United States
Environmental Protection
Agency

Office of
Drinking Water
Washington DC 20460

EPA 570/9-84-005
CCMS-112

Water

EPA

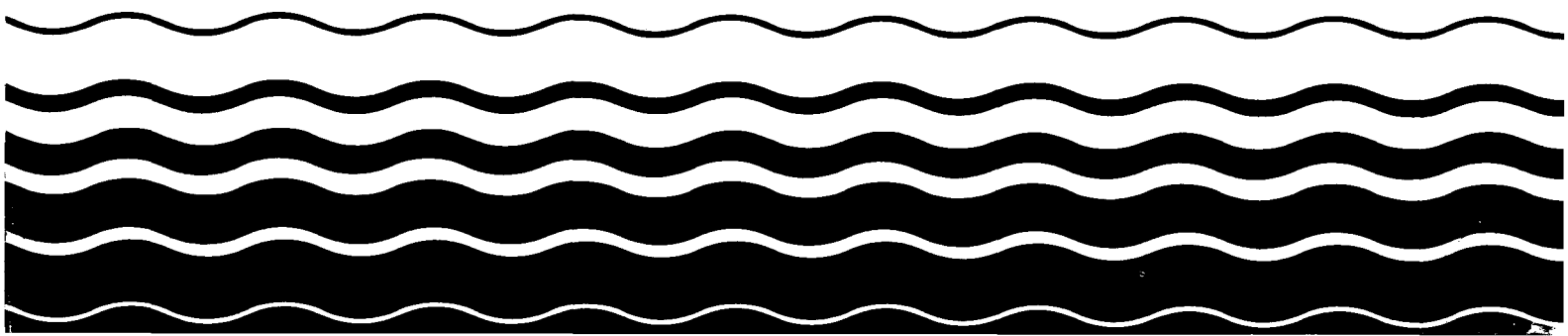
NATO – CCMS

Committee on the Challenges of Modern Society (NATO/CCMS)

Adsorption Techniques in Drinking Water Treatment

NATO/CCMS Drinking Water Pilot Project Series

CCMS 112



ADSORPTION TECHNIQUES IN DRINKING WATER TREATMENT

Papers and Discussion from the NATO/CCMS
Symposium held in Reston, Virginia, USA
April 30 through May 2, 1979

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Sponsored by

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U.S. Environmental Protection Agency
Washington, D.C. 20460

1984

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FOREWORD

Many of the industrial Nations today face problems related to population, energy, and protection of the environment. In order to optimize use of the scientific and technical expertise from different countries, the Committee on the Challenges of Modern Society (CCMS) was created between the Allied Nations of the North Atlantic Treaty Organization (NATO). This international society of scientists strengthens ties among members of the North Atlantic Alliance and permits NATO to fill a broader social role with non-member countries. CCMS has been responding to the increasingly complex, technological problems facing modern society.

The Drinking Water Pilot Study was initiated by the U.S. Environmental Protection Agency (EPA) in order to address a broad spectrum of drinking water quality and health related issues. Six subject areas have been studied by a number of groups representing individuals from eleven NATO countries and three non-alliance countries with technical participation from many others. The conclusions and recommendations reached by the participants are hoped to allow national programs to focus on specific areas of water supply research and to bring out the most up-to-date technology and practices. However, the recommendations and conclusions do not necessarily reflect the policy of the U.S. or any other participating countries. The work of the Pilot Project has been covered in a summary report.

In addition two international symposiums, "Oxidation Techniques in Drinking Water Treatment," and "Adsorption Techniques in Drinking Water Treatment," were held in Karlsruhe, Federal Republic of Germany, between September 9-13, 1978, and in Reston, Virginia, United States on April 30 through May 2, 1979, respectively. The first of these was supported by the Federal Republic of Germany and the second by the United States EPA. This volume contains the manuscripts of all the lectures and related discussions from the symposium held in Reston. In addition a summary paper was added by the editor. Herein is a comprehensive survey on the practical application of adsorption techniques for removing organics from drinking water.

Current uses of granular activated carbon (GAC) for controlling synthetic organic chemicals are discussed by representatives from the U.S., Canada and six European countries. GAC beds vary from shallow sand-replacement carbon filters (1 meter deep) with short contact times, to deep carbon contactors (as much as 4 meters deep) with long contact times, often following sand filters and ozonation. Performance of the GAC depends on the type of organics desired to be removed, the quality of the water, the preceding treatment, the depth and type of carbon used, and the throughput prior to carbon replacement or regeneration.

Laboratory techniques, adsorption models, and pilot testing can be used for predicting GAC performance. Organic removal effectiveness can be measured by total organic carbon (TOC), organic halogen (TOX), U.V. absorption, bioassays, and specific compound analysis using gas chromatography and mass spectrometry. Each of these methods, or the concurrent use of several methods, is appropriate for different concerns of treatment effectiveness.

GAC is often used most cost-effectively with on-site regeneration. Factors which determine the appropriateness of this include labor, energy, carbon costs, carbon loss, and reactivation frequency requirements. Different furnace types and operational modes need to be considered.

Although emphasis is given to GAC and biological activated carbon (i.e., GAC preceded by ozone or other oxidant), powdered activated carbon and ion exchange resins are also discussed. In particular situations, either of these may be a more suitable treatment alternative.

This workshop is a tribute to the efforts of all the participants involved. Paul Roberts, Scott Summers and Stig Regli were editors of the proceedings with assistance from Ross Pickford and Frank Bell. It is hoped that the ties established, and the good spirit of international cooperation that has prevailed during the symposium and through the finalization of this report, will continue in the development of future related projects.

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SYMPOSIUM OVERVIEW

NATO – CCMS

SYMPOSIUM OVERVIEW

Paul V. Roberts and R. Scott Summers

INTRODUCTION

This Symposium on Adsorption Techniques in Drinking Water Treatment was intended to bring together researchers and practitioners from a number of NATO member countries for an exchange of experiences regarding the application of adsorption technology in solving modern challenges in water supply. Foremost among these challenges is that of providing safe potable water. Our growing awareness of the health threat represented by organic trace pollutants, both those present in contaminated water supplies and those formed during treatment, is a reminder that meeting this challenge will not be a simple task.

Not surprisingly, a diversity of views was represented at the Symposium. Indeed, the value of the Symposium stems largely from the wide variety of nationalities, backgrounds, and views represented. To the extent that these diverse views can be synthesized, the proper role of activated carbon treatment in solving modern challenges to water supply can be defined more confidently.

It was not a goal of the Symposium to reach formal agreement in the form of resolutions or the like. Nonetheless, a substantial consensus was developed with respect to a number of important issues. The purpose of this overview is to point out areas of consensus, identify questions on which there is strong disagreement, and to compare the results of the investigations reported at the Symposium. Only information presented at the meeting is referenced; the reference numbers are keyed to the list appended to this summary.

We have chosen to emphasize a comparative evaluation of data on granular activated carbon (GAC) performance from a unified point of view, rather than to digest the arguments so well stated in the original papers. For the comparative evaluation of GAC column performance data presented at this Symposium, it is necessary to focus on the removal of total organic carbon (TOC) and total trihalomethanes (TTHM), because only these parameters were reported in a sufficient number of papers. In keeping with the spirit of the Symposium, the intent is to delineate the implications for practice.

GAC COLUMN PERFORMANCE

In a number of papers in this Symposium, data were presented that illustrate the breakthrough of organics, as measured by TOC, TTHM, UV-absorbance, and the concentrations of specific organic compounds in GAC columns. These data were derived from studies that were conducted under widely differing conditions--using raw waters of diverse composition, vastly different scales of operation size, various pretreatment configurations, diverse types of GAC, and differing values of empty bed contact time and bed depth. Hence, it is of interest to compare the results of the studies of organics breakthrough under such a wide range of conditions, with a goal of gaining insight into the range of variability that may be expected if GAC treatment is broadly implemented in practice.

TOC Removal

TOC is thought to be a useful, quantitative measure of the total amount of organic constituents present in a water. Hence, complete removal of TOC--or the equivalent measure, dissolved organic carbon (DOC), for filtered samples--is tantamount to complete removal of organic constituents. Virtually complete removal of TOC is one conceivable objective of GAC treatment.

In practice, however, it is found that complete removal of TOC by GAC treatment is infeasible under water treatment conditions. An immediate, partial breakthrough of TOC occurs when a column filled with fresh GAC is commissioned. This indicates that a portion of the influent TOC is not amenable to removal by GAC treatment. With increasing service time, the GAC becomes saturated with organics; the effluent concentration (C_E) rises and eventually assumes a steady state value. According to the theory of fixed-bed adsorption, the concentration in the effluent at steady state ought to equal the influent concentration (C_I). However, it has been observed that under water treatment conditions the effluent concentration of TOC seldom reaches the influent concentration; rather the effluent concentration rises to a steady state value lower than the influent concentration (41). In effect, the GAC column continues to remove a fraction of the influent TOC virtually indefinitely. This more-or-less constant steady state removal is attributed to biodegradation (8, 20, 36, 41).

Evidence of these phenomena--immediate partial breakthrough and indefinite steady state removal--can be inferred from the TOC breakthrough data presented at this Symposium. Table 1 includes all results for GAC columns which attained steady state removal or complete breakthrough. To facilitate reference, we have cited both the number of the paper and the figure number within that paper from which the referenced data were drawn. We have used letters as postscripts to the paper number to

Table 1

GAC Performance for TOC Removal

Data Designation Paper/ Expt.	Figure No. In Paper Cited	Initial Fraction Remaining $(C_E/C_I)_o$	STEADY STATE: Fraction Remaining $(C_E/C_I)_{ss}$	STEADY STATE: Throughput Bed Volumes θ_{ss}	Empty Bed Contact Time EBCT (min)	Hydraulic Loading v_o (m/hr)	Average Influent Concentration C_I (mg/l)	Pretreatment§§
3A	1	0.35	1.0	12,000	15	6	4	B.P.C./CLAR
3B	6	0.25	0.65	20,000	10	††	3	OZ/CLAR/FIL
4A	4	0.40	0.80	13,000	12	20	2-4	CLAR/OZ/FIL
4B	8	††	0.80	8,600	15	12	4-5.5	BPC/CLAR/FIL
4C	8	††	0.65	4,300	30	12	4-5.5	
4D	*	††	0.75	11,500	12	15	5	CLAR/FIL/CHL
4E	*	††	0.70	7,000	24	7.5	5	
7A	4	0.5	0.90	9,000	5.4	10	4-5	BPC/CLAR/FIL
7B	5	0.1	0.85	6,000	6	10	3-4	
8	4	0.55	0.90	11,000	††	††	1.5	††
13A	3	0.1	0.65##	6,500	11	5.4	3-4	
13B	3	0.1	0.60##	6,500	22	5.4	3-4	CLAR/
13C	7	0.1	0.70##	8,200	17	2.8	3-4	CHL/
13D	7	0.1	0.70##	8,700	21	2.2	3-4	FIL
13E	11	0.4	0.75	9,000	14	2.8	3-5	CLAR/
13F	11	0.15	0.70	9,800	17	2.6	3-5	CHL
15A	7	0.75	1.0	14,000	3	1.9	3-4	
15B	7	0.45	1.0	14,000	6	1.9	3-4	SET/CLAR/
15C	7	0.25	††	††	12	1.9	3-4	FIL/CHL
15D	7	0.2	††	††	18	1.9	3-4	
16A	10	0.15	0.80	10,400	6.2	7.4	6.4	
16B	10	0.4	0.85	5,500	6.2	7.4	6.4	CLAR/
16C	10	0.2	0.80	7,200	6.2	7.4	6.4	BPC/
16D	10	0.7	0.85	1,600	6.2	7.4	6.4	FIL
16E	13	0.2	0.65	3,800	19	7.4	6.5	CLAR
16F	13	0.1	0.70	3,800	19	7.4	5.4	CLAR/BPC/FIL
17A	5	0.15	0.80	10,000	4.5	6	2	
17B	5	0.15	0.75	9,000	7.5	6	2	
17C	5	0.15	0.65	9,600	7.5	6	2	
17D	10	0.15	0.90	12,600	3.2	17	2.5-1.5#	SET/CLAR/FIL
17E	10	0.15	0.85	11,000	7.5	17	2.5-1.5#	
17F	10	0.15	0.65	10,000	12	17	2.5-1.5#	
17G	10	0.15	0.55	7,700	16	17	2.5-1.5#	

Table 1

GAC Performance for TOC Removal (Continued)

Data Designation Paper/ Expt.	Figure No. In Paper Cited	Initial Fraction Remaining $(C_E/C_I)_o$	STEADY STATE: Fraction Remaining $(C_E/C_I)_{ss}$	STEADY STATE: Throughput Bed Volumes θ_{ss}	Empty Bed Contact Time EBCT (min)	Hydraulic Loading v_o (m/hr)	Average Influent Concentration C_I (mg/l)	Pretreatment§§
17H	11	0.15	0.95	13,500	3.2	17	2.5-1.5#	SET/ CLAR/ FIL
17I	11	0.15	0.85	11,000	7.5	17	2.5-1.5#	
17J	11	0.1	0.80	10,000	12	17	2.5-1.5#	
17K	11	0.1	0.75	7,200	16.	17	2.5-1.5#	
20A	9	0.1	0.70	5,300	34.	14	16†	‡
20B	10	0.15	0.60	3,000	34.	14	10†	§
21	9	0.1	0.70	9,000	20	7.5	3.2	CHL/CLAR/FIL
25	7	0.5	0.85##	5,100	††	††	2.0-3.5	††
32A	2	0	0.75	9,000	8	††	4.4	CHL/ CLAR/ FIL
32B	2	0	0.65	9,000	8	††	2.7	
41A	11	0.1	0.65	24,000	9	††	1-2	CLAR
41B	11	0.1	0.45**	29,000	9	††	1-2	CLAR/OZ
41C	15	0.1	0.70	30,000	10	19.	1-2	CLAR/OZ/FIL
41D	15	0.1	0.75	30,000	10	19.	1-2	CLAR/FIL
RANGES			0.45-1.0	1,600-30,000	3-34	1.9-20	1-16	
RANGES MINUS EXTREMES			0.6-0.9	3,000-14,000	5.4-24	2.6-17	2-6	
% IN RANGE			87%	87%	84%	80%	86%	

FOOTNOTES

* Data given in text of Paper No. 4.

† Constituent regularly measured and reported was chemical oxygen demand (COD). TOC calculated on given COD/TOC ratio of ~2.5.

‡ Wastewater treatment. TRICKLING FILTER/CLAR/AIR STRIPPING/RECARBONATION/FIL

§ Wastewater treatment. ACTIVATED SLUDGE/CLAR/AIR STRIPPING/RECARBONATION/FIL

\# Steady decrease in influent concentration with time.

** Influent concentration measured before O_3 addition.

†† Data insufficient to estimate this quantity.

General increase over a long period in C_E/C_I after rapid initial breakthrough

§§ Key to abbreviations regarding pretreatment:

B.P.C. -- Breakpoint chlorination
Chl -- Non-breakpoint chlorination
SET -- Pre-settling or storage
CLAR -- Clarification
FIL -- Sand Filtration
OZ -- Ozonation

distinguish among the individual experiments within a given paper. The influent TOC concentration was generally in the range of 3 to 6 mg/l. Exceptions were: two papers--(17) and (41)--concerning the treatment of Ohio River water, for which the influent TOC concentration was approximately 1 to 2.5 mg/l; and one paper (20), which dealt with the advanced treatment of wastewater having a TOC concentration in excess of 10 mg/l.

Immediate Breakthrough

The ratio of effluent concentration to influent concentration, defined as fraction remaining (C_E/C_I), generally was observed to be in the range of 0.1 to 0.5 immediately after start-up (Table 1). In only one case (32) was the initial effluent concentration reported as zero.

The initial breakthrough $(C_E/C_I)_o$ can be expected to depend on the composition of the organic constituents, as well as empty bed contact time (EBCT) or bed depth. Values of $(C_E/C_I)_o$ are plotted against bed depth in Figure 1. For the most part, $(C_E/C_I)_o \leq 0.2$; only one-fourth (9 of 36) of the values exceed 0.2, and 7 of these 9 positively deviating values of $(C_E/C_I)_o$ were observed in experiments in which the GAC bed depth was less than 1 m.

The plot of $C_E/C_I)_o$ versus EBCT (Figure 2) shows substantial scatter. It can only be said that the maximum value of $(C_E/C_I)_o$, observed at a given value of EBCT, decreases with increasing EBCT up to EBCT = 20 minutes.

Exhaustion of GAC and Steady-State Removal

With increasing service time, the (C_E/C_I) value begins to rise. The value of (C_E/C_I) continues to rise until an approximate steady state is reached. We have expressed the length of service in terms of the volume of water treated, normalized by dividing by the volume of the empty bed. This normalized quality is referred to as the throughput ratio:

$$\theta = \frac{V_t}{V_{GAC}} = \frac{Qt}{V_{GAC}} = \frac{t}{(EBCT)} \qquad (1)$$

where θ = throughput ratio, or cumulative number of bed volumes treated as of time t (dimensionless)

Q = volumetric flow rate (m^3/hours)

t = elapsed time (hours)

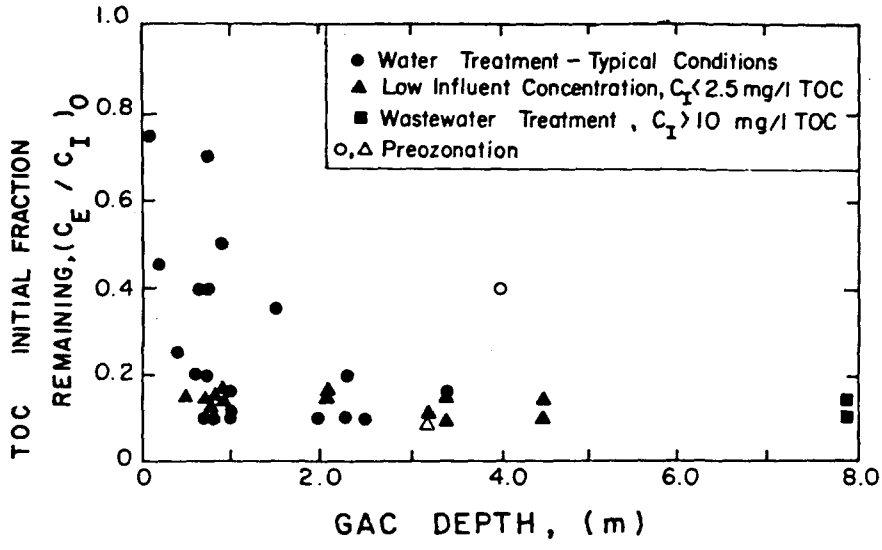

Figure 1. Dependence of Initial Fraction Remaining $(C_E/C_I)_o$ on GAC Bed Depth. Typical conditions are taken to be $2.5 < C_I < 10$ mg/l TOC, without preozonation

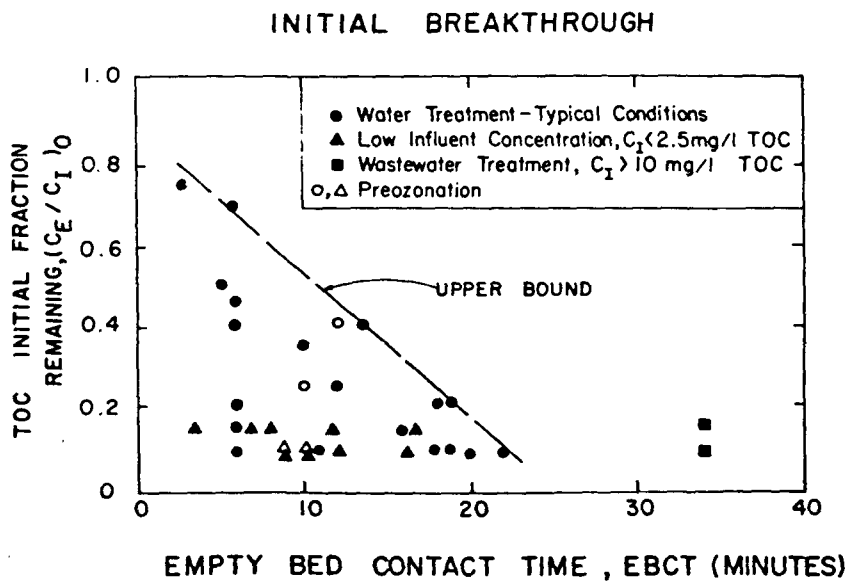

Figure 2. Dependence of Initial Fraction Remaining $(C_E/C_I)_o$ on Empty Bed Contact Time (EBCT)

V_{GAC} = bulk volume of GAC in the adsorbent bed (m^3)

EBCT = empty bed contact time (hours)

V_t = cumulative volume of water as of time t (m^3)

Hence, the throughput ratio serves as a dimensionless time parameter.

The value of (C_E/C_I) is shown as a function of the throughput ratio (θ) in Figure 3 for several representative data sets. The data shown are representative of the full spectrum of results presented at this symposium; the data from 16B constitute a relatively rapid approach to steady-state; the data from 32A represent approximately the median rate of approach to steady-state; and the 41A data indicate a much slower rate of exhaustion than do the data from the other studies (Table 1). The tendency in Figure 3 is clear: for most experiments (as in the examples of 16B and 32A), the fraction remaining rises at first rapidly, then ever more slowly toward an approximate steady state. There are some exceptions (such as 41A), in which the value of (C_E/C_I) shows a more symmetrical S-shaped breakthrough response: (C_E/C_I) at first remains nearly constant for an appreciable time period, before beginning to rise.

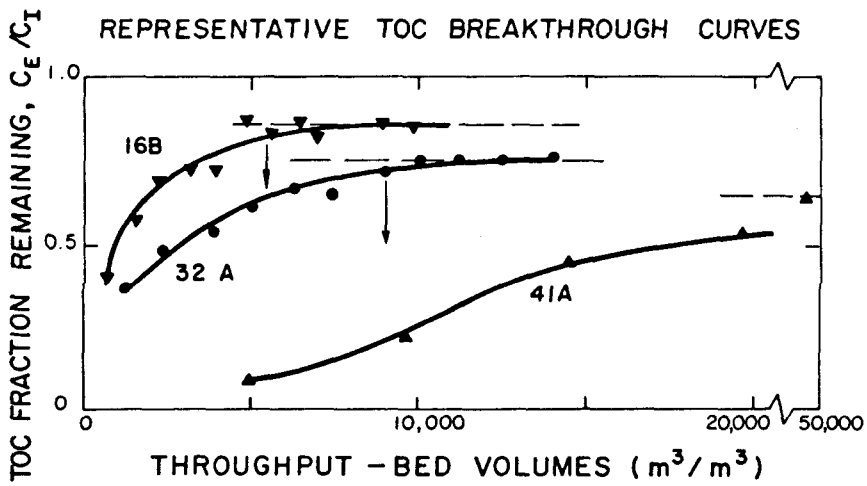

Figure 3. Representative TOC Breakthrough Curves

The point at which steady state is reached is an important characteristic of the GAC column's performance; it indicates the number of bed volumes that can be treated before the adsorptive capacity is exhausted. Thereafter, the removal of TOC is

achieved primarily by biodegradation. For purposes of comparison, we have estimated this exhaustion point for all cases shown in Table 1. Fluctuations in the rate of approach to the steady state condition will have a major impact on the throughput ratio at steady state (θ_{ss}). To account for these variations and their effects on θ_{ss}, an estimation of steady state is taken to be within 5 percent of $(C_E/C_I)_{ss}$, designated by the downward arrows in Figure 3. This arbitrary choice reflects an attempt to make a reasonable estimate of the point at which the remaining adsorption capacity becomes negligible.

Values of (C_E/C_I) at steady state and θ_{ss} (the number of throughput bed volumes at which $(C_E/C_I)_{ss}$ is approached within 5 percent) are given for all GAC breakthrough runs in Table 1. These values are plotted as $(C_E/C_I)_{ss}$ versus θ_{ss} in Figure 4 with the source of the data designated to facilitate references, and without designation to permit trends to be seen. The values of $(C_E/C_I)_{ss}$ lie mainly in the range of 0.6 to 0.9; only 13 percent (6 of 45) of the data points are outside that range. The mean and standard deviation for $(C_E/C_I)_{ss}$ are 0.76 ± 0.11. The values of θ_{ss} are clustered in the range of 3,000 to 14,000 bed volumes; only 13 percent (6 of 45) of the data points lie outside that range. Four of the six outlying values of θ_{ss} stem from a single investigation (41). The low outlying point (16D) corresponds to a GAC type that is seemingly ill-suited for TOC removal. The mean and standard deviation of θ_{ss} for all data are $10,200 \pm 6,600$ bed volumes. These values are averages of a large number of experiments representing a wide range of conditions, and hence must be interpreted with caution. Nonetheless, it can be said with some confidence that the capacity of GAC to adsorb TOC under typical water treatment conditions is exhausted before 14,000 bed volumes have been treated. The removal effectiveness thereafter is approximately 25 percent of the influent TOC, a level which presumably can be maintained indefinitely.

There is no apparent strong effect of preozonation on the value of $(C_E/C_I)_{ss}$. The data from 3B suggest that preozonation may increase θ_{ss}, effectively increasing the amount of TOC removed prior to exhaustion of the GAC's adsorptive capacity, but the direct comparison of 41C and 41D does not support that interpretation.

The value of θ_{ss} depends weakly on the empty bed contact time (Figure 5). This should be interpreted in the light of the definitions of θ and EBCT

$$\theta_{ss} = \frac{Qt_{ss}}{V_{GAC}} = \frac{t_{ss}}{(EBCT)} \qquad (2)$$

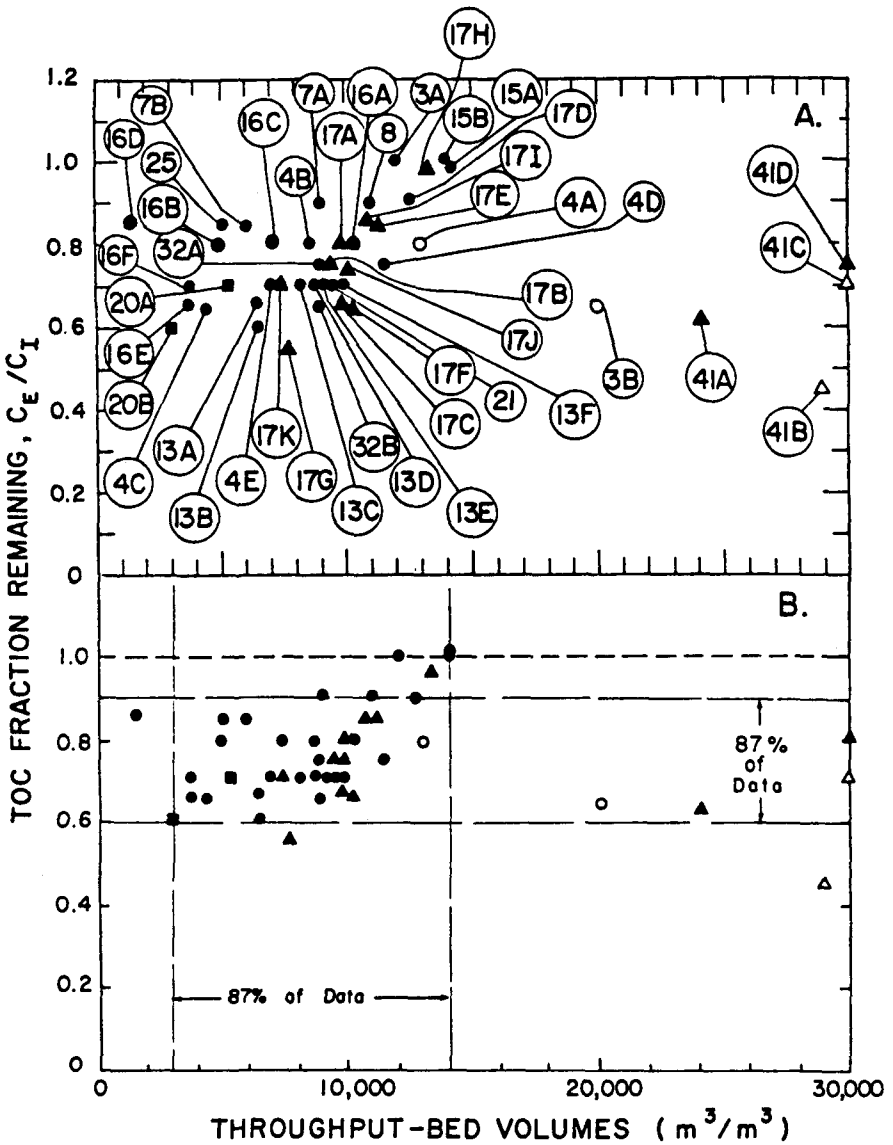

Figure 4. TOC Fraction Remaining at Steady State $(C_E/C_I)_{ss}$ and Throughput Ratio at Which It is Reached

A. (Above) - with designation of experimental data

B. (Below) - without designation of data

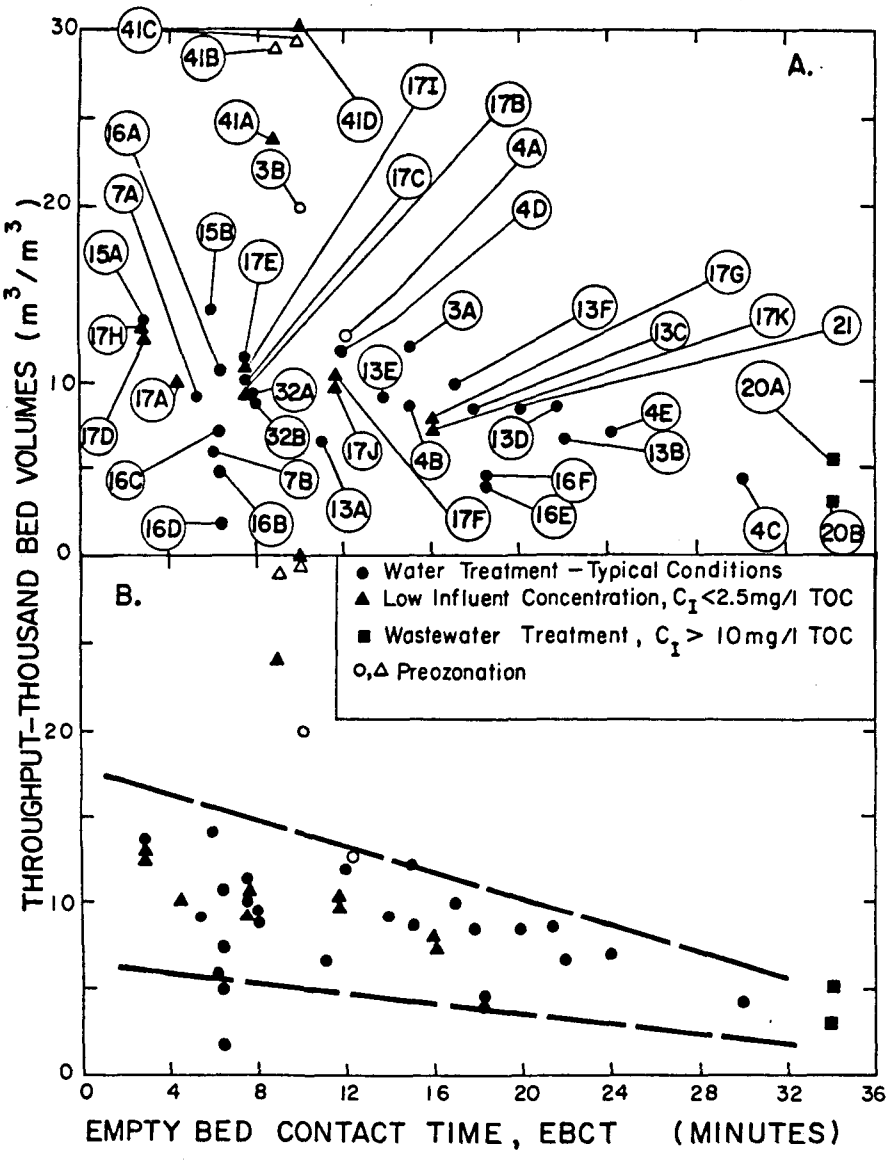

Figure 5. Throughput Ratio at Steady State θ_{ss} versus EBCT

A. (Above) - with designation of experimental data

B. (Below) - without data designation

where t_{ss} is the time at which steady state is reached within 5 percent. It can be seen from Figure 5 that θ_{ss} tends to vary inversely with EBCT. The dashed lines represent approximate upper and lower limits, ignoring data in which the influent concentration or GAC type (16D) were abnormal, or preozonation was practiced. In other words, t_{ss} increases with increasing EBCT, but in less than direct proportion. This is shown in Figure 6, in which t_{ss} is plotted versus EBCT, omitting the points that are anomalous because of abnormal GAC type or preozonation. From a regression of $\log(t_{ss})$ on $\log(\text{EBCT})$, it is evident that the data are correlated by an expression of the form

$$t_{ss} = \text{constant} \times (\text{EBCT})^{n} \qquad (3)$$

The estimate of n is 0.62 ± 0.20 (95 percent confidence interval). Hence there is a positive correlation between t_{ss} and EBCT under typical conditions of water treatment, but the dependence is weaker than linearity ($n<1$).

Performance of Adsorbers Operated in Parallel

At a large-scale treatment works, the GAC treatment typically will be accomplished in a large number of individual adsorbers connected in parallel. The number of individual contactors is approximately 12 for a 10 mgd plant and 60 for a 150 mgd plant (33).

A consequence of this multiple, parallel-unit configuration is that the activated carbon being used at any given time will tend to represent a broad spectrum of elapsed time in service, i.e., time since replacement or regeneration. This implies that, to achieve a given performance standard, it should not be necessary to regenerate or replace the GAC as frequently in a multiple contactor operation as would be the case with a single contactor.

The impact of the number of parallel units on required regeneration frequency can be illustrated by considering the case of m contactors operated in parallel, each of which is regenerated after a given number of throughput volumes. We assume that the contactors are regenerated sequentially, and also that the individual contactors treat equal flows. We further assume a typical breakthrough curve (e.g., for TOC in water treatment, as in Figure 3), as shown in Figure 7A. In this example, a fraction remaining value of 0.5 is reached when 5,000 bed volumes have been treated.

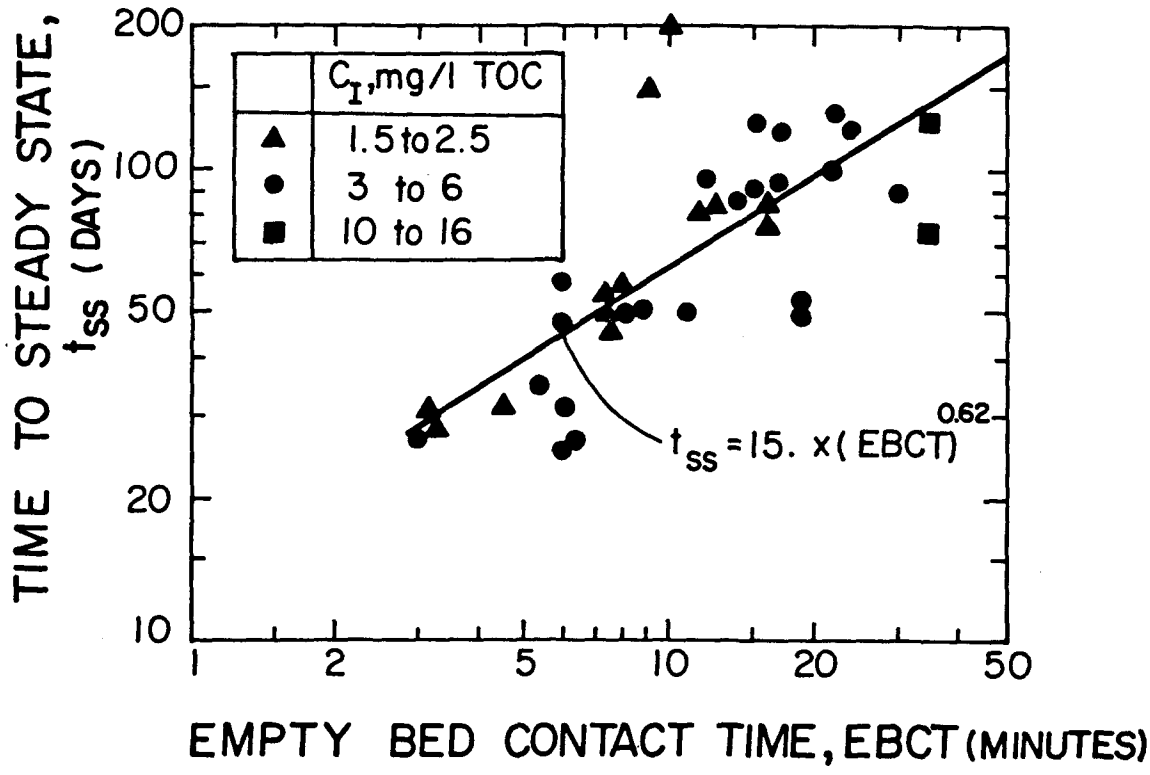

Figure 6. Observed Run Length at Which Steady State is Reached

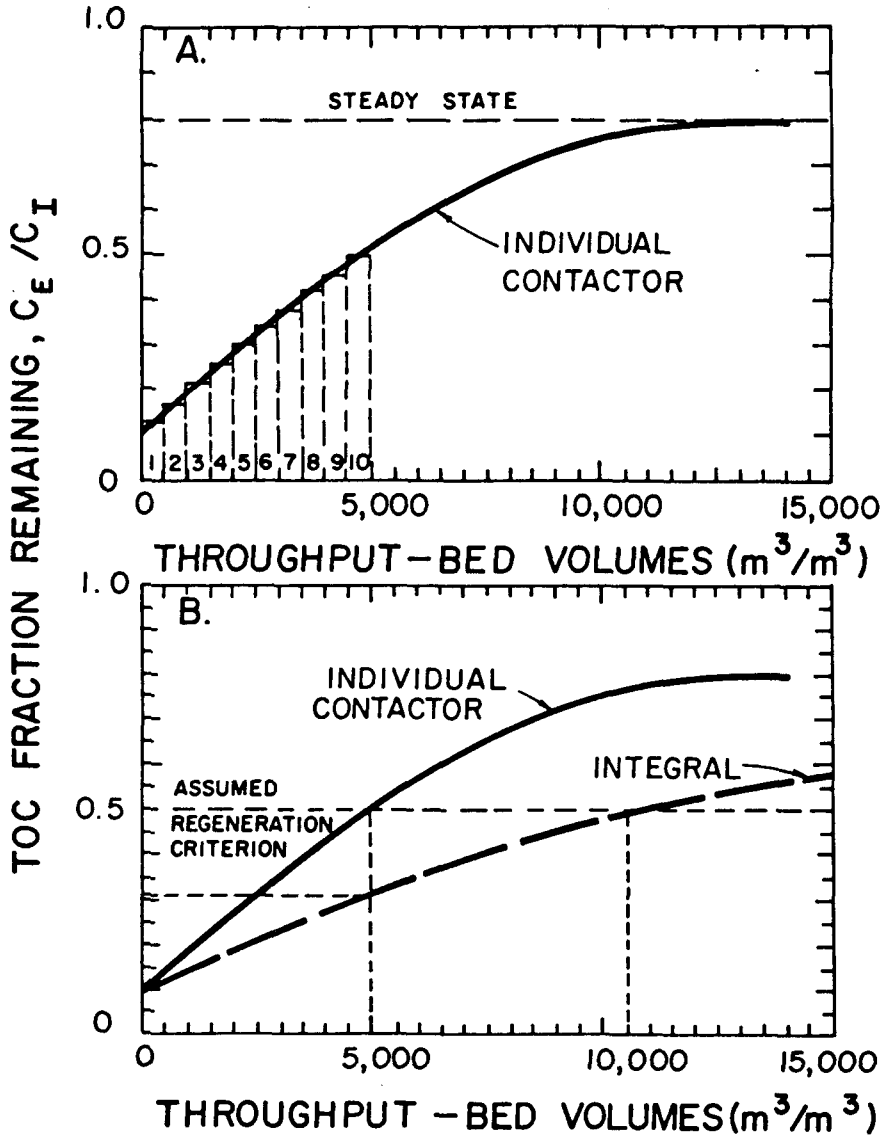

Figure 7. Integral Breakthrough Curve for Characterizing Performance of Multiple, Parallel Contactor Operation

Suppose that the individual contactors are regenerated regularly after 5,000 bed volumes have been treated. Assuming that EBCT = 30 minutes, the regeneration interval (run length) will be 2500 hours. Under these circumstances, the overall GAC plant performance will be superior to that predicted by the value of the fraction remaining $f = (C_E/C_I)$, at the chosen value of throughput ratio θ. The effluent average fraction remaining is given by

$$\bar{f} = \frac{\bar{C}_E}{C_I} = \frac{\sum_{i=1}^{m} f_i \cdot \left(\frac{\theta_R}{m}\right)}{\theta_R} = \sum_{i=1}^{m} (f_i/m) = \frac{1}{m} \sum_{i=1}^{m} f_i \qquad (4)$$

$$\bar{f} \cong \int_0^{\theta_R} f d\theta \quad \text{(for sufficiently large values of m)} \qquad (5)$$

where $f_i = (C_E/C_I)$ = fraction remaining = (1 - fraction removed)

$\bar{f}$ = plant effluent average fraction remaining

$\bar{C}_E$ = average effluent concentration

θ_R = regeneration interval in throughput bed volumes

m = number of contactors in parallel

subscript i refers to the i^{th} contactor

The integral in Equation 5 can be evaluated by numerical integration, as shown in Figure 7A where the breakthrough curve in the interval $0<\theta<5000$ is divided into ten increments. In the example shown, the average fraction remaining $\bar{f}$ of the combined GAC effluents would be only 0.31 (Figure 7B), if the GAC were regularly regenerated after a throughput of 5,000 bed volumes.

It is useful to estimate the limiting throughput ratio that would result in a desired average concentration of the combined effluent. This can be found by calculating the value of the integral

$$\bar{f} = \int_0^{\theta_R} f d\theta \qquad (5)$$

as a function of θ, plotting the result as in Figure 7B. For the example chosen, the limiting throughput ratio is 11,000 bed volumes estimated from the integral curve, compared to a value of 5,000 bed volumes estimated from the individual breakthrough

curve. This implies that, for the example shown, the GAC in a large-scale plant with multiple contactors will need to be regenerated slightly less than half as frequently as would be predicted by simply reading the value of the limiting throughput ratio for the individual contactor.

Integral TOC breakthrough curves for two experiments--16B and 32A (Table 1 and Figure 2)--are plotted in Figures 8 and 9, respectively. These experiments are chosen by virtue of their TOC breakthrough curves being typical of one of two types--rapid (16B), or average (32A) breakthrough. In both cases, the integral breakthrough is significantly slower than the instantaneous breakthrough, as expected. Choosing $\bar{f} = 0.5$ as a hypothetical criterion, the run length would be increased by a factor of two to three (Table 2) when judged according to the integral curve rather than the instantaneous curve for eight cases from Table 1.

Table 2

Comparison of Instantaneous and Integral Breakthrough Curves for Estimating GAC Run Length for 50 Percent TOC Removal

Paper	Figure No. in Paper Cited	Throughput θ At 50% Removal		$\left(\frac{\theta_{Integral}}{\theta_{Instan.}}\right)$
		Instantaneous (Bed Volumes)	Integral (Bed Volumes)	
16B	10	1,000	2,700	2.7
15B	5	1,800	3,800	2.1
32A	3	2,700	7,500	2.8
17B	10	6,000	12,400	2.1
21	9	3,000	8,600	2.9
17A	10	4,000	10,000	2.5
41A	11	17,000	~53,000	3.1
41D	15	18,000	~38,000	2.1

This indicates that the design regeneration frequency may be overestimated when based on breakthrough data from individual columns, as is commonly done. Because regeneration frequency is one of the most important determinants of the cost of GAC treatment, it is crucial to carefully consider how pilot plant data

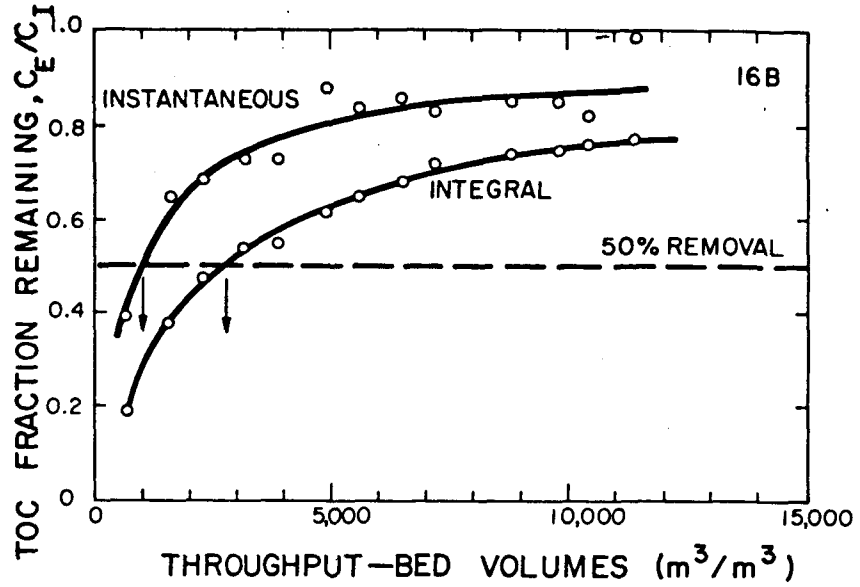

Figure 8. Importance of Multiple, Parallel Contactor Operation - Experiment 16B

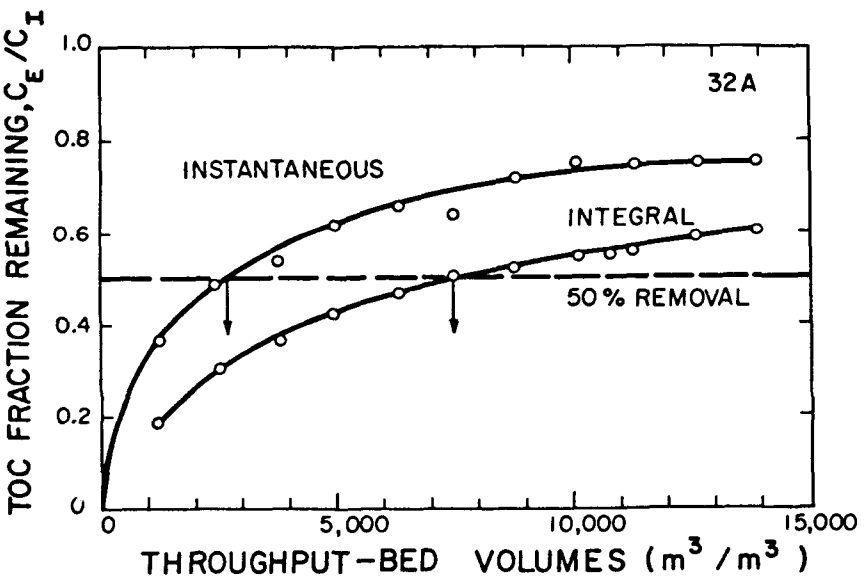

Figure 9. Importance of Multiple, Parallel Contactor Operation - Experiment 32A

should be used in estimating the regeneration frequency required to satisfy a given effluent standard.

Trihalomethane Removal

Trihalomethanes have significance as organic contaminants of public health concern, and also as indicators of the chlorinated organic hydrocarbons formed during water treatment by chlorination. The papers in this Symposium offer abundant evidence that trihalomethanes occur in appreciable concentrations in treated waters, and that they can be removed by GAC treatment, albeit for a limited time before the GAC is exhausted. The data are summarized in Table 3. The experiments are identified citing both the paper and the specific figure from which the data were taken; the code is consistent with Table 1. The results are difficult to compare. Some authors have reported measured total trihalomethane concentrations (TTHM); others have reported total trihalomethane formation potential (TTHMFP) data obtained at differing conditions of chlorine dose, reaction time, pH and temperature. It must be recognized that the collective parameters TTHM and TTHMFP are inherently different; therefore, direct comparison of their behavior may be misleading.

Immediate Breakthrough

The values of $(C_E/C_I)_o$ for TTHM and TTHMFP in the early stages of the experiments tend to cluster near zero. The initial concentration was significantly above zero for only six of the sixteen data points. Hence, the initial removal of TTHMs and TTHMFPs was in general substantially more complete than that of TOC.

Exhaustion of TTHM Removal Capacity

All of the TTHM and TTHMFP data in Table 3 exhibit an ultimate steady state fraction remaining in excess of 75 percent (Figure 10), except for 41A and 41B, experiments in which TTHMFP was measured and the influent TOC concentration was unusually low. It is useful to divide the data into two groups: one comprising data sets for which the influent TOC concentration was 3 to 6 mg/l (4, 13, 16) and a second set for which the influent TOC concentration was 2.5 mg/l or less (17, 41). The latter group, corresponding to low influent TOC concentration, exhibits substantially more prolonged TTHM and TTHMFP removal compared to the main group of data, for which the influent concentration was greater than 3 mg/l TOC. The values of θ_{ss} were two to three times higher for the group having the lower influent TOC concentration. This difference may be explained by lesser competition for adsorption sites between TTHMs and other organics when the TOC concentration is low.

Table 3

GAC Performance for TTHM and TTHMFP Removal

Data Designation Paper/ Experiment	Figure No in Paper cited	Analysis	Initial Fraction Remaining $(C_E/C_I)_o$	STEADY STATE		Empty Bed Contact Time EBCT (min)	Hydraulic Loading v_o (m/hr)	Average Influent Concentration C_I (µg/l)	Pretreatment
				Fraction Remaining $(C_E/C_I)_{ss}$	Throughput Bed Volume θ_{ss}				
4B	9	TTHM	††	1.0	11,500	15	12	130-30	BPC/CLAR/FIL
4C	9	TTHM	0.2	0.75	5,800	30	12	130-30	
13A	4	TTHMFP	††	1.0	7,800	11	5.4	300-100	
13B	4		††	0.65	7,000	22	5.4	300-100	
13C	8		††	0.85	~5,700	17	2.8	300-100	
13D	8		††	0.75	~4,700	21	2.2	300-100	
16G	6	TTHM	0	0.95	9,400	19	7	100-200	CLAR/BPC/FIL
16H	7	TTHM	0	1.0	12,300	6.2	7	126	
16I	8	TTHMFP	0	1.0	6,500	6.2	7	400-600	
16A	9		0.15	1.0	4,900	6.2	7	200-600	
16B	9		0.15	1.0	4,400	6.2	7	200-600	
16C	9		0.15	1.0	4,900	6.2	7	200-600	
16D	9		0.3	1.0	4,000	6.2	7	200-600	
17A	6	TTHM	0	0.9	27,800	4.5	6	20-80	SET/CLAR/CHL
17B	6		0	0.9	18,400	7.5	6	20-80	
17C	6		0	0.8	19,800	7.5	6	20-80	
18A	4		0	1.0	9,900	7.1	6.1	20-150	CHL/CLAR
18B	5		0	1.0	8,900	11	3.1	10-90	
23	6	TTHMFP	0	0.75	9,360	20	††	100-300	CLAR/CHL/FIL
41A	12		0.1	0.55	~19,000	9	††	40-80	CLAR
41B	12		0	0.35**	~29,000	9	††	40-80	CLAR/OZ

Footnotes consistent with Table 1

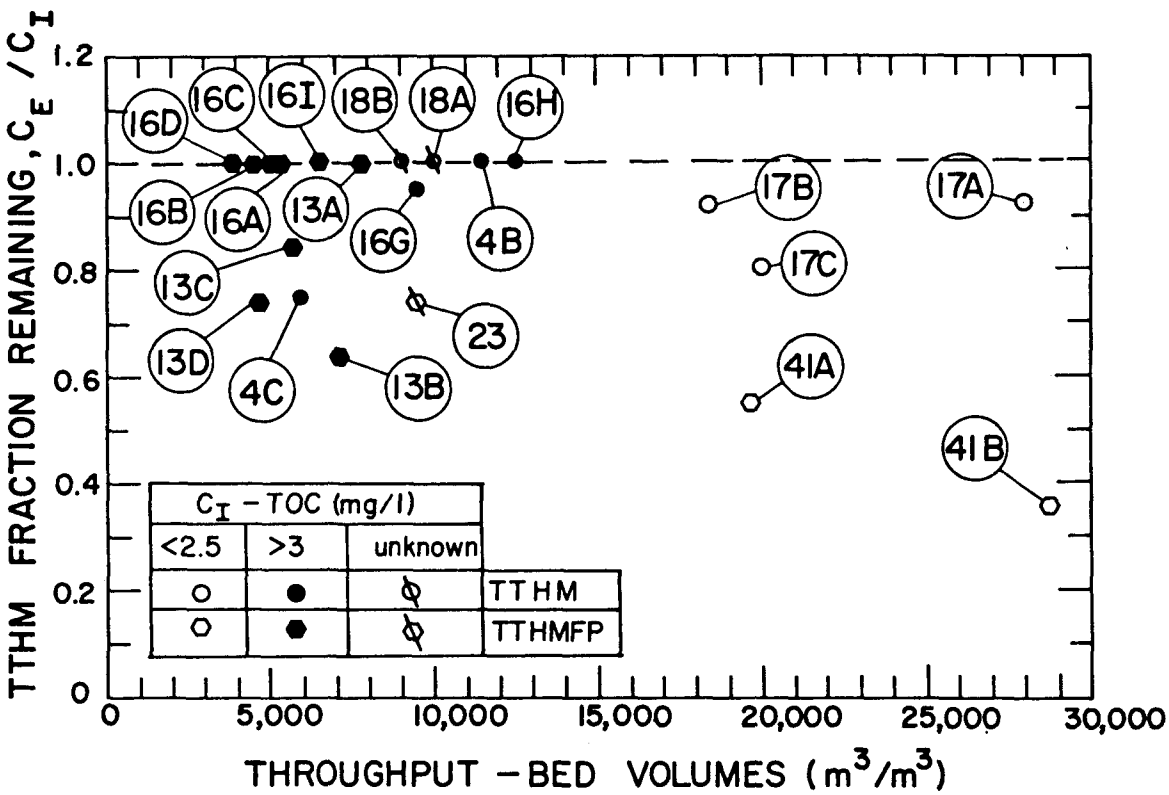

Figure 10. TTHM and TTHMFP Fraction Remaining at Steady State $(C_E/C_I)_{ss}$ and Throughput Ratio at Which It is Reached

REPORTING OF GAC COLUMN PERFORMANCE DATA

In reviewing the papers presented at this Symposium, the need for a standard format for reporting GAC data has become apparent. Authors with different research objectives report GAC data in a variety of forms, suitable and sufficient for their individual purposes. If, for example, an author is interested in reactivation frequency based on a maximum contaminant level (MCL) criterion, then the graph of most interest is the effluent concentration C_E versus time t. Others may be interested in the mass loading of an activated carbon or in the time to complete exhaustion of a carbon, and accordingly report their data in a form that best satisfies their objective. While reporting data in this objective-specific fashion satisfies the immediate needs of the author, it limits the interpretation of the data by others with different objectives. By including values for a few additional parameters and using a standard format for graphical presentation, some papers could be rendered more generally useful. Values of the following parameters should be specified if the potential of the data is to be fully realized.

Water Quality Characteristics

Knowledge of water quality parameters, in addition to the constituent of concern, is often helpful in the interpretation of the data, especially if abnormal conditions exist. Data on organic content (TOC or COD), chlorine residual, pH, dissolved oxygen, nitrogen species, and suspended solids should be reported. The measurements of collective organic parameters such as TOC or COD are helpful even if the objective of the study is to quantify the removal of specific organic pollutants. In reporting data from analytical methods that are not yet standardized (such as specific organic analysis), the detection limit and precision of the determination should be given.

GAC Physical Characteristics

GAC grain size, specific surface area, and bulk density ρ_B (g GAC per m^3 bed volume) are useful information for comparison of GAC performance. The value of ρ_B is needed for comparing mass loading per unit mass GAC. Carbon age, number of regenerations, has been shown to influence adsorptive capacity (28,32) and should be reported. Also, the manufacturer and type of activated carbon should be specified.

Pretreatment

This is normally reported, but often the level of pretreatment is not given. Sander (21) and Symons (41) report that chlorination and ozone-oxygen pretreatment have a substantial effect on GAC adsorption systems. Dosages and contact times for

pretreatment steps should be given if they are suspected of having an effect on the compounds of interest.

GAC Process Parameters

The following data are needed:

Empty bed contact time, EBCT;

Surface loading rate (superficial linear velocity), v_o;

GAC bed volume, V_{GAC};

Volumetric flow rate, Q; and

GAC bed depth, D.

Values of three of the last four parameters can provide enough information so that the other process parameters can be estimated and complete data analysis is possible. These parameters are related as follows:

$$EBCT = \frac{V_{GAC}\ (m^3)}{Q\ (m^3/hour)} = \frac{D(m)}{v_o(m/hour)} \qquad (6)$$

Clearly, the values of all parameters can be calculated if values are given for EBCT and either V_{GAC} or Q as well as D or v_o, or if any three of variables V_{GAC}, Q, D and v_o are specified. The superficial linear velocity v_o is normally defined as

$$v_o = Q/A\ \left(\frac{m^3 water}{m^2 area \cdot hour}\right) \text{ or } \left(\frac{m}{hour}\right) \qquad (7)$$

where A = cross-sectional area of the GAC bed, m^2, normal to the direction of flow.

Graphical Presentation

The most important measure of the performance is the difference between influent and effluent quality. Influent and effluent quality can be compared conveniently in several alternative ways.

Concentration normally is chosen as the dependent variable and commonly is plotted on the ordinate as: concentration in the influent C_I and effluent C_E; fraction remaining (C_E/C_I); or percent removed $\frac{C_I - C_E}{C_I} \times 100$. Several problems arise when

the latter two forms are used. When monitoring the constituents of water or wastewater, influent concentration C_I often varies considerably, which affects the breakthrough pattern of the GAC system. The extent of influent quality variation cannot be appraised if the concentration data are normalized. When C_I is reported as an average value and an MCL criterion is of interest, the latter two methods give only an estimate of C_E. If the data are to be transformed into a mass loading format, cumulative amount removed versus cumulative amount applied, then both C_I and C_E are required.

Laboratory studies differ from investigations at full-scale operating plants in that the influent concentration can be reasonably constant by dosing the influent with controlled amounts of solute. If the influent concentration can be maintained steady in this fashion, then the fraction remaining or percent removed can be used to represent the concentration variable. However, as a rule the individual data for influent and effluent concentration should be given, to permit interpretation of concentration fluctuations and trends and to facilitate estimation of the approach to steady state effluent quality.

The independent variable is normally reported as: time t in service; volume of water treated V_t; or throughput ratio θ, defined in Equation 1. The advantage of using throughput ratio θ over the other two alternatives is that GAC contractors with different EBCT values can be compared on an equalized basis. The interrelationships between θ, t, and V_t are defined in Equation 1.

RELATING GAC USE RATIO TO COLUMN PERFORMANCE

The rate at which GAC must be replaced or regenerated is an important factor influencing the cost of GAC treatment (33, 34). The GAC use ratio (34) is defined as the amount of GAC that must be replaced or regenerated per unit volume of water treated. The use ratio influences strongly the level of effluent quality resulting from GAC treatment. Conversely, the required degree of treatment dictates the necessary use ratio. For economic reasons, the use ratio will be chosen as small as possible, just large enough to satisfy the effluent quality criterion. The units of use ratio are chosen in (34) as pounds GAC per million gallons water treated; the corresponding metric units are g/m^3.

The use ratio can be defined in terms of the throughput ratio, as follows

$$UR = \frac{\rho_B}{\theta_R} \qquad (8)$$

where UR = GAC use ratio, $\frac{\text{g GAC regenerated}}{\text{m}^3 \text{ water treated}}$

How can the use ratio be estimated from GAC column performance data? Consider the example of the data for TOC removal from Passaic River water (32). We chose the data for previously reactivated GAC (32A in Tables 1 and 2 and in Figures 3 and 9) as being representative of long-term operation. The values of and UR corresponding to different levels of treatment for that example are summarized in Table 4. The values of the use ratio range from 49 to 160 g/m^3 (equivalent to mg/liter), or approximately 400 to 1300 pounds per million U.S. gallons, depending on the effluent quality criterion and the question of single or multiple columns. Any large water treatment plant would closely approximate multiple, parallel-column operation. Hence, for the example chosen, the use ratio to achieve an average TOC removal of 50 percent in a large treatment plant would be approximately 59 g/m^3, or 490 pounds per million gallons. The corresponding run length t_R (time between regenerations) would be:

$$t_R = \theta_R \times \text{EBCT (days)} = 7{,}500 \times \frac{8}{1440} = 42 \text{ days.} \qquad (9)$$

This example is intended for purposes of illustration only, and not as a general guideline. The methodology should prove useful in establishing a connection between papers that present GAC column performance data (3, 4, 7, 8, 13, 15-18, 20, 21, 23, 25, 32, 41) and those concerned with the costs of treatment and reactivation (33-35).

SUMMARY AND CONCLUSIONS

We have attempted to synthesize rather than summarize the Proceedings of this Symposium, by identifying areas of consensus and by applying a unified approach to interpreting GAC performance data.

There appeared among the experts, from the European and North American nations present at this Symposium, a remarkably strong consensus in favor of GAC treatment for control of dissolved organic contaminants, including those causing taste and odor as well as those of health concern.

There was general agreement in the following areas. GAC treatment has been shown to be effective for removing organic contaminants from water (1-8, 13, 15-23). The available technologies for GAC treatment and reactivation are felt to be relatively reliable and trouble-free (2-8, 14-20, 28-32). The understanding of GAC performance is reasonably well founded in theory (1, 9-12); pilot study results have improved our understanding of the breakthrough behavior of GAC columns (9, 13, 19,

Table 4

Estimating The GAC Use Ratio From

Column Performance for TOC Removal

Example--Data from (32), EBCT = 8 min, $(C_I)_{ave}$ = 4.4 mg/l TOC

Criterion for Reactivation	Throughput Ratio at Reactivation θ_R (bed volumes)	GAC Use Ratio[#] UR (g/m^3)	Resulting Fraction Remaining,[†] C_E/C_I	
			Single	Multiple
Steady State[§] reached in a single column	9,000[*]	49	0.75	0.53[**]
50% TOC removal in a single column	2,700[†]	160	0.5	0.3[**]
50% TOC removal in multiple columns operated in parallel	7,500[†]	59	0.7[††]	0.5

* Estimated from Figure 3 of this Overview

† Estimated from Figure 9 of this Overview

\# Calculated from Equation 8 using $\rho_B = 4.4 \times 10^5$ g/m^3
Units conversion: $(g/m^3) \times 8.34 = lbs/million$ U.S. gallons,

§ See the text of this Overview for a discussion of steady-state GAC column performance. For this case (32A, Table 1), $(C_E/C_I)_{ss} \cong 0.75$.

** Equivalent to the value of (C_E/C_I) for a single column over the entire period between reactivations.

†† Equivalent to the value of (C_E/C_I) at which an individual column would have to be reactivated.

41). The concurrent removal of organic solutes by biodegradation and adsorption in GAC columns is widely agreed upon; the GAC appears to serve a dual function as an adsorbent and an attachment surface for microorganisms (8, 20, 36, 37, 39, 42). GAC is almost universally accepted as being superior to powdered activated carbon for removal of collective organic substance (e.g., TOC) as well as specific organic contaminants; powdered carbon may be chosen as a short-term solution or as a low-cost means of controlling periodic taste and odor problems (3, 40). It is widely believed that GAC is justified for public health reasons in many cases where water supplies are prone to contamination by synthetic organic chemicals (1, 3-6, 8) despite the incremental cost (33-35) of GAC treatment; for such cases GAC presently is the only practical alternative to developing a new water supply (2-8). Macroreticular resins (38, 41) show promise for the long term, but have not as yet been demonstrated to be effective in practice.

Conflicting opinions were expressed in the following areas. Some speakers from European nations and a number of discussants voiced reservations regarding the feasibility and desirability of uniform, formal regulations for GAC treatment of water polluted by organic chemicals. Recommendations on a case-by-case basis are preferred by many. Also, concern was expressed about the rapid breakthrough of some specific compounds, notably chloroform. Furthermore, it was noted that chromatographic displacement can occur, resulting in effluent concentrations for some compounds being temporarily greater than the corresponding influent concentrations. The phenomena of elution and saturation observed in GAC columns, as well as the complex nature of the mixture of sorbing solutes, require that special attention be paid to characterizing effluent quality (1, 19, 20). Rapid progress is being made in developing and implementing chemical analytical techniques (24, 25, 27), but it is as yet unclear how bioassay techniques might be used effectively (26). It has been demonstrated how modern techniques of organic chemical analysis can be applied to quantitative characterization of the reliability of removal of specific pollutants in GAC treatment (20). It was observed that some organic priority pollutants continue to be removed effectively even after the steady state condition of TOC removal has been attained (20). This may be caused by either strong preferential adsorption or biodegradation, depending on the substance in question and other conditions. There was general enthusiasm for enhancing the microbiological activity in GAC columns to improve and prolong the removal of organics (3, 8, 14, 36, 37), but there was disagreement on the extent to which this can be accomplished (37, 42). Indeed, it is questioned whether GAC beds are more effective than beds of granular, non-sorbing media such as sand or coal (42). The process combination of preozonation and GAC has strong proponents (3, 8, 36); the technical arguments in favor are

convincing, but it is not yet clear that preozonation effectively improves GAC performance (41). These areas of divergent opinion are the subjects of intense research intended to clarify the issues.

A consistent approach to analyzing GAC column performance results was applied herein to the data on removal of TOC and trihalomethanes presented at this Symposium. The analysis showed order-of-magnitude agreement among studies conducted under an extremely broad range of conditions. Considering the disparities in conditions, the agreement should be considered heartening. The results of European investigations fell for the most part in the mid-range of the spectrum of results of studies conducted in the U.S.A. This too is encouraging; given the substantially greater body of experience with GAC in Europe, it would be an advantage to North American specialists to be able to draw on the European experience, in confidence that conditions are sufficiently similar. Indeed, the opening of communication channels for transmitting such experience was one of the main motivations of the Symposium.

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OVERVIEW OF PROBLEM - USA PERSPECTIVE

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THOMAS C. JORLING

ASSISTANT ADMINISTRATOR FOR
WATER AND WASTE MANAGEMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY

THE PROTECTION OF DRINKING WATER QUALITY

Tom Jorling is the Assistant Administrator for Water and Hazardous Materials from the Environmental Protection Agency. He has the overall responsibility for implementation of all environmental legislation relating to water--both drinking water and surface water protection--the construction of public waste treatment facilities, and solid waste disposal activities. That is a broad responsibility. Mr. Jorling has a very appropriate background to handle that position. He is an attorney and has an advanced degree in Biology, in effect a combination of law and technology. He was instrumental in the development of clean water legislation during his term working in the Congress.

Good morning. My purpose is primarily to welcome the guests from abroad--Dr. Sontheimer and his colleagues, as well as those from many other countries. No one disputes the fact that one of the first reponsibilities of government is to assure people that the water they are consuming is safe. In the United States we have a particularly good track record in assuring safety from conventional pollutants and pathogens. Like many others throughout the world, we now are coming to grips with the problems represented by the chemical revolution on one hand, and the growing awareness on the other of the pathways and risks associated with long-term exposure to those chemicals. That theme, I think, in large measure provides the motivation for a conference such as this.

Approaches to Drinking Water Quality Regulations

Drinking water is unique. It can be contaminated at its source, during the treatment process itself, and in the distribution system. Two of those--the treatment and distribution system--

are obviously within direct control. The source, on the other hand, may not be. But we must look at the overall implications for drinking water in the context of protecting the life support systems of our people in general.

I would like to take a moment to put the safe drinking water program, which comes under the Safe Drinking Water Act, into the context of the overall protection programs of the United States as administered by EPA and the States. I think it's clear that everyone is moving more and more toward source control of contaminants, especially synthetic contaminants. In the United States, we now have some people who are beneficiaries and others, especially those in my position, who are burdened by the very marginal legislative enactments directed at one or another of the threats and risks associated with protection of our environment. Over the last 10 years we have had 16 statutes enacted or amended in the United States, dealing with this question. Thus, we have been evolving into an overall program of environmental protection.

The task of the Environmental Protection Agency, at present, is to integrate these multiple authorities into a coherent, efficient theme and program of environmental protection. I believe, and I think most people agree, that we now have about as much authority as we need, with the possible exception of legislation that the administration will be recommending on abandoned hazardous waste sites. Our task now is to use that authority to implement the intent of the legislation.

Toxic Substances Control

We start with TOSCA. For those who are not familiar with our acronyms, TOSCA is the Toxic Substances Control Act. In principle, it is directed at preventing from entry into commerce those chemicals that pose an unreasonable risk. It also has residual authority, but it is designed to operate if other regulatory programs are inadequate to deal with the problems. A similar statute is designed to control the release into the environment of those chemicals used for pesticide purposes. Under the Solid Waste Act, amended and now called the Resource Conservation and Recovery Act (RCRA), we have full authority to regulate solid waste, with particular authority for that portion of the solid waste stream that is characterized as hazardous. The Clean Water Act is directed at release of chemicals into the environment that reach surface waters. The Clean Air Act is designed to control chemical release into the ambient air. So we have a full range of authority. And into that range of authority fits the Safe Drinking Water Act programs that will be covered by some of the subjects to be discussed at this conference.

The United States is implementing the Safe Drinking Water Act in several ways. We have established maximum contaminant levels for pollutants. We are in the process of dealing with the problems of additives associated with drinking water treatment and distribution. We are presently working on an agreement with the Food and Drug Administration that will enable us to address these problems. We are addressing the questions concerning corrosion, in both treatment and distribution processes. But today's concern, obviously, is the problem of synthetic organic materials, and those organic materials which are formed in the treatment process.

Regulations

All of you know that in February, 1978, the Environmental Protection Agency proposed regulations for control of trihalomethanes. These compounds, as well as being harmful themselves, are indicators of a multitude of other chemical contaminants formed during the treatment of water by reaction of chlorine with the naturally present organic substances. Moreover, EPA proposed requiring the use of treatment technology, such as granular activated carbon (GAC), to control the presence of other synthetic organic chemicals that reach the public drinking water through contaminated surface and ground-water supplies. There has been intense controversy concerning those two sets of regulations. The public comment period closed last fall. We have been evaluating those comments along with the written and oral comments we have received, and we will be translating these comments into a formal promulgation.

A great deal of controversy surrounds the subject of this meeting, so I personally look forward to the dialogue here. I must say one of the most frustrating aspects of my present job is my inability to stay through a session like this. I must, in fact, return to my office to convince the Governor of Mississippi that EPA was not responsible for the floods in Mississippi. I'm not sure I'll be able to succeed, but I do have to leave.

I do want to welcome you. I look forward to the proceedings of this conference because they are extremely important. Dealing with drinking water is a very controversial and yet a very significant responsibility of public officials. It's one that no one takes lightly, certainly no one in EPA. We will be as thorough as we can in the regulatory process, and much of what is to be said here bears on that kind of regulatory program. I welcome you and hope that you have a pleasant and very informative session. Thank you very much.

DR. COTRUVO: What would you say is your impression of the feelings of Congress and the present Administration on dealing with environmental quality matters? As we all know, there are pressures developing which include energy problems and inflation. What would you say is the mood of the Congress and the Administration?

JORLING: That's an open-ended question and one that I would have to answer personally rather than from my official position, although my perception is a function of that position and bears on the answer. In my opinion, the Administration's posture toward environmental protection is unchanged, unchanged from the President's earliest commitment before taking office. I also think that, in general, that position will prevail in Congress. That's not to say that there aren't many who are looking for easy answers to some of the more difficult problems that are facing our industrial society and all industrial societies, namely inflation and shortages of energy. There is a lot of rhetoric and dialogue, especially from very outspoken individuals both in Congress and the Executive Branch, concerning benefits and costs. But as a general matter, I do not expect any change in Congress or in the Administration to the commitment that both have given, historically, to environmental protection and public health problems. I think we will go through a phase when people will raise concerns about the benefits and costs, and empirical benefits versus the empirical costs. I do not, however, think it will change the basic thrust of our regulatory programs, including those under the Safe Drinking Water Act.

VICTOR KIMM

DEPUTY ASSISTANT ADMINISTRATOR
FOR DRINKING WATER
U.S. ENVIRONMENTAL PROTECTION AGENCY

U.S.A. POSITION--HISTORICAL AND REGULATORY

Mr. Victor Kimm is the Deputy Assistant Administrator for Drinking Water for EPA. He reports to Mr. Jorling and is specifically responsible for applying the Safe Drinking Water Act in all of its facets. Mr. Kimm has been in Government service for approximately 15 years. He is an engineer, has had experience and training in public policy in many respects, has been in the Safe Drinking Water Program since its beginning in 1974, and has carried it through to the present controversies in which we find ourselves.

I would like to welcome all those in attendance. To our good friend Professor Sontheimer, I would like to say that there's no way on earth that we're going to come close to matching the hospitality we received at the Oxidation Conference at Karlsruhe in 1978. Nevertheless, we hope to enlighten as well as entertain the participants. When we reviewed the program on Friday, we concluded that we had crammed at least a week's conference into a few days, and I suspect that those of you who stay with us for our evening and other activities, will discover this may become somewhat of an endurance test. At any rate, we hope that we can make these days as meaningful as possible for everyone.

Historical Perspective

There is a historical link to the challenges now facing water supply professionals throughout the industrial world and, in particular, the United States; fate has us at a very important crossroad. The primary public health concern at the turn of the century was about contaminants that had acute, immediate effects on public health. In the present context, we find ourselves becoming increasingly concerned about those contaminants

which do not have immediate effects, for which there are no clear linkages, but which nevertheless, have potentially serious risks that are a challenge to the public health world today. In 1900, in the United States, 36 deaths out of every 100,000 were attributed to typhoid. On a per capita basis, that corresponds to more than we currently lose to automobile accidents. It clearly was a major cause of death in the United States. With the advent of filtration and disinfectant practices that started in the early part of this century, and as those practices became more widely used, typhoid was virtually eliminated. This is often cited as one of the great public health benefits of the 20th century.

In regard to the current set of concerns in public health, the application of more sophisticated analytical techniques, beginning in the early 1970's, enabled us to inspect the organic fraction in drinking water and to identify and quantify a variety of contaminants. We then began investigating both the long-term health significance and the sources of such contaminants, as well as seeking ways of reducing the public's exposure to these materials. Simply stated, the contaminants have often been categorized into two basic groups: (1) trihalomethanes and other halogenated organic materials which arise as byproducts of conventional disinfection with chlorine, and (2) other man-made chemicals that are finding their way into drinking water through contamination of water sources. The second category is a byproduct of our chemical revolution; as mentioned earlier, approximately 20,000 chemicals are produced, commercially, in significant quantities. Enormous amounts of chemicals are transported via our major waterways, which are often used as drinking water sources. Spills and unplanned discharges pose serious problems that we face periodically. The effects are clearly significant and of major concern. The work done in the last few years has given us a better picture of the levels of the contaminants that confront us and of the almost overwhelming dimensions of the trace organic contaminant problems, when considered nationwide. Several papers in this Conference will give current data related to these problems.

When reviewing what we really know about the problem, we must realize that only a small portion is uncovered--at best, 30 percent of the total organic fraction can be identified as specific compounds. In many instances, we are dealing with chemical and physical phenomena that are just now beginning to be studied carefully and understood.

Regulatory Approaches with Respect to Technology

A regulatory problem can be approached by considering maximum contaminant levels or required treatment practices. I do not

wish or plan to rekindle the heated debate which we have had, over the last year, on the regulations, but merely to provide a context for our discussion of technology during the next few days. The need for reducing exposure to trihalomethanes has been generally accepted. The technology for reducing trihalomethanes is very similar to what we have used in the past and does not seem to present a problem as serious as the proposed use of granular carbon or equivalent alternatives. Adsorption techniques have not been widely used for drinking water treatment in the United States thus far; they have been used more elsewhere in the world. We will hear a great deal more about these technologies during this Conference. They are effective and they offer, in our judgment, a significant step in the direction of eliminating objectionable materials from our drinking water.

The National Academy of Sciences has listed some 22 carcinogens that have been detected, at least once, in drinking waters in the United States; two additional carcinogens have been added to the list since it was published. We anticipate that the list of chemicals will grow over the next few years as more and more specific materials are tested. We are relying on what has been the health community's guiding principle for at least a decade, namely to reduce human exposure to carcinogens to the degree that is feasible. Over the next few years, we must expect that the number of compounds of specific and immediate health concern will continue to grow, barring a major breakthrough on the health side. Faced with that, and in collaboration with other water supply professionals from all over the world, we are trying to determine the most effective means of reducing exposure to these materials. The effects are not immediate, and it is difficult to establish a link to adverse health effects. Nonetheless, these effects are deeply serious and of major public health concern.

I hope that in the next few days, as we review the experience of other countries, we may come to realize that the European experience with regard to use of granular activated carbon is somewhat different from what we are familiar with here in the States. I think that there will be many examples brought forth to show that many of the technical problems with deep-bed GAC filters and on-site regeneration facilities have, in fact, been overcome in a number of countries. There have been many, many years of experience in implementing this type of process, even though this has not been practiced extensively in the United States.

Much is known, yet much needs to be developed. I think that solving the technical problems associated with controlling trace organic contaminants is a major concern to all of us. EPA's role is: to support long-term research; to disseminate information; and, as we move into utility level experimentation and development, to provide technical assistance. The water utility

industry also will need to conduct pilot studies and research, to apply innovatively new technologies, and to maintain a continuing dialogue with the rest of the water supply profession. Together, Federal and State Government, industry, utilities and suppliers, and the professional engineers who support these activities can learn to effectively control trace organic contaminants in our drinking water. Thank you.

NATIONAL ACADEMY OF SCIENCE REPORT AN EVALUATION OF ACTIVATED CARBON FOR DRINKING WATER TREATMENT*

I.H. Suffet

INTRODUCTION

The National Academy of Science report on the use of activated carbon for drinking water treatment was divided into six major areas:

I. Adsorption Efficiency of Granular Activated Carbon (GAC) - discusses removal of organic compounds of health concern, effectiveness of pretreatment for removal of organic compounds, and competitive adsorption between organics in laboratory, pilot plant, and full scale plant operations.

II. Microbial Activity on GAC - discusses the extent of interaction of microbial activity with the adsorption process, the effect of pretreatment disinfectant processes, and the impact of microbial colonization on the water treated.

III. Production of Nonbiological Substances By or Within the GAC Bed - discusses the carbon surface in relation to catalytic reactions and reaction with disinfectants.

*Safe Drinking Water Committee of the National Research Council - Subcommittee on Adsorption - Chairman - I.H. Suffet - Members - M. Alexander, Cornell University, Ithaca, N.Y.; J.T. Cookson, JTC Environmental Consultants, Washington, D.C.; F. DiGiano, U. Mass., Amherst, Mass; R. Kunin, Consultant, Yardley, Pa.; J. Shands, U. Florida, Gainesville, Fl.; V.I. Snoeyink, U. Illinois, Urbana, Ill; M.J. McGuire, Brown and Caldwell, Pasadena, Ca. (Consultant)

Safe Drinking Water Committee: Chairman - J. Doull, U. Kansas Medical Center, Kansas City, Mo.; Safe Drinking Committee Staff - R. Housewright, R. Golden and R. Widdus

See complete report for all data (NAS, 1979)

IV. Regeneration of GAC - discusses the change of GAC including chemical leaching of GAC.

V. Adsorption Efficiency of Other Adsorbents - discusses the removal of humic substances by ion exchange resins and the removal of organic compounds of health concern by polymeric adsorbents.

VI. Analytical Methods to Monitor Adsorbent Unit Processes in Water Treatment - discusses monitoring of adsorbent processes by specific and nonspecific organic analysis for chemicals of health concern.

The results of the report are presented with the objective of defining the efficacy of adsorbents. The report did not evaluate toxicological, epidemiological, or economic and plant design aspects of the problem.

It is known that raw water sources and disinfected water supplies may contain organic compounds that have been demonstrated to be carcinogenic or otherwise toxic to experimental animals or in epidemiological studies. Many other compounds that are also present either have not been identified or their effects on health have not been characterized. At present, the compounds of known concern are synthetic organic chemicals or compounds produced by disinfection of potable water supplies. Lists of chemicals of health concern have been defined in a series of sources: (1) Categories of Known or Suspected Organic Chemical Carcinogens Found in Drinking Water (NAS, 1977, p. 794), (2) Carcinogens and Suspect Carcinogens in Drinking Water (NCI, 1978), (3) List of Chemicals Submitted by EPA for Evaluation by the Safe Drinking Water Committee Toxicology Subcommittee (NAS, 1979), (4) Interagency Regulatory Liaison Group Target List (IRLG, 1978), (5) Pesticides with established maximum contaminant levels (MCL's) (US EPA Interim Drinking Water Standards, 1975) and (6) Trihalomethanes (THM's) with proposed composite maximum contaminant level (MCL) values (US EPA 1978a). Table 1 shows an edited compilation from these lists.

The list of chemicals submitted by the EPA for evaluation by the Safe-Drinking Water Subcommittee on Toxicology added 5 compounds (Table 2), to the 22 Known or Suspected Organic Chemical Carcinogens Found in Drinking Water (NAS, 1977). Also, this subcommittee developed Suggested No Adverse Response Levels (SNARL's) on acute exposure for 27 synthetic organic chemicals. (Table 2 lists the SNARL's.)

Table 1. Available Adsorption Data for Organics of Health Concern[a]

Organic compounds	Molecular weight	Number of data points	Carbon type	Adsorption test method	Equilibrium concentration range mol/l	Maximum surface concentration, mol/g	Comments	Reference
Acrylonitrile	53.06	2	Unknown	Unknown	1.4×10^{-3}-9.2×10^{-3}	9.6×10^{-4}	Procedure unknown	Dahm et al., 1974
Aldrin	365	6	F300	Isotherm	2.5×10^{-9}-7.1×10^{-8}	3.0×10^{-5}		Mahon, 1979
Benzene	78.11	5	F400	Isotherm	2.6×10^{-5}-1.3×10^{-4}	3.4×10^{-3}		Fochtman and Dobbs, 1979
Benzo(a)pyrene	252.3	2	Norit NK	% reduction	Unknown	99.8% removal	Review article	Borneff, 1979
α-BHC	290.85	Unknown	Unknown	% reduction	Unknown	80% removal	Abstract	Schmidt, 1974
γ-BHC(Lindane)	290.85	1	OU-A	% reduction	7×10^{-8}	1×10^{-4}	Translated abstract	Shevehenko et al., 1974
Bis(2-chloroethyl)ether	143.01	11	F300	Isotherm	4.2×10^{-5}-1.2×10^{-4}	1.2×10^{-3}	pH 7 and 9 data pooled	Dobbs, et al., 1978
Bromodichloromethane	163.83	7	F300	Isotherm	7.9×10^{-9}-3.5×10^{-7}	1.3×10^{-5}		Dobbs et al., 1978
Bromoform	252.75	15	F400	Isotherm	2×10^{-8}-1.3×10^{-6}	1.0×10^{-4}		Weber et al., 1977
Carbon tetrachloride	153.82	11	F400	Isotherm	3×10^{-9}-2.6×10^{-7}	2.6×10^{-5}		Weber et al., 1977
Chlordane	764	3	F300	Isotherm	1.0×10^{-9}-2.3×10^{-8}	5.1×10^{-5}		Hansen, 1979[b]
Chlorobenzene	112.56	7	F300	Isotherm	1.2×10^{-5}-1.5×10^{-4}	1.5×10^{-2}		Dobbs et al., 1978
Chlorodibromomethane	208.29	7	F400	Isotherm	7.2×10^{-9}-1.9×10^{-7}	1.5×10^{-5}		Dobbs et al., 1978
Chloroform	119.38	7	F400	Isotherm	2.8×10^{-8}-1×10^{-6}	1×10^{-5}		Weber et al., 1977

Table 1. Available Adsorption Data for Organics of Health Concern[a] (continued)

Organic compounds	Molecular weight	Number of data points	Carbon type	Adsorption test method	Equilibrium concentration range mol/l	Maximum surface concentration, mol/g	Comments	Reference
DDE	318	5	F300	Isotherm	3.5×10^{-9}-1.1×10^{-7}	1.6×10^{-5}		Mahon, 1979
DDT	354.5	2	F300	Isotherm	1.0×10^{-8}-5.9×10^{-8}	2.3×10^{-5}		Mahon, 1979
Dichlorobenzene	147.01	3	F300	Isotherm	2.7×10^{-5}-6.8×10^{-5}	1.4×10^{-3}	1,4-dichloro-benzene	Mahon, 1979
1,2-Dichloroethane	98.96	7	F300	Isotherm	1.7×10^{-7}-6.6×10^{-7}	6.9×10^{-6}		Dobbs et al., 1978
2,4-Dichlorophenoxy-acetic acid (2,4-D)	221	Unknown	Aqua Nuchar A	Isotherm	2×10^{-7}-2×10^{-6}	4×10^{-4}	Sodium salt	Aly and Faust, 1965
Dieldrin	381	6	F300	Isotherm	2.1×10^{-10}-1.7×10^{-8}	1.7×10^{-5}		Mahon, 1979
1,4-Dioxane	88.12	8	F400	Isotherm	2.5×10^{-5}-1.5×10^{-3}	2.6×10^{-4}		McGuire et al., 1978
1,1-Diphenylhydrazine	184	5	F400	Isotherm	2.2×10^{-6}-4.9×10^{-5}	8.1×10^{-4}		Fochtman and Dobbs, 1979
Endrin	381	6	F300	Isotherm	1.8×10^{-10}-3.9×10^{-8}	6.2×10^{-5}		Mahon, 1979
Halogenated phenols (eg. pentachlorophenol)	266.4	5	F300	Isotherm	1.7×10^{-6}-2.9×10^{-5}	2.1×10^{-3}	Pentachloro-phenol, pH3	Dobbs et al., 1978
Heptachlor	373.3	2	F300	Isotherm	1.6×10^{-8}-1.5×10^{-7}	3.3×10^{-5}		Mahon, 1979
Heptachlor epoxide	389	Unknown	Unknown	% reduction	Unknown	>80% removal	Abstract	Schmidt, 1974
Hexachloroethane	236.74	1	F300	Column recovery	Unknown	Amount of carbon not specified	100% removal 100 ug/l influent	Chriswell et al., 1977
Methoxychlor	346	Unknown	Unknown	% reduction	Unknown	>80% removal	Abstract	Schmidt, 1974
Methylene Chloride (Dichloromethane)	84.9	17	F400	Isotherm	1.7×10^{-5}-5.0×10^{-5}	5.8×10^{-5}		Weber et al., 1977

Table 1. Available Adsorption Data for Organics of Health Concern[a] (continued)

Organic compounds	Molecular weight	Number of data points	Carbon type	Adsorption test method	Equilibrium concentration range mol/l	Maximum surface concentration, mol/g	Comments	Reference
Nitrosamines (eg N-Nitrosodiphenylamine)	198.07	17	F300	Isotherm	$5.0x10^{-8}$-$3.5x10^{-5}$	$2.2x10^{-3}$	N-Nitroso-diphenylamine	Dobbs et al., 1978
Polychlorinated biphenyls (PCB) (eg Arochlor 1254)	Mixture	6	F300	Isotherm	0.5ug/1-37ug/1	6.4 mg/g	Arochlor 1254	Mahon, 1979
Polynuclear aromatic hydro-carbons	Eight compounds	-	10 types	% reduction	ppb level	Variable	99% removal; Review Article	Borneff, 1979
Simazine	201.69	1	OU-A	% reduction	$7x10^{-7}$	$4x10^{-4}$	Translated abstract	Shevenhenk et al., 1974
Tetrachloroethylene	165.83	10	F400	Isotherm	$6x10^{-10}$-$2.5x10^{-8}$	$6x10^{-5}$		Weber et al., 1977
Toluene	92.15	4	F300	Isotherm	$1.7x10^{-5}$-$4.8x10^{-5}$	$9.5x10^{-5}$		Mahon, 1979
Toxaphene	412	Unknown	F300	Isotherm	$5x10^{-8}$-$4x10^{-7}$	$1x10^{-4}$		Hager and Rizzo, 1974
1,1,1-Trichloroethane	133.41	-	F300	Isotherm	$2.7x10^{-6}$-$1.2x10^{-3}$	$2.7x10^{-3}$		Hansen, 1979[b]
Trichloroethylene	131.39	7	F300	Isotherm	$1.1x10^{-9}$-$4.8x10^{-7}$	$4.2x10^{-5}$		Dobbs et al., 1978
2,4,5-Trichloro-phenoxypropionic acid (2,4,5-TP)	269	Unknown	Columbia LC	Isotherm	Unknown	Unknown	Follows Langmuir Isotherm	Weber and Gould, 1966
Xylene	106.2	4	F300	Isotherm	$1.4x10^{-5}$-$1.1x10^{-4}$	$1.2x10^{-3}$	Para isomer	Dobbs et al., 1978

Note: All values are for neutral forms of the molecules unless stated otherwise.

[a] There are no GAC data available for the following organic chemicals of concern to health: β-BHC, bis(2-chloropropyl)ether, butyl bromide, dibromochloropropane, 1,2-dibromoethane, dichlorofluoromethane, 1,1,-dichloroethene(vinylidene chloride), epichlorohydrin, ethylenethiourea (ETU), ethylene dibromide, ethylene oxide, kepone, methyl iodide, pentachloronitrobenzene (PCNB), polybrominated biphenyls(PBB), 1,1,2-trichloroethane, trichlorofluoromethane and vinyl chloride.

[b] Personal Communication.

Table 2. Summation of Acute and Chronic Exposure Levels and Carcinogenic Risk Estimates of Chemicals Reviewed

Chemical	Suggested No Adverse Response Level (SNARL) mg/l — Exposure Period: 24-hour	7-day	Chronic	Upper 95% Confidence Estimate[a] of Lifetime Cancer Risk Per ug/l
Acrylonitrile				1.3×10^{-6}
Benzene		12.6		
Benzenehexachloride	3.5	0.5		
Cadmium		0.08	0.005	
Carbon tetrachloride	14	2.0		
Dichlorodifluoromethane	350	5.6		
1-2-Dichloroethane				7.0×10^{-7}
Epichlorhydrin	0.84	0.53		
Ethylene dibromide				9.1×10^{-6}
Methylene chloride	35	5.		
Polychlorinated biphenyl	0.35	0.05		
Tetrachloroethylene	172	24.5		1.4×10^{-7}
1,1,1-Trichloroethylene	105	15		
Trichlorofluoromethane	88	8		
Toluene	420	35	0.34	
Uranium	3.5	0.21		
Xylenes	21	11.2		
Bromide	1400	224	2.3	
Catechol	2.2			
Chlorine dioxide			0.38	
Chlorite		0.21		
Chloroform	22	3.2		
Dibromochloromethane	18			
2-4-Dichlorophenol			0.7	
Hexachlorobenzene		0.03		2.9×10^{-5}
Iodide	115.5	16.5	1.19	
Resorcinol	11.7	0.5		

Note: See Drinking Water and Health (NAS, 1977) for details; Safe Drinking Water Committee - Subcommittee on Toxicology, headed by S. Murphy, U. Texas Medical School, Houston, Texas (NAS, 1979).

[a]An addition to the List of Known or Suspected Organic Chemical Carcinogens found in Drinking Water (NAS, 1979).

Human exposure data and sublethal animal data were used to develop single agent SNARL exposures.

ADSORPTION EFFICIENCY OF GAC

The adsorption efficiency of GAC includes the following major topics of study: Efficiency of GAC to Adsorb µg/l Quantities of Organic Compounds of Concern to Health, Effects of Pretreatment on GAC Treatment, and Competitive Effects on GAC.

This discussion includes competitive effects between trace organics, competition between humics and organics, and displacement vs. re-equilibrium effects.

Efficiency of GAC to Adsorb Organics of Concern to Health

The efficiency of adsorption of many organic compounds is shown in Figure 1 for over seven orders of magnitude of equilibrium concentration (McGuire and Suffet, 1979). The shaded area represents an attempt to describe a general isotherm. At relatively high equilibrium concentrations, C_e (depending on how well a compound is adsorbed), the slope of the isotherm is relatively flat. As the equilibrium concentration decreases, the slope increases until it becomes equal to 1.0, indicating compliance with Henry's law of adsorption (Radke and Prausnitz, 1972). The more poorly adsorbed compounds (urea for example) have a slope of 1.0 at high C_e values. The compounds which are more strongly adsorbed have a slope of 1.0 at much lower C_e values. For example, the isotherm for 2,4,6-trichlorophenol was determined over five orders of magnitude and the maximum slope is only 0.592 at 10^{-8} moles/l. Figure 1 also shows that for the isotherms determined on a comparative basis, substituted phenols adsorb much better than low molecular weight chlorinated organic compounds.

Our understanding of how specific organic compounds are adsorbed is generally derived from the work on well adsorbed, substituted phenols at mg/l concentrations. Figure 1 indicates that the poorly adsorbed and even the moderately well adsorbed compounds have steep slopes at the µg/l level (1×10^{-9} to 10×10^{-9} moles/l). Reducing compound concentrations two orders of magnitude into the ng/l range requires a much larger carbon dose or longer column contact time than a two-order-of-magnitude decrease at the mg/l level. Thus, reduction to subtrace levels of these specific organics of health concern is more difficult than would normally be expected based on the current understanding of the adsorption of organic compounds.

Although the isotherms in Figure 1 were determined by different investigators using different techniques and different carbons, there is surprising agreement between isotherms for the same compound. Clearly, other aspects of the experimental

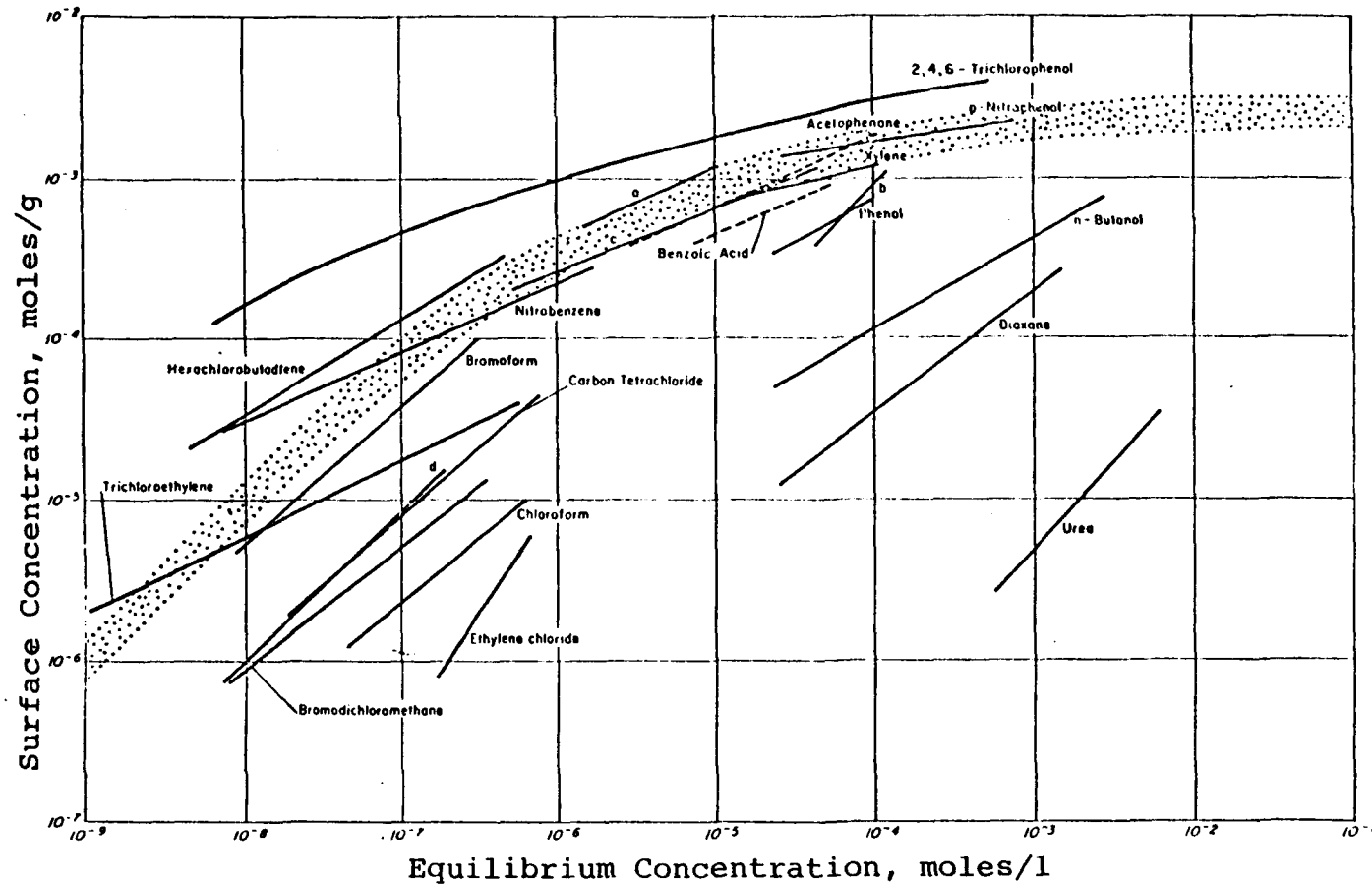

Figure 1. General and Specific Adsorption Isotherms
a)(Di)-n-butyl phthalate b)Bis(2-chloroethyl) ether
c)Dimethyl phthalate d)Dibromochloromethane

conditions including carbon type and water quality, affects the positions of the isotherms (McGuire, et al, 1978).

Available adsorption data for organics of health concern are shown in Table 1. Table 1 indicates that there are adsorption data pertaining to 40 of the 58 specific organics and classes of organic compounds on the lists. The data illustrate that a great number of the chemicals of concern are adsorbable on activated carbon; essentially all of the compounds tested have been shown to be adsorbable to some extent. However, competitive effects will be important in determining the capacity observed in specific water treatment applications. The isotherm data base should be expanded to provide the basic data for the adsorption characteristics of chemicals that are potentially harmful to health. Isotherms and mass transfer models have been reviewed by McGuire and Suffet (1978). These models, hopefully, will one day enable prediction of breakthrough curves of single solutes in multi-solute systems.

Effects of Pretreatment Steps on GAC Treatment

Because pretreatment processes remove adsorbable organic matter and consequently reduce the subsequent rate of saturation of the GAC column, these processes should be used to their maximum extent. Lowering the organic concentration will also result in a lower GAC regeneration frequency, less competitive adsorption, and lower demand for a disinfectant which could form undesirable end products. Table 3 shows the general positive effects of pretreatment steps on Total Organic Carbon (TOC), THM precursors, and specific organics. The application of powdered activated carbon (PAC) before GAC may be advisable in situations involving spills of specific chemicals. It is recommended that an adsorption process should be evaluated together with a clarification process that precedes it in a water treatment plant. In some cases, the removal of THM precursors by flocculation and clarification may be sufficient, eliminating the need for an adsorption process.

Competitive Effects on GAC

Competitive adsorption effects on GAC are created by the variability of a wide spectrum of trace organics which are found together in water supplies and generated within the treatment process (Suffet, et al, 1978a). Dynamic situations in GAC beds can be complicated due to a variety of competing species which have different adsorbabilities and concentrations. The variability of specific organics which can enter a water treatment process, their relative concentrations, their degree of competition, i.e., stronger vs. weaker adsorbing components, and their relative diffusion properties will influence displacement effects. Even if organics do not compete, shifts in influent

Table 3. The Effect of Pretreatment on the Removal of Adsorbable Organic Matter

METHOD	
COAGULATION - SEDIMENTATION AND FILTRATION	
A. Lower loading rates (25%-65% TOC),	(Kavanaugh, 1978; Semmens, et al, 1978)
B. Lower THM precursors ($\geq$ 70%)	(Babcock & Singer, 1977)
C. Lower specific organics -	
Phenols	(Sridharan & Lee, 1972)
Pesticides	(Robeck, et al, 1965)
Polyaromatic Hydrocarbons	(Andelman, 1973)
AERATION-VOLATILES - Needs study	
BANK FILTRATION - (< 65-76% DOC)	McCreary and Snoeyink, 1977)
PAC - Needs study	

concentration will cause the effluent concentration to re-equilibrate with it. The extent of the re-equilibration will be determined by adsorption equilibria in each case. Depending upon the relative concentrations of these organics, displacement also can lead to temporarily higher concentrations in the effluent of the GAC bed than in the influent for any given species.

Competition can be anticipated between trace organics, which account for only a small fraction of the TOC, and the majority of TOC, which is comprised of humic substances. It must be noted, however, that humic substances will vary in adsorption properties, thereby making competitive interactions more difficult to predict. Table 4 shows examples of competitive interactions between humic substances and trace organics (Snoeyink, et al, 1977). The data show why musty odors of methylisoborneol (MIB) and geosmin can be removed for many years, as these compounds compete favorably with humic substances. Because the source of humic substances may be different for each water supply and, in fact, seasonally variable, pilot plant studies at specific locations over the seasons of the year will yield the most useful information on the effects of competition. More basic data are needed in this area.

Table 4. Competitive Effects Between Humic Substances and Organics

COMPONENTS	EQUILIBRIUM CONCENTRATION RANGE	RELATIVE EXTENT OF COMPETITIVE DISPLACEMENT
Trichlorophenol (TCP)-Humic Substances[a]	10-50 mg/l 10^{-6} - 10^{-5} M	TCP >> Humic Substances
Humic Substances-Methylisoborneol (MIB)	10-100 mg/l 0.1-100 µg/l	MIB >> Humic Substances
Humic Substances-Geosmin	10-40 mg/l 0.1-100 µg/l	Geosmin >> Humic Substances
Humic Substances-Benzanthracene	10-100 mg/l 1-10 µg/l	None

[a]Aldrich Co.
After Snoeyink, et al., 1977.

The wide spectrum of organics that have been identified in water supplies represent an equally wide spectrum of adsorption behavior. This should also lead to competition among organics of differing adsorbabilities for sites on the carbon surface. However, there is little information on the mutual reduction in adsorption capacity for competing organics in the truly multicomponent mixtures that are encountered in drinking water treatment. The direct information provided by the pilot plant study seems to be an alternative to the more scientific, but as yet underdeveloped, approach that is provided by mathematical modeling of competitive adsorption.

The most immediate and presssing need is to determine whether significant displacement of any organics of health concern occurs in the operation of GAC beds for treatment of drinking water. The subcommittee recommends that even with the identification of those trace organics of concern in the raw water supply and measurement of their concentrations, including the concentration variability, pilot plant studies will still be necessary to confirm the relative order of breakthrough of each contaminant and to assess the importance of any displacement effect. This displacement effect can be caused both by a variable influent composition and by competitive adsorption. Although it is difficult to distinguish between these two causative factors in pilot plant studies, every effort should be made to determine which is more important.

MICROBIAL ACTIVITY ON GAC

The microbial activity on GAC includes the following major topics of study:

- Interaction of Microbial Activity with Adsorption on GAC
- Effects of O_3 vs. Cl_2 Pretreatment on Microbial Activity on GAC
- Impact of Microbial Colonization on Drinking Water, including:
  - Microbial Contamination of Drinking Water
  - Microbial Products
  - Microbial Toxins

Interaction of Microbial Activity with Adsorption on GAC

Electron micrographs provide clear evidence of the presence of microorganisms on the surface of GAC (Weber, et al., 1978; McElhany and McKeon, 1978). The types and number of microorganisms will depend upon the amount and nature of the available substrates. Table 5 divides organics in four categories of adsorbability and degradability. While the classification is simple, it also is ambiguous because the term nonbiodegradable is not easily defined. The term recalcitrant, rather than non-biodegradable, has been used by Alexander (1973) to describe substances that persist for extended periods under all environmental conditions thus far tested. Alexander (1973) lists 15 possible mechanisms to explain recalcitrance.

The organics that are most likely to be attacked microbially fall into the non-adsorbable, biodegradable category (Table 5). In treatment with GAC, these organics could be removed by the biofilm surrounding the carbon granules without affecting the adsorption process. The adsorbable, biodegradable category (Category 4, Table 5) of organics is of more interest because of the strong interaction expected between biological and adsorption processes (Ying and Weber, 1978; Tien, 1978; Benedek, 1977). This sets GAC apart from sand or other nonadsorbing media.

In water treatment, the removal of adsorbable, biodegradable organics (Category 4, Table 5) by microbial activity, rather than by adsorption, enhances the opportunity for the GAC bed to remove the adsorbable, nonbiodegradable organics (Category 3, Table 5). Category 3 is generally of the most concern because it contains many of the synthetic organics that are suspected carcinogens. Thus, the question of whether or not GAC can be regenerated biologically needs to be addressed. The evidence reported thus far is incomplete and contradictory.

Table 5. Interaction of Microbial Activity with Adsorption on GAC

Category	Adsorbability	Degradability
1[b]	Non	Non
2[b]	Non	High
3[a]	High	Non
4[b]	High	High

[a] Synthetic Organic Category-Chlorinated Organics

[b] More sites for category 3, the organics of health concern shown in Table 1.

While the GAC bed is a suitable environment for microbial activity, questions regarding which specific organics are biodegradable and at what rate also remain unanswered by research. In addition to accessibility, the concentration of the substrate is an important factor. Clearly, many organics of concern are present in drinking water in such low concentrations that the opportunities for microbial action may be quite limited unless adsorption occurs first; however, adsorption into the pores of GAC may prevent biodegradation if the substrate becomes inaccessible to the microorganism. One factor which could influence substrate availability is re-equilibration when influent concentration decreases in a dynamic situation. In this case, sorbed substrate could be released and once again become available to microorganisms.

Category 3 from Table 5 (adsorbability and nondegradability) is the area of particular interest for organics of health concern. No direct evidence has been given for removal of specific organics of health concern by microbial activity. Only one study (at the Jefferson Parish Water Works, which was reported by Brodtmann, et al., 1979), implied that precursors to THM formation were removed by microbial action. An indirect benefit of microbial activity may be the lengthening of GAC service time by removing organics that would otherwise occupy adsorption sites, but this in itself does not imply more effective removal of organics of health concern.

Much of the recent interest on the effect of microbial activity and GAC performance stems from European research and experience. While operation of GAC beds for 6 months to 2 years without regeneration has shown that microbial activity removes organics as measured by group parameters, such as TOC, potassium permanganate demand, chemical oxygen demand (COD), and UV-absorbance, the efficiency of biodegradation is less than that of adsorption. Removal of about 1.5 mg/l TOC by microbial degradation requires about 30 minutes of GAC contact (Eberhardt, et al., 1974; Jekel, 1977; Benedek, 1977) while adsorption only requires approximately 10 to 15 minutes.

More careful investigation is needed to determine if adsorbed organics, which are more resistant to biodegradation, can be acted upon by microbes.

Effects of Ozone vs. Chlorine Pretreatment on Microbial Activity on GAC

Miller, et al. (1978) and Benedek (1977) have reviewed pilot scale tests of preozonation before GAC at Bremen, Amsterdam, and Morsang-Sur-Seine and full scale tests at Düsseldorf, Mülheim, and Rouen-la-Chapelle. These tests have shown that organics, measured by collective organic parameters (e.g., TOC:UV) are efficiently removed through the total system, including the flocculation and adsorption steps; however, the ability of microbial action to aid in removal of specific organics of health concern was not reported. Thus far, one study, at the U.S. EPA Cincinnati pilot plant (U.S. EPA 1978b) implied that precursors to THM formation were somehow altered by ozonation in such a manner that their removal was made more effective.

The role ot ozone in promoting microbial activity remains unclear. Conversion of organics to more biodegradable forms and addition of oxygen to the biofilm are two advantages implied by Rice, et al. (1978) and Sontheimer, et al. (1978). On the negative side, less adsorbable, polar organics, such as carboxylic acid and aldehydes have been identified in drinking water (Safe Drinking Water Subcommittee on the Chemistry of Disinfectants NAS, 1979). Benedek (1977) also shows that ozone may decrease the adsorbability of some organics.

While prechlorination does not stop microbial growth on GAC, there is some evidence to suggest that it results in the formation of chlorinated organics (Safe Drinking Water Subcommittee on the Chemistry of Disinfectants, NAS, 1979). These organics are considered much more resistant to biodegradation on the GAC surface (Sontheimer, et al., 1978). Studies are needed to determine the changes in biodegradability and adsorbability which are brought about by ozonation or chlorination of specific organics of concern to public health.

Impact of Microbial Colonization on Drinking Water

The attachment of microbes to GAC surfaces has been described by Marshall (1976) and Daniels (1972). Data from studies on microbial numbers in effluents of GAC filters indicate detachment is a negligible problem, controllable by backwashing (Eberhardt, et al., 1974; Klotz, et al., 1976; Mueller and Bernhardt, 1976; Sontheimer, et al., 1978; Schalekamp 1976).

Microbial Contamination of Drinking Water--

The bacteria that have been reported on GAC beds are considered nonpathogenic. Genera identified include Flavobacterium and Xanthomonas (U.S. EPA, 1978b); Acinetobacter, Pseudomonas, Caulobacter, coryneforms, Flavobacterium, Alcaligenes, actinomycetes, Bacillus, Planctomyces, and Moraxella (Ben Blanken, 1978); Pseudomonas, Enterobacter agglomerans, Acinetobacter, Alcaligenes faecalis, Moraxella, and Flavobacterium (Love and Symons, 1978, reporting the work of Parsons), and ten species of Pseudomonas (McElhaney and McKeon, 1978). Although it is unlikely, the possibility that some pathogens may be able to colonize GAC beds should be tested. Of primary importance are enteric pathogens, such as Salmonella, Shigella, Vibrio, Yersinia enterocolitica, and the enterotoxigenic E. coli.

Microbial Products--

The published research does not indicate which compounds are or are not acted upon by microbial activity on GAC and what compounds may be generated as a consequence of bacterial growth. Attention has been focused on bulk organic materials in water and not on discrete classes of molecules.

Microorganisms can generate a variety of highly potent, low molecular weight toxicants in culture. Studies of several model environments and some natural systems indicate that toxicants may be or are indeed formed during GAC treatment (Boethling and Alexander, 1979).

Microbial Toxins--

Endotoxins are lipopolysaccharides from gram-negative bacteria. Endotoxin levels in water that have been filtered through GAC are either not increased or not significantly increased (Love and Symons, 1978 and Jorgenson, et al., 1976). The measured levels are very low and should pose no risk.

Discussion of Microbial Activity on GAC

If the use of GAC is to become widespread, research is necessary to identify the factors that are responsible for the initiation of microbial growth on the GAC surface and the microbiological generation of organic compounds during carbon treatment. Attention should be given to the compounds that are present and retained in the bed as well as to those that are

released and could appear in the effluent. Research should be directed toward compounds generated from innocuous, natural precursors as well as toward those that may be formed as a result of microbial action on synthetic organic chemicals. The investigation should identify the specific organic molecules thus formed and not simply the quantity of organic carbon that is emitted from GAC. The toxicological significance of such compounds and the possibility of their occurrence in concentrations sufficiently high to be of concern to public health should be assessed.

PRODUCTION OF NONBIOLOGICAL SUBSTANCES BY OR WITHIN THE GAC BED

One potential source of chemical breakthrough from a GAC column is chemical change on GAC surfaces. This section evaluates the significance of this potential source of toxic organic chemicals in drinking water. Few studies have addressed the ability of carbon to catalyze reactions producing new chemical components and their release to water that is being purified for human consumption. Emphasis has been placed on adsorption and removal. Table 6 shows examples of physiochemical interactions on GAC. It appears that reactions on GAC involve surface oxides and other impurities in the carbon structure (Cookson, 1978). Surface oxides are formed for example by the reduction of disinfectants.

Table 6. Physiochemical Interactions on GAC

1.	CATALYSIS BY GAC - Bush -S-S- (Ishizaki and Cookson, 1974)
2.	OXIDATION OR REDUCTION REACTION ON GAC - MALONIC ACID (Garten and Weiss, 1959)
3.	CATALYSIS BY METALS ON GAC - Fe (Rideal and Wright, 1926)
4.	RELEASE OF CHEMICALS FROM GAC - Oxidation of GAC itself
5.	REDUCTION OF DISINFECTANTS - Cl_2 BY GAC - C* CO + Cl^- (Magee, 1956) O_3 BY GAC - C* CO + O_2 (Dietz and Bitner, 1972)
6.	RELEASE OF CARBON FINES - 2.5-25 m diameter (McCarty, et al, 1979)

Because there is a limited amount of data on catalysis on activated carbon, one is handicapped when attempting to draw specific conclusions. In addition, generalizations are extremely risky, making it difficult to project the possible significance of catalysis during the process of adsorption of organics on GAC. Reaction products that were not originally present can be released to the water solution and behave as typical solutes in their adsorption equilibrium and competition for carbon sites. This subject needs further research.

There is a possibility that carbon may undergo significant changes via its patterns of use and regeneration procedures. The studies that were reviewed point to the effects of adsorbed ions on carbon's catalytic potential for a number of reactions. Thus, it appears possible that the recycling and regeneration of activated carbon can result in a material that is radically different than the virgin material. This may indicate the need for a control program that prevents the carbon utilized for drinking water from being used for any other purpose.

Chlorine, chlorine dioxide, and ozone react readily with carbon and may react with compounds adsorbed on carbon. There is no evidence to indicate that such reactions, under the conditions that exist in water treatment plants, will or will not produce potentially hazardous compounds. Research is needed to identify the end products of reactions between activated carbon and disinfectants, especially chlorine and chlorine dioxide. Also the interaction of oxygen with the carbon surface must be evaluated.

Carbon fines can be released during use. McCarty, et al. (1979) found four times the number of fines released during upflow filtration versus downflow filtration. Studies should be conducted to determine levels of carbon fines that pass into drinking water and their biological significance.

REGENERATION OF GAC

Regeneration procedures influence the chemical properties of GAC and this in turn will also influence adsorption, catalytic properties, and leachable chemicals. The ash content, surface oxides, and pore size distribution of GAC are examples of the properties which can change by regeneration processes and which can effect adsorption (Cookson, 1978). Sufficient data are not available to determine differences in adsorption between regenerated and virgin GAC. At present, no significant health problems have been documented.

The leaching of toxic organics from carbon to water has not been studied sufficiently to draw general conclusions. Although small amounts of polycyclic aromatic hydrocarbons (PAH's) have been detected (Borneff, 1979), they are well adsorbed and do not appear to readily leach off. The analytical studies are few,

emphasizing the need for evaluation of various regenerated carbon types and virgin carbons.

The leaching of metals from carbon to water appears to be slight, producing concentrations too low to affect health (Love and Symons, 1978).

Pollutants are discharged during the GAC regeneration process. Few studies have sufficiently characterized the air pollutant discharges to evaluate their health effects. These studies are also needed.

ADSORPTION EFFICIENCY OF OTHER ADSORBENTS

Two distinctly different processes were considered: The use of anion exchange resins for the removal of humic material and the use of polymeric adsorbents, e.g., Ambersorb XE-340 (Rohm and Haas Co.), for removal of low molecular weight organics of health concern. The physical and chemical nature of the resins must be considered. Attrition of resin by abrasion or osmotic forces should be minimized to maintain long-lived beds and to minimize escape into the water distribution system. Chemical degradation by oxidants such as Cl_2 and ozone should be minimized by reduction to Cl^- and O_2 since oxidants can alter the activity of a resin by changing the nature of the surface (Kunin, 1976).

Removal of Humic Substances by Ion Exchange Resins

The use of ion exchange resins other than cation exchange resins for softening potable water has been quite limited. Most data on the use of anion exchange resins for the removal of humic material comes from treatment of cooling water for power utilities (Kunin, 1973, 1976). There is sufficient evidence indicating that the technology can be applied to drinking water prior to chlorination to remove precursors of $CHCl_3$ production, the so-called trihalomethane formation potential (THMFP) and humic material in general. Davis (1977) and Boening, et al. (1979) showed that strong base anion exchange resins were the best in adsorbing humics (Table 7). Thirty to 64 % of the exchange capacity was regenerated with NaOH by both authors. Boening et al. (1979) cautioned that although strong base resins remove more organics, they are that much harder to regenerate than weak base resins and regeneration is critical for the use of anion exchangers.

Pilot plant studies by Kölle (1976), Gauntlett (1975), Jayes and Abrams (1968), Tilsworth (1974), and Wood and DeMarco (1979) have shown the ability of anion exchangers to remove color, total organics, and THM precursors from ground and surface waters. Wood and DeMarco (1979) found that the anion exchange resin IR-904 removed more THM precursor (≈50%) from raw and lime softened

Table 7. Adsorption of Humic Acids by Anion Exchange Resins

Resin	Humic Acid[c] Removed, % pH 2.2	pH 7
IRA-410[a]	97	70
IRA-410[a]	92	52
A-57[b]	79	22
A-30B[b]	71	44
ES-340[b]	82	59

Source: Davis (1977)

[a] Rohm and Haas, Corp. - Strong base resin
[b] Diamond Shamrock, Corp. - Intermediate base resin
[c] Commercially available humic acids

water than GAC or Ambersorb XE-340, but GAC removed slightly more from finished water. The anion exchanger did not remove 22 purgeable organics and in fact, in the presence of chlorine the anion exchange process catalyzed formation of high concentrations of these organics [e.g., chloroform (1.75X), and trichloroethylene (10X)].

Present studies indicate that nitrosamines may be generated by passage of water over a strongly basic resin (Fiddler, et al., 1977; Cohen and Backman 1978; Gough, et al., 1977). The exact mechanism has yet to be demonstrated. This is not surprising since the resins concentrate the potential reactants for forming nitrosamines and also accumulate potential catalysts (iron and copper). The published data on the formation of nitrosamines on anion exchange resins suggest that the use of such resins for potable water should be reconsidered. It may be possible to use anion exchange resins in conjunction with GAC; the resin would remove the bulk of the humic material and the GAC would remove the remainder of the humic material as well as any nitrosamines that had been generated. However, there are no data for such possible systems.

More research on anion exchange resins and their use in potable water treatment is needed. Present data on the use of anion exchange resins are based upon those that were regenerated only a few times or have been used in their virgin states. Such data are highly unrealistic for the water treatment industry.

An acceptable loss of capacity upon regeneration can be addressed only after many regenerations are completed.

Adsorption Efficiency of Polymeric Adsorbents

Experience with polymeric adsorbents to remove organic compounds from drinking water and regeneration of these materials are limited in comparison with the use of GAC. Laboratory studies and a few recent pilot plant studies indicate that the synthetic carbonaceous adsorbents of the Ambersorb XE-340 type do not have the broad-spectrum adsorption properties of GAC, and that they selectively adsorb lower molecular weight organics but apparently do not readily adsorb humic material (Chudyk, et al., 1979; Neely, 1979). However, the data indicate some promise for special situations, such as the removal of toxic organics from sources contaminated with low molecular weight organics (Wood and DeMarco, 1979).

Compounds of health concern for which isotherm data are available include only chloroform (XAD-4, XE-340), bromodichloromethane (XE-340) and dieldrin (XAD-4, XE-340) (Neely, 1979; Rohm and Haas, 1977; and Chudyk, et al., 1979). Chudyk, et al., (1979) found 10 mg/l of a commercially available humic acid did not affect adsorption of µg/l amounts of $CHCl_3$ on XE-340. $CHCl_3$ adsorption on XE-340, relative to GAC, has been shown to be 3:1 to 5:1 at high $CHCl_3$ concentrations (Neely, 1979) and approximately 1:1 at low $CHCl_3$ concentrations (Chudyk, et al., 1979). The degree of competition between organic compounds needs to be studied.

In a series of small column studies, extremely small adsorptive capacities were exhibited by the non-carbonaceous resins XAD-2 and XAD-7 in comparison to GAC and XE-340 (McGuire, 1977). This is in agreement with results from pilot plant studies (Suffet, et al., 1978 a and b) in which they compared Filtrasorb 400, XAD-2 and XE-340 as post treatment adsorbers for chlorinated Philadelphia drinking water from the Delaware River. XAD-2 was shown to be of much lower capacity (Suffet, et al., 1978a). XE-340 removed low molecular weight organics, whereas GAC removed high and low molecular weight organics. Caution was expressed that the data were largely qualitative and interpretation is complicated by the highly variable nature of the organic content at the influent to the adsorption columns.

Wood and DeMarco (1979), during a pilot scale study of a groundwater supply at Miami, reported that XE-340 did not remove THMFP where GAC removed 20 percent from finished water. However, XE-340 did remove 24 percent of the THMFP from raw water. XE-340 always removed a greater amount of individual volatile compounds than GAC per unit weight, e.g., chloroform (4X), cis-1, 2-dichloroethane (3X), bromodichloromethane (2.8X), and dibromochloromethane (1.5X) from finished water.

To further define resin uses, studies on resin regeneration systems are needed to determine the efficiency of different types of regenerants, attrition rates, and oxidant effects on the adsorbent. The resin to be cycled should be used for treating contaminated well water to provide direct interpretations of removal efficiencies. Slejko and Meigs (1979) state that XE-340 may be regenerated by steam with periodic alcohol washes but only preliminary data are available. Crucial questions remain concerning how to regenerate efficiently, what type regenerant to use, and the actual rate of loss of capacity.

ANALYTICAL METHODS TO MONITOR ADSORBENT UNIT PROCESSES IN WATER TREATMENT

The focus of this report has been on the individual compounds of potential harm to health. Thus, the primary purpose of this section is to evaluate if analytical methods are available to monitor the operation of adsorbent processes for these compounds at a water treatment plant.

The variability of the complement of organic compounds (Table 8) in the influent to the GAC column affects the efficiency of the adsorptive process for compounds and must be monitored. Chemical compounds in the effluent may be the same as those that entered the carbon bed or they may have been changed

Table 8. Organic Compounds in Drinking Water Functionally Defined by the U.S. EPA, (1978b)

Class	
I	CAUSES OF TASTE AND ODOR
II	SYNTHETIC ORGANIC COMPOUNDS[b]
III	PRECURSORS-CLASS IV REACTIVE[c]
IV	DISINFECTANT BYPRODUCTS[b]
V	NATURAL ORGANIC COMPOUNDS-NOT CLASS III[a]

[a] 90% by weight of the TOC are high molecular weight compounds of Class V.

[b] Compounds of health concern are present in these classes. These compounds are represented in Table 2.

[c] Precursors primarily of Class IV are represented by THMFP.

by chemical or microbial action within the bed. The variability of species type and concentration in the column influent are also reflected in variable effluent concentrations from competitive and reequilibration effects discussed in the Competitive Effects section of this report.

Thus, infrequent grab sampling might not be sufficient for an adequate evaluation of material entering or leaving a GAC column. Since minute-to-minute sampling is presently impractical, the variability of these organics in the influent and effluent can best be followed by on-line composite sample collection augmented by grab samples.

Two different analytical approaches can be used to determine specific organic compounds of health concern. In one approach, individual compounds are analyzed that have been selected because of health implications. In the second, a general "screening" procedure for the isolation of organic compounds is used and the compounds of interest are selectively determined from the same sample matrix.

Table 2 lists specific pollutants of potential health concern that should be monitored. Specific analytical methods for each compound or groups of compounds are being developed at the present time and are reviewed by Keith and Telliard (1979).

The second approach to analysis uses screening procedures. The screening procedure consists of a qualitative analysis for individual compounds of health concern and subsequent quantitative evaluation of the constituents that were found. A general sequence that is followed for screening of trace organics is:

Sample ----> Isolation Method ----> Concentration ----> Chromatographic Separation ----> Qualitative Identification ----> Quantification

Suffet and Radziul (1976) have described the methods that can isolate chemicals with health implications. For example, the less polar volatile organics of health concern are isolated by methods such as the purge and trap volatile organic analysis (b.p. $\leq$ 150°C) (Grob, 1976), liquid-liquid extraction (Yohe, et al., 1979), and macroreticular resin accumulators (Chriswell, et al., 1977). These methods must be supplemented by specific analysis for compounds that are not isolated by the specific extraction methods.

The complex group of trace organics in the extracted sample is chromatographed and a sample profile or fingerprint is obtained. This consitutes an information pattern in each chromatographic analysis. When the profile is compared to a profile of a set of standards of the compounds of health concern, a tentative identification of the sample components can be made. When

many profiles of influents and effluents are plotted in the same manner, chromatographic profiles can be compared and differences noted. GC/MS analyses must be used to confirm the identification of the compounds tentatively identified by the isolation method. Examples of the screening have been reported for purge and trap analyses (Steiglitz, et al., 1976, and Wood and DeMarco, 1979), resin accumulators (Suffet, et al., 1978a), and liquid-liquid extraction (Yohe, et al., 1979). When monitoring an adsorption process for volatile pollutants of health concern that can be detected by GC techniques, only selected GC/MS analyses may be necessary. GC analysis can be used for monitoring purposes if defined concentration limits for pollutants are established.

Nonspecific Organic Analyses

Nonspecific organic analyses lump together a large number of organic compounds into one collective measurement heap. The analysis of specific organic compounds with suspected health implications (Table 2) should be the criteria by which all of the nonspecific analyses are evaluated.

Nonspecific organic analytical techniques for monitoring the performance of adsorbent beds need further development. Correlations between nonspecific measurements and compounds of health concern should be completed on a site-specific basis, because the specific organic compounds which must be controlled will probably vary among water supplies. The correlation of such measurements as UV absorbance, fluorescence, or analyses of organic carbon (e.g., TOC) with GAC-breakthrough of specific organic compounds of health concern has not been observed (Brodtmann et al., 1979; Wood and DeMarco, 1979; Symons, et al., 1975). However, TOC remains an important measure of the mass loading of an adsorption column.

The correlation of Total Organic Halogen (TOX) in the aqueous or absorbed phases with organic compounds of health concern has not been sufficiently studied. This should be developed for routine use as many compounds of health concern are chlorinated, Table 2.

THM precursors which participate in the haloform reaction have not been shown to correlate with nonspecific organic analysis. Although fluorescence has been used to monitor humic material (Snoeyink, et al., 1977; Sylvia and Donlon, 1979), it has not been shown to correlate with THMFP. TOC and THMFP did not correlate well in pilot column studies (Wood and DeMarco, 1979; and Cairo, et al., 1979). Organic carbon is a collective measure of all organic constituents and only a few of these are haloform precursors.

GENERAL CONCLUSIONS AND RECOMMENDATIONS

Raw water sources and disinfected water supplies may contain organic compounds that have been demonstrated to be carcinogenic or otherwise toxic in experimental animals or in epidemiological studies. Also present are a large number of compounds that either have not been identified or their effects on health have not been characterized. Properly operated GAC systems can remove or effectively reduce the concentration of many of the compounds described above. Less is known about synthetic resins than about GAC, but it is known that they can be applied to remove certain types of organic contaminants.

The information available as of this date on the treatment of water with GAC provides no evidence that harmful health effects are produced by the process under proper operating conditions. However, there are incomplete studies on the possible production of such effects with virgin or regenerated carbon through reactions that may be catalyzed by the GAC surface, reactions of disinfectants with GAC or compounds adsorbed on it, reactions mediated by microorganisms that are part of the process, or by the growth of undesirable microorganisms on GAC. Studies are also needed on the properties of regenerated activated carbons and on the adsorption of additional contaminants with potential health effects.

The frequency of GAC regeneration is determined by the organic compounds in the water and their competitive interactions. The types and concentrations of organic compounds may vary widely in different locations and seasons of the year. Competitive interactions are complex and presently cannot be predicted without data from laboratory and/or pilot scale tests on the water to be treated.

While there is ample evidence for the effectiveness of GAC in removing many organics of health concern, more data are needed on the quantification of any harmful health effects related to the use of GAC. This need, however, should not prevent the present use of GAC at locations where analysis of the water supply clearly indicates the existence of a potential health hazard greater than that which would result from the use of GAC.

Clarification processes (coagulation, sedimentation, filtration) remove significant amounts of some organics, especially some types of THM precursors and relatively insoluble compounds that may be associated with particulates. In some cases, the removal of THM precursors by clarification may be sufficient to eliminate the need for an adsorption process.

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U.S.A. EXPERIENCE WITH GRANULAR ACTIVATED CARBON ADSORPTION

Richard H. Moser

INTRODUCTION

In 1975, the United States Environmental Protection Agency conducted a survey of water treatment plants using granular activated carbon for taste and odor control. The results have been summarized by Symons[1]. They found 33 plants using GAC; 30 on a routine basis and three on an experimental basis. Thirteen other plants have converted some, but not all, of their filters to GAC. The average quantity of water treated at these plants was about 8 mgd, ranging from 0.3 to 33.5 mgd. The average media depth was 28 inches with the range of 11 to 84 inches. A sand layer was being used under the GAC at 77 percent of these plants. In 95 percent of these cases, water was gravity fed to the GAC but only 14 percent had the water pre-filtered prior to passing through the adsorbent. At 35 percent of these plants, 2 gpm/ft^2 was the filtration rate, with the remainder about equally divided above and below this value. Finally, 82 percent of the plants were installed in the years 1970 to 1975.

More recently, larger GAC plants have been placed into service, with Chattanooga, Tennessee (part of the American Water Works System) being the largest at 72 mgd nominal capacity.

Of the 46 plants in the EPA survey, 13 were part of the AWW System; therefore, our experience constitutes at least one third of the USA experience with granular carbon in drinking water plants.

We did not know exactly why GAC did a better job of controlling taste and odor than did powdered carbon and the chemical oxidants, nor did we feel it was essential to know. The material worked--and that's what counted. Still, today, the precise mechanics of GAC adsorption are a subject of controversy. Researchers did ascertain that this "magical" granular black material phenomenally removed dissolved organics from water, especially those large molecule organic chemicals

associated with taste and odor problems. Yet it was not enough to know that GAC did work, we had to know how it worked, and why in some cases it did not work. We wanted to be able to predict how well it would work and for how long. Lastly, we had to know if any problems were being created by its use. All of these concerns are rightfully addressed by the GAC developers and researchers. However, those of us who had experience with GAC also became aware of these concerns and are now able to assist in the development of the answers.

TASTE AND ODOR CONTROL

The American Water Works System began its GAC experience at Hopewell, Virginia, in 1960 and currently has 19 systems with GAC. Table 1 shows the current list. Hopewell, interestingly, is the only one which uses GAC as a post contactor; even as long ago as 1960, it was recognized that post contactors are better, especially in cases of heavy organic loading where bed life is a matter of weeks. Such was the case at Hopewell, where only 30 to 60 days of carbon life could be expected to remove the earthy odor now known to be caused by geosmin.* Figure 1 shows the Hopewell plant flow diagram. The Appomattox River, source of supply for Hopewell, receives back water from the nutrient-rich James River during high tide, thereby providing ideal conditions for growth of Actinomycetes. Thankfully, the James River water quality has improved over the years so that we now get a one year service life.

Regeneration was not installed at Hopewell because this was our first GAC experience. After the first few exchanges of GAC, the operating personnel decided to replace some sand with partially spent GAC to get a longer contact time. They found that the carbon could still dechlorinate after it was exhausted for taste and odor control. Since they had been dechlorinating with sodium bisulfite, enough sand filters were converted to spent carbon filters to accomplish the same degree of dechlorination. The carbon was tested in parallel with sand for suspended solids removal and it was found that carbon did slightly better than sand without affecting its dechlorinating properties. (See Table 2). Today, some carbon has been in service for almost 10 years and is still effectively dechlorinating. Since then, many other locations have verified GAC's ability to remove suspended matter and now it is routinely accepted as a filter medium.

Over the years, we found that the iodine number (an indication of available surface area) of GAC decreases with use, which means that the carbon spaces are becoming filled with organic compounds. Experience taught us that when the iodine number

*Identified by Dr. J.K.G. Silvey of North Texas State University

Table 1

American Water Works System Locations Presently Using GAC

	Bed Depth (In.)	LBS. GAC
Illinois		
E. St. Louis	18	412,200
Granite City	18	174,000
Peoria	30	165,000
Indiana		
Kokomo	20	162,000
Muncie	24	90,500
Richmond	24	100,900
Terre Haute	30	127,000
Iowa		
Davenport	24	331,700
Kentucky		
Lexington	14	177,600
Ohio		
Ashtabula	24	75,000
Marion	18	80,000
Pennsylvania		
New Castle	30	190,800
Pittsburgh	30	1,947,400
Tennessee		
Chattanooga	30	927,400
Virginia		
Hopewell	60	81,000
West Virginia		
Huntington	30	337,500
Madison	18	7,300
Princeton	18	24,300
Weston	18	14,600
Total 19	--	5,426,200

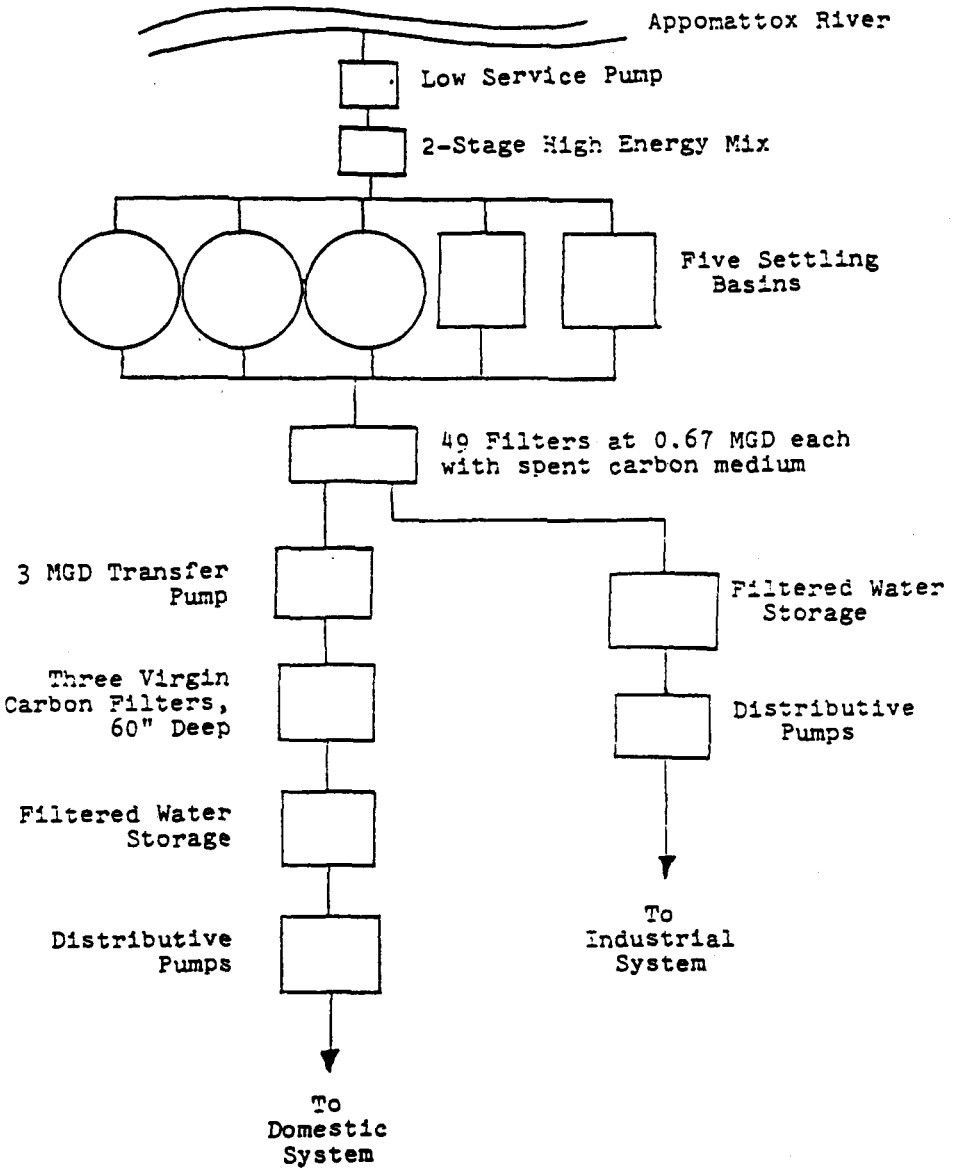


Figure 1. Virginia-American Water Company
Hopewell, Virginia

Table 2

Impurity Removal by Adsorption - Filtration by Carbon Beds* and by Sand Medium (Hopewell, Virginia)

Impurity	Influent	Carbon Bed Effluent	Sand Medium Effluent
Threshold Odor Number	35-140	0-4+	35-70+
Color	4-14	0-2	1-2
Manganese (ppm)	0.066-0.15	0.008-0.017	0.008-0.017
Iron (ppm)	0.2-0.37	0.006-0.025	0.012-0.087
Turbidity (JTU)	0.45-1.4	0.07-0.15	0.10-0.25
Chlorine (ppm)	1.4-2.8	0-0.25	1.4-2.8

*24" Deep at 2 gpm/ft^2.

+Odor samples over 60 day period; other data 150 day period.

Extracted from: "Removal of Organic Contaminants by Granular Carbon Filtration" by Hager and Flentje, JAWWA, November, 1965.

is reduced to about 300 (virgin material ranges from 650 to 1100) that the carbon is no longer effective enough to assure taste and odor control. While the iodine number drops, the apparent density (the weight of carbon per unit volume) increases, also indicating pick-up of organic chemicals. An increase of about 20 percent (0.42 to 0.50 gm/cm^3) seems to accompany the drop in the iodine number. Figures 2 and 3 show these effects. A threshold odor number of three seems to correlate with the iodine number and the apparent density as described above, so they make good operating parameters.

When the American Water Works Co. purchased several properties in West Virginia, the plant serving the City of Nitro was a prime candidate for GAC. Figure 4 shows the plant layout. The Kanawha River contained innumerable organic wastes because of the high density of chemical industry in the Charleston area. Not only was GAC considered to be necessary, but tests showed that taste and odor removal could only be assured for a few months. During these tests, some specific compounds were identified and shown to be adsorbed by virgin GAC (Tables 3 and 4). Data on CCE and COD was also generated, but not included here because these parameters are no longer considered significant. To minimize capital expenditure, GAC was used as a sand replacement. With the cooperation of Calgon Corp., a multiple hearth furnace (Figure 5) was leased and installed at the Nitro Water Plant for exclusive use by our people for regeneration every few months. The furnace was larger than needed and was therefore used periodically. Probably because of the start/stop operation, the regeneration facility performed very unsatisfactorily. The furnace was difficult to start up, carbon losses in handling were about 10 percent, and temperature was hard to control.

Because the furnace was so difficult to operate, regeneration was not conducted as often as needed. Threshold odor became a secondary concern as regeneration frequency was changed to once per year. Regeneration efficiency was determined only by periodic tests for apparent density, so data is inconclusive on that question. Table 5 shows a regeneration cost breakdown done after a few years' operation. Finally in 1973, the Nitro Plant was replaced by a new facility using an unpolluted stream. The Nitro installation constitutes our only (and until recently the nation's only) plant scale regeneration experience in a drinking water plant.

Since then, we have learned considerably more about GAC, how it is used, how it works, and its pitfalls. The remaining 17 systems that we have in service were installed as filter/adsorbers, because it was known or guaranteed that the GAC would have a multiyear life for taste and odor removal. The difficult task of removing GAC from a conventional filter box need not be

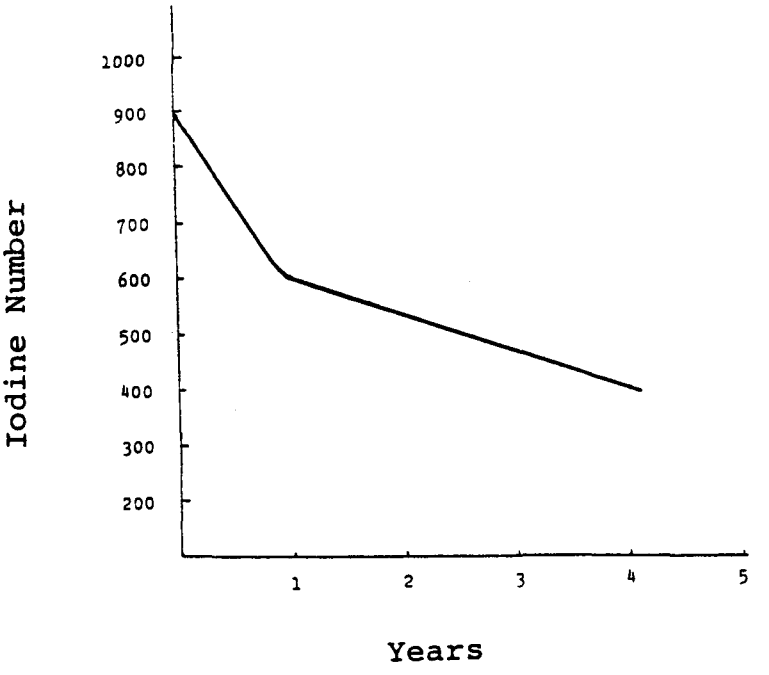


Figure 2. Typical Iodine Number vs. Time Relationship

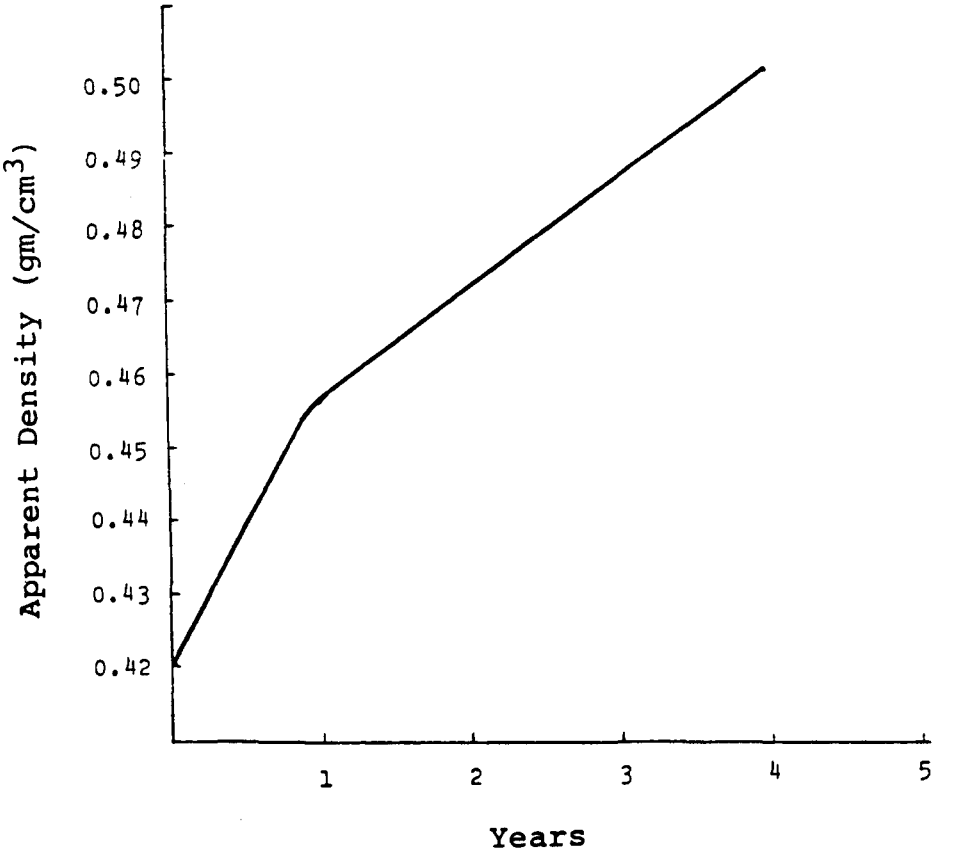


Figure 3. Typical Apparent Density vs. Time Relationship

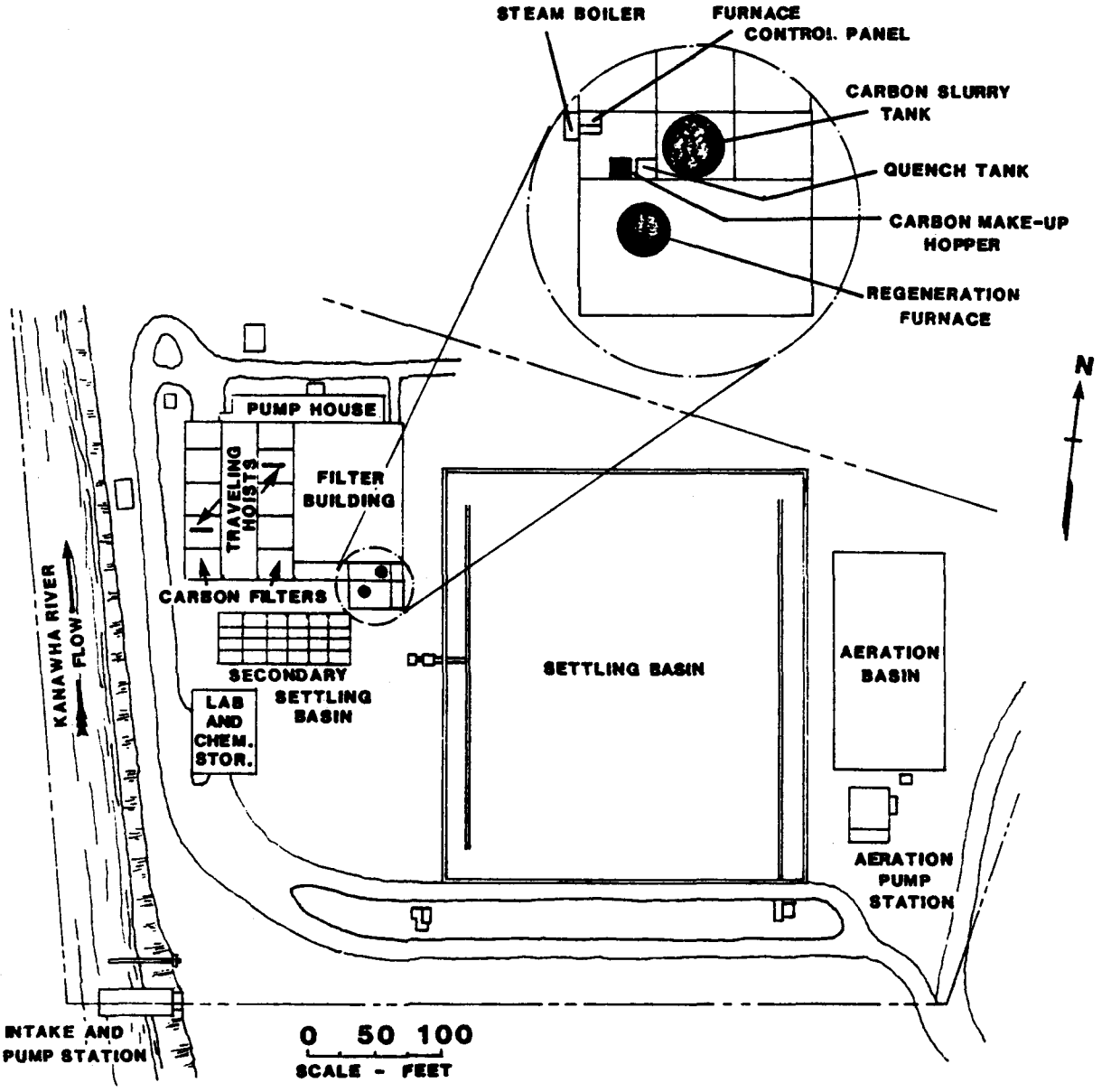


Figure 4. West Virginia Water Company Plant Layout Showing Location of Carbon Filters and Carbon Reactivation Equipment

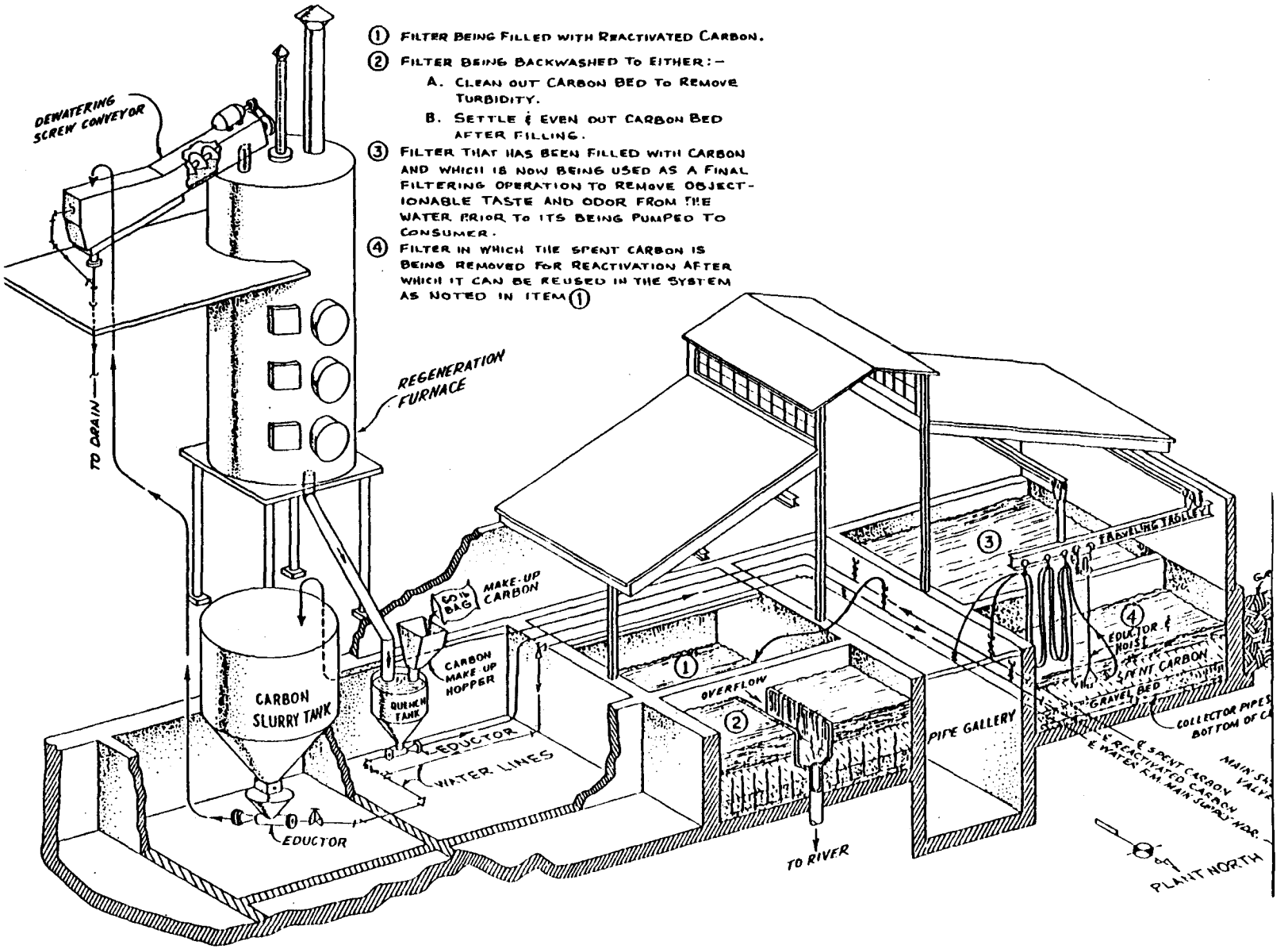


Figure 5. Granular Carbon Purification System, West Virginia Water Company Nitro, West Virginia

Table 3

Concentrations of Suspected Contaminants in Parts per Billion

Contaminant	Nov. 13, 1963		Nov. 21, 1963		
	Raw Kanawha	Sand Filtered*	Raw Kanawha	After Aeration	Carbon Filtered
Ethylbenzene	11	11	<D+	<D	<D
Styrene	18	<D	<D	<D	<D
Bis (2-chloroethyl) ether	55	10	154	104	<D
2-Ethyl hexanol	110	8	<D	7	<D
Bis (2-chloroisopropyl) ether	24	<D	48	23	<D
Methyl benzyl alcohol	<D	<D	26	12	<D
Acetophenone	19	<D	29	17	<D
Isophorone	90	<D	25	16	<D
Tetralin	<D	<D	57	103	<D
Total	327	29	361	296	
Threshold odor number (25°C)	128	6	237	181	<1

*Sample dechlorinated before analysis.

+Value below detectable concentration.

Extracted from: "Carbon Bed Design Criteria Study at Nitro, West Virginia" by Dostal, Pierson, Hager and Robeck, JAWWA, May, 1965.

Table 4

Influence of Contact Time on Passage of Specific Contaminants, Experiment 1

Contaminant	Contact Time-min			
	1.9	3.8	5.6	7.5
	Depth-ft			
	5	10	15	20
	Concentration*-ppb			
Ethylbenzene	20	18	15	5
Bis (2-chloroethyl) ether	94	44	<D+	<D
2-Ethyl hexanol	57	20	<D	<D
Bis (2-chloro-isopropyl ether	26	10	<D	<D
Methyl benzyl alcohol	62	13	<D	<D
Acetophenone	11	<D	<D	<D
Isophorone	12	9	<D	<D
Total	285	114	15	5
Threshold odor number (25°C)	32	25	5	2

*Sampled Dec. 30, 1963.

+Value below detectable concentration.

Extracted from: "Carbon Bed Design Criteria Study at Nitro, West Virginia" by Dostal, Pierson, Hager and Robeck, JAWWA, May, 1965.

Table 5

Direct Costs of Granular Carbon Reactivation*

	Estimated Daily Costs†	
	U.S. Dollars	Pounds Sterling
Fuel ($21.20/1000 m^3)	5	2.08
Power ($0.01/kWh)	3	1.25
Steam ($4.40/1000 kg)	5	2.08
	13	5.41
Make-up Carbon (5% loss/ cycle)	25	10.42
Labor (existing personnel normally adequate)	--	----
	38	15.83
Cost per kg**	3.3 cents	1.4 pence

*Excludes amortization, insurance, and taxes (if any).

†Based on a 75 cm I.D. x 6 hearth furnace

**Based on 1135 kg/day of carbon being reactivated.

Extracted from: "Adsorption and Filtration with Granular Activated Carbon" by Hager and Fulker, Journal of the Society for Water Treatment and Examination, Vol. 17, 1968.

done so often as to be a burden. Service life of GAC beds has ranged from two to six years, except for Hopewell.

GAC can provide benefits beyond taste and odor removal as we found out when the James River was contaminated with kepone in 1974. Naturally, Hopewell's supply was affected. Hundreds of tests were conducted by the Commonwealth of Virginia and ourselves which showed without a doubt that the carbon removed virtually all of that contaminant (Table 6). Thanks to GAC, we had no urgent need to be concerned about kepone in the drinking water.

Table 6

Kepone Removal by Granular Carbon at Hopewell, Virginia

	River Water	Pre GAC	Post GAC
Kepone (ppb) Avg.*	0.017	0.011	0.001

*60 samples taken over a two year period.

HANDLING OF CARBON

During these past 20 years, we have handled millions of pounds of carbon. We have used hand shovels, pails, drums, eductors, eductors on hoists with trolleys, cranes with buckets, and vacuum trucks--all of which work. Undoubtedly, the Hopewell plant personnel had more experience than anywhere else in our company. The method employed for carbon removal from the filters uses the water eductor with a periodic backwash at low rate. By maneuvering the suction hose around the filter, virtually all the carbon can be removed, even where gravel is supporting it. When sand is present, it is more difficult to remove all the carbon without getting the sand mixed with it. But the system works very well, and with a little equipment and a little experience removing 800 ft^3 from a 1 mgd filter, it can be done in less than four man-hours.

PROBLEMS WITH GAC USE

Most of our experience has been with bituminous material, but lately we have had good success with lignite. Not all the experiences with GAC have been good. Since GAC is lighter than other media, backwash rates had to be lowered to prevent loss of material. Not only lower backwash rates, but the rate

as a function of water temperature, suddenly became a crucial operating parameter. A more precise wash flow control had to be installed to prevent loss of the relatively expensive material. Figure 6 shows that relationship. Recently, we have found that some carbons require higher wash rates as shown in Figure 7, which also shows the effect of particle size. This may demonstrate a change in carbon raw materials or in processing, but with variation like this, filter washing requires closer operational control. Even with good control, some carbon gets washed away - perhaps one inch per year.

Another problem is the possible accumulation of mud in the media. This does not happen in all cases, but where floc particles are particularly cohesive, as in a high polymer-dosed water, the floc does not readily wash away at these low wash rates, even when wash times have been extended. Contrary to what might be expected, wash water consumption does not decrease with use of GAC (because of lower rates). In actuality, wash water consumption often increases due to the extended times required to clean the bed.

Another operating problem is due to carbon's affinity for chlorine. In many cases, the absence of chlorine has caused bacteria to multiply in the bed causing the filtered water to contain bacteria many-fold higher than the inlet water. Total plate count bacteria have been controlled by backwashing with water containing up to 50 ppm of combined chlorine residual in all but one case. Pittsburgh is the exception, where bacteria counts in filtered water are tens of thousands per ml during the summer. Fortunately, post chlorination lowers the total plate count to less than 10 colonies/ml. Since this is not a national problem, I presume there is not much concern. Contrarily, there are some who contend that the bacteria should be encouraged to multiply. Those of us who have for years strived to reduce general bacteria to as close to zero as possible, throughout the treatment process, have difficulty in accepting that concept, although it seems to have merit in reducing organics.

Despite having some problems, granular activated carbon is an excellent operating tool - at a cost which is not exorbitant for taste and odor control. Table 7 gives some recent cost data for GAC treatment after several years operation. These costs do not reflect the decrease in other taste and odor chemicals, changes in wash water, changes in chlorine consumption, or any savings in sludge disposal. The overall cost reduction for just taste and odor control at these locations has been 34 percent.

SPECIFIC ORGANIC REMOVAL

While we installed granular carbon only where severe, chronic taste or odor problems occurred, we recognized that

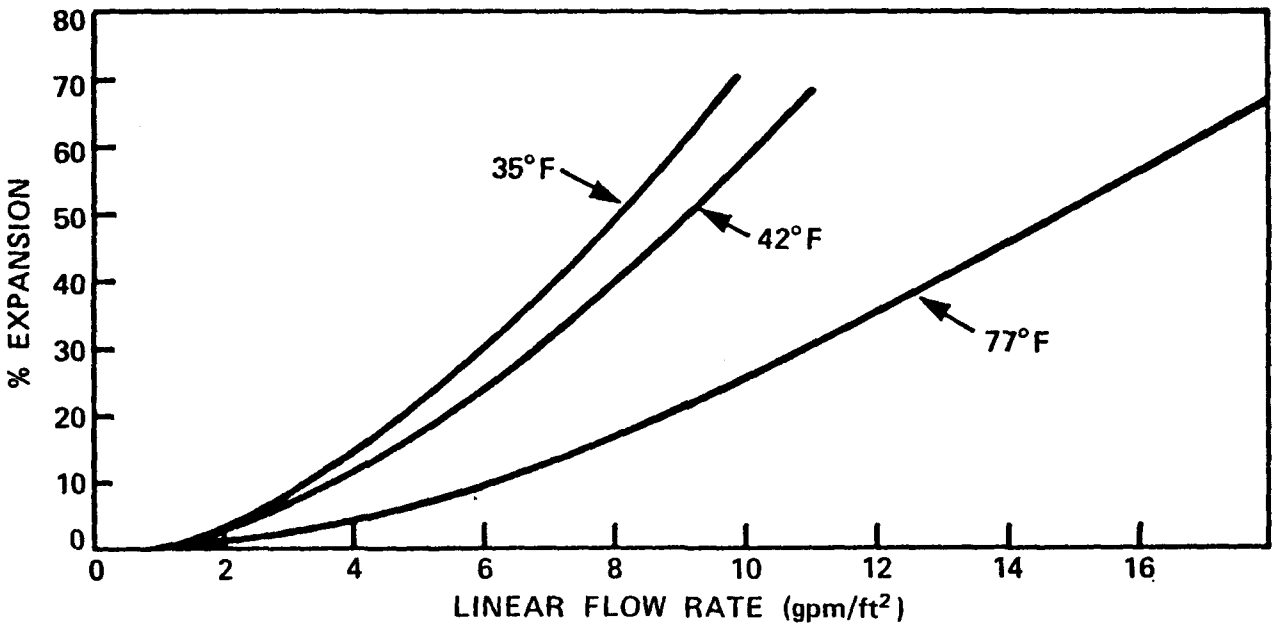
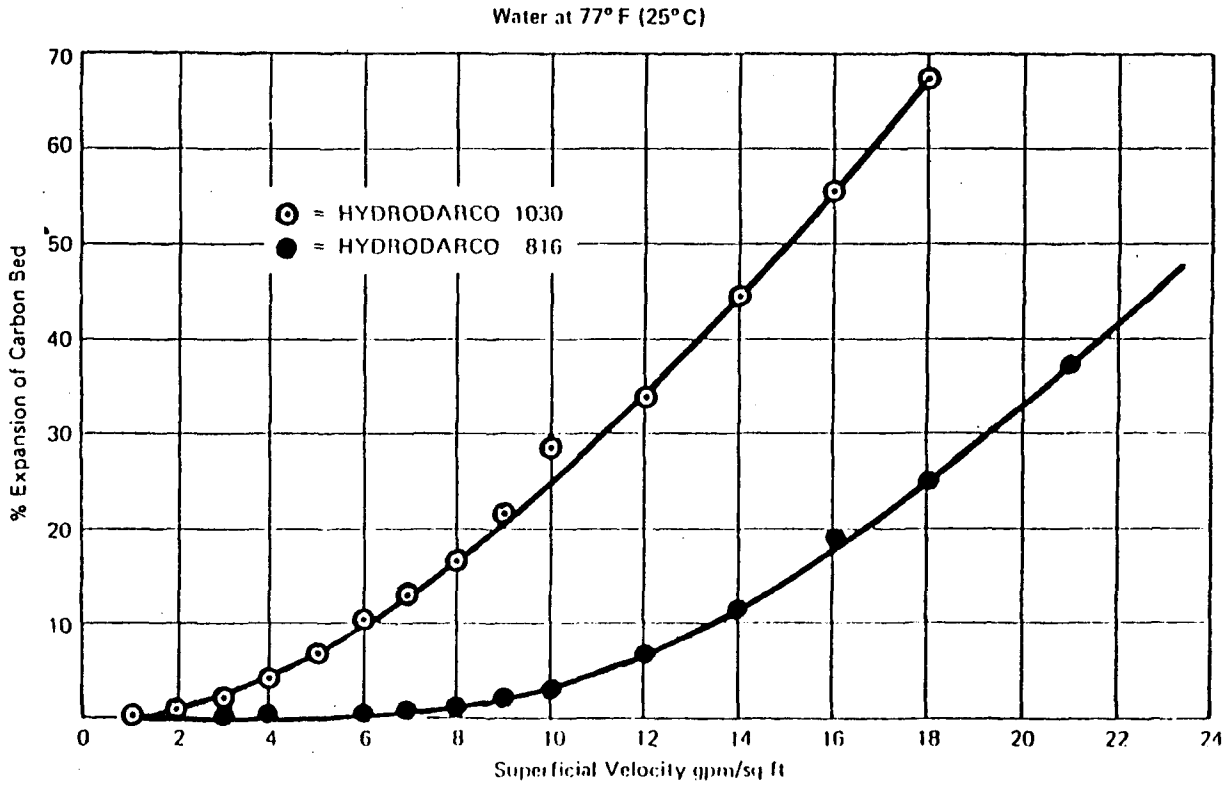


Figure 6. Bed Expansion of Hydrodarco 1030 (10x30 Mesh) At Various Temperatures (Water)



Effective size of 1030 = 0.8 to 0.9 mm
Effective size of 816 = 1.2 to 1.3 mm

Figure 7. Bed Expansion Curves for Hydrodarco 1030 and Hydrodarco 816

Table 7

Cost Data

Plant	Capacity (MGD)	Raw Water Source	$/MG
Ashtabula, OH	4	Lake Erie	3.70
Chattanooga, TN	81	Tennessee River	5.73
Davenport, IA	30	Mississippi River	16.30
E. St. Louis, IL	35	Mississippi River	3.38
Granite City, IL	13	Mississippi River	8.35
Kokomo, IN	11	Wildcat Creek	4.63
Lexington, KY	20	Private Reservoir	3.95
Marion, OH	7	Wells and Scioto River	3.71
Muncie, IN	8	White River	6.57
Peoria, IL	30	Illinois River	11.68
Richmond, IN	8	Private Reservoir	6.19
Terre Haute, IN	6	Wells and Wabash River	3.47
Total	253		6.47 AV.

other organics were being removed. However, it was not until recently that such data have been generated. We participated in the ORSANCO study, replenishing some filters with virgin GAC at Huntington and also evaluated the partially spent GAC at Pittsburgh. Mr. Miltner will present that data later in this conference.

We have conducted trihalomethane analyses throughout our entire system and have found that most GAC installations were already exhausted. However, at Hopewell, after 9 months, considerable THMs were still being removed (see Table 8). The same phenomenon occurred at Davenport, Iowa after 7 months, as Table 9 reveals. Therefore, we can say that one cannot predict bed life for THM removal without specific, case-by-case evaluation.

I have also reviewed some of our data looking for possible desorption effects. Table 10 is an example of how a particular compound can be at a higher concentration in the carbon-filtered water than in the applied water. Researchers now say one can expect this to occur when carbon is used long after its removal life, which can explain the results in this table. However, with all the compounds which granular carbon can remove, how does one know when (and even if) desorption occurs? This question and others cannot be answered in this paper. Future studies will hopefully answer this and other questions being raised about applications of granular activated carbon in water treatment.

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Table 8

Trihalomethanes at Hopewell, Virginia Plant Effluent

	Concentration, ug/l			
	7 month old GAC		9 month old GAC	
	Pre GAC	Post GAC	Pre GAC	Post GAC
Chloroform	77	55	261	68
Dibromochloromethane	22	5	1.9	3.3
Dichlorobromomethane	17	<1	191	27
Bromoform	20	2	<1	<1
TTHM	136	62	454	98
% Removal TTHM	54%		78%	

NOTE: All samples were quenched at collection and analyzed at NUS Corporation laboratory in Pittsburgh, Pa.

Table 9

Davenport Water Company

Date	Location	Trihalomethanes (ug/l)			% Reduction
		Quenched	Formation Potential	Terminal	
November 1978	Filter Influent	152	87	239	
	Filter Effluent	120	15	135	44
December 1978	Filter Influent	93	56	149	
	Filter Effluent	97	8	105	30
January 1979	Filter Influent	71	26	97	
	Filter Effluent	62	7	69	29

Table 10

Example of Possible Competitive Adsorption and Desorption

Western Pennsylvania Water Company - Pittsburgh, Pa.

Concentration, ug/l

	Filter #18		Filter #2	
	Influent	Effluent	Influent	Effluent
Chloroform	30	16	11	26
Dibromochloromethane	3	23	6	9
Dichlorobromomethane	1	9	<1	<1
Bromoform	28	15	5	7
TTHM	62	63	22	42

NOTE: 1. Influent and effluent samples taken at same time. Analyses done by NUS Corp., Pittsburgh, Pa.

2. Granular carbon approximately 20 months in service.

DISCUSSION

Following Monday Morning Session (April 30)

Q PROFESSOR McCARTY: Mr. Moser, I'd like to know more about the one case in which you used spent activated carbon in the filters for dechlorination. Do you feel it is a good idea to use carbon loaded with organics for dechlorination? Did you consider the organics problem at all? Did you investigate the possible formation of chlorinated organics?

A MR. MOSER: In 1961 it seemed like a good idea, and I don't mean to say we wouldn't do it again; however, I think we would probably investigate some other factors first. We have virgin carbon after the prefilters, so in a sense I don't see how that differs from having carbon in one filter and expecting the organics to be removed on the top. We really are relying on the virgin material on the bottom to remove substances that might tend to bleed through or slough off from the top portion of the filter. The carbon in those primary filters has effectively dechlorinated for up to 10 years without replacement. The purpose of putting it there was to take advantage of its dechlorination and filtration properties, rather than for organics removal. What was the second point of your question?

Q McCARTY: Have you studied whether organics are formed in that process?

A MOSER: No, we have not. I think the best way to get an answer to your question is to refer back to the person who was instrumental in obtaining that data. Vern Snoeyink is here. Vern, do you want to comment on chlorination of organics in the carbon column or chlorination of the carbon itself?

SNOEYINK: Yes. We did one experiment I think that relates quite nicely to Professor McCarty's question. We chlorinated a carbon bed that was loaded with humic substances and measured the amount of chlorinated organics formed. The principal halogenated compound found in the effluent was chloroform; there was no bromide present, so we were not getting any of the brominated compounds. When we analyzed the data carefully, there was evidence that the chlorine was reacting preferentially with carbon rather than with the humic substances. So although chloroform was produced from the saturated carbon, not as much

was produced as would have been if that compound had not been attached to carbon. Chlorinated compounds are certainly formed, but carbon destroys a lot of the chlorine before it can react to form halogenated organics.

Q CHARLES BUSCHER, Continental Water in St. Louis: I'd like to ask Mr. Moser a question concerning the criteria employed to decide whether or not to use carbon in specific areas. You have indicated that your company uses granular activated carbon at only 19 of its 100 water treatment facilities.

A MOSER: To put it briefly, customer complaints. We use carbon where we have chronic taste and odor problems. It doesn't always work out that the granular carbon reduces treatment costs, so we generally try to do what we can by using powdered activated carbon, potassium permanganate, or other simple alternatives. We avoid the expense of granular carbon installations unless we have a problem that's so severe or so chronic that GAC is the only way to handle it.

Q MR. BUSCHER: In the 19 plants that you have operated over various periods, have you monitored TOC or trihalomethane concentrations to check the effectiveness of your particular GAC. Can you control your GAC operation in that way?

A MOSER: We haven't tried to do that. If we still had the Nitro facility operating, we could go back and check. Nitro is the only plant at which we had a multiple, regenerated carbon. We had some data on COD and CCE from Nitro, but nothing conclusive. We haven't attempted to monitor for trace organic compounds ourselves. We have participated in the ORSANCO study and Dick Miltner will later in this conference present some data from two of our plants, Pittsburgh and Huntington, on GAC's ability to remove many compounds. Perhaps that will answer part of your question.

Q CHARLES BUSCHER: In review of the American operations of GAC to date, have you found anybody who has used any of the parameters prescribed in the proposed regulations to measure the efficiency of the GAC?

A MOSER: I believe there's some data available from the Passaic Valley installation where they have an infrared furnace. They are regenerating carbon in that furnace and, as part of that study, are measuring volatile organics and TOC to try to determine its life with respect to the criteria in the proposed regulation.

I don't have that data, but to my recollection it was a couple of days before one of the volatile organics having a concentration greater than a half of a part per billion passed through

the carbon. That's the only installation I know of where data may be available.

COTRUVO: I believe there are data available from other sources. Patrick Cairo from Philadelphia probably has some and he might be able to mention it when his time comes.

Q ART BUSCH, North Texas State University: Dr. Suffet, I'd like to continue the discussion of monitoring breakthrough using a surrogate or a correlation. I share Dr. Cotruvo's position I think, but I'm also a little bit confused. EPA has stipulated a TOC standard that could be used, or considered, as a general characterization, but it's several orders of magnitude higher than their limit on THM's, for example. As long as the standards are written in terms of specific compounds, it seems to me that we have to address those compounds. However, we certainly don't have any list at the present time. The question is, do we have any general techniques that would approach the level of the THM standards?

A DR. SUFFET: If specific standards are developed by EPA for particular organic compounds of health concern, such as THM, there are methods available to measure these at the levels of concern. Screening procedures can and are being developed for this purpose, but the expense is the key question. It would be ideal if a surrogate parameter could be developed that correlated with the compounds that need to be removed. Right now, there is insufficient information on how these organics are simultaneously affected by a treatment process to develop these correlations. I'd like to see them developed. I think everybody would. It's much easier to use surrogate than specific standards.

Q BUSCH: Perhaps so, but isn't there a legal problem in imposing a surrogate standard for a specific compound? It appears that, legally, we are going to have to identify specific compounds.

A COTRUVO: I think I can answer that. This discussion falls into EPA's province. It is possible for both to exist simultaneously. There can be standards for individual chemicals and there also can be standards for surrogates. For example, coliform bacteria are a surrogate standard which are intended to indicate overall biological quality. The same kind of thing could exist for organics. There could be a standard for trihalomethanes and, at the same time, there also could be standards for TOC, TOCL, or whatever. Of course, both specific and collective standards would have to be satisfied.

MOSER: The development of surrogate parameters would require collecting an immense data base to convince people that they provided satisfactory correlation with specific

contaminants. More typically, those types of correlations are developed for a particular place with a fairly consistent raw water situation. There are convenient ways for determining such a relationship between parameters, and using that as an operating criterion.

COTRUVO: Although we have some flexibility under the statute when setting standards, we have a fairly strong directive for setting a numerical standard when there is clearly an adverse health risk, as in the case of carcinogens, and when the measurement is manageable. That may not turn out to be the optimum approach in situations where a large number of chemicals might be present.

SUFFET: I think the screening methodology is an approach that requires consideration of water quality fluctuations and their implications for sample collection. Sample collection is sometimes neglected in devising systems for collecting data. Grab samples don't show you the whole story. You have to see things over the longer span of time.

COTRUVO: By the way, we are not only concerned with trihalomethanes; we consider the trihalomethanes as both a chemical MCL and as a surrogate because they represent, at least qualitatively, the formation of a whole range of chemicals during the chlorination process.

Q MR. PANAGIOTAKOS: I'm from the Lowell Water Treatment Facility. We are just installing a GAC unit. We have been using PAC for about 15 years. I have a question concerning chlorine residuals. In our State, we are required to maintain a free chlorine residual in the effluent. With GAC we are going to be removing the chlorine, and we are going to have to post-chlorinate in order to satisfy the State's standard. What is EPA's stand on this matter? Will it be possible in the future to lower or eliminate the free chlorine standard?

A COTRUVO: There are no EPA chlorination or disinfection regulatory requirements. That is a State matter. Our intent is to minimize the unnecessary introduction of synthetic chemicals into drinking water while assuring protection from pathogens. Disinfectants and their by-products are synthetic chemicals. Nevertheless, there are definite benefits from disinfection as well as from the maintenance of a disinfectant residual in the distribution system. The appropriate combination of treatment processes has to be worked out in each specific system.

Q PANAGIOTAKOS: What I was really trying to find out is, if current studies show that we may cause more harm by post-chlorinating after GAC than if we didn't.

A COTRUVO: The point is, that after the GAC has been applied, the total organic loading of the water is lower than it was in the influent; therefore, the amount of by-products that are formed from post-chlorination are generally going to be less than they would have been in the absence of GAC.

MOSER: Given that granular carbon is going to remove the chlorine anyway, and that the pre-chlorination only makes your trihalomethane problem worse, it would seem to make sense to rely upon post-chlorination for much of our disinfection.

Q RHODES TRUSSEL, Montgomery Engineers: Mr. Moser, I'm concerned about the implication that GAC may be effective for removing trihalomethanes for periods as long as 9 months. I noticed that data from two points in time at the Hopewell Facility were presented. In the first instance, the trihalomethane levels were rather low and there was about a 50 percent removal. Then, 9 months later, 78 percent removal was observed with levels between 400 and 500 ppb coming in. Other studies have generally shown that carbon is usually exhausted much earlier than either of these two periods. I wonder if it wouldn't be reasonable to suppose that the trihalomethane concentration in the influent to your carbon is varying a great deal, that the carbon isn't just serving to smooth out the trihalomethane levels in the effluent, and the actual mass of trihalomethane discharged from the carbons over a long period of time probably equals the mass coming in.

A MR. MOSER: I admit that you certainly could be right. Only after we collect more data from a greater number of samples and average them out will we determine whether you're right or not.

MR. TRUSSEL: I'd like to see much more frequent monitoring of that plant. It would be very interesting.

MR. MOSER: We're going to do so.

Q MOHSIN SIDDIQUE, the Washington Suburban Sanitary Commission: Mr. Moser, in your work on the regeneration of carbon, did you analyze the gaseous products of regeneration?

A MR. MOSER: No. We weren't concerned with that since it had not yet been shown to be a problem.

LUNCHEON PRESENTATION

(Beginning of Luncheon, April 30)

DR. STEPHEN J. GAGE

I am very pleased to be here today for this luncheon speech. First, I'd like to extend my congratulations to Professor Sontheimer and Dr. Cotruvo for this very successful CCMS pilot project and also for this very successful technical conference. I have been involved wth CCMS for more than 6 years in one way or another. I think that I can whole-heartedly say that this is by far the most successful technical conference yet hosted by the CCMS. I hope that the success of this conference is some reasonable indication of the interest, in this country and abroad, in the very important subject of protecting the health of our people from contaminants in the drinking water supply.

I would like to make a few remarks about CCMS. The organization was formed in 1969 as the civilian arm of NATO, the North Atlantic Treaty Organization. At that time, considerable thought was given to strengthening the role of NATO, especially with the success of the economic restoration of the European countries. It was felt that it would be most appropriate to establish a civilian analogue to the military and technological activities of NATO. The author of this idea, it's reputed, was Patrick Moynihan, who was working in the White House at the time. Since then, Mr. Moynihan has gone on to become our Ambassador to the United Nations and more recently, a Senator from the State of New York. He started this program and was the first American chairman, and it has been running successfully ever since. In fact, this Fall, here in Washington, we'll celebrate the tenth anniversary of the Committee on the Challenges to Modern Society. The U.S. has volunteered to host this meeting and all of the other CCMS countries have heartily concurred. We will be holding the tenth anniversary plenary session here in the latter part of October. I hope some of you who are working on the CCMS projects will be able to join us.

I understand that eleven of the NATO countries and three countries outside of NATO are participating in this pilot project. That representation is probably typical for the projects that

have developed in recent years. We have had some projects with as many as 20 or 25 countries taking part, and other projects with as few as three or four countries. All of them have had the same basic goal, to improve the living conditions of the people of the NATO countries and of the people of other countries around the world. CCMS has emphasized concerns in health and safety, environment, and energy that have strongly influenced our public policies during the past decade.

All of the other CCMS Projects are run in essentially the same way as this one. Typically, two to three countries agree that they will sponsor the pilot project and thus become the project leaders. In this case, the project leaders are the United States, the Federal Republic of Germany, and the United Kingdom. I think all of the NATO countries have sponsored a project at one time or another. While the U.S. has played a major role in supporting many of the projects, we have had excellent sponsorship from throughout the North American and Western European continents.

We have had some excellent projects, which include work on air pollution surveys and control strategies, hazardous waste disposal systems, and automotive safety. I might just mention that I am packing my bags to attend the next CCMS plenary session in Brussels, which opens Thursday morning. We are going to propose three new pilot projects. One is on estuarine management, for which the Greek government will be proposed as the project leader. The United States will contribute with our massive study of the Chesapeake Bay estuary system. That gives you some idea of how closely such international projects are tied to our interests. The other two projects range far afield in other directions. One new project is on plastics recycling, which will look at ways to reduce the amount of plastic waste products burdening the environment and to reclaim more of those valuable materials that can then be used as feed stocks for other plastic processing operations. The third new project is related to the protection of monuments from air pollution. Right now, interestingly enough, the Greeks and the French are competing for sponsorship of that project, both having expressed a great deal of enthusiasm for it. Given the effect on the cathedrals and other public buildings in France, or on the historic buildings such as the Acropolis and Parthenon in Athens, this is a very important new project.

The United States receives a great deal of benefit from these CCMS projects. First, it always leads to an improved understanding among the various Western nations involved. In some instances, other nations from around the world have been included. Australia, New Zealand, Japan, and some of the African countries have participated in some of these projects. So in a sense, CCMS provides a forum for improved understanding

throughout the world. It encourages the sharing of technical information, as exemplified by this meeting, and just as importantly, the sharing of information concerning institutional and social development for improving health, safety, and the environmental quality of the various countries.

Institutional and social concerns are probably the most sensitive areas in the design of a new pilot study. The argument always presented is that the work will interfere with the political aspects of the individual countries or that working cooperatively would be difficult. Frankly, the lessons we have learned in these many projects--over 30 to date--cover the institutions and the social structures of the other countries. In that way, we have benefited greatly in the approach to using the technologies that we have identified through the projects.

I would like to pass on to you a couple of anecdotes that I have found quite interesting. One of the earliest projects started, I believe in 1970, was on automotive safety. This was a project in which several automobile companies were presented with the challenge to design new safety features, such as side rails, collapsible bumpers, and other devices that are now generally accepted and are used in most automotive design. But as you will recall, back in 1970, there was still a great deal of hostility and skepticism toward those ideas in some quarters, stemming from the belief that these innovations would make the cars too heavy and/or that the benefits from such improved safety design would not merit the additional cost and effort.

The United States wanted to be the major pilot on this project, but the people who were organizing the project could not convince any of the Detroit auto manufacturers to participate. The Department of Transportation had to issue a competitive contract and actually hire three companies with no previous automobile manufacturing experience, to make modifications in automobiles and to test the various types of innovative safety designs. The automobile industries of Germany, Sweden, and Japan, on the other hand, all took the project very seriously and divided the responsibilities among themselves according to the size of the car. One took a small car, another took an intermediate size car, and the third took the larger car. They began designing and constructing automobiles and testing them, and committed a substantial amount of resources to carry out destructive testing of a full-scale automobile. About 1974, when the success of the pilot project became obvious here in the United States, Detroit suddenly became interested. I'm speaking of General Motors, Ford, and Chrysler. They started their own independent work, or at least made public some of the work that they were doing. If I had a lesson to bring from that particular example, it would be that the institutional changes that we helped bring about in this country, as a result of our involvement in this

international technology transfer project, were more important than the technologies themselves. Although we did have safer Volvos and Datsuns driving around on American streets, hopefully we also have safer American automobiles.

I will mention another project, or a series of projects, in which I first became involved with CCMS. After Mr. Moynihan left the White House to become Ambassador to the United Nations, the responsibility for the CCMS chairmanship went to Mr. Russell Train, who was then the Chairman on Environmental Quality and subsequently administrator of the Environmental Protection Agency. I was working for Mr. Train in 1973, at the time of the Arab oil embargo. Mr. Train asked me to put together some ideas for some projects on energy that would not conflict with the interests of other U.S. agencies, and that in fact, would help increase their interest and attract interest from other countries. Three ideas resulted. One was a project on solar energy, another on geothermal energy, and another on energy conservation.

The first attempt to determine interest on the part of CCMS countries resulted in a mixed response. In fact, we were discouraged at that time. Basically, the countries said, well, we're either too far north in Europe to use solar energy or we're too far south in Europe, or we're too poor to be able to invest enough in additional research to make a significant contribution to solar energy development. We heard different reservations for the geothermal and energy conservation projects. As it turned out though, the world's perception of their use of energy, or at least those of the western industrial nations, changed so markedly during the intervening 3 years that when these three pilot projects were reported in Brussels this past fall, it was apparent that CCMS had actually fostered an overwhelming success in international cooperation. Over 20 countries took part in the solar energy project. Over 15 countries became involved in the geothermal project, which entailed drilling geothermal wells in Turkey, Greece, Portugal, as well as in the United States. We were soon able to recruit New Zealand, Mexico, and other countries for cooperation in the CCMS projects.

Probably the best story of all was that connected with energy conservation which was renamed, as Rational Use of Energy. From that project, we discovered that throughout the world some very sophisticated research was being done on how best to use available energy for space conditioning, heating, or air conditioning.

That project, up until then, probably contributed the most to the United States' National Energy Conservation Program, by providing a good substantive technological base.

Recently, I was associated with the Flue Gas Desulfurization Project. This was interesting for me in that it goes back to

my first experience with international technology transfer. I will conclude with this anecdote.

In the Spring and Summer of 1972, it became obvious that the U. S. Environmental Protection Agency's support for using scrubbers, or flue gas desulfurization units, had aroused a great deal of adverse reaction from the electric utility industry, which was to be forced to use scrubbers in many of their installations. The scrubber that had been used as the basis for the administrative decision had been dismantled and moved from the site of the electric power plant. Therefore, it was not feasible to return to that same scrubber and operate it for longer periods of time and under different operating conditions to show the utility clearly that scrubbers could work. Consequently, a group of us were asked to investigate the status of flue gas desulfurization units in Japan. We spent 3 weeks there in the summer of 1972 and prepared an interagency report on our findings. The effectiveness of the flue gas scrubbers in Japan supported the EPA Administrator's decision and made it tenable. We found that there were a number of scrubbers operating at full-scale there, including one scrubber operating on medium sulphur, high-ash coal at over 90 percent reliability without any serious chemical problems. We brought that experience back with all the documentation that the Japanese company provided us, and that particular scrubber became the most important scrubber in the world for the next several years.

These anecdotes are an indication that we are willing in this country to capitalize on the experience of the other advanced technological nations in making economic decisions. To put it another way, where we can find demonstrated technology in other countries that can be transferred to this country, we will incorporate it into our environmental decisions. The reason why I brought the scrubber case up now is that we are going back. In fact, I started about 2 years ago to recap the Japanese experience. We also found operating scrubbers in Norway and in West Germany to add to that bank of experience. At this time, the Japanese now have over 200 operating scrubbers, nearly all of which have had excellent success. They have increased the number of coal-fired power plants using scrubbers from one to five, and each of those installations are effective. In fact, the one plant that was mentioned earlier has had a record of close to 100 percent reliability for the last 5 years. That's a tribute to Japanese engineering, but also, it should be recognized that when good technologies can be developed and dedicated, capable people are there to employ them, some of the technological problems that seem to pester us all the time can be mastered.

I will conclude by pointing out that we take the activities of these CCMS pilot projects very seriously. The Congress of the United States requires us to prepare a 5-year plan and submit

annual updates of that plan to them. In our 5-year plan, our research outlook for 1979 which was submitted to the Congress in the early part of February, one paragraph from the chapter on drinking water states that: ". . . water treatment practices in other countries are similar to those used in the United States with the important exception that greater use is made of granular activated carbon and disinfectants other than chlorine. New developments in the drinking water area are transmitted through contacts among individual scientists, the NATO Committee on the Challenges to Modern Society, the World Health Organization, and other professional organizations." This shows that we have built the CCMS project on Adsorption Techniques in Drinking Water Treatment into our 5-year plan. We hope that this technical conference, and the many exchanges that I know occur among our scientists and the scientists from the various countries, will enable this project to live up to our expectations as being one of the most successful that we have yet sponsored under the Committee on the Challenges to Modern Society.

EUROPEAN EXPERIENCE IN THE USE OF ACTIVATED CARBON TREATMENT

EPA
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OTAN
CCMS
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AN EVOLUTIONARY APPROACH TO ACTIVATED CARBON TREATMENT IN FRANCE

Pierre Schulhof

In France as in other industrialized countries, the treatment of river waters to produce drinking water requires the elimination of most of the organic substances.

The various types of organics present in raw water, as categorized by engineers specializing in water treatment rather than by chemists, have long been classified as

1. Organic materials with unpleasant taste
2. Organic materials without taste, but which acquire a taste through treatment, notably chlorination
3. Organic materials without taste and unaffected by treatment
4. Organic materials that interfere with treatment, for example by causing foaming.

For years, because the pretreated raw waters were still of adequate quality, this classification was the sole consideration in water treatment. It is principally centered on taste problems and more particularly on taste related to chlorine treatment. The taste of chlorine has long been unacceptable in France.

This aversion to chlorine taste has resulted in the use of ozonation since the beginning of the century and of activated carbon for the last twenty years.

Recently however, a new classification of organics has been superimposed on the first one because of the decline in raw water quality. This second list is not only linked to the organoleptic quality of the treated water, but it also takes into consideration possible long-term effects of some chemical compounds. The second classification includes:

1. Organic materials of natural origin that are not transformed by treatment (especially chlorination)

2. Organic materials of natural origin that are transformed by chlorination

3. Organic materials that are of synthetic origin.

The elimination of materials in the second category requires treatment without chlorination; the elimination of materials in the third category can be achieved by different suitable means.

This being the case, a new treatment concept has evolved in which the role of activated carbon remains very important but is associated with a function quite different from that for which it originally had been provided. Today biochemistry governs water treatment technology. Activated carbon no longer acts only as an efficient adsorptive agent but also as a favored site for biological degradation.

Beginning in 1970 a few plants were constructed according to this new concept and have been in operation since 1975. Construction of other plants is in progress and some are expected to begin operation at the end of 1979. In several places pilot plants have been operating for several years.

The role of activated carbon should not be considered independently, however. Its combination with other treatment processes, now available, should be emphasized.

EXPERIENCE WITH POWDERED ACTIVATED CARBON

In the past, activated carbon was used essentially to eliminate tastes of natural origin from raw waters. These tastes are very often associated with the presence of algae in rivers. Indeed, in most cases they are not strong but are exacerbated by the action of synthetic organics, especially those produced through chlorination.

Progressively increasing quantities of organic substances and ammonia are contained in the rivers. The need for chlorine addition to eliminate ammonia made the taste problem difficult to solve, but fortunately activated carbon is very effective in this respect.

In some cases when the water to be treated contains a particular synthetic organic that has a bad taste or interferes with the treatment process, its elimination is obtained by activated carbon. At first powdered activated carbon was used, it being readily available in France at low cost and easy to implement. (Table 1 lists principal plants using powdered activated carbon.)

Table 1

Principal Drinking Water Plants in France Using Powdered Activated Carbon (Output >50 x 10^3 m^3/day)

Plant	Output m^3/day	Raw Water Origin	District Supplied	Treatment	Date of PAC Going Into Service	Average Treatment Rate mg/l	PAC Function	Storage and Supply	Carbon Origin
Choisy-le-Roi	800,000	Seine River	Paris southern suburb	Chlorination; aluminum polychloride coagulation; powdered activated carbon treatment; flocculation-sedimentation; rapid sand filtration, part on sand, part on activated carbon; ozonation; addition of Cl_2	1964	0 to 30	tastes	2 silos (90 T each); weighing systems	coconut
Neuilly-sur-Marne	600,000	Marne River	Paris eastern suburb	Chlorination; aluminum polychloride coagulation; powdered activated carbon treatment; flocculation-sedimentation; rapid sand filtration; ozonation; addition of Cl_2	1968	0 to 30	tastes	1 silo (70 T) (plus containers); screw conveyor; proportioning	coconut
Orly	300,000	Seine River	Paris southern suburb	Chlorination; $Al_2(SO_4)_3$ plus activated silica coagulation; powdered activated carbon treatment; flocculation-sedimentation; rapid sand filtration; ozonation; addition of ClO_2	1970	0 to 20	tastes	3 silos; 2 gravimetric batchers	coconut and peat
Mery-sur-Oise	200,000	Oise River	Paris northern suburb	Present treating line: chlorination; aluminum polychloride coagulation; powdered activated carbon treatment; flocculation-sedimentation; rapid sand filtration, part on sand, part on activated carbon; ozonation; addition of ClO_2	1964	0 to 30	tastes; organic matter	Containers; proportioning; screw conveyors	coconut

Table 1

Principal Drinking Water Plants in France Using Powdered Activated Carbon (Output >50 x 10^3 m^3/day) (continued)

Croissy	120,000	Seine River	Outer western suburbs	Coagulation; flocculation (aluminum sulfate plus activated silica); powdered activated carbon; sedimentation with powdered activated carbon; aerated sand filtration; ground level replenishing through sand pits	1958	10	detergent removal (avoiding foams in sand pits)	containers; proportioning	coconut and peat
Aubergenville	120,000		Outer western suburbs	Coagulation; flocculation (aluminum sulfate plus activated silica); powdered activated carbon; sedimentation with powdered activated carbon; nitrification (bacteria beds); sand filtration; ozonation; addition of Cl_2	1961	Varies widely	Tastes (in connection with algae and bacteria)	Containers; proportioning	coconut and peat
Morsang (first section)	75,000	Seine River	Outer southern suburbs	Prechlorination; coagulation (alumina sulfate plus activated silica); powdered activated carbon; flocculation-sedimentation with powdered activated carbon; sand filtration; ozonation; addition of Cl_2	1969	15	tastes; organics removal	1 concrete silo (60 m^3)	peat and anthracite
Suresnes-pont-Valerien	50,000	Seine River	Paris north-western suburbs	Chlorination; powdered activated carbon; coagulation; flocculation-sedimentation; rapid sand filtration; addition of ClO_2	1959	40	tastes	containers; proportioning	peat and anthracite

The activated carbon treatment technique has been steadily refined. Activated carbon input locations were studied with respect to the application points of other reagents. It was found that the carbon should be introduced last, as far as possible from the flocculating agent and chlorine or chlorine dioxide. It was also found that adding the carbon in lots at two different locations improved the economy of treatment.

Activated carbon in powdered form remains widely used in France. It is very effective in eliminating taste from treated waters containing low concentrations of organic substances and ammonia. It is also particularly well adapted to meet organic matter peaks of short duration, without heavy capital costs. In such cases the treatment consists of injecting large doses of carbon, up to 100 mg/l, for a short period.

Thus while the effectiveness of powdered activated carbon in eliminating organic substances economically is somewhat limited, substantial removal can be achieved. Combined with a well-designed and well-operated flocculation-sedimentation process, a dose of 20 to 30 mg/l can reduce the total of dissolved organic matter by about 60 percent. However, the constant increase of chlorination doses accompanying the rise of dissolved ammonia creates taste problems that powdered activated carbon cannot eliminate. This is why, at the end of the 1960's, French engineers responsible for water treatment looked to granular activated carbon, not to replace the use of powdered carbon but to extend its range when the yield was low. Initially this modification took place in the simple filtration stage through the exchange of granular carbon for sand in the filter beds.

GRANULAR ACTIVATED CARBON AS A FILTER BED

The concern for taste problems, especially chlorine taste, contributed to the initial development of granular activated carbon (GAC) filtration. However, it is not possible to stop the reaction of organic substances with chlorine used at the breakpoint rate to eliminate ammonia. This is evidenced by current required chlorine doses of more than ten times the amount of dissolved ammonia that is present, although a factor of seven is sufficient to control the ammonia.

In addition, the competition between ammonia and organic substances for chlorine consumption is sometimes difficult to predict because the kinetics are very complex. This may lead to an underestimation of the chlorine dose, resulting in a partial oxidation of ammonia stopped at the chloramine level. Chlorinated organic substances and chloramines give water the improperly named "chlorine" taste to which consumers object.

Also, odor thresholds as high as 20 may be measured in raw waters chlorinated to breakpoint, while they were measured at 4 before treatment.

Chlorine taste is difficult to remove with powdered activated carbon. Organic materials should be eliminated before they combine with chlorine. Very high doses of powdered activated carbon are necessary to obtain reliable taste removal.

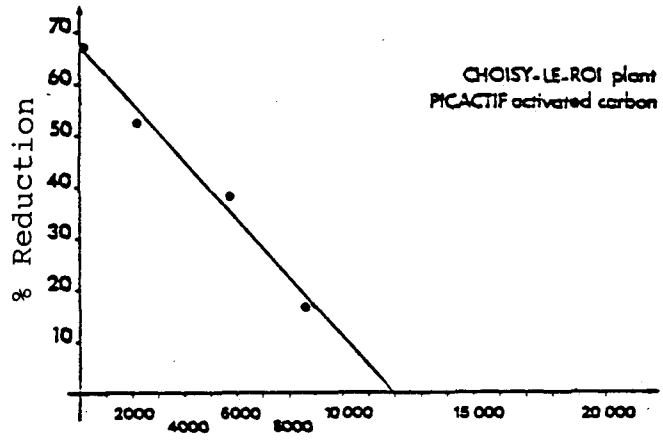
The mechanism of granular activated carbon placed in a filter bed is quite varied. First, it acts as a chlorine removal agent and decomposes chloramine to regenerate ammonia, which is eliminated fairly well by nitrifying bacteria contained in the filter, yielding an ammonia-free water at the output. Second, it adsorbs taste- and odor-causing organochlorinated compounds which because of their slow kinetic reaction, remain at low levels during the filtration process. Consequently they can be effectively adsorbed by carbon for a long period.

Under such conditions it is not unusual for carbon filtration effectiveness on the taste of water to be maintained over one or two years, whereas effectiveness in removing total dissolved organics lasts only a few months. This is illustrated in Figures 1 and 2, which show the results of two years of testing at the Choisy-le-Roi plant. Tests at this plant also indicate that chlorine added to GAC-treated waters is consumed quickly (Figure 3), indicating a new generation of organochlorinated substances.

With some precautions, good results can be obtained in the removal of chlorine taste in treated water through simple filtration on activated carbon. A number of plants in France have applied or are still applying the technique of breakpoint chlorination followed by flocculation-sedimentation-activated carbon filtration (Table 2). Disinfection is usually by ozonation, and distribution network protection requires addition of chlorine or chlorine dioxide. Carbon is regenerated every year or every two or three years, depending on the case. Some carbon beds have been regenerated up to five times without any difficulty. Regeneration criteria are most often based on the taste threshold test.

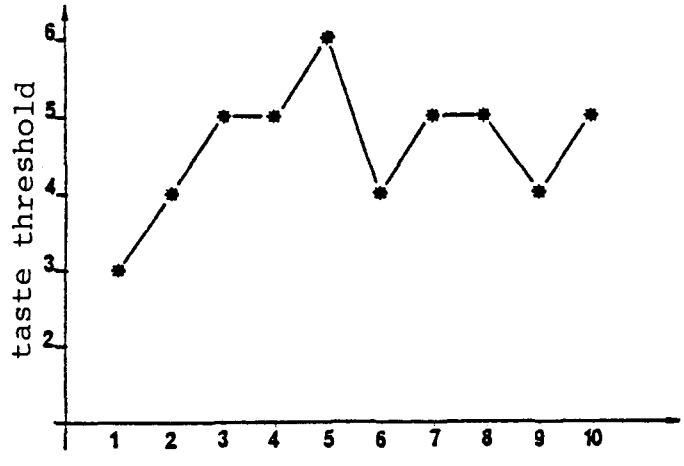
Filters are usually of the open type, made of concrete in rectangular shapes with a surface area of up to 120 m^2. Carbon layer depth and empty bed contact time vary from 0.70 to 1.0 m and from 6 to 20 min, respectively. In most cases washing is carried out with air and water.

An extended range of carbon grades is used, most of which give satisfactory results with respect to the taste of treated



Filtered Water Volume (m^3) Per m^3 of Carbon

Figure 1. Reduction in Total Organic Carbon by Single Filtration on Activated Carbon Beyond That Achieved by Sand Filtration



Duration of Test - Months

Figure 2. Taste Removal by Single Filtration on Activated Carbon

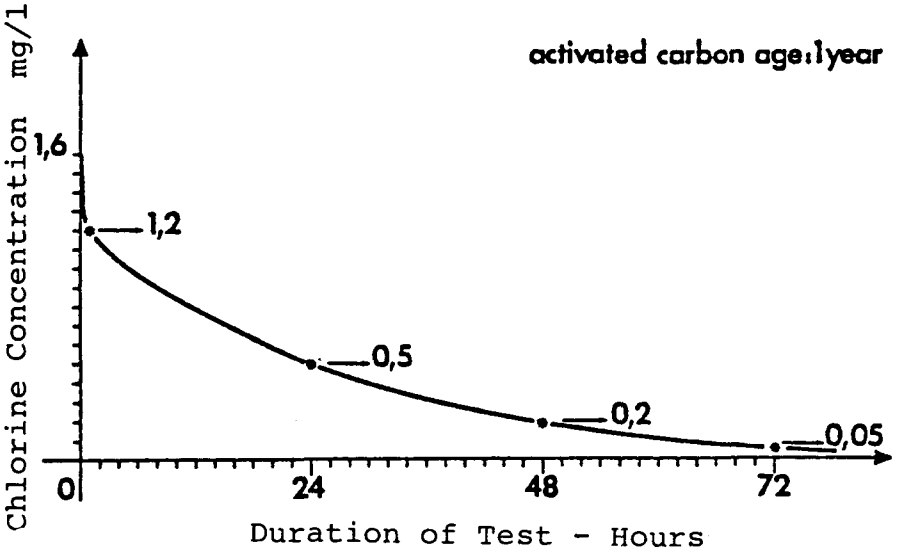


Figure 3. Chlorine Consumption in Filtered Water After Single Filtration on Activated Carbon

Table 2

Principal Drinking Water Plants in France Using Granular Activated Carbon for First Filtration (Output >50 x 10^3 m^3/day)

Mery-sur-Oise	100,000	Oise River	Paris northern suburbs	Chlorination; aluminum polychloride coagulation; flocculation-sedimentation; GAC filtration; ozonation; chlorination	1970	tastes; organic matter	6	108	15	12	1 filter Picactif 2 filters Picafil 2 filters Picaflo G 1 filter F300
Viry-Chatillon	100,000	Seine River upstream of Paris	Paris southern suburbs	Prechlorination; aluminum polychloride coagulation; flocculation-sedimentation; GAC filtration; ClO_2 disinfection	1973	tastes; organic matter	15	9 at 40 6 at 32	10	30	F 300 E; Row 0.8 supra
Saint-Charles	100,000	Moselle River	Nancy	Prechlorination; coagulation; 5A plus alginate flocculation-sedimentation; GAC filtration; ClO_2 disinfection	1974	tastes; organic matter	22	48	15	36	NCY 103 at F300
Vigneux-sur-Seine	50,000	Seine River upstream of Paris	Outer western suburbs	Prechlorination; aluminum; sulfate plus activated silica coagulation; flocculation-sedimentation; GAC filtration; ClO_2 disinfection	1970	tastes; organic matter	10	23	6	12	F300; F500; Row 0.8 supra; BS12
Houille	50,000	Houille River	Dunkerque	Prechlorination; coagulation; flocculation (Fe-ClO_2 plus starch), sedimentation, in part; flotation, in part; GAC filtration; replenishment basins	1973	organic matter	7	50	10	6	Row 0.8 supra
Choisy-le-Roi	30,000	Seine River	Paris southern suburbs	Chlorination; aluminum polychloride coagulation; flocculation-sedimentation; GAC rapid filtration; ozonation; chlorination.	1978	tastes	2	117	15	Not yet regenerated	1 filter Picaflo B 1 filter F300
Annet-sur-Marne	25,000	Marne River	Paris eastern suburbs	Aluminum polychloride coagulation; flocculation-sedimentation; activated carbon filtration; ozonation; chlorination.	1971	tastes; organic matter	2	45	13	36	1 filter Picactif 1 filter Picaflo

water. The selection depends on performance and cost considerations. In given circumstances, carbon grades may be mixed. Reactivation is carried out by the manufacturers.

In addition to removing taste, activated carbon filtration can be used when the water to be treated usually contains low concentrations of synthetic organics, but is subject to occasional contamination by industrial wastewaters that create peaks of synthetic organics for short periods. Even when already saturated with total organic carbon, activated carbon adsorbs these peaks and releases less harmful organics. In such cases, powdered activated carbon is also effective at high doses, but a monitoring device is required to detect the need to adjust the treatment, whereas a carbon filter is continuously available. For this reason, granular activated carbon filtration has sometimes been preferred over powdered carbon injection.

The experience acquired in France with simple filtration has permitted carbon manufacturers and water treatment engineers to master the technologies of carbon design (type and grain size) applicable to water treatment, selection of bed depth and contact time, filter backwash, and carbon regeneration techniques. It has been confirmed that carbon is an excellent filtering medium and that disinfection of filtered water is not a problem in spite of the large numbers of microorganisms contained in the filtering beds.

French experience also has shown that dissolved ammonia in raw water can be partially removed through biological action. The elimination of ammonia in this way, with a corresponding reduction in chlorination of raw waters, constitutes a definite move toward the elimination of chlorinated organics simply by avoiding their generation in the course of treatment.

Finally, with respect to total organic carbon, complete elimination tests have shown that a satisfactory result could be obtained at the cost of reiterated regeneration. From Figure 1 and Table 2, it can be estimated that if the average filtration velocity is 6 m/hr, regenerations at six-month intervals provide a 20 percent reduction in organic carbon content, which combined with flocculation-sedimentation-sand filtration gives a total reduction of 60 percent of the raw water content. At present regeneration costs, such a process stream is expensive.

NEW TECHNIQUES

The presence of substantial amounts of synthetic organics in river water is a rather recent concern. This analysis of the problem will essentially be centered on the Seine River flowing through Paris, which supplies, directly or indirectly from

related underground sources, the city's five million inhabitants, one tenth of the population of France (Figure 4).

Within ten years, micropollution of the river has increased considerably even in the area upstream of Paris. In terms of total organic carbon, the Seine River contains an average of 6 to 7 mg/l of dissolved organic carbon, including at least 3 to 3.5 mg/l of synthetic carbon. However, the proportion of volatile organochlorinated material, particularly THMs, is very small (< 10 µg/l).

As a result of increased amounts of ammonia and organic matter, chlorine demand (breakpoint rate) has increased substantially, as has coagulant demand (jar test rate) which is influenced by organic substances.

Despite the rise of total organic carbon content or chlorine doses, trihalomethane levels have never been very high in the treated waters, usually about 20 µg/l and in exceptional cases 50 µg/l. This is perhaps due to the brief contact time between chlorine and haloform precursors in the treatment plants.

Nevertheless, it is desirable to limit organochlorinated substances as well as taste- and odor-causing substances in supplied water. This implies severe restriction of the use of chlorine and elimination of organic matter to the extent possible.

The new techniques combine step-ozonation with sand and activated carbon double filtration. The second filtration on carbon is always preceded by ozonation, which efficiently promotes the elimination of organic substances, as demonstrated through tests begun in 1970 and subsequent research. This does not mean that the use of powdered or granular activated carbon without ozonation will be discontinued; they will still be used where applicable.

To illustrate these new technologies while remaining in the operational field of the Seine River and Paris district, data obtained from a pilot installation in the 800 x 10^3 m^3/day Choisy-le-Roi plant upstream of Paris will be presented in detail, followed by reports on full-scale developments that preceded or accompanied the pilot tests. These are the Morsang plant (150 x 10^3 m^3/day), which treats water from 40 km upstream of Paris; Rouen-la-Chapelle (50 x 10^3 m^3/day), which treats groundwater affected by the Seine River downstream of Paris; and Mery-sur-Oise (300 x 10^3 m^3/day), which treats water from the Oise River, a tributary of the Seine.

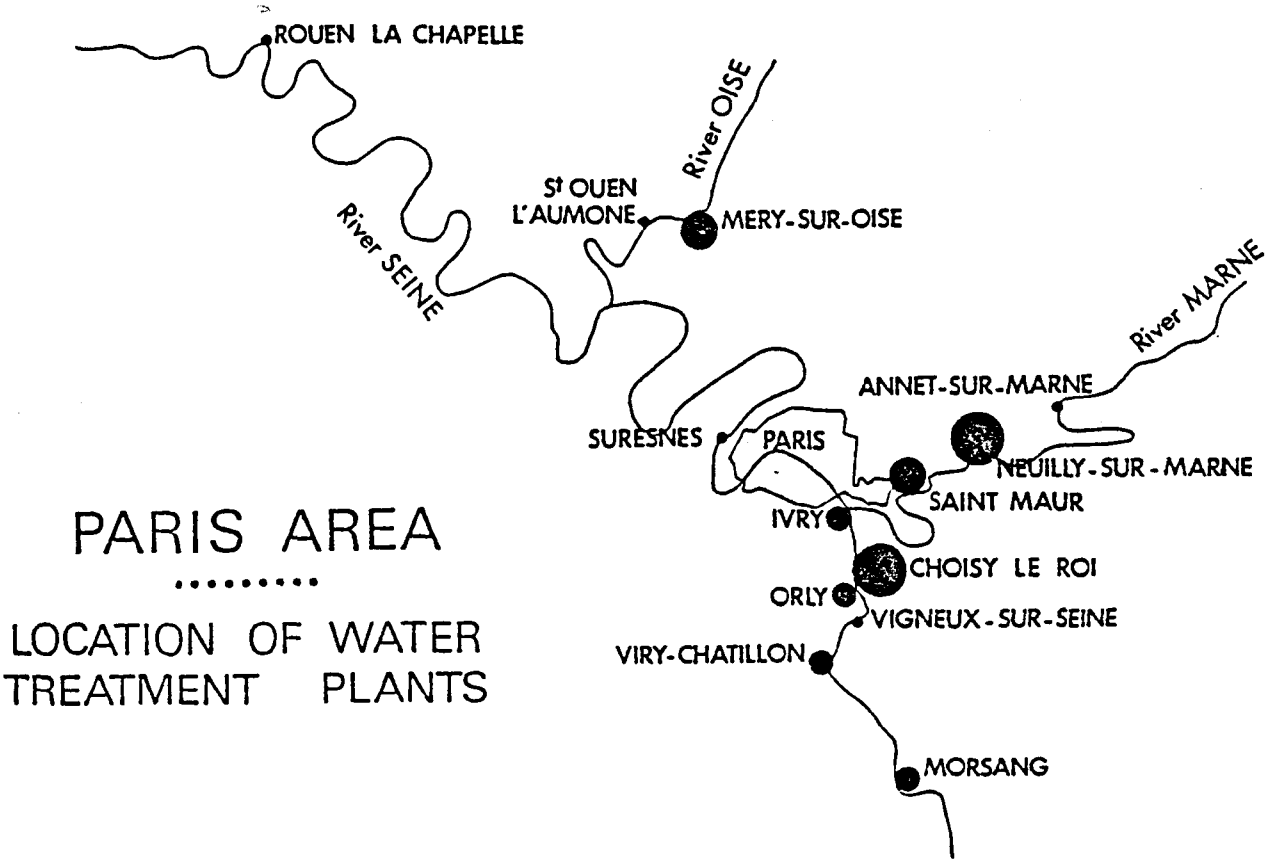


Figure 4. Location of Water Treatment Plants in the Paris Area

THE CHOISY-LE-ROI PLANT

The former treatment train at Choisy-le-Roi consisted of breakpoint chlorination (to an average of 6 mg/l); flocculation-settling; sand filtration at a maximum velocity of 6 m/hr and ozonation with 10-min contact time; and an ultimate chlorination step with a dose of 0.8 mg/l resulting in 0.4 mg/l of chlorine residual at the plant effluent.

The distribution network is long, and residence time is currently 72 hr. In summer, water temperature is high, sometimes exceeding 25°C.

The plant is equipped with powdered activated carbon devices whose performance has already been described. As a test, sand has been replaced by granular activated carbon in some of the plant's 54 filters of 117 m^2 surface area each. The supplementary reduction in total organic carbon produced by the use of activated carbon is plotted in Figure 1.

The results seeming insufficient, a pilot plant was installed which has been in operation for two years, permitting comparison of alternate treatments. Two essential modifications were tested in this pilot plant (Figure 5):

1. The suppression of prechlorination and its replacement by step-ozonation of rather short duration (about 2 min)

2. A second filtration with activated carbon after initial ozonation. Various carbon-water contact times were tested.

It was found that using the same ozone dosage as in the original installation (and thus with no extra cost) but distributing it differently--i.e., partially at the head of the train and partially after sand filtration--resulted in the total elimination of ammonia without the use of chlorine.

In addition, the combined effect of the first step-ozonation and a properly selected coagulant dose has made it possible to reach a 50 percent reduction in raw water total organic carbon at the sand filter bed effluent.

Data from the second filtration on activated carbon, after step-ozonation, are more difficult to analyze. As observed, when carbon was used as a simple filter bed, the reduction across the filter bed (between input and output) decreased to a final plateau after a throughput of 15-20 x 10^3 m^3 water per m^3 carbon during which organics were effectively eliminated. Contrary to the case of simple filtration, where the decrease in the

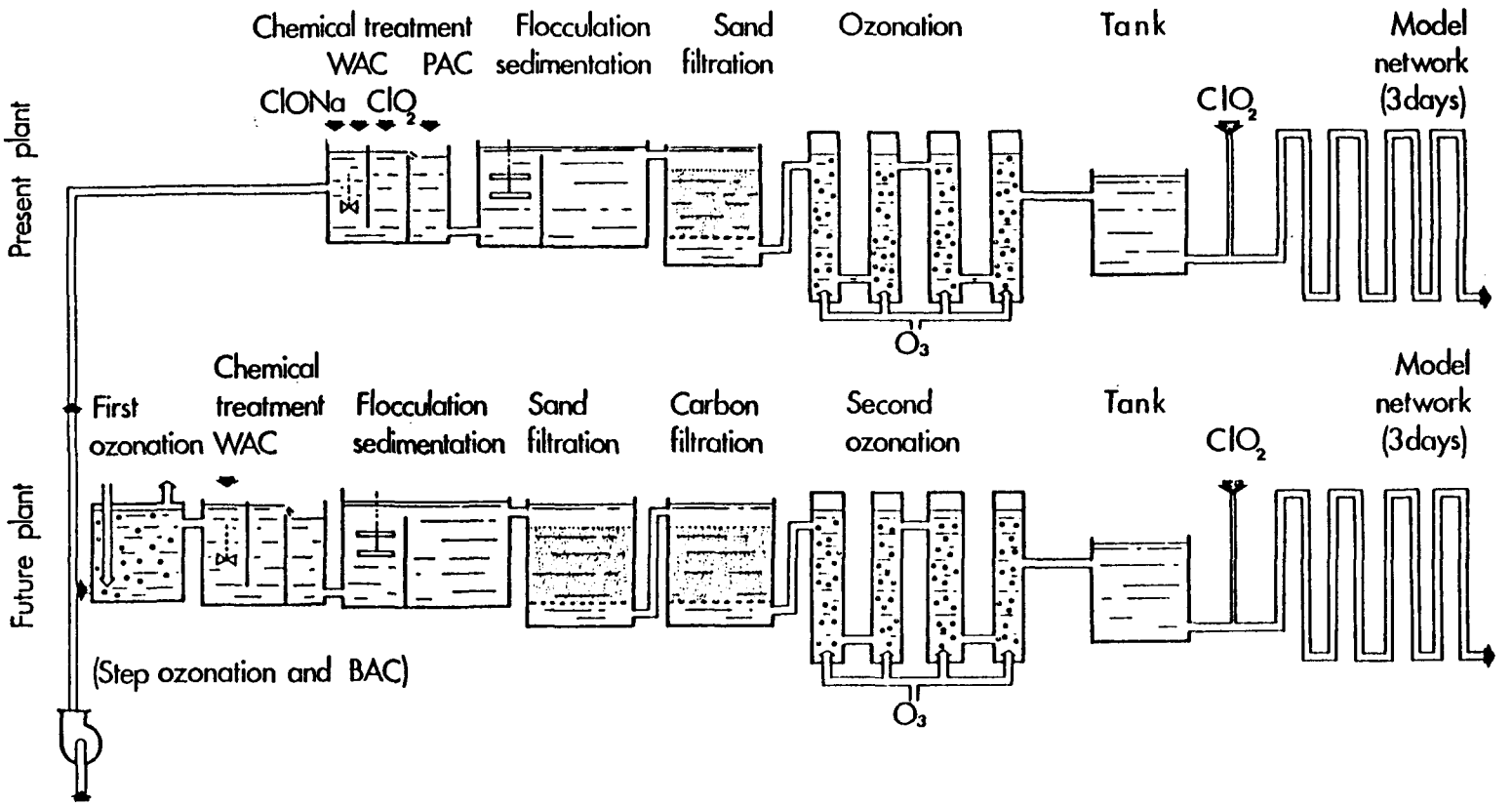


Figure 5. Choisy-le-Roi (800,000 m^3/day) General Flow Scheme of Pilot Plant

reduction nears zero, the final plateau shows a steady state reduction of about 30 percent of the total organic carbon at the influent (Figure 6). This plateau remains unchanged for one or two years without the need for regeneration.

The reduction of organics through the complete treatment process (step-ozonation, flocculation-sedimentation, double sand and carbon filtration) has been between 65 and 85 percent during tests carried on for more than a year. At the same contact time, the second filtration on activated carbon without regeneration resulted in a reduction of total organic carbon at least equivalent to the reduction obtained with simple filtration with activated carbon regenerated every four months.

Three empty bed contact times were tested with carbon: 10 min, 30 min, and 1 hr. No appreciable differences were observed in the organics level of the reduction plateau. A threshold was observed, however, in respect to filtration velocity. At 17 m/hr the reduction of detergents was limited to 50 percent, whereas the reduction was 100 percent at 12 m/hr.

Another interesting parameter is the chlorine demand of filtered water. The dose of chlorine injected for network protection depends strictly on the chlorine demand of the treated water. Therefore, using the pilot network of treated water, free chlorine is measured as a function of time, and the chlorine demand of the treated water is given by the difference between chlorine dosage and chlorine residual. Because this demand varies with the temperature and the initial dose of chlorine, these parameters must be well defined. (These tests were conducted with one-year-old carbon; i.e., when the reduction plateau had been reached.)

The second filtration on activated carbon is very important in stabilizing chlorine in the treated water. It has already been indicated that organics reduction was substantial, though limited. Significantly, the major portion of the organic substances eliminated are those that react with chlorine to form organochlorinated compounds. It is worthwhile to note that preozonation, prior to carbon filtration, has considerable influence on the rate of disappearance of chlorine (Figure 7), while the influence of preozonation on total organic carbon reduction is not so marked. Thus, ozonation acts preferentially on organics that consume chlorine, which is the desired objective. Under such conditions the quantities of organochlorinated compounds in the treated waters are extremely small. The decrease in the dissolved oxygen shows the biological nature of this phenomenon.

Many other studies are required to explain the basic mechanisms operating during the second filtration on activated

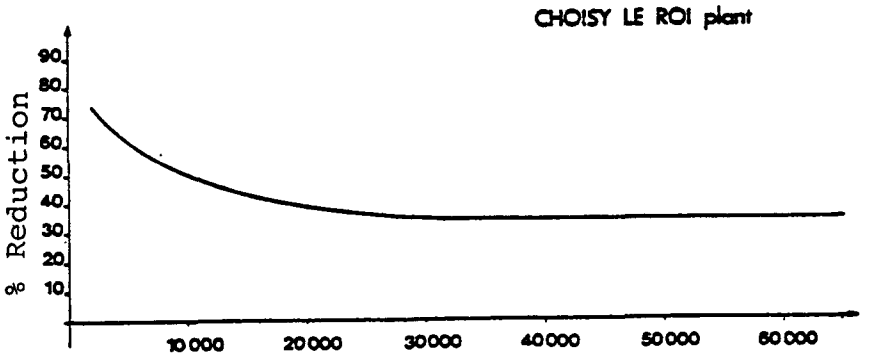


Figure 6. Reduction in TOC by Second Filtration on Activated Carbon Versus First Filtration on Sand

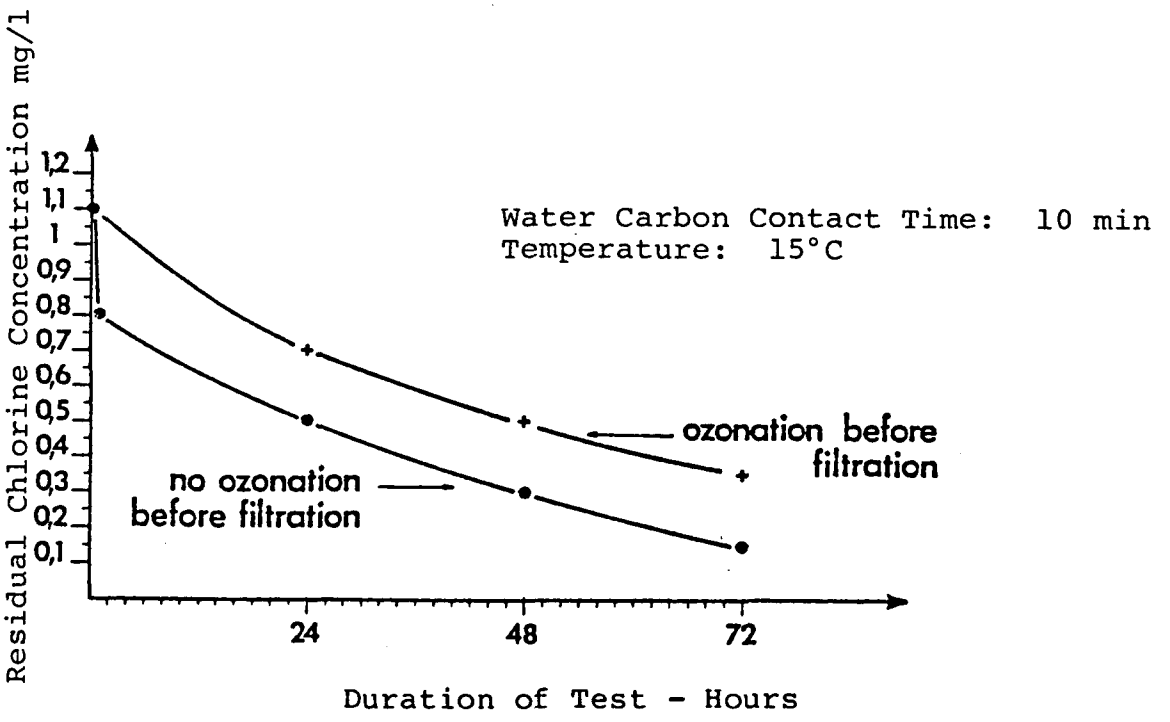


Figure 7. Chlorine Consumption in Filtered Water After Second Filtration on Activated Carbon

carbon after ozonation. With further research, optimum ozonation contact times in each particular case will be better defined.

Above all, an activated carbon should be specially developed for water treatment, to foster the effects of biological regeneration and take full advantage of this new technique. It is unlikely that activated carbon standards, determined for other applications, are suitable for specific water treatment operating conditions. French manufacturers are marketing a wide range of carbons and have agreed to cooperate in the development of specific carbons oriented to water treatment with a good quality-cost ratio.

Choisy-le-Roi plant modifications. From the pilot tests, what improvements are suggested for the Choisy-le-Roi plant?

At a rather reasonable cost, half of the 54 filters can readily be filled with carbon and operated in series following the other half of the filters, which would remain filled with sand. With preliminary step-ozonation to reduce the chlorination of raw water, the modified treatment would consist of sand and carbon double filtration and a second step-ozonation.

The Choisy-le-Roi plant was initially designed to process 800×10^3 m^3 of water per day with a filtering velocity of 6 m/hr through 54 filters. With the same filtering velocity, the new output would be reduced to 400×10^3 m^3/day.

However, the process of double filtration employs an increased velocity of 9 m/hr through the 54 filters arranged in two filter series. The same turbidity level would be maintained since two sequential filtrations at 9 m/hr give results equivalent to a single filtration at 6 m/hr. Thus, the expected production would be 600×10^3 m^3/day. Output over this maximum value would require that the two batteries of filters be operated parallel and arranged in a single filtration mode.

Modified to produce 600×10^3 m^3 of water per day by a double filtration process while retaining the possibility of producing 800×10^3 m^3/day by simple filtration, the installation at Choisy-le-Roi would remain flexible to handle peak demands.

Figure 8 shows organics reductions resulting from single filtration and double sand-carbon filtration after ozonation as a function of estimated additional cost, including capital and operating costs and regeneration expenses. When activated carbon is not used, organics reduction from initial concentrations in the raw water amounts to 50 percent. Obviously the double filtration after ozonation appears to be the most promising technique. It was on this basis that the decision was made to modify the Choisy-le-Roi plant (Figure 9).

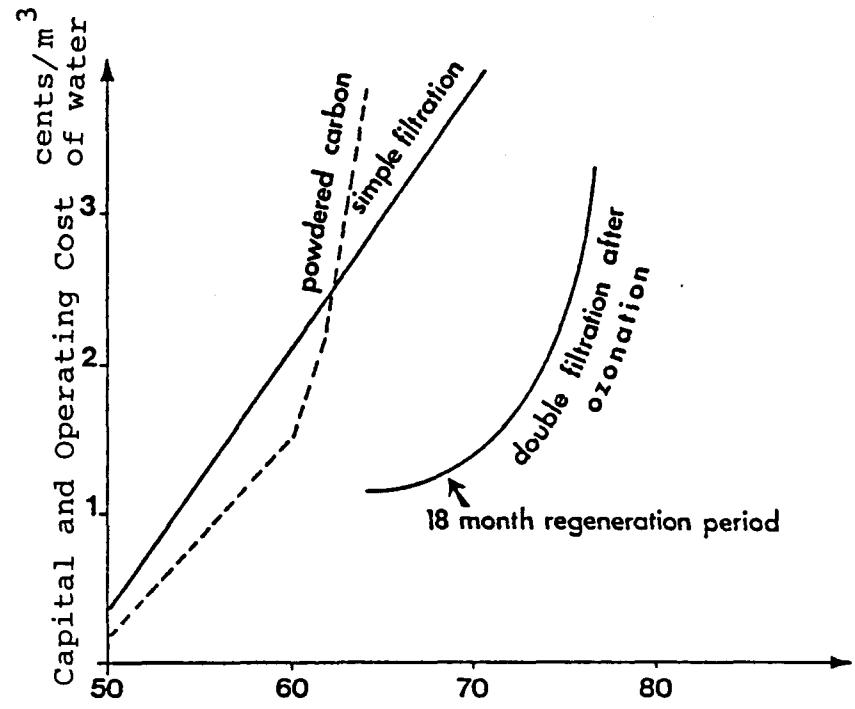
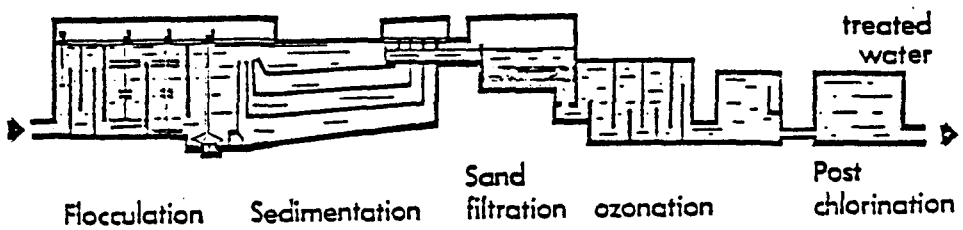


Figure 8. Organics Reduction Versus Capital and Operating Cost

800 000 m^3 /day

PRESENT PLANT



600.000/800.000 m^3/day

FUTURE PLANT

(Step ozonation and second stage active carbon filtration)

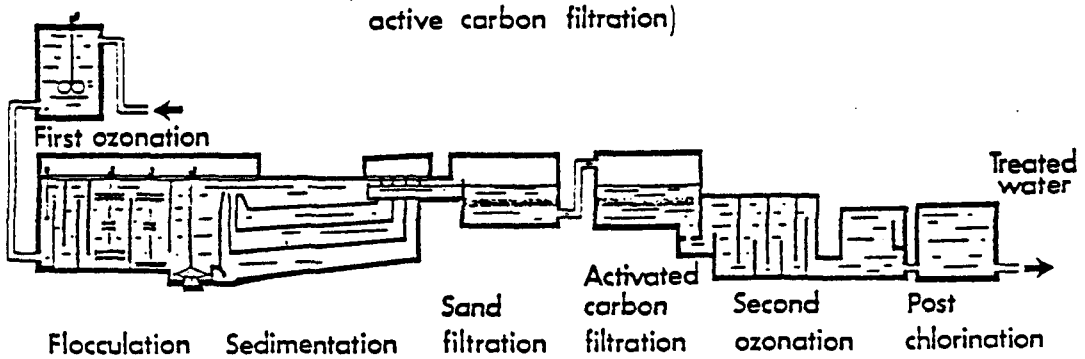


Figure 9. Original and Modified Treatment Processes at Choisy-le-Roi

The regeneration criterion will be based on the chlorine demand of treated water; a carbon regeneration period of eighteen months is expected. Organics reduction is anticipated to be 70 percent. Including capital, operating and maintenance, and regeneration costs, the added charge is estimated to be only 1.4 cents per cubic meter of water, corresponding to about one more dollar per year per consumer. For this small extra cost, a 40 percent reduction of synthetic organics in the water supplied will be gained, the improvement being mostly related to organochlorinated substances. Higher reduction percentages are possible, but the cost of additional gains increases sharply.

THREE NEW TREATMENT PLANTS

The primary reason for deciding to modify the largest water treatment plant in France was the confirmation of test results from the pilot plant at Choisy-le-Roi by experience with other plants using step-ozonation followed by double filtration which had been operating at full scale for four years. Three of these plants are described below. Plant characteristics and conditions of step-ozonation are summarized in Tables 3 and 4.

The Morsang plant. The 150 x 10^3 m^3/day capacity of the Morsang plant is obtained from three parallel trains. The first line uses powdered activated carbon; the second line, in operation since 1975, uses a second filtration on granular activated carbon. Half of the second line constitutes a third train in which an ozonation step is inserted before the carbon filtration so that the full treatment line comprises flocculation, sedimentation, sand filtration, ozonation, activated carbon filtration, and chlorination. This line yields a 70 percent reduction in organics, as measured by TOC.

The Rouen-la-Chapelle plant. Following a pilot testing program begun five years ago, the Rouen-la-Chapelle plant (Figure 10) was put into service at the end of 1975. The treatment sequence consists of a first ozonation with a short (3 min) contact time, a sand filtration, an activated carbon filtration with a contact time of 10 min, and finally a second ozonation, also with a contact time of 10 min. Before pumping the treated water to the distribution system, a 0.4 mg/l chlorine dose is added.

The first ozonation plays three roles:

1. It provides oxygen to water very depleted in dissolved oxygen.

2. It oxidizes and precipitates iron and manganese.

Table 3

Principal Drinking Water Plants Using Step-Ozonation Before a Second Filtration on Granular Activated Carbon

Plant	Capacity	Raw Water Origin	District Supplied	Treatment	Date of GAC Going Into Service	GAC Function	Number of GAC Filters	Filter Volume per Unit m^3	Average Empty Bed Contact Time min	Regeneration Period years	Carbon Type
Mery-sur-Oise	300 000	Oise River	northern suburbs	First ozonation; raw water storage; coagulation by aluminum chloride; flocculation-sedimentation; sand filtration; second ozonation; GAC filtration; chlorine disinfection; dechlorination; ClO_2	1979	organics elimination; chlorine stability & NH_4 elimination	12	108	13	Not yet regenerated	2 Picactif 2 Picafil 4 PicafloG 2 F 300
Morsang(second section)	75 000	Seine River upstream Paris	remote southern suburbs	Prechlorination; coagulation; flocculation; sedimentation; sand filtration; ozonation (half the plant); GAC filtration; final disinfection chlorination	1975	organics elimination	4	90	10	3	F400
Rouen-la-Chapelle	50 000	groundwater	Rouen southern suburbs	First ozonation; sand filtration; activated carbon filtration; second ozonation; chlorination.	1975	micro-pollution & NH_4 elimination	6	75	13	1 filter regenerated after 4 yrs testing	5 Picactif 1 Picafil

Table 4

Conditions of Step-Ozonation

Plant	First Ozonation		Second Ozonation			
	O_3 Concentration in the Air (g/m^3)	Treatment Rate ($g\ O_3/m^3$) of water	Contact Time in Minutes	O_3 Concentration in the Air (g/m^3)	Treatment Rate ($g\ O_3/m^3$) of water	Contact Time in Minutes
Mery-sur-Oise	15 to 20	0.8 to 1	3	12 to 18	2 to 4	10
Morsang				12 to 18	average 2.85	10
Rouen-la-Chapelle	residual second ozonation: 1.5 to 2; with addition of new O_3 12 to 15	1	3	12 to 15	1	10

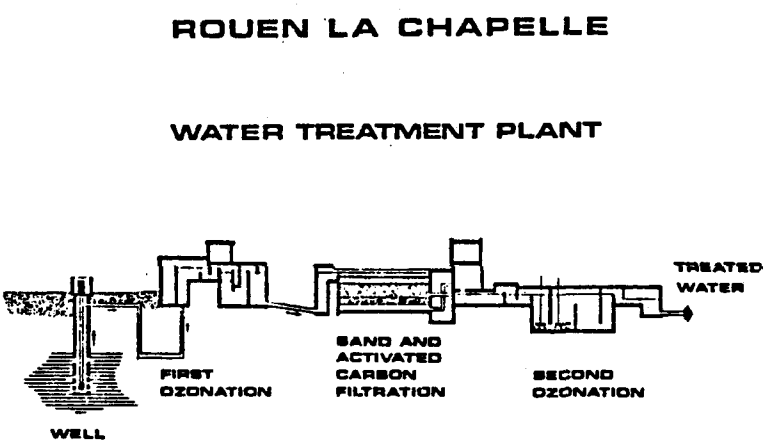


Figure 10. Treatment Process at Rouen-la-Chapelle

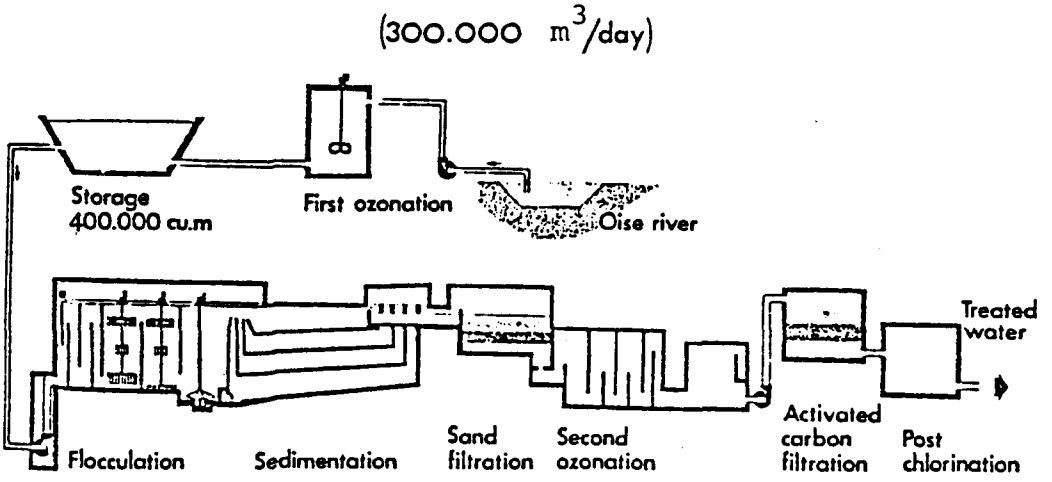


Figure 11. Treatment Process at Mery-sur-Oise

3. It transforms the organic micropollutants into substances that can be adsorbed on the activated carbon for a long period of time.

Ozonation coupled with activated carbon constitutes the technique termed biological activated carbon (BAC). Ammonia is biologically eliminated in the sand filter, for the most part, while the activated carbon filter, through the BAC effect, completes the elimination of organics. The organic content in treated water averages 25 percent of organic content of the raw water.

The reduction rate of 75 percent, observed at Rouen-la-Chapelle, is slightly higher than the 70 percent rate noted at the Morsang and Choisy-le-Roi plants, but this difference may be due to the nature of the dissolved organic content of the source water. After three years, the carbon has not needed regeneration.

At the Rouen-la-Chapelle plant, unlike the Morsang plant, the last stage of ozonation is introduced at the end of the treatment line, rather than before carbon filtration, and is followed only by chlorination at low dosage to protect the distribution system. Postozonation has sometimes been suspected of fostering regrowth of bacteria in the distribution network. No evidence for this has been found at Rouen-la-Chapelle or in other French water treatment systems using the same final ozone-chlorine combination. Plants at Toulouse and Nice, in fact, have been disinfecting with ozone only, without post-chlorination, for many years with satisfactory results.

The Mery-sur-Oise plant. Another plant under conversion by the end of 1979, will be the largest in France, and perhaps in the world, using step-ozonation and BAC to eliminate organics and limit the use of chlorine. This plant is located at Mery-sur-Oise, 20 km north of Paris, and is supplied from the Oise River, a Seine tributary severely polluted by industrial wastewaters (Figure 11).

Mery-sur-Oise was originally a conventional plant using simple filtration and ozonation, with a maximum output of 300×10^3 m^3/day. It is being modified by the addition of a riverside storage reservoir with preozonation and by the separation of the conventional filters into two batteries, in series, as at Choisy-le-Roi.

The raw water storage reservoir will hold 400×10^3 m^3 of water, corresponding to a little more than two days of average output of the plant. Such facilities allow the smoothing out of pollution peaks by pumping and storing water from the river when its quality is higher. The storage reservoir also will improve

the quality of the water through a natural purification process. To promote this prepurification, an ozonation stage is placed before the reservoir, eliminating some of the inhibitors of natural purification as well as phosphates that could encourage proliferation of algae in the reservoir.

After the storage basin the treatment line is comprised of flocculation-sedimentation and sand filtration, at which level ammonia is biologically eliminated; ozonation with a contact time of 10 minutes; and filtration on activated carbon in twelve filters of 100 m^2 surface area, with an empty bed contact time averaging 13 minutes. This stage eliminates organics as far as possible before a final chlorination preceding pumping into the distribution system. Only in this last operation is chlorine used in the plant.

It can be noted that step-ozonation is carried out in these three plants in three different ways: one ozonation between the sand and activated carbon filtration at Morsang; a first ozonation before sand and carbon filtration and a second after carbon filtration at Rouen-la-Chapelle; and a first ozonation before the sand filter and a second before the carbon filter at Mery-sur-Oise. The particular quality of the raw water at each plant leads to the particular treatment scheme. The common feature is that in every case double filtration is used with at least one ozonation step before the second filtration on activated carbon.

Conclusions

Experience in France covers a full range of the possibilities offered by activated carbon. During recent years, research has been accelerated and new developments have brought about continual improvements, with further progress in sight.

Two basic processes are used. The first, employed by six treatment plants with a combined output of 500 x 10^3 m^3/day, is adsorption--i.e., simple filtration on activated carbon beds. This requires a rather high frequency of regeneration.

The second process, used by four plants with a total output exceeding 400 x 10^3 m^3/day, is biologically enhanced adsorption entailing double filtration on sand and carbon beds with step-ozonation. Most conventional French treatment plants can be converted to this process at reasonable cost. Regeneration is still required, but less frequently.

Either of these processes can improve the quality of treated water, but in each case there is an optimal choice between the two. The choice depends both on the pollution level of the raw

water and on the quality requirements for treated water. The higher these are, the greater the inclination toward the double filtration process.

It has proved possible to obtain a 70 percent removal of organics and to control chlorination, at reasonable cost.

OBJECTIVES AND PROCEDURES FOR GAC TREATMENT IN THE NETHERLANDS

Adriaan P. Meijers, Johan J. Rook, Bart Schultink,
Johan G.M.M. Smeenk, Johan van der Laan, and Cees L.M. Poels

The annual production of drinking water in the Netherlands amounts to approximately 1 billion cubic meters, of which 40 percent is drawn from the Rhine and Meuse rivers, the Yssel Lake, and the Haringvliet. The Rhine is seriously polluted by many contaminants, while the other sources are polluted to a lesser extent. Given the quality of the sources for the production of drinking water, the Dutch waterworks are unanimous in their opinion that at least a 1-month reserve supply should be permanently available. Reserve water suplies are collected in storage basins and by infiltration in the dunes. Selective intake of raw water prevents serious pollution from reaching the purification plants. The collection of reserve supplies substantially improves and equalizes water quality, but pollution is so high that treatment with activated carbon remains indispensable. Powdered activated carbon is still widely used, but many waterworks now are changing over to granular activated carbon (GAC) treatment.

This paper describes several currently operating carbon filter installations and pilot plants, focusing on the criteria for contact time and operating time between regenerations, referred to as running time.

ROTTERDAM WATERWORKS, KRALINGEN

Water Quality

Rotterdam obtains its water from the Biesbosch storage basin where the water taken from the Meuse River has a residence time of approximately 3 months. The river is slightly contaminated by micropollutants. Table 1 shows the water quality of the Meuse at Keizersveer.

While the water is held in the storage basin, it satisfactorily improves in quality as the concentration peaks of pollutants taken in are attenuated. Algal growth in the deep basin is suppressed by screens of rising air bubbles that ensure the circulation of the water. The average chlorophyll content is 5 µg/l with occasional peaks of 40 µg/l.

Table 1

Water Quality of the Meuse at Keizersveer, 1977

Parameter	Minimum	Average	Maximum
Flow-m^3/s	23	270	1,015
Temperature-°C	2	12	22
Suspended matter at 110°C-mg/l	7	19	214
pH	7.5	7.7	8.1
DOC-mg/l	3.0	4.4	5.8
Color-mgPt/l	9	15	25
Taste	1	3	6
Phenols-µg/l	1.5	2.5	5
Oil-mg/l	<0.1	0.1	0.9
Pesticides-µg/l	<0.1	0.1	0.14
Detergents-µg/l	40	60	130
Chlorophyll-a-µg/l	1	22	86
Ammonia-mg/l	0.1	1.3	4.7
Total phosphate-mg/l	0.7	1.5	2.2

DOC-Dissolved organic carbon

From this storage basin the water is transported 30 km to the plants at Berenplaat and Kralingen. Transport chlorination with 5 mg/l chlorine takes place during the summer months; the dose was reduced to 1 mg/l chlorine in 1978.

Purification Processes

The plant at Berenplaat has been in operation since 1966 and has a capacity of 12,000 m^3/hr. The storage basin, located where water from the Oude Maas formerly was taken in, has a residence time of 2 weeks. The water is purified successively by breakpoint chlorination with 4 mg/l chlorine, dosing with powdered activated carbon, coagulation in a sludge blanket flocculator, rapid sand filtration, and safety chlorination with 0.8 mg/l chlorine.

In 1977 a new 5,000-m^3/hr plant was built at Kralingen. The water is purified by coagulation and sedimentation in lamella separators, ozonation with 3 mg/l ozone, secondary iron dosing, double-layer filtration, carbon filtration, and safety chlorination with 0.8 mg/l chlorine.

Both plants supply good quality water, although the taste of the water from the Kralingen plant is said to be better.

Objectives of Carbon Filtration

Carbon filtration is employed at Kralingen for protection against occasional pollutants and toxic substances, for removal of substances produced by chlorination, and for removal of assimilable organic matter produced by ozonation. The additional precaution of carbon filtration along with ozonation is deemed necessary because ozone fails to oxidize numerous substances including highly chlorinated organic compounds.

The Rotterdam waterworks is not primarily concerned with trihalomethanes, but by the chlorinated substances having a higher molecular weight that are represented by the parameter AOCl (adsorbable organic chlorine) (1). The AOCl determination method is still in the developmental stage, however, and cannot yet be used as a criterion for contact times and running times of filters. The same caveat applies to the toxicity tests of effluents presently being developed by KIWA. The operating conditions of the carbon filters at Kralingen are given in Table 2.

Table 2

Conditions for the Carbon Filters at Kralingen*

Filter Condition	Value
Particle size-mm	0.8
Quantity of adsorbent per filter-m^3	116
Depth of adsorbent-m	4
Free board-m	3
Filter diameter-m	6
Contact time-min	12**

*Adsorbent used was Norit ROW 0.8 Supra and N.

**5 empty bed volumes/hr.

Results

During the summer months, transport chlorination was maintained at 5 mg/l chlorine, which led to the formation of trihalomethanes (THM). The residence time in the pipeline to Berenplaat was 8 hours, and to Kralingen it was 15 hours. During the 1977-1978 winter season the transport chlorination was discontinued; consequently, no THM formation occurred.

Table 3 shows the THM concentrations in the influent at Berenplaat and in the water supplied by the plant. Prechlorination with 0.5 to 1 mg/l chlorine and safety chlorination with

0.8 mg/l chlorine in summer causes an increase in THM concentrations from 68 to 84 µg/l. The trihalomethane formation potential (THMFP) of the raw water after 48 hours at 20°C is 160 µg/l. During the winter period when only breakpoint chlorination with 4 mg/l chlorine and postchlorination with 0.8 mg/l are applied, the THM concentration in the Berenplaat drinking water is 38 µg/l.

Table 3

THM Concentrations (µg/l) in the Water of Berenplaat*

Season and Type of Water	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	Total THMs
Summer raw water	30	22	14	1.5	68
Summer finished water	40	28	14.5	1.5	84
Winter raw water	<1	0	0	0	<1
Winter finished water	18	13	6	1	38

The plant in Kralingen began operations in July 1977. During the first month no carbon filtration was applied. Table 4 shows the THM concentrations during that period. The raw water was subjected to transport chlorination with 5 mg/l chlorine for 15 hours. The effect of safety chlorination with 0.8 mg/l chlorine was measured after 6 hours. During the coagulation process the THM concentration decreases slightly, but this decrease is offset by the increase resulting from the safety chlorination.

The effect of the removal of THM precursors can be seen in Table 5. During the first 5 months of GAC operation the influent contained approximately 100 µg/l THM. In the first month the THM concentration was reduced to 2 µg/l. The decrease in the production of THMs by safety chlorination (by 16 µg/l as compared to 33 µg/l without carbon filtration) indicates a partial elimination of the precursors. After a few months the trihalomethanes started to break through, with the brominated compounds appearing in the lowest concentrations. In this period 20 µg/l THMs were generated by safety chlorination.

Table 4

THM Concentrations (µg/l) at Kralingen
Without Carbon Filtration, July 1977

Type of Water	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	Total THMs
Raw water	50	32.5	18	2.5	103
After coagulation	32	22	13	1.5	68
After ozonation	32	23	12	2	69
After safety chlorination	49	35	16.5	1.5	102

Table 5

THM Concentrations (µg/l)at Kralingen
With Carbon Filtration

Running Time of Carbon	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	Total THMs
1 month, after carbon filtration	1.2	0.8	0	0	2
1 month, after safety chlorination	3.2	3.7	5.4	5.7	18
2-5 months, after carbon filtration	17	11	4	0	32
2-5 months, after safety chlorination	18	12.5	13.5	8.5	52
2-10 months, after carbon filtration	5	3	1.5	0	9.5
2-10 months, (winter) after safety chlorination	6.5	6.5	9.5	6.5	29

During the winter period, transport chlorination was discontinued; consequently, no THMs were formed. However, after carbon filtration small concentrations of THMs caused by elution were still detected, while the removal of precursors continued. This is illustrated by the constant increase of 20 µg/l THM after safety chlorination, which yielded a proportionately high concentration of brominated compounds. For these reasons, the Rotterdam waterworks does not consider GAC treatment for THM removal economically feasible.

This moderate reduction, especially for chloroform, is illustrated by Figures 1 to 3. The breakthrough curves of the DOC, UV extinction, and the reduction of detergents are shown in Figures 4 to 6. At the end of 5,500 empty bed volumes (6 weeks) the DOC had dropped from 2.4 to 1.0 mg/l, or by nearly 60 percent. After 6 weeks there is a rapid breakthrough, amounting to 80 percent after 12,000 empty bed volumes.

A similar breakthrough occurs for compounds represented by the UV extinction. Anionic detergents are also only partly eliminated. The concentrations of phenols and pesticides after carbon filtration are generally $\leq$1 µg/l and $\leq$0.04 µg/l, respectively.

The carbon filters are expected to be able to cope with a sudden high influx of pollutants. A test filter that had been running for 2 years and therefore was in equilibrium with the existing pollutants, was dosed with 10 µg/l lindane for 7 months. On the average, 0.6 µg/l lindane was detected in the effluent, indicating that the carbon filter functioned effectively as a safety filter.

Eliminating chlorination before the coagulation process does not lead to sliming of the installations. The water evidently matures sufficiently in the Biesbosch. Since the plant is indoors, weather conditions are not a factor.

At present, research is being conducted to determine the most suitable type of adsorbent for a given set of analytical and toxicological parameters.

PROVINCIAL WATERWORKS OF NORTH HOLLAND (PWN), ANDIJK

Water Quality

The PWN depends on the Yssel Lake for part of its water supply. Table 6 shows the water quality of the Yssel Lake at Andijk for 1977.

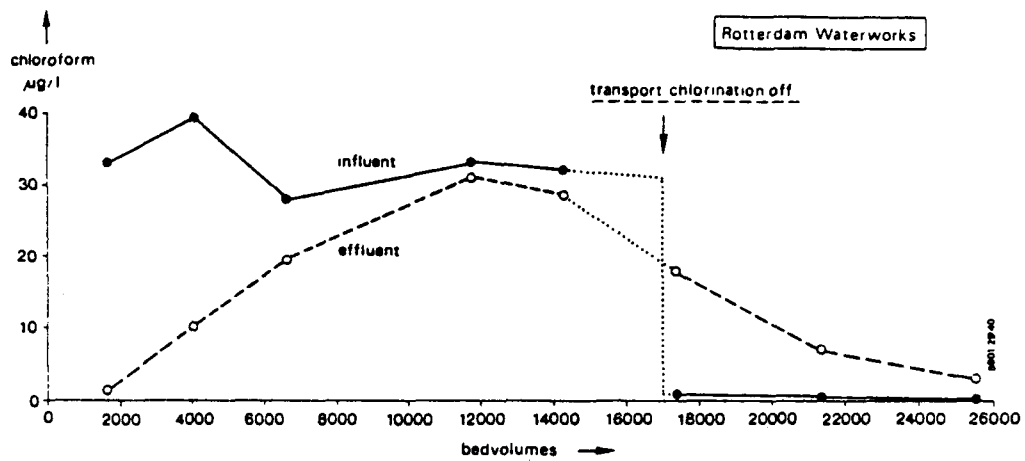


Figure 1. Chloroform Content before and after Carbon Filtration at Kralingen

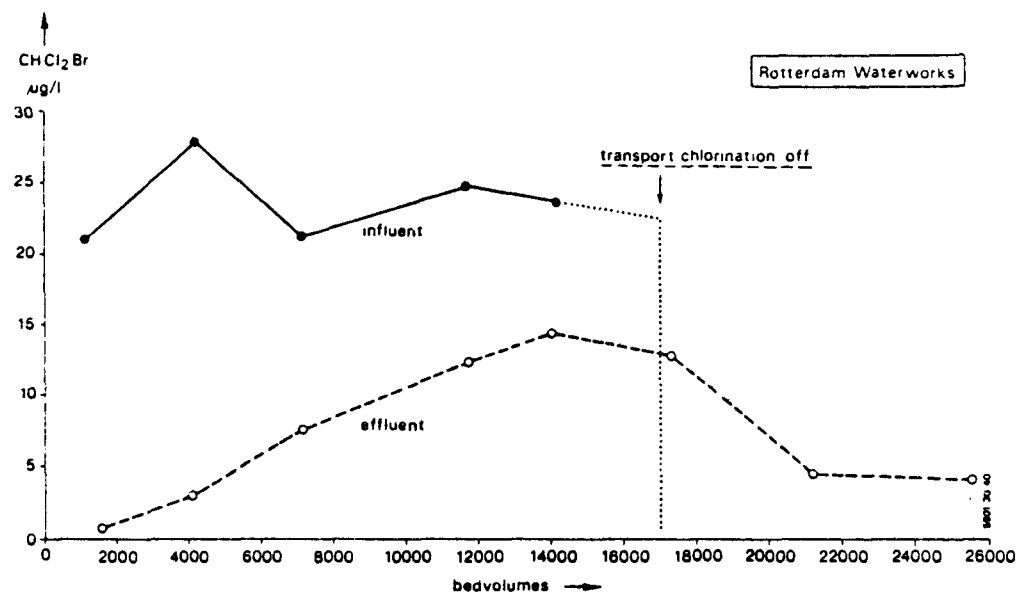


Figure 2. $CHCl_2Br$ Content Before and After Carbon Filtration at Kralingen

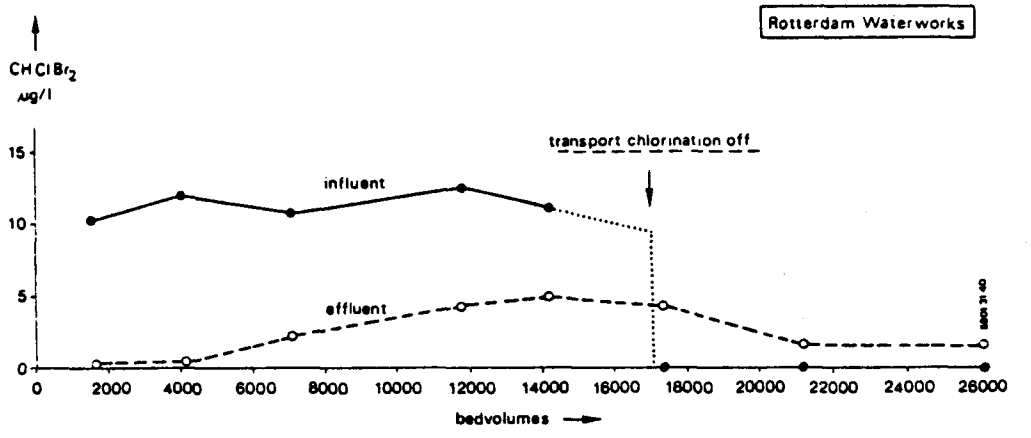


Figure 3. $CHClBr_2$ Content Before and After Carbon Filtration at Kralingen

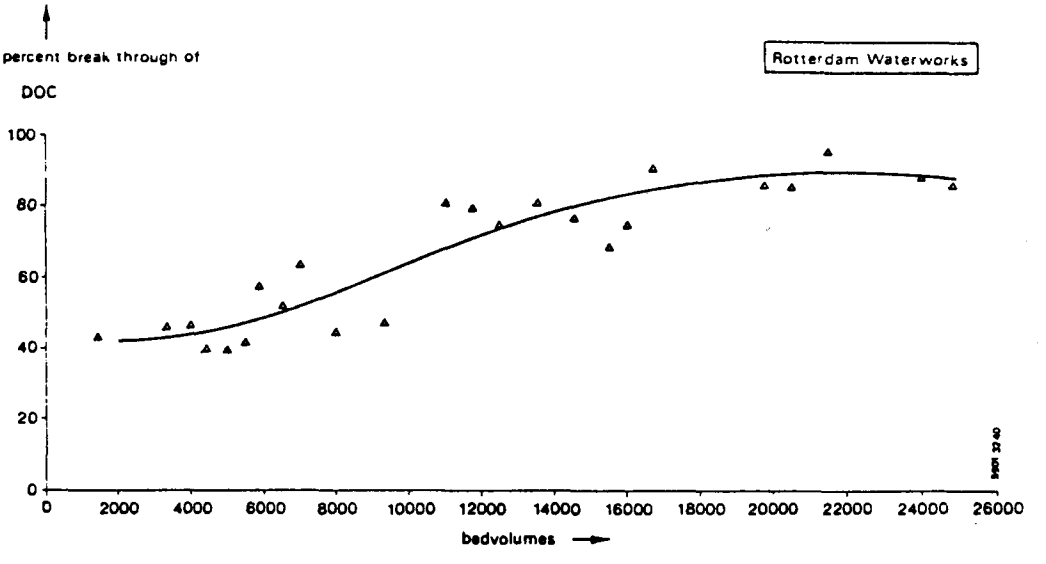


Figure 4. DOC Breakthrough Curves in Case of Carbon Filtration at Kralingen. DOC_o = 2 to 4 mg/l.

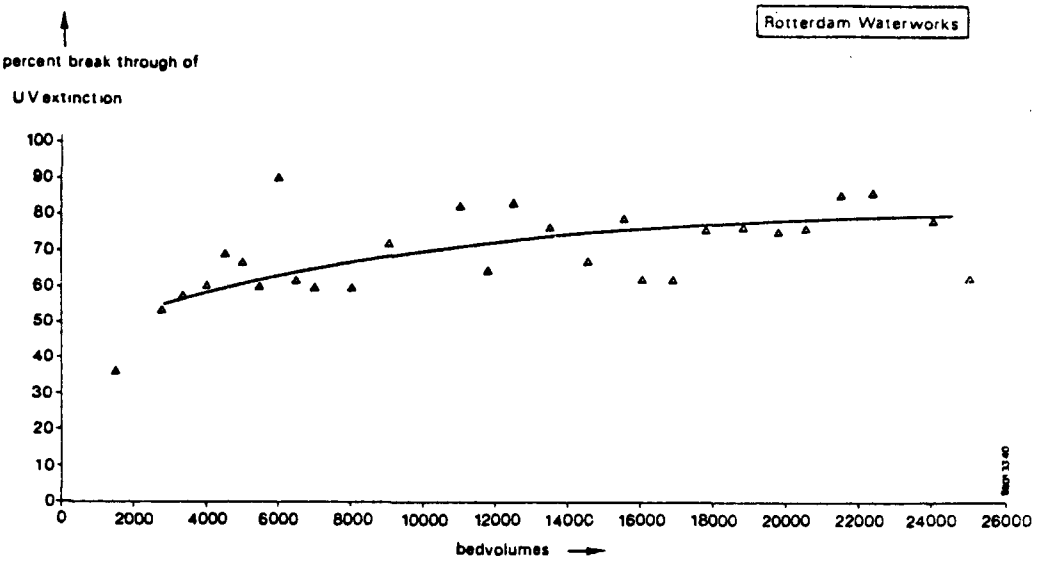


Figure 5. UV Extinction Breakthrough Curves in Case of Carbon Filtration at Kralingen

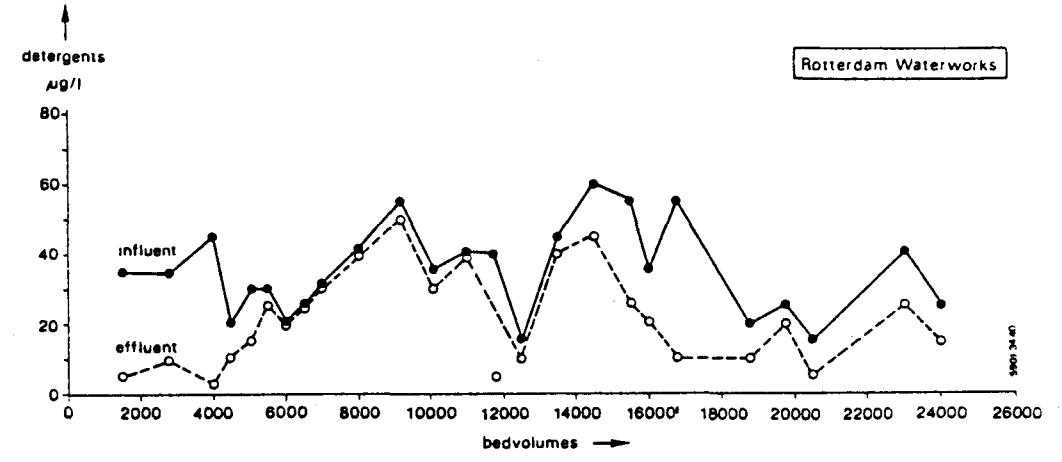


Figure 6. Decrease of Anionic Detergents by Carbon Filtration at Kralingen. Methylene Blue Method.

Table 6

Water Quality of the Yssel Lake at Andijk, 1977

Parameter	Minimum	Average	Maximum
Temperature-°C	1	11	20
Suspended matter at 110°C-mg/l	2	18	49
pH	7.7	8.6	9.5
Chloride-mg/l	164	223	340
DOC-mg/l	6.2	8.6	12.2
Color-mgPt/l	12	21	30
Taste	1	2	4
Phenols-mg/l	<1	7	28
Oil-mg/l	0.01	0.07	0.15
Pesticides-µg/l	<0.01	0.02	0.22
Cholinesterase inhibitors-µg/l	0.2	1.4	6.6
Anionic detergents-µg/l	<10	62	170
Chlorophyll-a-µg/l	5	78	220
EOCl-µg/l	0.4	3.4	8.2
Ammonia-mg/l	0	0.3	2.3
Total phosphate - mg/l	0.2	0.7	1.8

Usually the contamination by micropollutants is slight, but higher concentrations of phenols, cholinesterase inhibitors, extractable organic chlorine compounds (EOCl), and chlorophyll (algal growth) may occur occasionally, so that a sophisticated purification system is still necessary.

Purification Processes

The pumping station at Andijk has a maximum purification capacity of 4,000 m^3/hr and was put into operation in 1967. Water from the Yssel Lake is received in a basin with a storage capacity of 3 weeks. Algae are removed by microsieves with a mesh size of 35 µm. The water then is subjected to breakpoint chlorination with an average of 9 mg/l chlorine disinfection in a detention basin with a 30-min. contact time, coagulation in hydrotreaters, double-layer rapid sand filtration, carbon filtration, and a second straining with microsieves to remove large organisms. Finally, safety chlorination is applied with 0.03 mg/l chlorine and chlorine dioxide. The dose can be kept low because after breakpoint chlorination and carbon filtration the chlorine demand of organic compounds is negligible. Thus the concentration of trihalomethanes does not increase.

Recently, static mixers have been used in the coagulation process, making it possible to reduce the coagulant dosage.

However, elimination of organic compounds has been less effective since this change.

Objectives of Carbon Filtration

The reasons for applying carbon filtration at Andijk are to restrict bacterial growth in the distribution system; to protect against occasional pollutants and toxic substances; and to improve taste. The criterion for the restriction of bacterial growth is that the water supplied be of sufficiently high quality to preclude further oxygen consumption in a slow sand filter. This criterion may be interpreted as a requirement for the removal of the DOC.

Trihalomethanes were not recognized as a significant health risk before the carbon filters were installed. Hence, their elimination was not considered in establishing the original criteria for the carbon filter running time.

Conditions for Carbon Filtration

Table 7 describes the operating conditions of the carbon filters at Andijk. A 4,000-m^3/hr flow is maintained through the carbon filters. Since only 2,000 m^3/hr are withdrawn on the average, the water recirculates over the carbon filters from 1.7 to 2.5 times.

Every fortnight one carbon filter is regenerated by the manufacturer; in the future this process will be done by the waterworks. After the first carbon filtration step (12 filters) the water is collected, pumped to the second carbon filtration step, collected again, and 50 percent of it recirculated. The filters have been operating in this way since the end of the startup period in April, 1978.

The adsorption loading of the GAC rises to between 20 and 25 percent weight during the course of a filter run. To achieve comparable results with one carbon filtration step, the run time would have to be decreased by 50 percent and the regeneration rate correspondingly increased. In spite of the additional pumping step between the two carbon filters, this process proves to be cheaper because of the lower consumption of activated carbon. Preliminary research has revealed that for DOC reduction a residence time of 30 min. yields the optimum cost-performance ratio (2).

The preliminary tests also proved that the performances of the two carbon brands tested, type A* and type B** were virtually identical. Lower regeneration costs determined the choice of adsorbent; the initial cost of the carbon is of far less importance.

* Norit N.V., Amersfoort, The Netherlands
** Chemviron S.A., subsidiary Calgon Corp., U.S.

Table 7
Conditions for the Carbon Filters at Andijk*

Filter Condition	Value
Particle size-mm	0.8
Quantity of adsorbent per filter-m^3	85
Depth of adsorbent-m	3
Free board-m	to 3
Filter surface-m^2	27
Contact time-min	30**
Bed volumes before regeneration	16,000 (11 months)
Number of carbon filters	2 by 12
Type of carbon filters	open, concrete
Backwash cycle***	once every 4 months

*Adsorbent used was Norit ROW 0.8 Supra, slightly smaller pores than normal.
**The maximum permissible flow variation is 10 percent; 2 empty bed volumes/hr.
***Stratification is attempted by gradually reducing the backwash velocity.

Results

The manner in which the filters are operated makes it possible to obtain fairly constant effluent quality, as shown in Figures 7 to 9, for UV extinction, DOC, and THM reduction. Table 8 shows the average reduction of DOC, UV extinction, THMs, and EOCl. The DOC and UV extinction decrease by a constant percentage. The decrease in EOCl is satisfactory during the entire period; the average effluent concentration of EOCl is 1.0 µg/l. The reduction of trihalomethanes varies widely, reflecting the fluctuations in the THM content of the influent (Figure 9). The high summer concentrations were reduced satisfactorily; their removal led to a new criterion for the running time of the filters at the plant. The regeneration cycle has to be adjusted in such a way as to ensure that the effluent will not contain more than 50 µg/l THM.

Table 8
Average Percent Reduction of Some Collective Parameters

Parameter	April-June	July-December
DOC	35	31
UV extinction	55	56
THM	83	36
EOCl	79	68

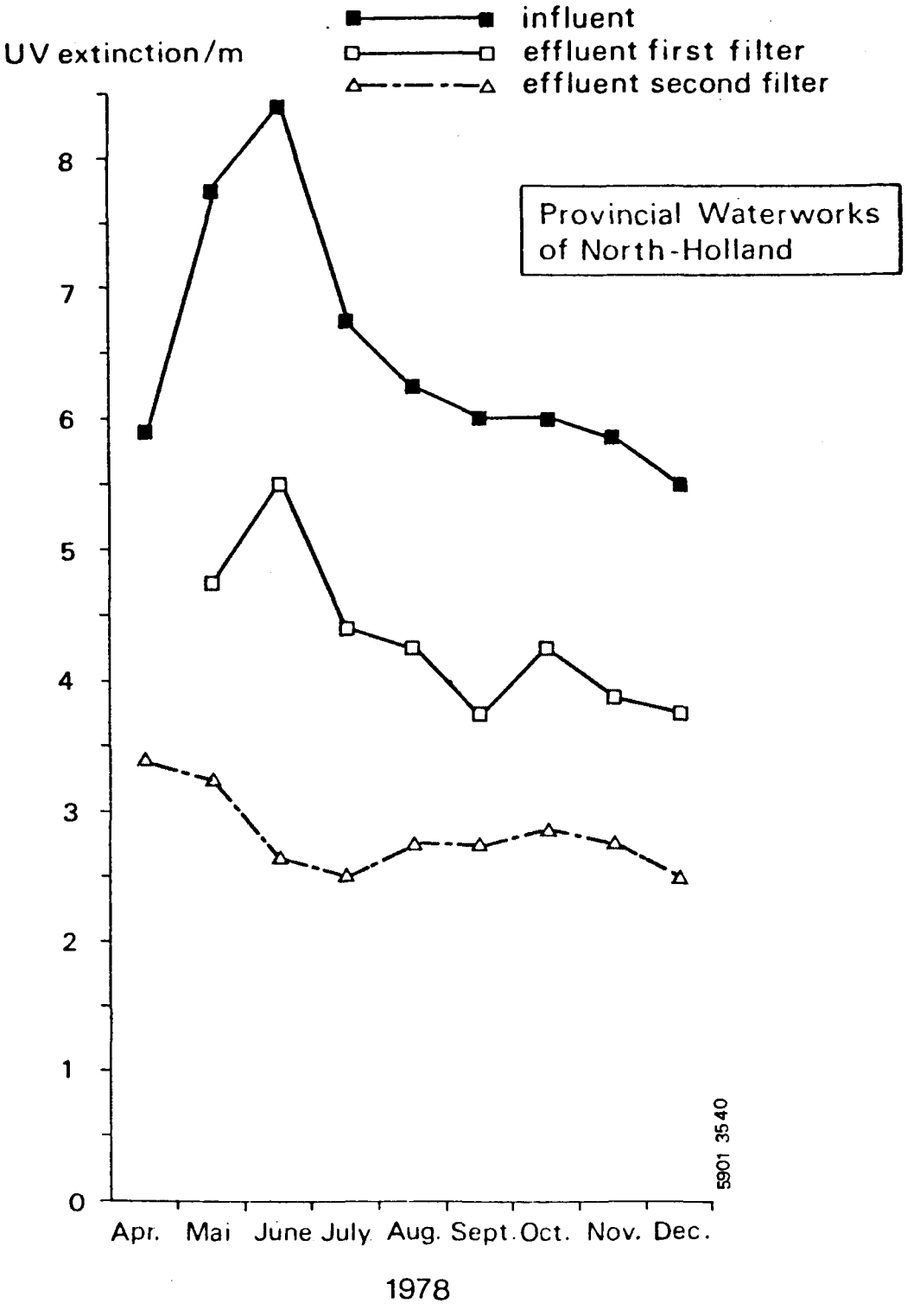


Figure 7. Decrease of UV Extinction (254 nm) in GAC Treatment at Andijk.

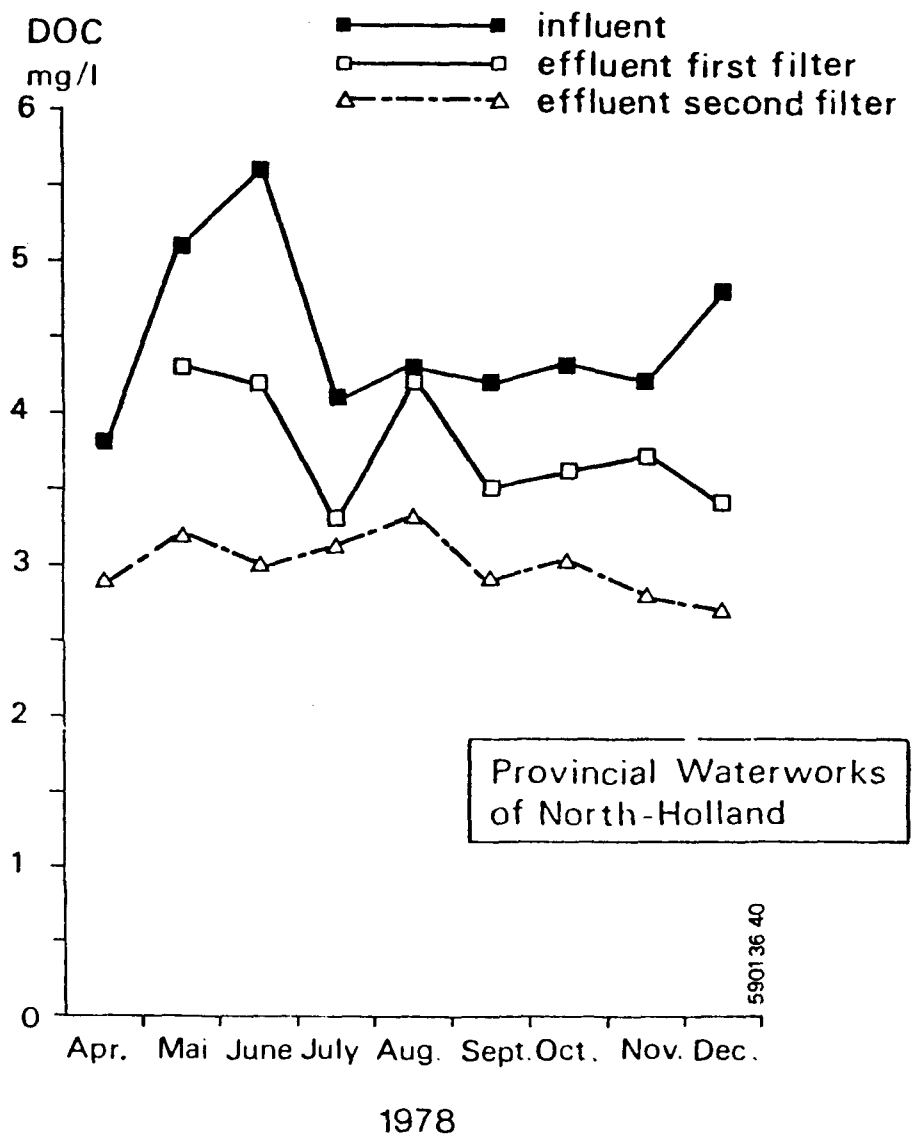


Figure 8. Decrease of DOC in GAC Treatment at Andijk

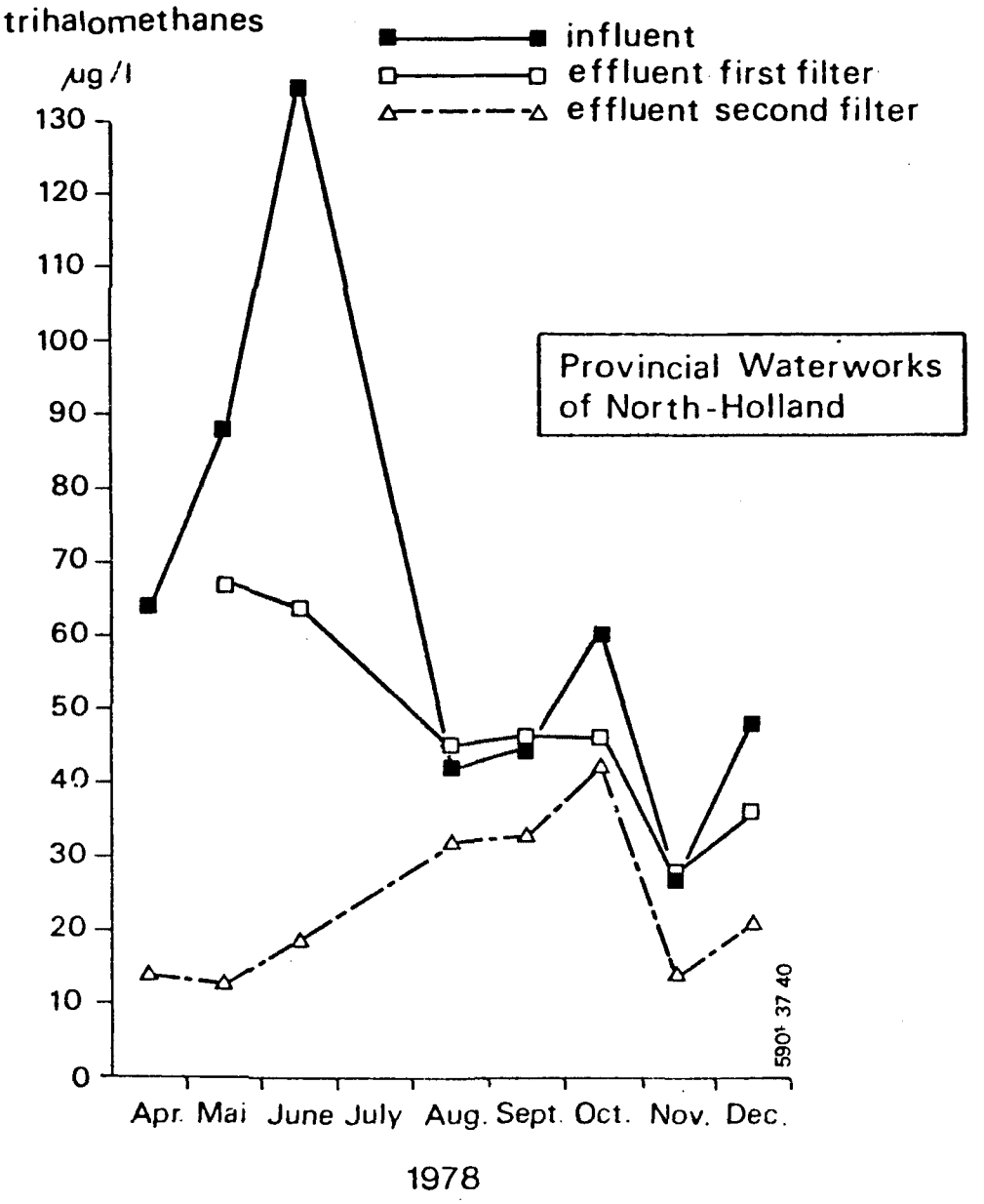


Figure 9. Decrease of Trihalomethanes in GAC Treatment at Andijk

After carbon filtration the bacterial counts measured at 22°C ranged from 800 to 10,000. Safety chlorination reduces their numbers to between 10 and 100, and bacterial growth in the distribution system is clearly diminished. However, carbon filtration leads to a marked increase in the number of higher organisms such as rotifers and worms. These organisms are removed using 35-µm mesh microsieves. A striking phenomenon is that when high bacterial counts occur, few higher organisms are found after startup and backwashing, whereas bacterial counts decrease when higher organisms occur in large numbers.

Taste-causing and harmful substances have been effectively eliminated. The concentrations of pesticides and phenols lie below the detection limit. Blue algae are removed by rapid sand filtration and carbon filtration.

The oxygen consumption per filter is 1 to 2 mg/l. The water is aerated between and after the two filters. In winter virtually no oxygen consumption occurs.

AMSTERDAM MUNICIPAL WATERWORKS

Water Quality

The Amsterdam Municipal Waterworks obtain the major part of their water from the Lek Canal near Nieuwegein. This canal is fed indirectly by the Rhine River. The water quality characteristics are shown in Table 9.

Table 9

Water Quality of the Lek Canal at Nieuwegein, 1977

Parameter	Minimum	Average	Maximum
Flow of the Rhine at Lobith-m^3/s	1,050	2,200	6,300
Temperature-°C	1	11	23
Suspended matter--mg/l	12	38	111
pH	7.4	7.7	8.1
Chloride-mg/l	76	151	233
DOC-mg/l	2.9	4.8	8.3
Color-mgPt/l	7	19	60
Taste	31	44	67
Pesticides-µg/l	0.1	0.2	1.6
Detergents-µg/l	50	150	430
Chlorophyll-a-µg/l	0.1	17	49
Oil (Bergambacht)-mg/l	<0.1	0.1	0.3
EOCl (Ochten)-µg/l	2	12	45
Ammonia-mg/l	0.1	0.9	3.4
Total phosphate-mg/l	0.7	1.7	4.7

In addition to the compounds named in Table 9, numerous organic micropollutants are found in the untreated water, including organic phosphates, chlorinated and nitro aromatic compounds, chlorinated ethers, aromatic bases, and phthalates. The concentrations measured in the Lek with the aid of gas chromatography and mass spectrometry totalled 20 µg/l on October 30, 1977, and 30 µg/l on December 6. These compounds are assumed to be partly responsible for the taste of the water and for its toxicity to fish.

After pretreatment the water from the Lek is infiltrated in the dunes, satisfactorily eliminating these compounds and equalizing the quality of the water.

During artificial recharge the volatile compounds virtually disappear. The concentrations of the remaining micropollutants are generally much lower than 1 µg/l, with the exception of the phthalates. Nevertheless, the infiltrated water is not free from taste and numerous pollutants from the Rhine still are present, albeit in substantially reduced concentrations.

Purification Processes

At Nieuwegein water has been drawn from the Lek Canal since 1957. Coagulation and sedimentation take place in a basin, followed by rapid sand filtration. After chlorination the water is transported over a distance of 55 km to the dunes where it is infiltrated. The water is aerated, dosed with 3 mg/l powdered activated carbon, and further purified by rapid sand filtration, slow sand filtration, and safety chlorination. These operations take place at Leiduin. When the temperature of the water from the Lek falls below 10°C, the water to be transported is no longer chlorinated. Above this temperature a dose of 2.4 mg/l chlorine is added, which leads to the formation of approximately 100 µg/l trihalomethanes. The THMs are eliminated by infiltration in the dunes. At present the doses of chlorine vary, the criterion being that after 20 min 0.2 mg/l chlorine should still be present. The resulting concentration of THMs is 15 to 25 µg/l.

Objectives of Carbon Filtration

Since the results of dosing with powdered activated carbon have not been entirely satisfactory, the municipal waterworks is considering GAC treatment. This change is intended to eliminate the remaining substances causing taste, to reduce bacterial growth in the network system, and to remove unknown and possibly toxic substances. GAC treatment will be placed after rapid sand filtration in the treatment sequence. The results of the test filters are being evaluated.

Conditions for the Test Filters

In the test filters three types of adsorbents were tested at different contact times. Table 10 lists the test conditions. Every 2 weeks the filters are backwashed, gradually reducing the backwash velocity to maintain the stratification to the extent possible.

Table 10

Conditions for Seven Test Filters at Leiduin

Filter Condition	Type of Carbon						
	Type A			Type B			Type C
Quantity of adsorbent per filter-l	393	147	147	393	147	147	393
Depth of adsorbent-m	2	3	3	2	3	3	2
Filter diameter-m	0.5	0.25	0.25	0.5	0.25	0.25	0.5
Contact time-min	40	24	12	40	24	12	24

Results

Collective Parameters--

For the type A and type B carbons it was observed that with a residence time of 12 min, a constant TOC breakthrough of 75 to 80 percent occurs after 11,000 to 12,000 empty bed volumes, while the permanganate consumption and the UV extinction reach breakthrough levels of 80 and 70 percent, respectively. These constant breakthrough levels last until 25,000 empty bed volumes regardless of the hydraulic loading rate.

With a residence time of 24 min, constant breakthrough levels are reached after 6,000 to 8,000 empty bed volumes. For carbons A and B the breakthrough is then approximately 70 percent for TOC and permanganate consumption, and 50 percent for UV extinction.

Carbon type C* shows a higher breakthrough for these parameters, from 75 to 80 percent. For these parameters no difference in performance between the type A and type B carbons was observed. Type C carbon clearly gives poorer results.

*Lurgi Apparate Technik GMBH, Frankfurt, Fed. Rep. Germany

With a residence time of 40 min the constant breakthrough is probably reached sooner (4,000 empty bed volumes) with lower breakthrough levels. However, this residence time gives rise to anaerobic conditions and its use in daily practice is therefore not recommended.

Trihalomethanes are not detected after infiltration. Other micropollutants, however, can still be discovered by measuring the AOCl. The concentrations of AOCl before carbon filtration amount to 100 to 250 µg/l. For these parameters, too, the behavior of type A and type B carbons is identical. With a residence time of 24 min, the AOCl is reduced by 45 percent up to a throughput of 11,000 bed volumes. After that, almost complete breakthrough occurs. The type C carbon is also inferior in removing these parameters. The initial reduction of 40 percent soon drops to 20 percent. With shorter residence times the reduction of AOCl is even poorer, while longer residence times bring no improvement. The adsorption of AOCl is no better than that of the TOC, which may be explained by the assumption that in this case the AOCl represents fairly polar chlorinated compounds of little volatility. Furthermore, the safety chlorination raises the AOCl concentrations to their original levels. During the last stage of these experiments two EOCl determinations also were carried out. The concentrations were very low, however, ranging between 0.2 and 0.6 µg/l before carbon filtration and 0.1 and 0.2 µg/l after carbon filtration. Subsequent chlorination caused an increase to approximately 4 µg/l. No difference was observed in the performance of the three types of carbon.

Micropollutants--

In several samples, micropollutants were determined by gas chromatography and mass spectrometry. The results are listed in Table 11. The concentrations are very low and no clear distinction can be drawn in the performance of the three types of carbon. The overall precision of this analytical method is certainly no better than 0.1 µg/l.

Trihalomethanes--

Trihalomethanes are not present before carbon filtration, and consequently they also are absent afterwards. However, trihalomethanes are formed during safety chlorination with 0.7 mg/l chlorine. After a 2-hr contact time the THM concentrations average 30 µg/l, with slight differences associated with the design of the preceding carbon filtration. In a purification system without carbon filtration or with ozonation, safety chlorination produces lower concentrations of 20 µg/l. When the carbon filtration process is added with a contact time of 12 min, a substantial increase to 40 to 50 µg/l occurs during the first few months; later this level falls to 20 to 30 µg/l. If carbon filters with a residence time of 40 min are installed, a

Table 11A

Analysis of Micropollutants Before and After Carbon Filtration at Leiduin on May 8, 1978 - Concentration in µg/l

Type of Micropollutant	Influent	Effluents		
		Carbon Type A	Carbon Type B	Carbon Type C
Acids	0.4	---	---	---
Phthalates	1.2	1.7	1.3	1.6
Organic phosphates	0.2	---	---	---
Dichloroisopropyl ether	0.3	---	---	---
Chlorinated aromatics	---	0.1	0.1	0.2
Polyaromatics	---	0.1	0.2	0.1
Trimethyloxindole	0.4	---	---	---
Aromatic bases	0.2	---	---	---

Table 11B

Analysis of Micropollutants Before and After Carbon Filtration at Leiduin on July 12, 1978 - Concentration in µg/l

Type of Micropollutant	Influent	Effluents		
		Carbon Type A	Carbon Type B	Carbon Type C
Acids	0.1	0.5	0.8	0.1
Phthalates	1.2	1.0	0.9	1.1
Organic phosphates	1.1	---	---	---
Dichloroisopropyl ether	<0.1	---	---	---
Chlorinated aromatics	0.1	---	---	---
Polyaromatics	0.2	0.2	0.1	0.5
Trimethyloxindole	---	---	---	---
Aromatic bases	---	---	---	---

slight reduction to 15 µg/l takes place during the first few months. However, after 3 to 6 months the THM content increases again to 30 to 50 µg/l. Bromoform is primarily responsible for these high concentrations.

Conclusive evidence indicated that installation of carbon filters followed by chlorination with 0.7 mg/l chlorine causes an increase in the THM concentrations. The THM concentrations can be reduced to 20 µg/l, if the chlorine is dosed*after a 20-min contact time the chlorine residual does not exceed 0.2 mg/l.

* (in an amount such that)

Evaluation of GAC Treatment

The Amsterdam Municipal Waterworks anticipates few problems with regard to the elimination of unknown toxic substances as well as those substances causing taste. It is also expected that the bacterial growth in the distribution system will decrease. During the testing of the carbon filters it was found, however, that the concentrations of chlorinated products are decreased little or not at all by carbon filtration. The significance of the residual AOCl and THM concentrations will have to be demonstrated with the aid of toxicity tests. At the present state of these investigations, however, the choice of the optimal contact and running times is not conclusively indicated.

MIDDEN NEDERLAND WATERWORKS PUMPING STATION AT ZEIST

WATER QUALITY

At Zeist very pure groundwater with extremely low levels of organic substances is pumped. In recent years, however, pollution by trichloroethene has been observed in concentrations of 500 to 1,000 µg/l. Such pollutants have also been found in the groundwater elsewhere in the Netherlands; for example, tri- and tetrachloroethene at Hilversum, tribromoethene at Almelo, and trichloroethene at Nijmegen, while chloroform also occurs at various locations.

PURIFICATION PROCESSES

The groundwater at Zeist is aerated and filtered over $CaCO_3MgO$ filter material* which results in deacidification and elimination of iron and manganese. A number of wells have been equipped with carbon filters with a total capacity of 300 m^3/hr. The entire pumping station has a capacity of 900 m^3/hr. The quality of the treated water is shown in Table 12.

*Akdolite-Werk GMBH, Hochdahl, Fed. Rep. Germany

Table 12

Quality of the Drinking Water at Zeist

Parameter	Value
Temperature-°C	12
Color-mgPt/l	1
pH	8.2
Permanganate consumption - mg/l	<1
Total hardness-meq/l	2

GAC treatment is intended to reduce trichloroethene levels to less than 1 µg/l. Table 13 describes the operating conditions of the carbon filters at Zeist.

Table 13

Carbon Filter Characteristics at Zeist

Filter Condition	Value
Particle size-mm	1
Quantity of adsorbent per filter-m^3	12
Depth of adsorbent-m	1.5
Free board-m	1
Filter diameter-m	3.3
Contact time-min.	12
Expected empty bed volumes before regeneration	>25,000
Number of carbon filters	3 by 2
Backwash cycle	first filter only

RESULTS

In the course of the preliminary experiments it was found that GAC treatment is most effective when inserted into the sequence following filtration over $CaCO_3$/MgO filter material. This reduces the need for frequent backwashing and prevents the risk of premature breakthrough.

An attempt was made to fix the adsorbent within a packed bed in a test filter. During backwashing the tension is released only in the uppermost 50 cm. This backwashing method and a contact time of 8 min yielded a running time of 4 months. The trichloroethene concentration front advanced regularly through the GAC bed during the course of the test run, as expected (Figure 10). At the equilibrium stage the load of the adsorbent proved to be 50 g/kg carbon.

For regeneration all the carbon has to be removed from the filter. If not, desorption and breakthrough occur immediately. The operational filters have been in actual use since December 1, 1978. Two filters have been placed in series, with a total contact time of 12 min. The running time is expected to be 7 to 8 months. The costs for this small capacity are hfl. 0.15/m^3 carbon ($0.075/$m^3$ carbon at the May 1979 exchange rate).

KIWA PILOT PLANT AT NIEUWEGEIN

The water quality of the KIWA pilot plant at Nieuwegein is illustrated in Table 9.

Purification Processes

At Nieuwegein water is taken in from the Lek Canal. The raw water is presettled in a basin and then coagulated and filtered over a double-layer filter. This step is followed by parallel ozonation, GAC treatment over a fresh carbon filter, and GAC treatment over a filter that has been running for 7 months.

Objectives of Carbon Filtration

The most suitable criteria for contact time and running time are TOC, UV extinction, EOCl and AOCl, and taste. However, the toxicological significance of the remaining concentration is not known.

The operating conditions of the carbon filters used at Nieuwegein are shown in Table 14. At the start of the experiments on August 10, 1977, one carbon filter had been running for 2 weeks, whereas the other one had been in operation for 7 months. A great difference in the quality of the effluents from these two filters was expected.

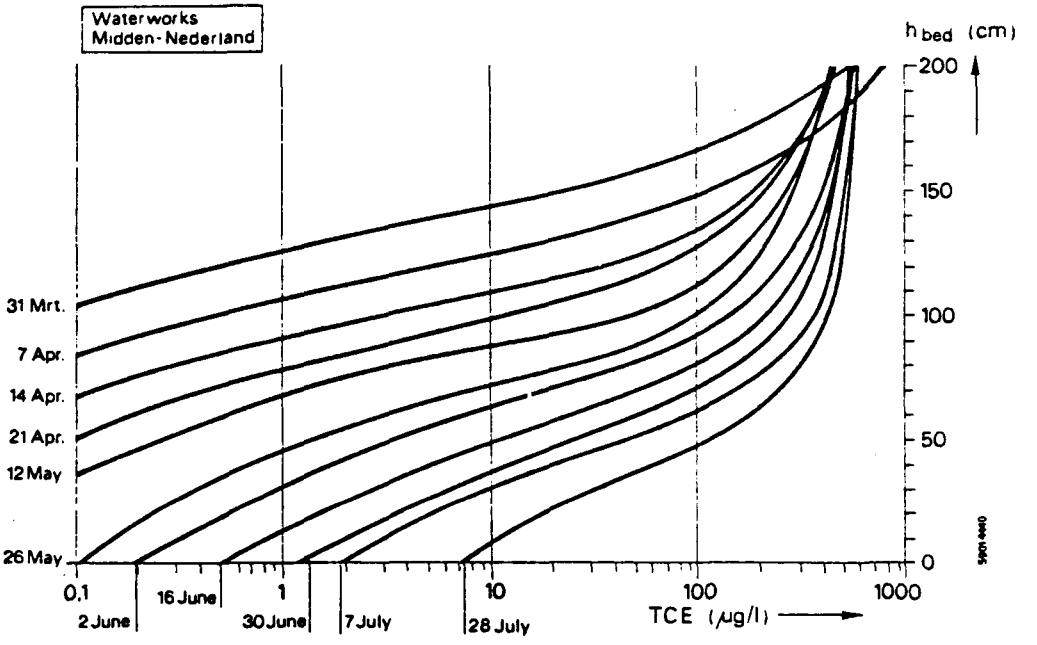


Figure 10. Breakthrough Curves of Trichloroethene by Carbon Filtration at the Zeist Pilot Plant. Contact Time 8 Minutes.

Table 14

Conditions for the Carbon Filters at Nieuwegein

Filter Condition*	Value
Particle size-mm	0.8
Quantity of adsorbent per filter-l	42.5
Depth of adsorbent-m	0.85
Free board-m	0.65
Filter diameter-m	0.25
Contact time-min	21
Backwash cycle	every two weeks at 25 m/hr

*Adsorbent used was Norit ROW 0.8 Supra.

Results

For 4 months, weekly analyses were made of DOC, UV extinction, and EOCl. On two occasions analyses were made using gas chromatography and mass spectrometry. The toxicological research was carried out on tropical tadpoles (Xenopus laevis) raised in aquarium tanks with a constant water supply of varying water qualities. During the larval development and the growth period after the metamorphosis, it was not possible to find criteria for judging the toxicology of the water. Two parameters eventually proved suitable, namely the mortality rate up to the sixth day after egg deposition in the tanks, and the enlargement of the liver in the tropical tadpoles after 4 months at the end of the tests. The enlargement of the liver was expressed as the liver somatic index (LSI); i.e., the weight of the liver related to the total body weight of the tadpole. The liver is the organ in which toxic substances (e.g., chlorinated and aromatic hydrocarbons) are metabolized, causing liver enlargements.

In order to find relations, the mean values of the DOC, UV extinction, and EOCl were computed on the 8th, 15th, and 22nd of August and compared with the mortality rate of the tropical tadpoles after 6 days. Table 15 and Figure 11 show the results.

The mortality rate of the tropical tadpoles proved to be a less changeable criterion than the chemical parameters. This cannot be a logical assumption, however, because of the totally different nature of the toxicological parameters. In living organisms there is often a threshold value that has to be exceeded before toxicological effects become apparent. The

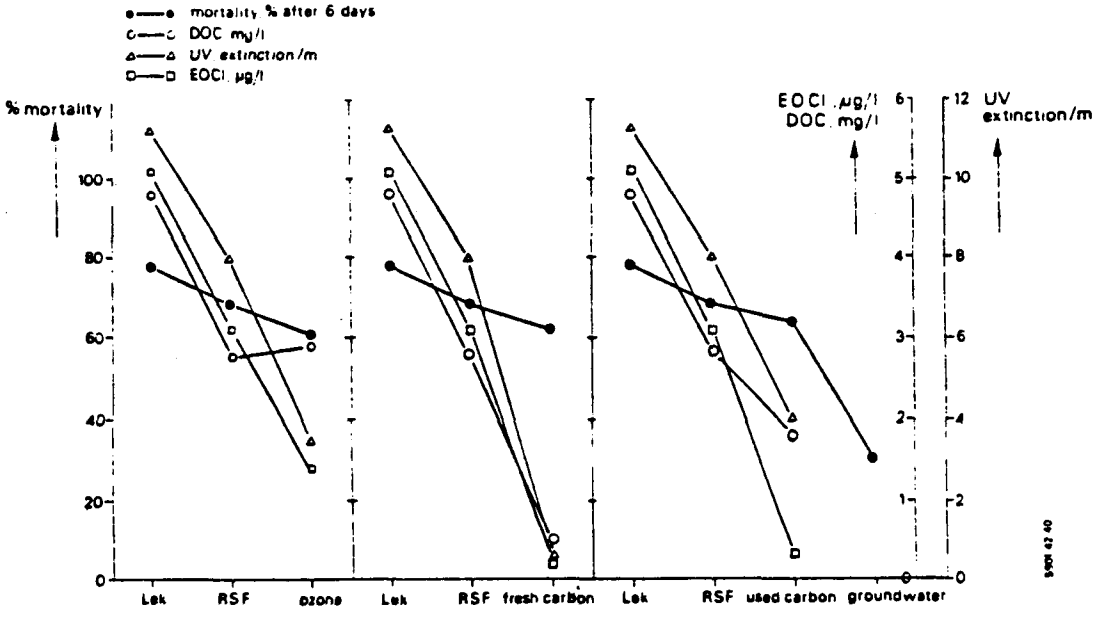


Figure 11. Relation Between the Mortality of Tropical Tadpoles After Six Days and DOC, UV Extinction and EOCl
Lek = raw water; RSF = rapid sand filtrate

Table 15

Comparison Between DOC, UV Extinction, and EOCl and the Mortality Rate of Tropical Tadpoles After Six Days

Type of Water Used as Habitat	DOC mg/l	UV Extinction per m	EOCl µg/l	Percentage Mortality After Six Days
Lek water	4.8	11.3	5.1	78
Rapid sand filtrate	2.8	8.0	3.1	69
Effluent ozone	2.9	3.5	1.4	61
Effluent carbon (old)	1.8	4.1	0.3	64
Effluent carbon (fresh)	0.5	0.3	0.2	62
Groundwater			0.1	31

mortality rates of the tropical tadpoles in the effluents of ozonation and of the fresh and old carbon filters hardly differed. However, a vast difference exists in the mortality rates between the effluent of a fresh carbon filter and groundwater, although the analytical parameters of the effluent of the fresh carbon filter yield favorable results. There seems to be no linear relation between the mortality rate and the DOC, UV extinction, and EOCl. All that can be deduced at present is that a decrease in the value of the chemical parameters most often goes hand in hand with a decrease in the mortality rate of this test animal.

The chemical parameters have also been compared with the LSI value. The mean values for the chemical parameters have been computed over the entire test period. Table 16 and Figure 12 give the results for the comparison of the LSI values and DOC, UV extinction, and EOCl. Table 17 and Figure 13 compare LSI values with various groups of organic compounds.

The values of the groups of organic compounds have been calculated by taking the average over the entire test period. For the Lek water, five samples were taken at Bergambacht. The other samples were taken weekly at Nieuwegein. The LSI as such proves to be a sensitive parameter as compared with the differences between the chemical parameters. An accentuation of the differences is obtained if the LSI value is related to the decrease in the LSI of animals in Lek water and the control animals by the formula:

$$\Delta \text{LSI percentage} = \frac{\text{LSI} - \text{LSI (groundwater)}}{\text{LSI (Lek water)} - \text{LSI (groundwater)}} \cdot 100 \text{ percent}$$

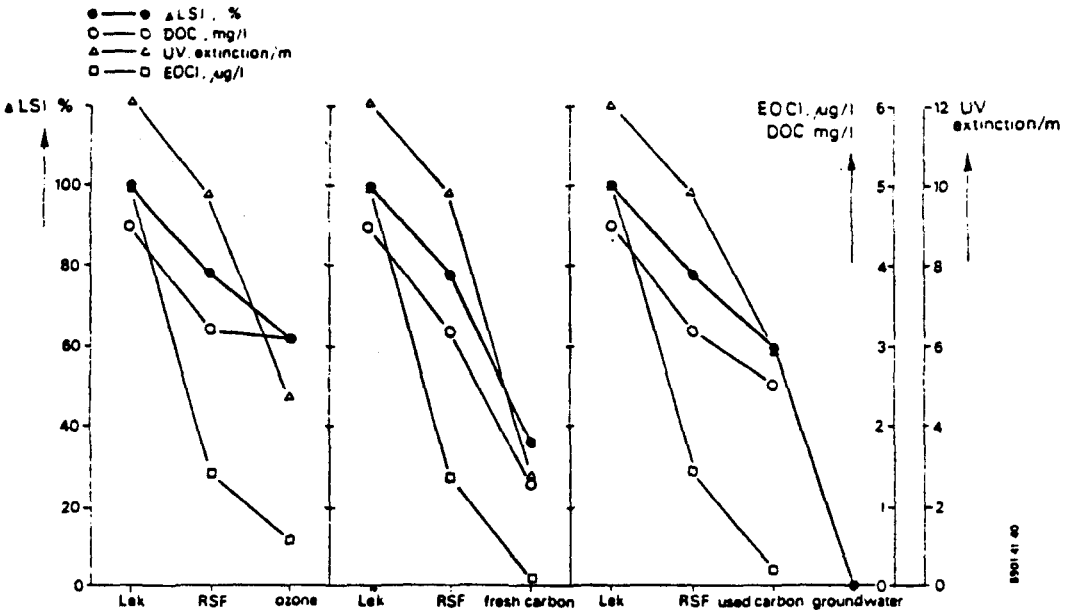


Figure 12. Relation Between the Relative Value of the Liver Somatic Index and DOC, UV Extinction and EOCI

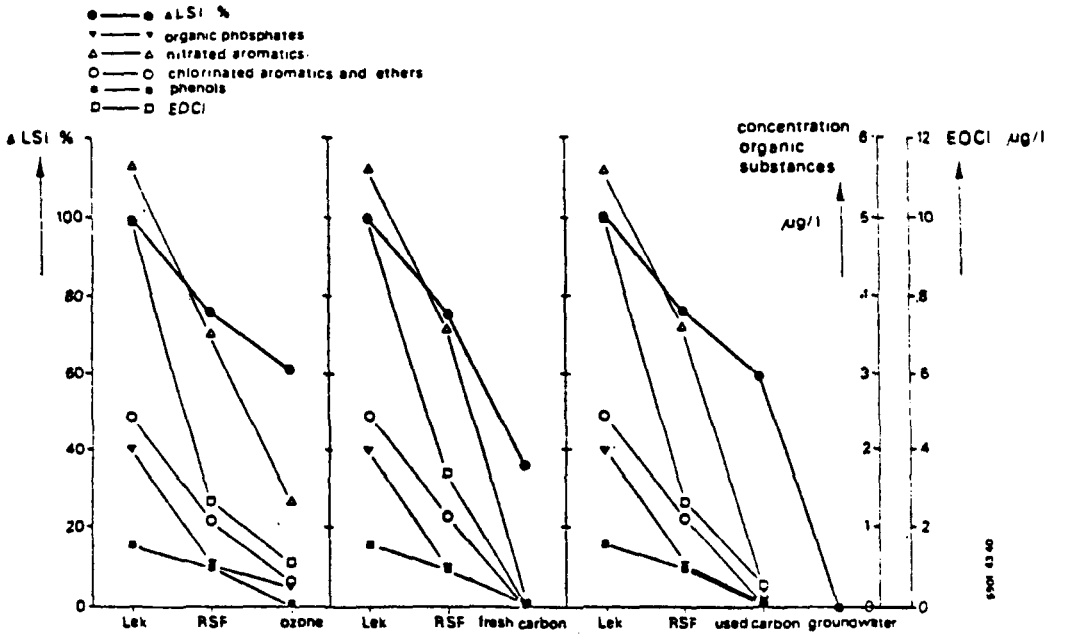


Figure 13. Relation Between the Liver Somatic Index and the Concentration of Different Groups of Organic Substances

Table 16

Comparison of DOC, UV Extinction, and EOCl with the LSI Percentage

Type of Water	DOC mg/l	UV Extinction per m	EOCl µg/l	ΔLSI Percentage	LSI Increase In Relation to Control Animals
Lek water	4.5	12.1	10.1	100	36.0
Rapid sand filtrate	3.2	9.9	2.7	78	28.2
Effluent ozone	3.1	4.8	1.1	62	22.2
Effluent carbon (old)	2.5	5.9	0.3	60	21.6
Effluent carbon (fresh)	1.3	2.4	0.1	36	13.0

Table 17

Comparison Between Some Groups of Toxicologically Suspect Compounds, EOCl, and LSI Percentage

Test Parameter	Lek	Rapid Sand Filtrate	Ozone	Old Carbon	Fresh Carbon
Organic phosphates-µg/l	2.0	0.5	0.3	0.1	0.05
Nitrates aromatics-µg/l	5.65	3.6	1.3	0.15	<0.1
Chlorinated aromatics and ethers-µg/l	2.45	1.15	0.25		
Phenols-µg/l	0.8	0.5	0.05		
EOCl-µg/l	10.0	2.7	1.1	0.3	0.1
ΔLSI percentage	100	78	62	60	36

The direct relation between the ΔLSI percentage and DOC and UV extinction appears to be better than the corresponding relation with the mortality rate. Each decrease in the value of the chemical parameters, except for the DOC after ozonation, parallels a decrease in the ΔLSI percentage. The difference in LSI between the effluent of the fresh carbon filter and the groundwater is smaller than the differences in the mortality rate.

In this connection it should be noted that the carbon filter had been running for 4 months at the end of the test period. The relation between LSI and EOCl is less favorable since the differences in EOCl concentrations do not parallel the differences in Δ LSI percentage.

Figures 11 to 13 reveal that the various groups of organic micropollutants follow the trend indicated by the EOCl fairly closely. The relation between micropollutants and the ΔLSI percentage appears to be less clear, given the large disparity in ΔLSI percentage between the two carbon filters and the slight differences in the concentrations of the micropollutants. Therefore, little purpose would be served by conducting a great deal of GC-MS work in this type of research. At present it is sufficient to observe the collective parameters, such as EOCl, and to carry out occasional GC-MS research if the identity of the substances that constitute the collective parameters is unknown, acute or highly toxic effects occur, or a sudden increase in the value of the collective parameters occurs. Although the tropical tadpole is apparently not the most suitable test animal for the toxicological evaluation of water quality and the tests did not lead to optimum results at certain points, some important findings were obtained. It was determined that the toxicological effects on the tropical tadpole decrease as the water quality improves, and that given its biological effects on the tropical tadpole, the Lek water quality--even after coagulation, rapid sand filtration, and (fresh) carbon filtration--is inferior to groundwater quality. This is not confirmed by the chemical parameters, however.

Evaluation of Toxicological Parameters

From these tests, and from the research on full-grown trout and trout eggs carried out some time ago at KIWA, it is known that measuring toxicological parameters for the evaluation of the water quality may yield useful results. Rapid measuring methods need to be developed both for the toxicological and for the chemical parameters. This type of research should be continued, but with parameters that can be measured in a relatively short time, such as TOC, UV extinction and EOCl, the Ames test, and short-term biolarval tests. If these rapid tests are conducted at frequent intervals the results may be related to each other more effectively than were the test data resulting from this investigation.

ACKNOWLEDGEMENT

The author would like to thank J.J. Rook and A.J. van der Veer of the Rotterdam Waterworks; L.J. Schultink and J. Zwaagstra of the Provincial Waterworks of North Holland; J.G.M.M. Smeenk and E.A.M. van Soest of the Amsterdam Municipal Waterworks; and J. van der Laan of the Waterworks of Midden Nederland, who generated most of the data described here. Thanks also are due to my colleagues at KIWA, C.L.M. Poels, M.A. van der Gaag, S.H.H. Olrichs, and R.Chr. van der Leer, for carrying out the toxicological, analytical, and technological parts of the KIWA investigations.

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PRACTICAL APPLICATIONS OF ADSORPTION TECHNIQUES IN DRINKING WATER — BELGIAN EXPERIENCES

Dr. W.J. Masschelein

INTRODUCTION

Belgium has a surface area of about 30,600 km^2 and 10 million inhabitants. The average water consumption per capita is 220 liters per day, including industrial consumption.

The average rainfall is between 800 and 900 mm/year. The theoretical potential groundwater capacity amounts to 2.6×10^9 m^3 of which 0.65×10^9 ($\pm$25 percent) m^3 are effectively used.

About two-thirds of the reserves are situated in the South of the country and one-third in the North. Fifty percent of the reserves are potentially exploitable, but only 900×10^6 to 1000×10^6 m^3 are potentially usable groundwater because a considerable amount in coastal areas or in coal mining zones is brackish. Furthermore, the percolation yield (1 $m^3/m/h$ for free infiltration galleries) limits the exploitation in a given area although the yield by pumping reaches 1 to 50 $m^3/m/h$. For this reason, it is easily understandable that most of the water (presently about 80 percent) originates from groundwater.

Well water has always occupied an important place in Belgian water supply, as in Belgian art (e.g. in the Ghent alterpiece of Van Eyck or in the well construction of Breughel). However, the use of surface water is increasing and experience with advanced techniques such as adsorption is expanding.

The available surface waters are those of the Yser River in the coastal area, the Scheldt River in the northern and western parts of the country, and, in the south-eastern part, the Meuse River, including the North Albert canal fed with water from the Meuse. At present, the two former lowland rivers are often heavily polluted and their use necessitates bank-side storage.

Hence, the most used source of surface water is that of the Meuse River. The Meuse is a "flashing river ", the flow being influenced by rainfall and seasonal sources.

PRINCIPLES OF THE USE OF ACTIVATED CARBON APPLIED IN BELGIUM

In the practical uses of activated carbon, already in operation or to be used in the future, there is a tendency to use fixed beds, e.g., rapid filtration through granular activated carbon (GAC), or pulsed beds, e.g., powdered activated carbon (PAC) in a flocculator. Expanded fluidized and moving bed techniques have not yet found use.

Practical data on full scale experience with rapid filtration on GAC, at a surface loading of 4 to 6 m/hr in the treatment of the lowland water stored at the Blankaart station, are indicated in Table 1 [data given by the national "Institut d'Hygiene et d'Epidemiologie" (I.H.E.)].

Table 1. Typical Examples of THM Adsorption in Lowland Waters

Sampling Point	Concentrations					
	TOC g/m^3	$CHCl_3$	CCl_4	$CHCl_2Br$ mg/m^3	$CHBr_3$	THM m Mol/m^3
Intake	23-11	3	0.1	0.6	0.3	(0.03)
After chlorination	12-8	40	3.2	5.6	12	0.74
After flocculation	12	40	1.4	14.6	14	0.54
After filtration on Norit ROW	6	35	1.2	14.5	2.6	0.40
After filtration on Norit PKST	7	32	1	14.5	2.6	0.36
After filtration on Chemviron 400	6	3.5	(0.1)	0.3	0.3	0.03

In some instances the quality may become critical and research is intended to diminish the residual THM content in the treated water by the use of appropriate carbons. Significant differences appear in the adsorption capacity for THM, even among carbons with equal TOC removal capacities. Adequate treatment

includes storage, pre-chlorination, coagulation-flocculation (either with aluminum sulphate or ferric chloride), settling, and filtration.

The Tailfer Plant

The Tailfer plant of the Brussels Intercommunal Waterboard (CIBE) incorporates the most modern treatment technology in the country. The station is located on the Meuse River, which has its source in France and is a typical "rain-river" of the moderate climatic zone. Upstream from Tailfer, the wastewater from about five hundred thousand inhabitants (equivalents) is discharged into the Meuse River. The natural tributaries to the Meuse result from spongy peat-soil. In dry summer periods the water is peaty. To enable navigation, the Meuse is forming a cascade of locks and reaches. During the summer period, actinomycetes develop in the river. The organic content is increased by decaying vegetation during the fall. Consequently, color, taste and odor removal are among the objectives of the treatment.

The treatment sequence consists of pH adjustment, prechlorination (can be by-passed), preoxidation with chlorine dioxide, coagulation (aluminum sulphate + activated silica), flocculation in a "pulsator", settling, filtration, ozonation, and post-disinfection (Cl_2 + NH_3 and/or ClO_2).

The powdered activated carbon in the sludge zone of the pulsator acts as a coagulation-flocculation aid. At the normal sedimentation rate, 0.011 m^3/s of sludge is withdrawn for a water flow of 0.73 m^3/s, hence about 1.5 percent volume. The concentration factor of the solids (carbon) is then 70. If 2 to 20 g/m^3 PAC are injected, the concentration can attain 140 to 1400 g/m^3. This has a favorable effect on the density of the floc and also improves the coagulation. The differences between the injection, during or after the coagulation phase, are shown in Figure 1.

The quality improvement in the water through use of PAC must be considered in conjunction with coagulation-flocculation. Typical data are shown in Table 2. The whole process of removing dissolved compounds is kinetically controlled and the best improvements require longer contact times. This appears to more favorably apply to the use of PAC, rather than GAC, with an appropriate and specific technology. PAC has a higher surface area per unit weight than GAC.

Except for the formation of small amounts of volatile brominated halomethanes, ozonization did not exert any significant effect on preexisting trihalomethanes (THM's) (Table 3).

Although the mixed waters from different origins, distributed by the Brussels' Intercommunal Waterboard, contain less than

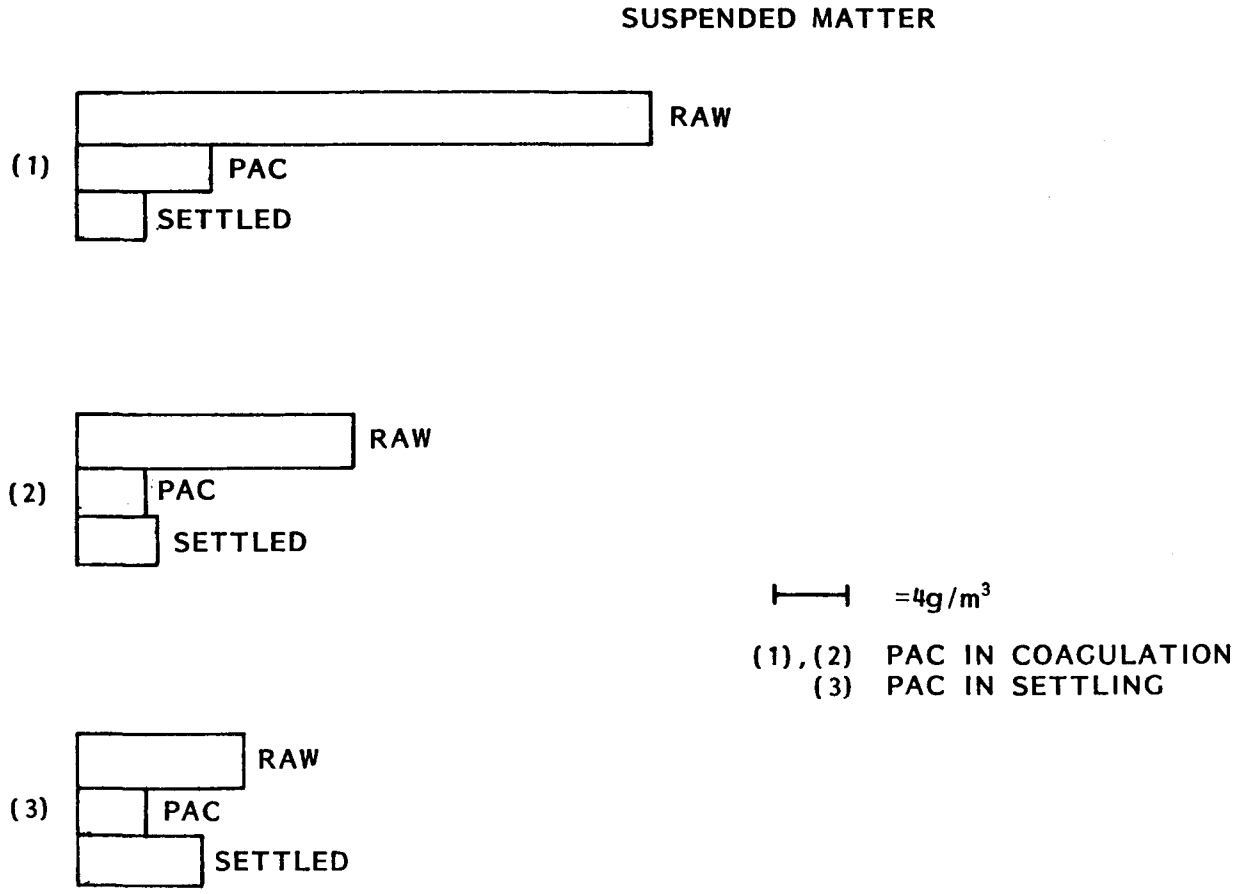

Figure 1. Effectiveness of PAC as a Coagulant - Flocculant Aid for Removing Suspended Solids

Table 2. Effect of PAC-Aided Coagulation/Flocculation

Parameter	Raw Water	Water Treated with PAC and Settled
TOC g/m^3	7 ± 2	2.5 ± 1
Phenols mg/m^3	35 ± 30	18 ± 13
MBAS mg/m^3	48 ± 32	43 ± 31
COD g/m^3	15 ± 4	8 ± 5
Carbon dose g/m^3	27.5 ± 12.5	—

Table 3. Trihalomethane Concentrations at Tailfer with Prechlorination

	$CHCl_3$	CCl_4	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THM
	expressed in mg/m^3					m mol/m^3
Raw Water	2	-	-	-	1	-
Prechlorinated ($2-5\ g/m^3$) (10 min)	15-20	-	5-7	0.5	-	0.2
Chlorine dioxide ($0.7\ g/m^3$) (30 min)	20-22	-	8-11	1	-	0.26
After carbon & settling (30 min)	10-15	-	8-11	1	-	0.20
2nd chlorination & filtration ($1\ g/m^3$) (3 hrs)	15-17	-	8-11	1	-	0.20
After postozonization	17-20	-	10	2-3	0.5	0.20

0.1 mg/m^3 of total THM's, the laboratory will focus more attention on this question in the future. The possible formation of haloalkanes of higher molecular weight, as well as other chlorinated compounds, requires very close attention.

From the data in Table 3, one can deduce that the formation of THM essentially results from the prechlorination phase. Considering the possible destruction of the precursors of the meta-cresol type, prechlorination was discontinued and the ClO_2 dosage and post chlorination were reinforced. Single data, comparative to that in Table 3, is shown in Table 4.

Table 4. Trihalomethane Concentrations at Tailfer without Prechlorination

	$CHCl_3$	CCl_4	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THM's
			(mg/m^3)			($mMol/m^3$)
Raw water	2	-	-	-	0.5-1	0.02
Chlorine dioxide (1.2 g/m^3) (30 min)	2	-	2-3	-	0.5	0.035
After carbon and settling (30 min)	3	-	4	-	0.5	0.04
Post chlorination (1.5 g/m^3) (3 hrs) + filtration	4-6	-	3-5	-	0.5	0.07
After post-ozonation	5	-	4	-	0.5	0.08

It appears that the use of chlorine dioxide as a pre-oxidation-predisinfecting agent largely reduces the formation of THM's. This is probably caused by the destruction of precursors which otherwise would form THM's during chlorination. Chlorine dioxide is believed to be capable of oxidizing certain organic structures which chlorine cannot. The present data are inconclusive; an investigation conducted over a whole year is needed to indicate possible seasonal effects. Also the effect of ClO_2 treatment needs to be more closely studied.

The PAC also removes chlorine from water. This effect is considered of secondary importance in Belgium since no objective for research on dechlorination in treatment plants currently

exists. From experience in the Tailfer plant, chlorine dioxide appears much more stable than chlorine in the presence of PAC under similar conditions. Laboratory experiments have indicated that the reaction proceeds by at least two consecutive steps; the integrated rate expression may be described by an exponential function (1).

$$\text{Percent Remaining} = b \times e^{-mt}$$

The half-life time of ClO_2 in the presence of PAC is about ten times greater than that of (free) chlorine applied under the same conditions.

PILOT EXPERIMENTS

There is no other experience at full scale with GAC or PAC in Belgium. The method, however, receives considerable attention at pilot-plant scale.

When considering overall quality improvement, the removal of TOC constitutes one of the most critical criteria. At filtration velocities of 15 to 20 m/hr, the thickness of the GAC layer must be at least 2 to 3 m in order to obtain a satisfactory removal of TOC.

Experiments with a column of 2.5 m Chemviron 400 carbon (see also Table 1) indicated that for an extended service time of several months, the level of abatement of TOC or THM remains limited (2) (Table 5).

Table 5. TOC and THM Abatement

TOC Abatement (mg/m^3)	THM Abatement ($m\ Mol/m^3$)	Service Time (months)
1	-	8.6
1.25	-	7.2
1.5	-	6.0
1.75	-	4.8
2.0	-	2.9
-	0.1	6.2
-	0.15	4.1
-	0.2	3.1
-	0.25	2.5
-	0.3	2.1

Pilot experiments have been carried out at the Havre treatment works (also managed by CIBE) to help in the design of a biologically regenerable GAC filter eliminating simple phenols (including cresols) and monocyclic aromatic hydrocarbons (toluene and xylene). These compounds had polluted a groundwater catchment. The concentration of these organics, which previously ranged from 50 to 100 mg/m^3, has been lowered to less than 5 mg/m^3, usually 1 mg/m^3. The carbon used was Norit ROW 0.8 supra, at a surface loading of 0.72 m/hr, during 6 to 10 months of operation.

Other characteristics of the raw water were: oxygen, 1 g/m^3; iron, 150 to 200 g/m^3; COD, 4 to 5 g/m^3; TOC, 3 g/m^3; and less than 50 mg/m^3 ammonia.

In-depth aeration was attempted by using hydrogen peroxide in association with the GAC filter. Typical data for the oxygen content (in g/m^3) are given in Figure 2.

The final population of bacteria (on the surface of the activated carbon) in the presence of H_2O_2 reaches a stationary state at about one organism per 4 mm^2. Even at this rather low count (populations up to one bacterium per 40 m^2 have been reported), the filter remained sufficiently active in biological degradation.

Bacterial concentrations in the filtered water from the pilot plant, using adsorption and biological treatment, have varied from 50 to 45,000 total counts per ml. No systematic explanation has been given yet, but the point illustrates the need for an accurate post-disinfection after GAC filtration.

No treatment combining ozonation with adsorption on GAC exists at present in Belgium; however, the technique is considered to be promising for the future.

OTHER TECHNIQUES

The CIBE has two full-scale plants using diatomaceous earth in occasional operation. One plant has a capacity of 0.2 m^3/sec for final polishing filtration of water coming from the River Meuse. Another plant has a capacity of 0.12 m^3/sec for treatment of raw water that is temporarily stored in open reservoirs to meet potential peak consumption. In both cases, the adsorption effects on organics (COD, TOC, detergents) are negligible.

COSTS

It appears that in Belgium, under most conditions, the problems related to organics can still be solved by the use of PAC.

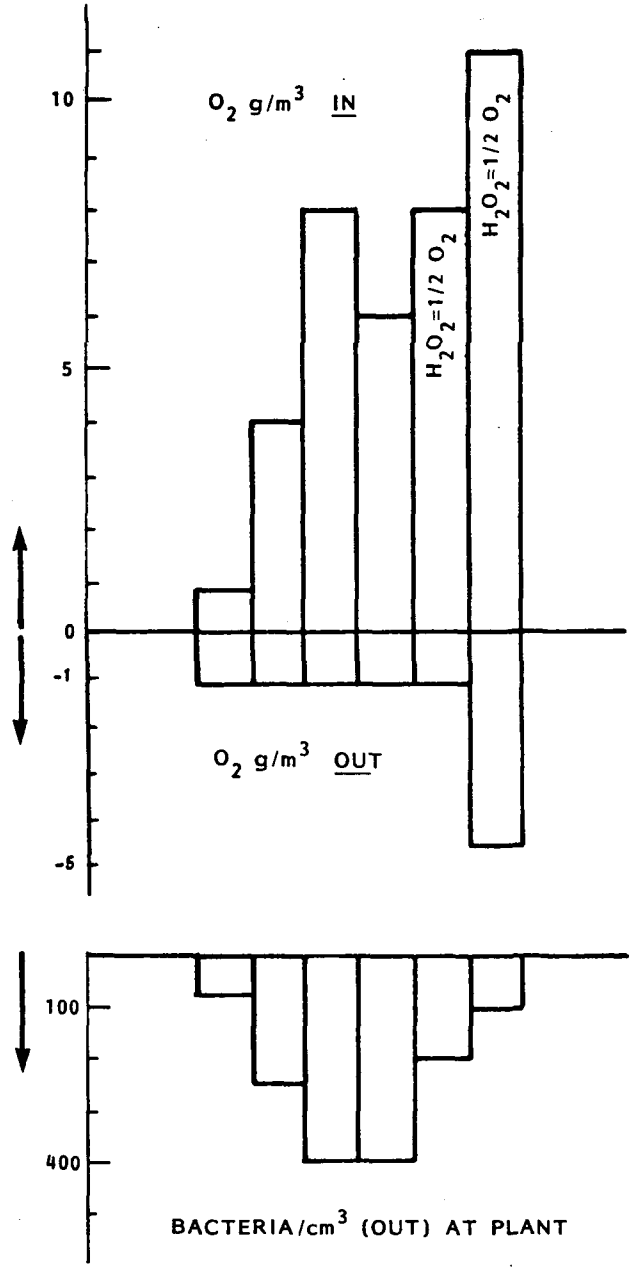

Figure 2. Bacteria Counts in the Effluent as a Function of Oxygen Presence

However, there is growing interest in the use of GAC, particularly if, in the future, more polluted resources in central and northern Belgium must be exploited.

On the Belgian market, prices are respectively 15 BF/kg for PAC and 55 BF/kg for regenerable GAC (May 1979 exchange rate: 30 BF to 1 $U.S.).

The estimated regeneration loss is 10 percent per cycle, with two regenerations per year in rapid filtration. The cost of carbon losses is 11 BF/kg/year and the cost of regeneration (thermal) is equal to 10 BF/kg/year. Total estimated regeneration costs are 31 BF/kg/year.

Example: To treat 0.28 m^3/s (1000 m^3/h) at a filtration velocity of 10 m/hr and through a GAC bed depth of 2 m, the total surface of the filters is 100 m^2. Hence about 80,000 kg GAC could be necessary.

Annual charges are:

carbon 55 BF/kg x 80,000 kg x 0.1 (investment)	= 440,000
filters: (1500 BF/m^3/d) 27,000,000 x 0.1	= 2,700,000
carbon losses and regeneration costs (includes costs of emptying and filling carbon beds) - 31 BF x 80,000	= 2,480,000
Total, BF/year (This includes power and maintenance costs for regeneration, but does not include operational costs; i.e., backwashing and power costs for filtration)	= 5,620,000

At a net production of 8,500,000 m^3/yr, these estimated costs amount to 0.66 BF/m^3 or $0.022 US/$m^3$. If only one annual regeneration is necessary, this production cost amounts to 0.52 BF/m^3 or $0.017 US/$m^3$.

On a comparative basis, the cost of using powdered activated carbon is less than 2,000,000 BF corresponding to a nominal production cost of less than 0.025 BF/m^3. The cost of using PAC amounts to 0.15 BF/m^3 or $.005 US/$m^3$ at a dose of 10 g/m^3, and is approximately proportional to the dose.

Various Impacts on Production Costs

Besides the above factors, other parameters have an effect on the costs:

The average peak factor in Belgium, that is maximum day consumption to average day, is on the order of 1.30 to 1.35. This can involve, in local circumstances when only considering treated surface water, an increase in the above mentioned production costs of 30 percent, or as in the example given, an additional expense of 0.12 BF/m^3 or \$.004 US/m^3.

Labor for PAC dosing in the Tailfer station, operated at 130,000 m^3/day, amounts to less than 0.5 man/day/week or less than 0.003 BF/m^3 water produced. Estimates for the use of GAC, regenerated twice a year, indicate three working days/year/20 m^3 GAC. Assuming filtration at 10 m/hr, corresponding labor costs amount to 0.016 BF/m^3 or \$.005 US/m^3.

The use of GAC necessitates a transfer procedure. During these periods, the production must continue. Hence, a supplementary filter or storage area may be necessary. The minimum required volume is 20 m^3, or an additional investment of about 2,700,000 BF, or an annuity of 270,000 BF/yr to be imputed with the production (respectively \$90,000 and \$9,000 US).

CONCLUSION

Belgium relies on its groundwater resources for about 80 percent of its water supply.

PAC is used in the Tailfer plant of the CIBE to improve color, sometimes taste and odor, and, in conjunction with ClO_2, to reduce trihalomethane formation potential. The level of trihalomethanes found until now does not justify the introduction of GAC in most plants; however, the technique is being evaluated seriously.

Several pilot plants are operated to investigate the use of GAC for abatement of TOC and THM, and as biologically active filters. Examination of representative small scale columns is necessary to shorten the delay until a conclusion can be reached.

On a comparative basis, estimated costs in Belgium are in the ratio of 1/0.2 to 1/0.5 for regenerated GAC compared to PAC.

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THE USE OF GAC FILTRATION TO ENSURE QUALITY IN DRINKING WATER FROM SURFACE SOURCES- Swiss Experiences

Maarten Schalekamp

The lake waterworks in Switzerland use granular activated carbon (GAC) filtration, despite the relatively high quality of their water sources, because of the proximity of oil pipelines to drinking water storage basins and the occurrence of two phenol spills in the St. Gallen and Zurich drinking water supplies, respectively.

When the oil pipeline from Genoa to Ingolstadt was laid adjacent to Lake Constance and its surroundings, the possibility of oil leakage had to be taken into account. The consequences of oil leakage into a drinking water storage basin could be disastrous. As a result of the efforts of several waterworks, the Energia Nationale Italiana (ENI) financed the installation of ozone or GAC treatment facilities for all the waterworks in the critical area. Thus, water contaminated by slight amounts of oil can be purified for potable use.

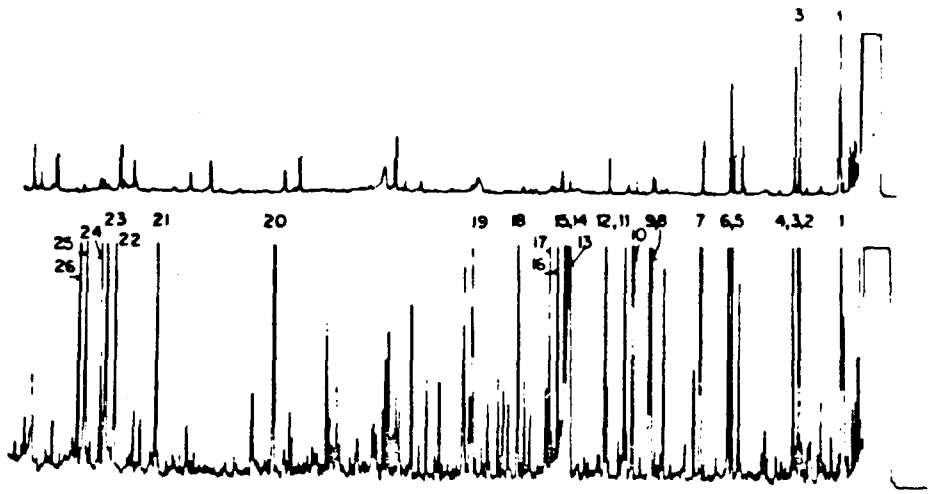
The need for GAC filtration was further demonstrated by the phenol spills that contaminated the water supplies of the cities of St. Gallen in 1957 and Zurich in 1967. On both occasions, the drinking water supplies were highly contaminated and their tastes and odors were adversely affected.

These two events led to the installation of a GAC filtration system at the waterworks of St. Gallen by Lake Constance. The phenol spill in Zurich had consequences so severe that it provided sufficient impetus for the installation of a GAC filtration step in the Lengg and Moos treatment plants. In most of the other lake waterworks in Switzerland, the sudden appearance of the floating mussel Dreissena polymorpha pallas (DPP) made necessary chlorination and subsequent GAC filtration for dechlorination.

The consumption of oil and gasoline has increased sevenfold during the past few years; therefore, the organic load of the rivers also has increased. It has been reported that many organic substances found in the lake waters are almost completely absent from pure well water (Figure 1). Investigations carried out in the laboratories of the Zurich waterworks confirmed the presence of such substances in treated water drawn from Lake

Zurich (Figure 2). Since each Swiss waterworks must ensure that the quality of the drinking water obtained from surface water is in no way inferior to the quality of water found in well and groundwater, particularly with respect to the load of organic substances, the need for purification of surface water by GAC filtration is manifest.

Well Water from Dolder, July 5, 1973



Surface Water from Lake Zurich, July 7, 1973

Figure 1. Organic Substances in Well and Zurich Lake Water (Each numbered peak represents an identified organic substance.)

DECHLORINATION EFFICIENCY OF GAC

Several waterworks in Switzerland use chlorine to prevent DPP from attacking raw water pipelines. The chlorine is then removed through GAC filtration. Experiments have shown that a concentration of 0.5 mg/l chlorine remains after a dose of 1.0 mg/l Cl_2 has been added to the raw water catchment installation, completely eliminating the DPP larvae within 14 days (Figure 3).

This amount of chlorine is sufficient since it has been shown that the larvae remain in the rapid filter for up to 15 days. Because a residual chlorine concentration of only 0.05 mg/l in drinking water is permitted in Switzerland, the excess chlorine must be removed from the water.

Although the chlorine could be neutralized with thiosulfate, GAC was selected instead as a safety measure. The GAC is applied either as a second upper layer in the rapid filters,

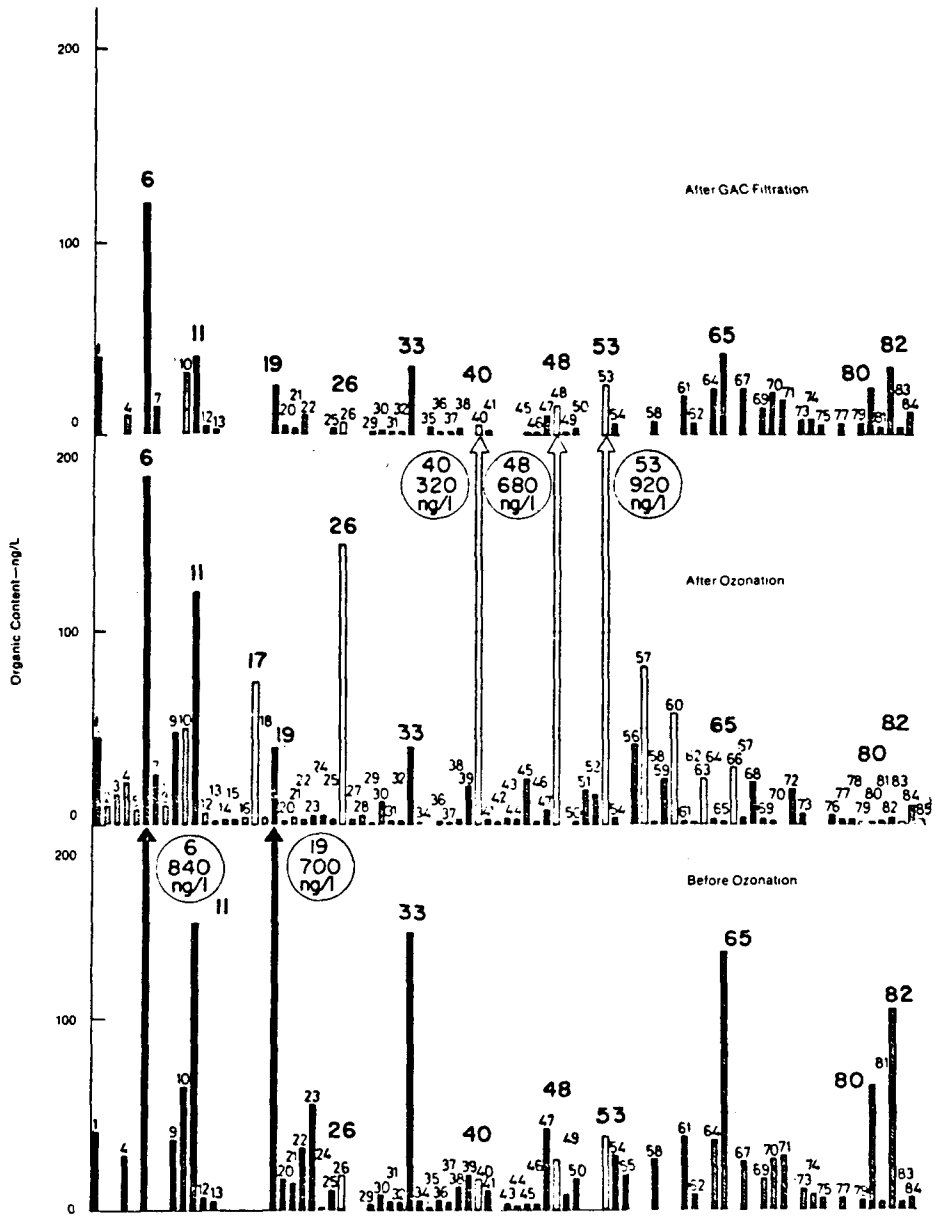


Figure 2. Modification of Organic Matter During Water Treatment

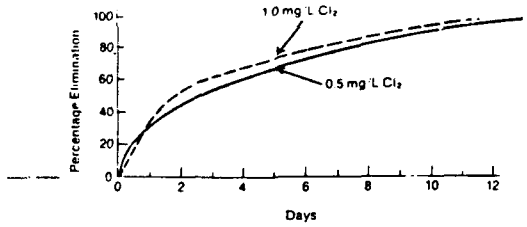


Figure 3. Elimination of Dreissena Polymorpha Pallas Larvae in Raw Water

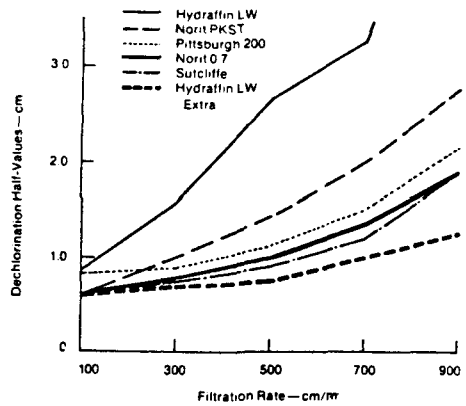


Figure 4. Dechlorination Half-Values of Various Types of GAC at Different Filtration Rates

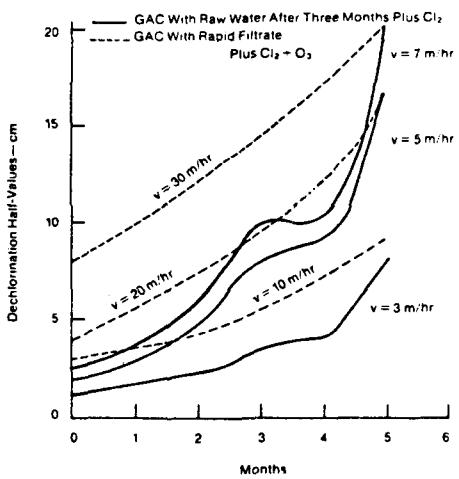


Figure 5. Decrease in Declorination Efficiency of Norit 07 GAC at Different Filtration Rates

as a 5 to 10 cm thick layer above the sand in the slow filters, or as a top layer in GAC filters.

To select the most suitable type of GAC, experiments were conducted to test the different types of GAC for dechlorination at the velocities of the slow as well as the rapid filters. All the carbon types were suitable for the slow filters. For the rapid filters, however, Hydraffin LW extra, Sutcliffe, Norit 07, and Pittsburgh 200 were most suitable (Figure 4). Since the effectiveness of dechlorination decreases with time, different types of GAC were tested for several months at different velocities (Figure 5).

It was also discovered that the efficiency of dechlorination depends upon the grain size of the GAC: the smaller the grain size, the higher the efficiency. GAC also was employed to eliminate any ozone remaining in the treated water.

DOUBLE-LAYER RAPID AND SLOW FILTERS WITH GAC

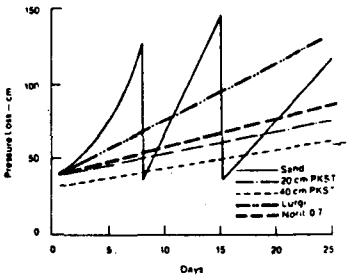
Additional experiments were performed with one-layer and double-layer rapid filters. The double-layer filters, consisting of 60 cm quartz sand and 20 cm GAC, were compared with a one-layer filter filled only with 80 cm quartz sand.

The operating time was five times longer for the double-layer GAC filters compared to the single-layer filter (Figure 6), with the cleaning efficiency being equal. The pressure loss takes place in the GAC layer (Figure 7). The longer or shorter operating time for the double-layer filter is also dependent upon the grain size of the GAC. After intensive air rinsing, it was possible to rigorously separate the quartz sand and the GAC with a backwash water velocity of only 15 $m^3/m^2/hr$.

Until the completion of the GAC filters, most of the lake waterworks in Switzerland augmented their rapid filters with GAC for dechlorination. In Zurich, dechlorination was accomplished with the slow filter, with 10 cm of GAC as the top layer, until the completion of the GAC filter. This modification resulted in operating times at least five times better than those of the single-layer slow filters (Figure 8).

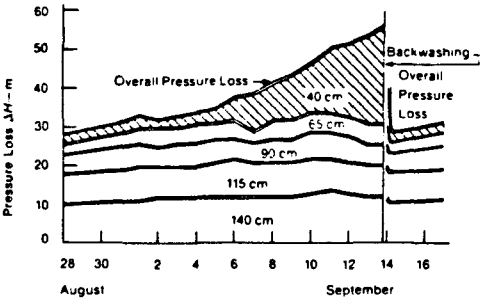
A new cleaning process with cyclic and continuous systems was developed (Figures 9, 10) eliminating the necessity of removing the GAC during the backwashing process. The advantage of this new process is that the slow filters no longer need to be shut down.

Although the results of using the GAC layer on slow filters were excellent, the recharge basins of the new Hardhof plant were covered with 10 cm of GAC.



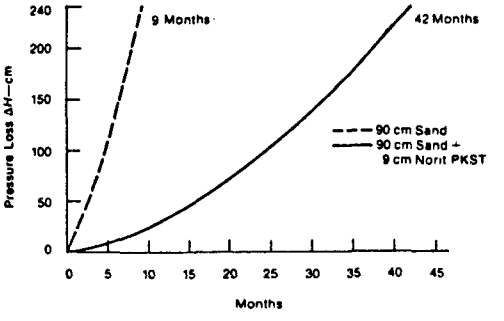
V = 3.75 m/hr

Figure 6. Operating Times of Single- and Double-Layer GAC Rapid Filters



Q = 5000 m³/hr; V = 5.6 m/day

Figure 7. Pressure Loss in Each Layer of a Double-Layer GAC Rapid Filter



V = 15 m/day

Figure 8. Operating Times of Single- and Double-Layer Slow Filters as a Function of Loss of Pressure

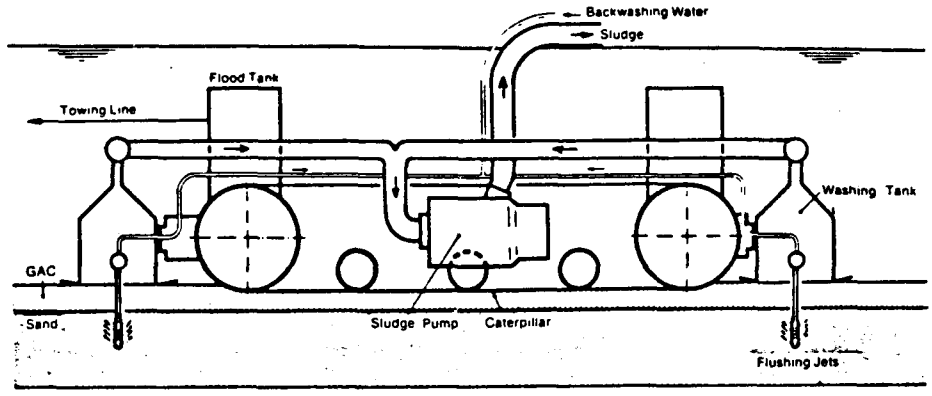


Figure 9. Slow Filter Cleaning Instrument (Cyclic System)

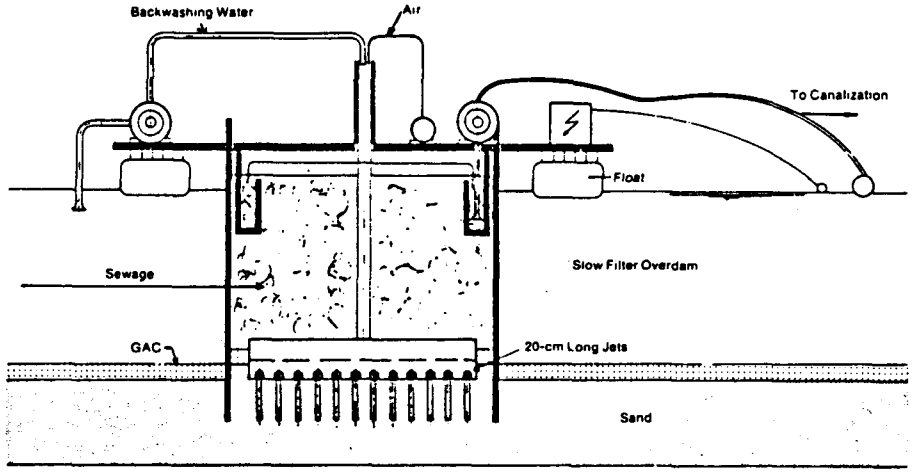


Figure 10. Slow Filter Cleaning Instrument (Continuous System)

THE REMOVAL OF ORGANIC SUBSTANCES BY THE GAC FILTER

Experiments in Zurich showed that, depending on the kind of GAC, up to 75 g of organic substances can be removed from water per kg of GAC. These substances are referred to as the sum of dimethylformamide (DMF) plus dioxane extracts.

The removal of organic substances by several types of GAC was investigated in Zurich. Table 1 shows the types of GAC tested and the amount of organic substances removed from the raw water of Lake Zurich. The best removal efficiencies were achieved with Pittsburgh F400 and Lurgi LS-Supra.

Table 1. Cumulative Removal for Various Types of GAC for Zurich Lake Raw Water

Carbon Type	Experiment 1* Cumulative Removal‡ g/kg	Experiment 2† Cumulative Removal‡ g/kg
Pittsburgh F400	61	61
Norit PKST	41	41
Lurgi LS-Supra	34	40
Norit 07	21	28
Lurgi LW	28	
Pittsburgh F300		30
Norit 08		34
Zetclef		26

*Duration nine months
†Duration three months
‡Measured as sum of DMF plus dioxane extracts.

A new GAC, ROW 08 Supra from Norit, was tested and compared with Pittsburgh F400. Experiments in larger plants had already confirmed that the ROW 08 was equal to the Pittsburgh F400 after 1 month (Table 2). This was further substantiated by long-term testing.

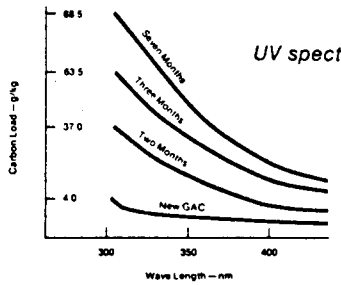
Table 2. Load Comparison of Various Types of GAC*

Carbon Type	DMF Extract g/kg GAC			DMF Extract Extinction at 300 nm (Light Path = 1 cm)		
	Total Load	New GAC	Effective Load	Total Load	New GAC	Effective Load
ROW 08 supra	5.5	1.6	3.9	0.062	0.044	0.018
ROW 08 supra M	4.1	1.6	2.5	0.093	0.044	0.049
F400	6.1	3.7	2.4	0.121	0.109	0.012

*34 days; throughput—4.5 m^3/kg GAC

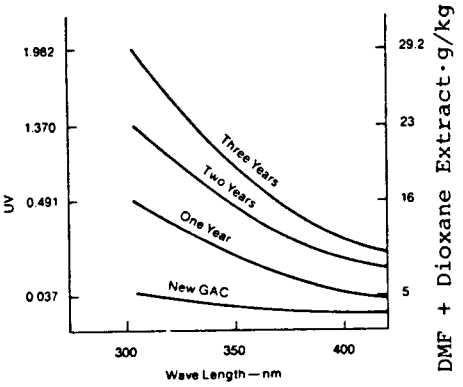
Pittsburgh F400 carbon was used later in the GAC filtration process of the Lengg waterworks. After a 2-month operating period, a load of 37 g/kg in the upper GAC layer was attained. The fresh carbon showed a load of 4 g/kg DMF + dioxane extract, increasing after 3 months of operation to 63.5 g/kg, and attaining the highest capacity of 68.5 g/kg after 7 months (Figure 11).

The slow filter in the Moos waterworks was supplemented with a 5-cm layer of PKST GAC. This new carbon initially adsorbed an organic load of 5 g/kg; after 3 years the load was 29.2 g/kg (Figure 12). The effectiveness of this carbon



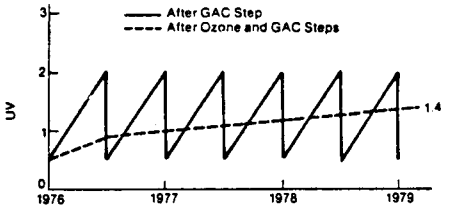
UV spectra of DMF extracts; DMF + dioxane extract

Figure 11. GAC Loads Over Time in the Upper Layer of the Filter



UV spectra of DMF extracts

Figure 12. GAC Loads Over Time in a Slow Filter



UV = 254 nm; light path = 1 cm

Figure 13. UV Extinction Over Time After GAC Filtration and After Ozone Treatment Plus GAC Filtration

in removing organic substances (i.e., UV extinction) in the treated water remained constant over a 3-year period.

Thus, the construction of a separate GAC filter for the recharge of groundwater at the new Hardhof waterworks was not necessary because the recharge basins performed with equal efficiency when they were augmented with GAC. The operating time of the recharge basins also increased by five times.

The operating time of GAC with Swiss lake water is only 6 months if the ozonation process is not used. When the ozonation process is placed before GAC filtration, the GAC can be used for about 3 years (Figure 13), thereby increasing the GAC operating time sixfold at a significant cost savings since the GAC does not have to be reactivated as often. If halogens are present in the water, they will be more efficiently removed by ozone than by GAC. Figure 14 shows an 80 percent decrease in chloroform following ozone treatment and a 33 percent further decrease after GAC.

Figure 15 illustrates the increase of the most important aldehydes through ozonation. In plants without a GAC stage, the continued oxidation of the aldehydes causes the formation of acids that promote the reproduction of bacteria. To prevent this problem, GAC filtration is used immediately after ozonation.

There are three situations when the GAC should be changed or regenerated: first, when the halogen level in the drinking water approaches the maximum level permitted, at 25 µg/l (Swiss drinking water normally contains only 10 to 15 µg/l halogens (Figure 16)); second, when the UV extinction does not decrease further after the GAC filtration step (Figure 17); and third, when the load of DMF + dioxane extract in the upper layer of GAC is very near the maximum possible and that in the bottom layer is 70 percent of the maximum possible load.

Figure 18 shows that with the GAC ROW 08 Supra, the maximum load is 40 g/kg. The bottom layer is regenerated at 28 g/kg, or 70 percent. With the GAC Pittsburgh F400 the maximum load is 75 g/kg, and regeneration is done if the bottom layer is 52 g/kg, or 70 percent.

TESTS AND MONITORING

In view of the danger to the consumer's health presented by certain organic pollutants, it is imperative that water suppliers know instantly when changes occur in the drinking water, as monitored by biological and physio-chemical tests. Nonspecific chemical tests such as oxidizability, TOC, DOC, DOCl (dissolved organic chlorine), and DOCl-N (dissolved organic chlorine-nonpolar, measured in the liquid-liquid extract by microcoulometric technique) are slow and laborious to carry

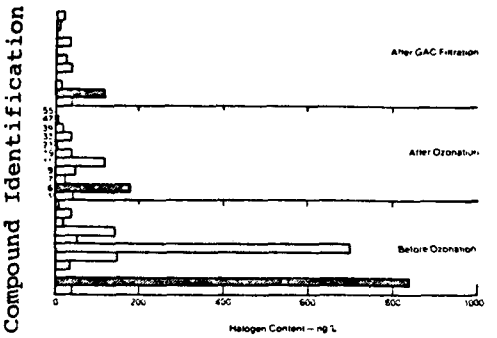


Figure 14. Decrease of Halogens After Ozonation and After GAC Filtraton

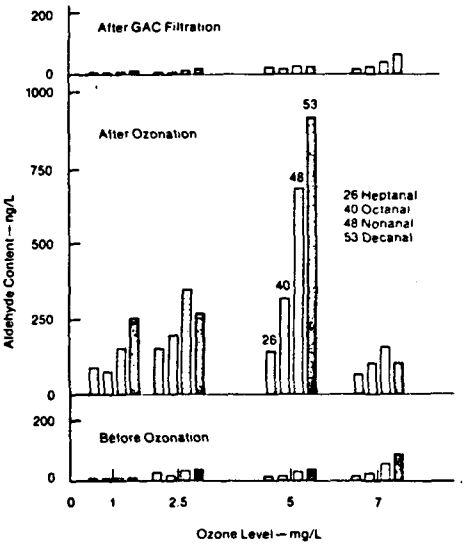


Figure 15. Aldehydes Before and After Ozonation at Different Ozone Concentrations and After GAC Filtration

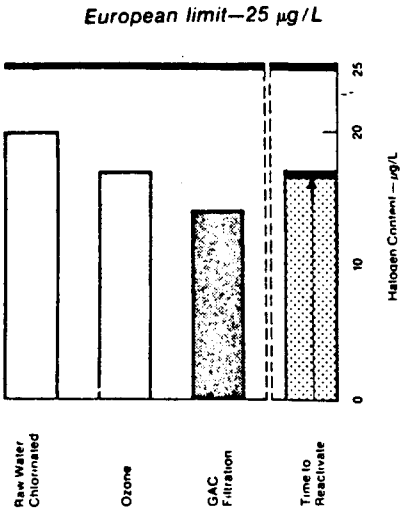


Figure 16. Halogens in Raw and Finished Water from Lake Zurich Supplies

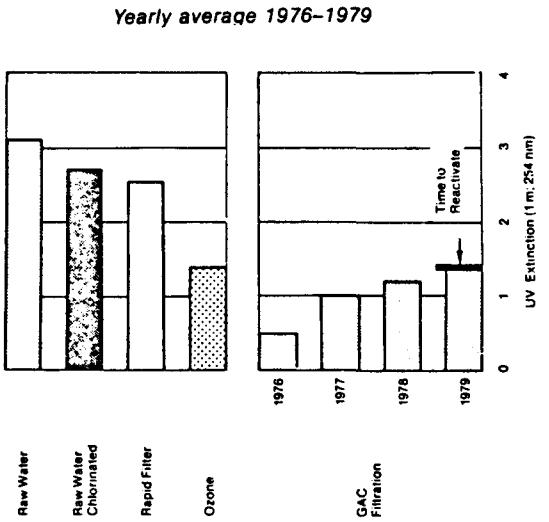


Figure 17. Variation of UV-Extinction Levels During Water Treatment

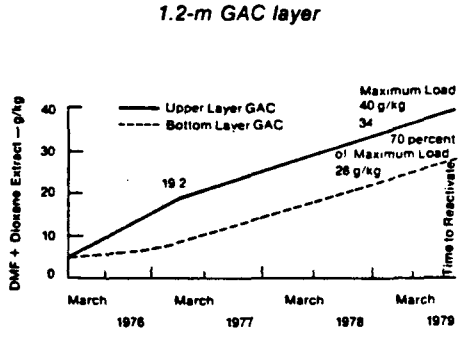


Figure 18. Loads of Upper and Bottom GAC Layers as a Function of Time

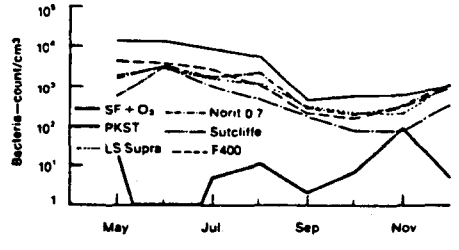


Figure 19. Bacterial Count After Three Days at 20°C in 1 ml of Chlorinated Rapid Filtrate and Various GAC Filtrates

out and are not continuous. Besides these tests, an instrument for continuously monitoring organic matter in raw water, groundwater, and finished water is employed. It measures UV extinction, which enables organic pollution to be detected immediately. With this instrument, it is also possible to monitor the amounts of organic matter during the treatment of drinking water. The results obtained by UV extinction correlate satisfactorily with those given by DOC or TOC, and they are available instantaneously in the Hardhof control center.

BACTERIAL REGROWTH

Experiments in pilot plants in Zurich have proved that GAC treatment leads to bacterial regrowth. Figure 19 shows that the Norit PKST carbon initially had the highest bacterial count. The bacterial count of the Pittsburgh F400 was about half that of Norit PKST and the Lurgi LS-Supra count was a little lower than the Pittsburgh F400. The Sutcliffe carbon showed the best results. Nearly all the counts for the GAC types tested were equally high, except for the Sutcliffe carbon. Its bacterial count (343 colonies/ml) was only a third that of the others.

A close relationship exists between the reduction of organic substances and bacterial regrowth, especially for PKST GAC. Initially, PKST was the most effective GAC for removal of organic substances, but its use also resulted in the highest regrowth count. As shown by experiment 2 (Figure 20), with monthly backwashing all carbon types already exhibited a 5-digit bacterial count after 1 month of operation. The weekly backwashing of Sutcliffe 206A and Norit PKST carbons reduced the bacteria to a 4-digit count, and after 5 weeks they had a 60 percent recurrence of bacteria. It must be concluded that the carbons have a significantly lower reinfection when the GAC filter is more regularly backwashed. Full-scale tests with rapid filters at the Lengg waterworks confirmed this hypothesis.

In previous experiments, Lurgi LS-Supra and Norit PKST produced no regrowth; however, they were fed with chlorinated water. The new GAC filter in Lengg, which is backwashed twice a week, has never produced a count of more than 10 to 50 colonies/ml. These are extraordinary results (Figure 21).

REACTIVATION

The reactivation is done by Norit's fluid-bed process. The GAC must be either replaced or reactivated every 2 years. The fluid-bed process was selected because it ensures the lowest loss of carbon of all processes currently available. The volume loss from filter to furnace and back to the filter totals only 3.5 percent (Figure 22).

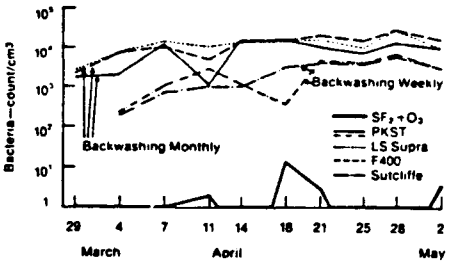


Figure 20. Bacterial Count After Three Days at 20°C in 1 ml of Ozonized Slow Filtrate and Various GAC Filtrates

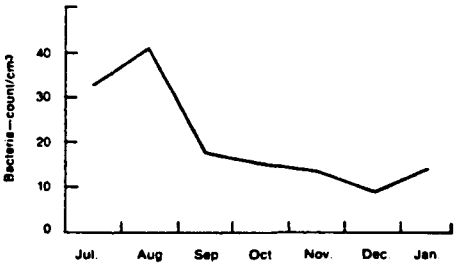


Figure 21. Bacterial Count After Three Days at 20°C in 1 ml of GAC Filtrate

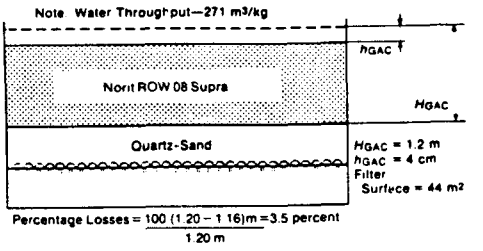


Figure 22. Loss of ROW 08 Through Reactivation

UV spectra of DMF extracts

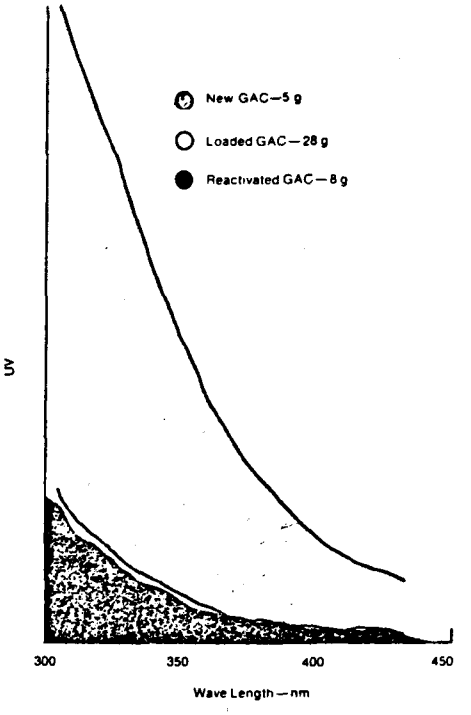


Figure 23. Results of GAC Reactivation

The author was present when Norit ROW 08 Supra from Duisburg and PKST 1-3 from the Zurich waterworks were reactivated (Table 3). Later, a low density GAC, Norit PKST 1-2, was reactivated in the same furnace. Although this carbon is not usually suitable for reactivation, the losses were only 50 percent of those incurred with common processes. The effectiveness of the reactivation was excellent. The PKST carbon had a small load of only 28 g/kg (Figure 23). Whereas fresh carbon had a load of 5 g/kg, the value for the reactivated carbon was slightly higher (8 g/kg).

Table 3. Reactivation Efficiency of Two Types of GAC*

Carbon Type	DMF Extract g/kg GAC			DMF Extract Extinction at 300 nm (Light Path = 1 cm)		
	Total Load	New GAC	Reactivated GAC	Total Load	New GAC	Reactivated GAC
ROW 08 supra	28.5	1.6	3.1	1.576	0.044	0.066
PKST 1-3	20.9	2.2	4.5	1.055	0.045	0.057

*Reactivated in the Norit installation Mar. 26, 1974
†Throughput—3800 m³/kg GAC

This kind of reactivation plant was installed in the Lengg waterworks and was put into operation at the beginning of 1976. The reactivation of the GAC was excellent. The used Pittsburgh F400 had a total load of 32.1 g/kg dioxane + DMF; the new GAC, 6.9 g/kg; and the reactivated GAC, 6.2 g/kg. The reactivated GAC was better than the new GAC at a furnace capacity of 110 kg/hr. The ROW 08 had a total load of 22.1 g/kg dioxane + DMF; the new GAC, 2.3 g/kg; and the reactivated GAC, 5.8 g/kg. The reactivated ROW 08 GAC was not as efficient as the new GAC, but was as good as the F400. With a furnace capacity of 110 kg/hr the reactivated GAC was also better than the new GAC (Table 4).

Table 4. Effectiveness of the Lengg Reactivation Furnace for Two Types of GAC

Carbon Type	Dioxane Extract g/kg GAC			DMF Extract g/kg GAC			Total g/kg GAC		
	Total Load	New GAC	Reactivated GAC	Total Load	New GAC	Reactivated GAC	Total Load	New GAC	Reactivated GAC
F400*	7.8	2.9	1.8	24.3	4.0	4.4	32.1	6.9	6.2
ROW 08†	5.4	1.0	2.7	16.7	1.3	3.1	22.1	2.3	5.8

*Throughput—181 m³/kg GAC; furnace capacity—110 and 130 kg/hr
†Throughput—271 m³/kg GAC; furnace capacity—130 kg/hr

CONSTRUCTION OF THE GAC FILTERS IN ZURICH

In Lengg, 12 GAC filters are in use, six on each side of the pumping station. The filters are closed pressure filters of smooth-faced concrete with an area of 44 m^2 each (Figure 24). The bottom of the filters contain 75 plastic nozzles per m^2. The filter bed consists of a 50-cm layer of quartz sand, grain size 0.7 to 1 mm, and a 1.2-m layer of Pittsburgh F400 GAC above. Because this carbon exhibited a very high filtration resistance, it was replaced during the reactivation by Norit ROW 08 Supra which resulted in considerably lower pressure loss. Nevertheless, the F400 carbon has very good adsorptive characteristics and is still used in the Moos waterworks where pressure losses cause no problem.

The cleaning of the GAC filters is accomplished by backwashing, first with air and then with the same type of treated water as that used for the rapid filters. The backwashing velocity is 25 $m^3/m^2/hr$; if necessary, it can be increased to 50 $m^3/m^2/hr$. The normal velocity of the filter is 21.5 $m^3/m^2/hr$ when one of the 12 GAC filters is backwashing. For reactivation, the GAC can be transported hydraulically to their respective reactivation plant silos.

In the construction of the filters, measurements must be taken to ensure that enough free space is available for the expansion of the carbons, which is often greater than the estimates of the supplier (Figure 25). The construction of recharge basins as two-layer filters with 10 cm of GAC can be seen in Figure 26.

THE COSTS OF GAC FILTRATION AND REACTIVATION

The construction costs for the 12 GAC filters with a total area of 528 m^2 and a daily output of 250,000 m^3 are:*

Buildings	$2,749,970
Technical installations	$3,014,030
Consolidation of the filter	$ 120,370
Total	$5,884,370

The costs of the reactivation plant are not included in this list. The capital costs per cubic meter daily capacity are therefore $22. The whole lake water treatment in Lengg, including the pumping station, will cost $220 per daily cubic meter. Ten percent of the total capital costs must be spent on the GAC filtration system.

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*Based upon an exchange rate of $1 = 1.67 Swiss francs.

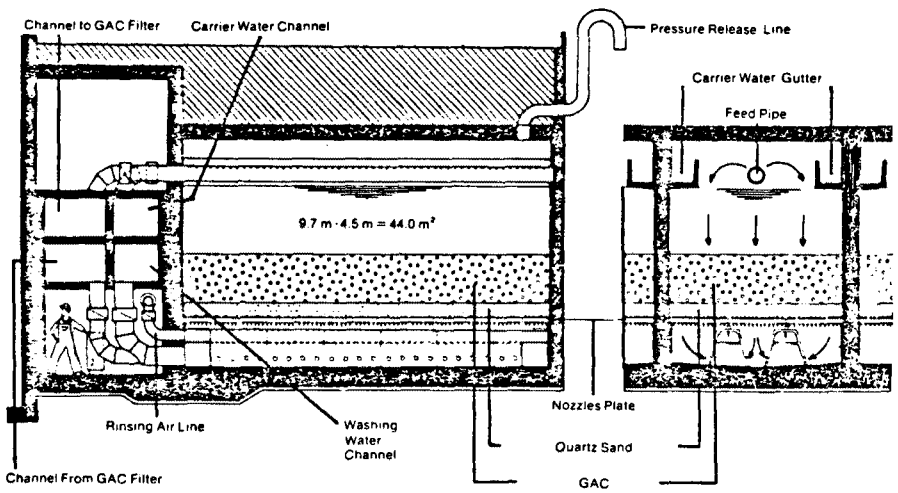

Figure 24. Profile and Cross Section of GAC Filter

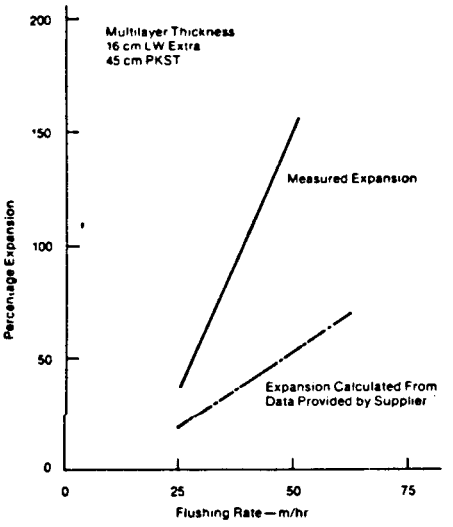

Figure 25. Expansion of GAC Layers as a Function of the Backwashing Rate

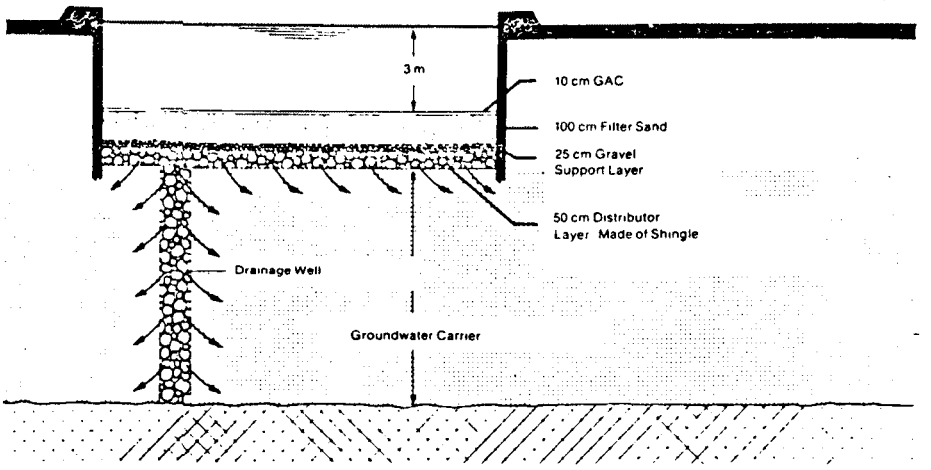

Figure 26. Composition of the Recharge Basin at Hardhof Plant

The operating costs for interest and amortization (25 years at 6 percent interest) are $560,000 per year. An additional $80,000 should be included as annual maintenance costs. With an annual output of 40 x 10^6 m^3, the capital investment costs are $0.016/$m^3$. The operating costs for the annual reactivation are:*

Capital costs	$106,670
Maintenance	$ 26,670
Heating	$ 21,330
Service	$ 21,330
Loss GAC at 5 percent (effectively only 3.5 percent)	$ 37,340
Annual total operation costs	$213,340

With an output of 40 x 10^6 m^3/year, the operation costs for the reactivation, including the loss of GAC, are $0.0055/$m^3$. The total costs will be $0.0215/$m^3$. With an annual output of 40 x 10^6 m^3, the treatment costs of the Lengg waterworks total $0.17/$m^3$. Thus the costs for GAC filtration come to only 12.5 percent of the total operating costs.

To ensure that the quality of drinking water derived from surface water is not inferior to that of well or groundwater, GAC filtration is indispensable. At a cost of one eighth of the total treatment costs, the use of GAC is also economically feasible.

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*Construction costs of the reactivation plant and transfer installations = $560,000 (10 percent amortization, 6 percent interest).

CURRENT UNITED KINGDOM PRACTICE IN THE USE OF GRANULAR ACTIVATED CARBON IN DRINKING WATER TREATMENT

J.B. Goodall
and
R.A. Hyde

INTRODUCTION

Water suppliers in the United Kingdom are legally required to supply water which is wholesome - this is generally taken to mean water which is clear, palatable, and safe.

The facility for using activated carbon is available in approximately 100 potable water treatment works throughout the country. In most applications, activated carbon is used for controlling unpleasant taste and odor, particularly the earthy/musty taste and odor that occur as a result of the presence of actinomycetes and algal matter in water. Because these taste and odor problems are seasonal and often short lived, most water undertakings find it more economical to use powdered rather than granular activated carbon.

At present, the United Kingdom has four water treatment works employing granular activated carbon, three of which use the carbon after rapid filters and one where the carbon has partially replaced the media in the rapid filters. One of the treatment works employs granular activated carbon to remove "chemical" taste and odor, the remaining three are for earthy/musty taste and odor control. Only one of the treatment works has regeneration facilities on site.

Research on the use of granular activated carbon for synthetic organic control in drinking water treatment is being undertaken by the Water Research Center and a number of water suppliers.

Bough Beech (East Surrey Water Company)

Water from the unpolluted Eden River is pumped into a 9.1 x 10^6 m^3 (2 x 10^9 gallons; 2.4 x 10^9 U.S. gallons) reservoir from October to April each year. Water from the reservoir that feeds the carbon filters is prechlorinated to maintain 1 g/m^3 free

chlorine in the water and then split into two parallel streams (Figure 1); two thirds of the water is clarified by coagulation with aluminum sulphate at pH 7.1 and floc blanket sedimentation. The remaining one third of the water is softened and coagulated by addition of sodium hydroxide and aluminum sulphate at pH 11 and clarified by floc blanket sedimentation. The two clarified streams are combined, resulting in a blended pH of 8 to 8.3, filtered through five rapid gravity sand filters, then pumped through four horizontal pressure filters containing granular activated carbon, rechlorinated, and stored prior to distribution. During the summer months 27.3 x 10^3 m^3/d (6 mgd; 7.2 U.S. mgd) of water is treated; in the winter this is reduced to 13.6 x 10^3 m^3/d.

The Eden River is the only surface water treated by the East Surrey Water Company and treatment with activated carbon was considered necessary to avoid taste and odor complaints from customers accustomed to water supplied from deep borings in the chalk and Lower Greensand. Consequently, it was decided that the treatment works, commissioned in late 1970, should contain granular activated carbon filters.

The activated carbon horizontal pressure filters are 2.44 m (8 ft) in diameter by 9.14 m (30 ft) long and contain 0.91 m (3 ft) of media. Initially, the bed was 0.69 m (2 ft 3 in) of 0.3 to 0.85 mm (18/52 BS mesh) granular activated carbon on 0.23 m (9 in) of sand and was later changed to 0.84 m (2 ft 9 in) of carbon on 0.08 m (3 in) of sand. At present, the filters contain 0.76 m (2 ft 6 in) of 0.3 to 0.85 mm (18/52 BS mesh) carbon on 0.15 m (6 in) of 0.7 to 2.8 mm (6/22 BS mesh) carbon. The filters are cleaned once every 2 days by air scour followed by backwashing.

Under summer treatment conditions, the carbon filters are operated at a downflow velocity of 12.7 m/h (4.3 gal/min/ft^2: 5.2 U.S. gal/min/ft^2) and an empty bed contact time of 4.3 minutes. In the winter the treatment rate is halved and consequently the contact time is doubled.

To date, one coal-based and two different coconut-based activated carbons have been used; the approximate bed life for taste and odor control was 2 years for the coconut-based carbons and somewhat less for the coal-based carbon. The granular activated carbon ceased to remove organics (monitored as permanganate value) after only a few days of operation. Every spring, exhausted activated carbon from two of the four adsorbers is replenished with virgin and/or regenerated activated carbon. During the last cycle of operation (2 years of treating water, mechanical handling and carbon transfer, carbon regeneration) it was estimated that 40 to 50 percent of the carbon was lost.

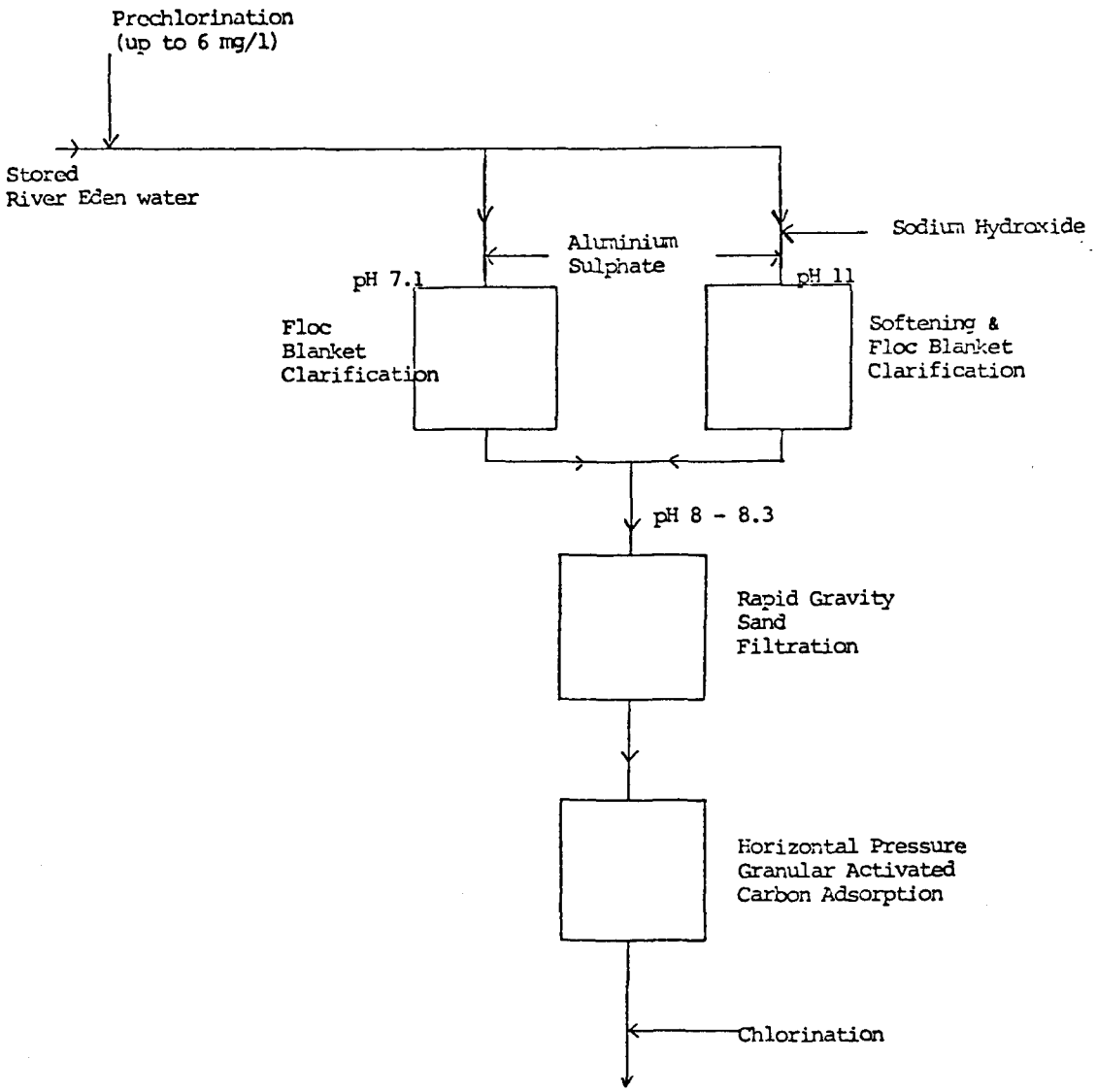

Figure 1. Schematic Diagram of the Bough Beech Treatment Works

Church Wilne (Severn Trent Water Authority)

The Derwent River, a tributary of the Trent River, at Church Wilne contains the industrial and municipal effluents from the city of Derby. At a flow rate of 22.7 x $10^3 m^3/d$ (5 mgd; 6 U.S. mgd), stored Derwent River water is treated by prechlorination (to maintain a residual of 0.05 to 0.1 g/m^3 through the carbon filters), coagulation with chlorinated copperas, floc blanket clarification, rapid gravity filtration, granular activated carbon adsorption, and disinfection with chlorine dioxide (Figure 2). This works has the only on-site regeneration furnace, at a potable water treatment plant, in the United Kingdom. Details of the design and operation of the granular activated carbon adsorbers and the regeneration furnace are described elsewhere (1, 2). The granular activated carbon filters are used for controlling unpleasant taste and odor that results from industrial and municipal effluent contamination of the source water. Prior to the commissioning, in 1975, of the granular activated carbon filters, up to 40 g/m^3 of powdered activated carbon were needed for effective taste and odor control. Granular activated carbon was selected as the most suitable method of using activated carbon after pilot trials had shown that if powdered carbon was used, continuous dosing would be necessary. A minimum of 20 g/m^3 powdered carbon would be required and, under the most severe conditions, doses of 90 g/m^3 were not adequate. Trials also showed that oxidation using chlorine dioxide or ozone was ineffective for taste and odor control and, in fact, the use of potassium permanganate increased the problem.

The coal based granular activated carbon is contained in twelve 4.11 m (13 ft 6 in) diameter by 3.75 m (12 ft 3 in) high vertical pressure filters operating in parallel. Initially, the carbon bed depth was 1.53 m (5 ft); at a later stage this was increased to 2.28 m (7 ft 6 in), but due to backwashing problems (carbon loss at 50 percent bed expansion) this had to be reduced to the present bed depth of 2 m (6 ft 6 in). The carbon adsorbers are operated at 6 m/h (2 $gal/min/ft^2$; 2.4 U.S. $gal/min/ft^2$) down-flow velocity and have an empty bed contact time of 20 minutes. The beds are backwashed daily, with water only, to alleviate compaction of the bed.

The approximate bed life for controlling the "chemical" taste and odor is 6 months. One adsorber is taken off line at a time and the carbon transported as a slurry to the multi-hearth furnace for regeneration. Regeneration of activated carbon takes 1 week per adsorber, resulting in a 4 to 5 percent loss of carbon, and achieves a 95 to 98 percent recovery of activity.

FOXCOTE (ANGLIAN WATER AUTHORITY)

This 9.1 x $10^3 m^3/d$ (2 mgd; 2.4 U.S. mgd) treatment works can receive water from three separate sources: a gravel pit;

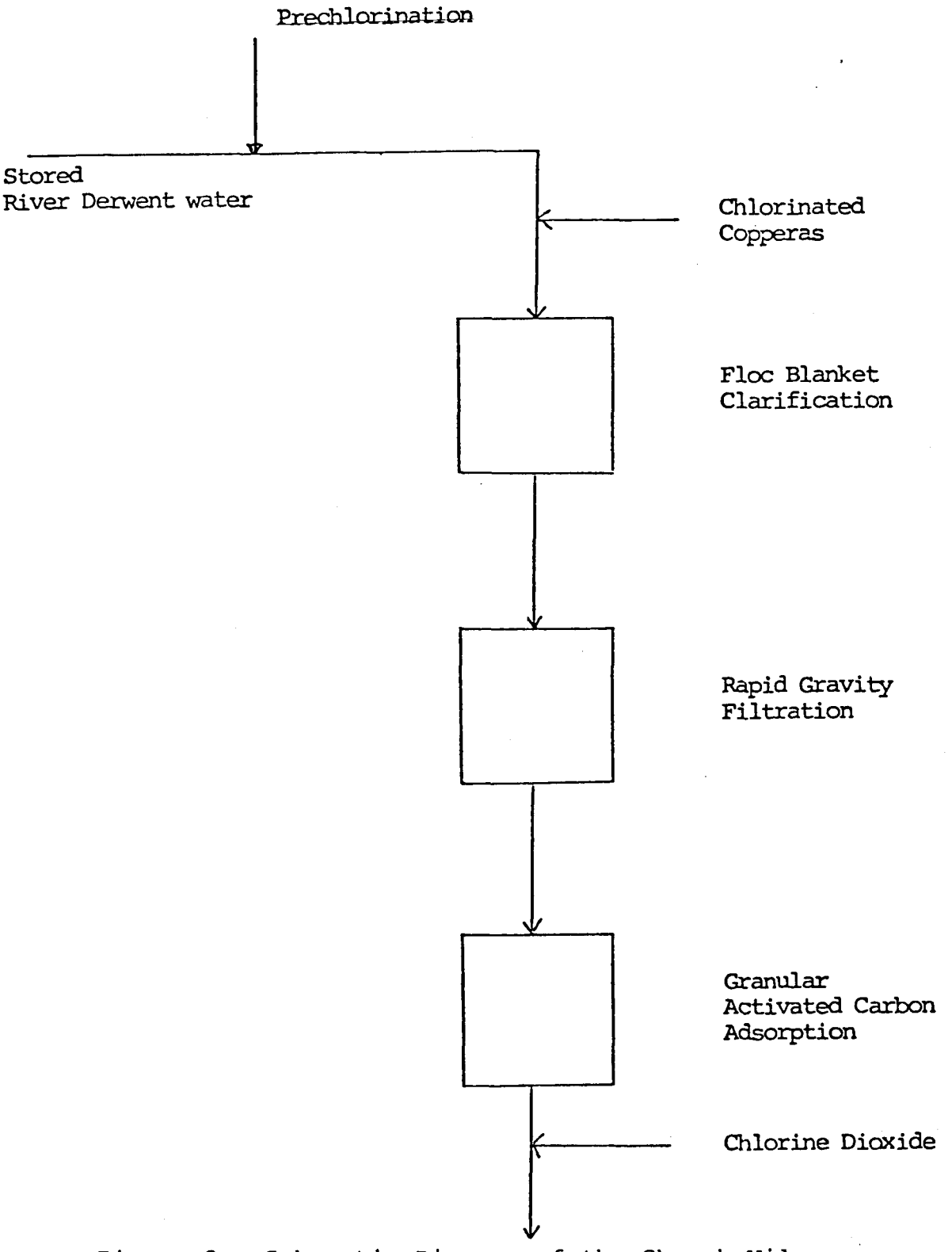

Figure 2. Schematic Diagram of the Church Wilne Treatment Works

direct abstraction from the Great Ouse River; or from a 614 x $10^3 m^3$ reservoir. Treatment is breakpoint chlorination (to maintain 0.6 to 0.7 g/m^3 free chlorine onto the carbon filters); coagulation with ferric or aluminum sulphate; floc blanket clarification; rapid gravity sand filtration; adsorption with granular activated carbon; rechlorination; and ammoniation (Figure 3).

Prior to the installation of the granular activated carbon adsorbers, consumer complaints were received about an unpleasant earthy/musty taste in the water. Ozonation, permanganate dosing, lime softening, and chlorination (both free and chloramine residual) all failed to control the taste problem. The use of chlorine dioxide, though successful, was rejected on the grounds of cost. Powdered activated carbon was found to be effective, but at the doses required, up to 40 g/m^3, filtration difficulties were encountered. Thus, after pilot trials in 1957 and 1958, granular activated carbon filters were installed and operational in 1960.

The 17.3 x 10^3kg (17 tons; 19 U.S. tons) of coconut-based granular activated carbon is contained in eight 2.44 m (8 ft) high, 2.44 m diameter, vertical rubber-lined steel pressure vessels. The activated carbon beds, initially 0.91 m (3 ft) deep but now 1 m (3 ft 3 in), are supported on floors of porous stainless steel tiles. Water flows downwards through the bed at a rate of 10 m/h (3.5 gal/min/ft^2; 4.1 U.S. gal/min/ft^2) giving an empty bed contact time of 6 minutes.

The carbon beds are backwashed twice per week; there is an initial high rate water wash (31 m/h; 11 gal/min/ft^2; 13 U.S. gal/min/ft^2) for 1.5 minutes, followed by 0.5 minutes for settling, and finally a 20 minute water wash at 15 m/h. Design and operation details of this system have been described elsewhere (3).

The useful bed life of the granular activated carbon for taste control is 4 years, after which time the carbon is returned to the supplier for regeneration. Approximately 25 percent of the carbon is lost during the 4 years of operation, its transfer from the filters to the furnace, and subsequent regeneration.

Although the carbon effectively controlled taste in the drinking water for periods of up to 4 years, its capacity for organics removal (measured as TOC and COD) was much more limited (Figures 4 and 5). In an earlier paper about this plant (3), it was reported that the effluent from the granular activated carbon adsorbers had a substantially higher plate count (3 days at 22°C) than the influent to the adsorbers. This observation has been confirmed by more recent findings (Table 1).

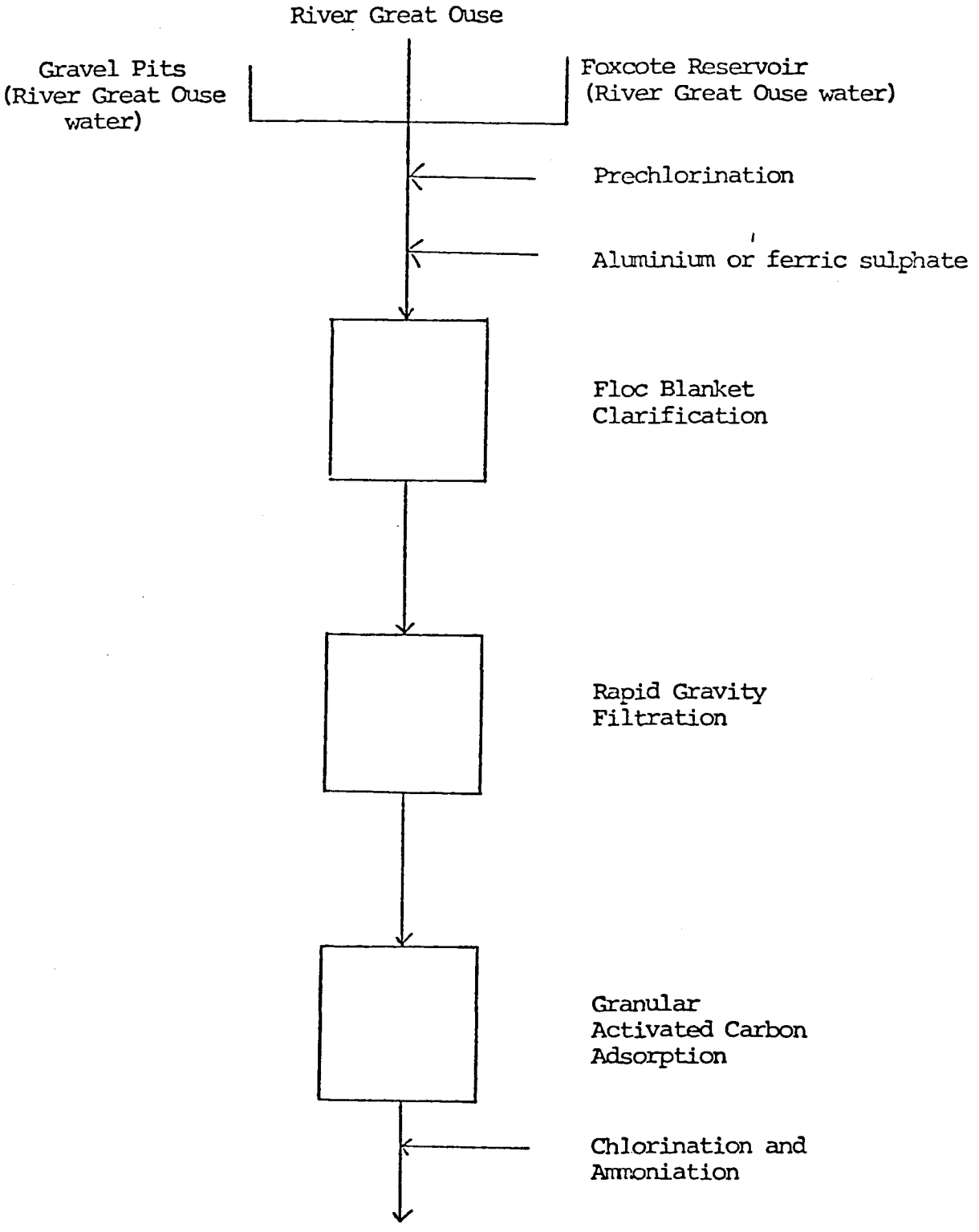

Figure 3. Schematic Diagram of the Foxcote Treatment Works

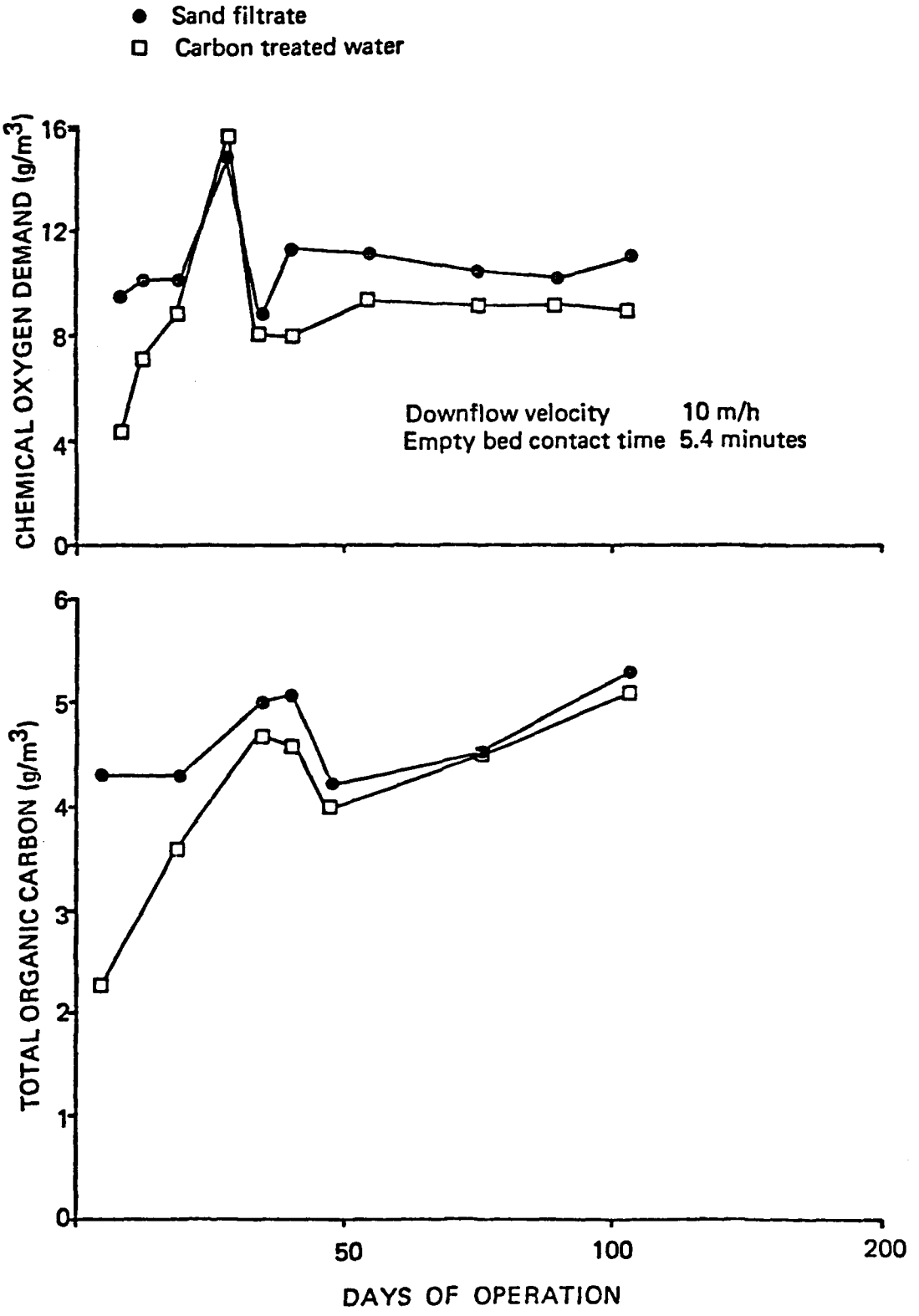

Figure 4. Organics Removal on Foxcote No. 6 Filter
29 November 1972 to 12 March 1973

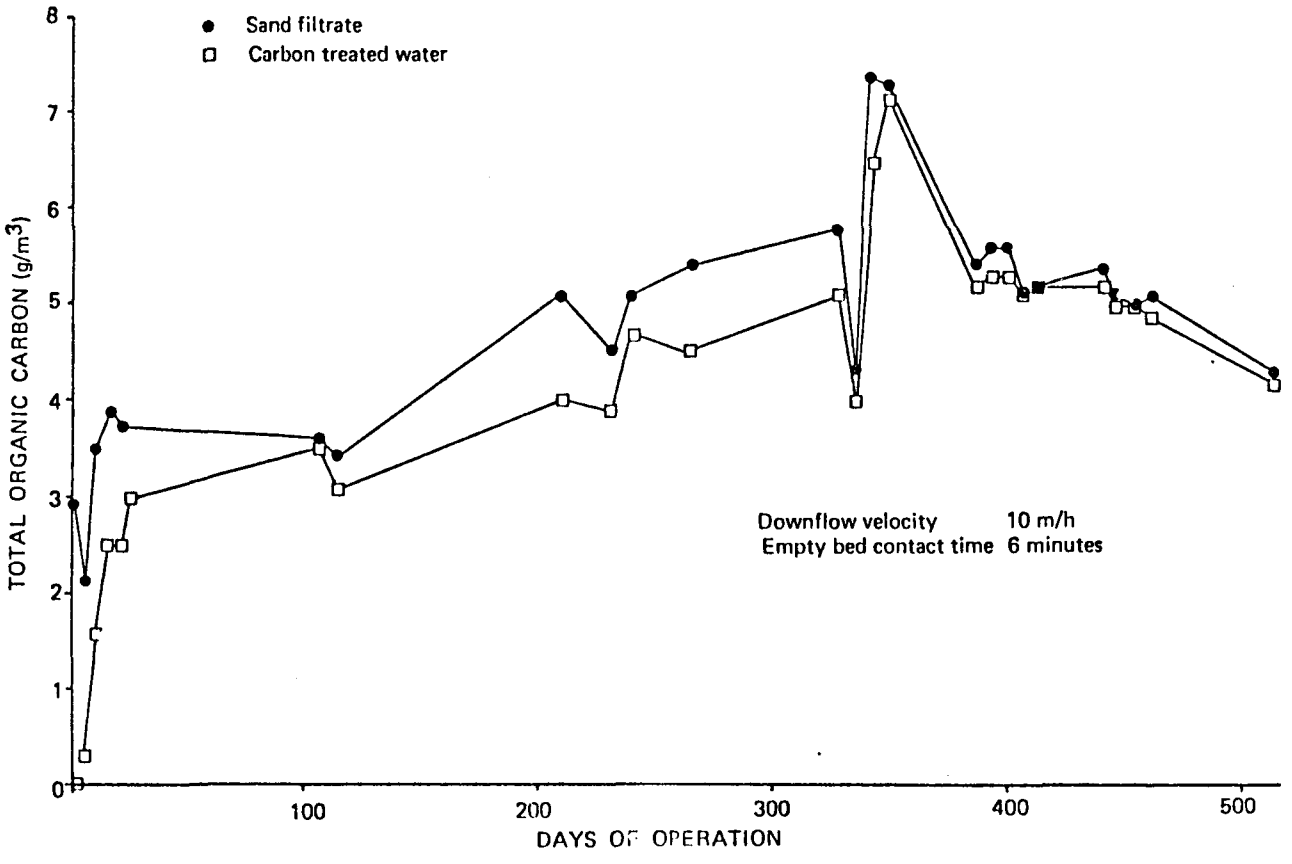

Figure 5. Organics Removal on Foxcote No. 7 Filter
21 October 1975 - 23 March 1977

Table 1. 3 Day 20°C Plate Count

	No of samples	Colony count/ml	Percent sample
Sand filtrate	53	0-10	98.1
		11-100	1.9
Carbon filtrate	83	0-10	60.2
		11-100	34.9
		100+	4.8
Final water	231	0-10	74.9
		11-100	24.7

LLANDEILO-GRABAN (WELSH WATER AUTHORITY)

Water from Llan Bwch-Llyn, at a rate of 1.1 - 2.3 x $10^3 m^3/d$ (0.25 to 0.5 mgd; 0.3 to 0.6 U.S. mgd), is treated by direct injection of aluminum sulphate and filtration through five 2.44m (8 ft) diameter pressure filters.

A heavy bloom of blue-green algae gave rise to taste and odor problems during 1978. As an emergency measure, at the end of September 1978, the 0.3 m (1 ft) of anthracite was replaced with 0.3 m of granular activated carbon. Since that time, no taste and odor problems have been reported.

RESEARCH

The increasing need to use polluted surface waters to satisfy the demand for potable water has led to increasing concern about the presence of organic compounds in water supplies. These compounds may constitute a health hazard or be esthetically undesirable. Research work is being carried out by the Water Research Center and a number of water suppliers on the use of granular activated carbon for removal of trace organics in potable water production.

In a program carried out by the Water Research Center, jointly financed by the Severn Trent Water Authority and the Directorate General Water Engineering of the Department of the

Environment, pilot studies were undertaken to investigate the treatability of the industrially polluted River Trent to a potable standard (5). Part of this program was to investigate the efficiency of granular activated carbon to remove organics from water. Results showed that activated carbon, even with an empty bed contact time of up to 78 minutes, could not reduce the total organic content to non-detectable levels. As an extension of the River Trent studies, pilot plant trials are being undertaken on River Thames water that has been pretreated (coagulation, floc blanket clarification, rapid gravity filtration) before being spiked with selected organic compounds. The spiked compounds have been chosen to represent a wide range of molecular weights and chemical types. The studies are to determine the efficiency of commercially available adsorbents as well as the effect of bed design and plant operation on the removal of these compounds.

Preliminary work has concentrated on the removal of six chlorinated compounds; chloroform, bromodichloromethane, α and γ isomers of hexachlorocyclohexane ($\alpha$and γ HCH also known as α and γ benzene hexachloride), dieldrin, and 1,2-dichlorobenzene. Initially, these were dosed into treated River Thames water via a methanol stock solution (6). The use of methanol was necessary to assist in getting the chlorinated organics into solution in the aqueous phase. It was desirable to keep the methanol concentration in the spiked water as low as possible in order to minimize the associated biological activity. In later work (7) it was possible to eliminate the use of methanol by dissolving the solid organics (αHCH, γ HCH and dieldrin) into the liquids (chloroform, bromodichloromethane and 1,2-dichlorobenzene) and adding these at the required flow rate (approximately 0.3 ml/h) using a syringe pump into 1 m^3/h of treated River Thames water.

Results have shown that 1,2-dichlorobenzene was the most readily removed of the six compounds; in general, pesticides are more readily adsorbed than haloforms and bromodichloromethane is better removed than chloroform. There was also a tendency for the carbons that were best for haloform removal to be worst for pesticides, and for the worst for haloforms to be the best for pesticides removal (Figures 6 and 7). Over the range investigated (2, 5 and 10 m/h), downflow velocity did not appear to influence the performance of granular activated carbon filters. Similarly, increasing bed diameter from 0.15 to 0.3 m (0.5 to 1 ft), while maintaining the same downflow velocity and contact time, did not influence performance.

THE FUTURE

It is unlikely that the use of granular activated carbon for potable water treatment in the United Kingdom will greatly increase unless legislation makes this necessary or there is organic contamination of source waters where no alternative source is available.

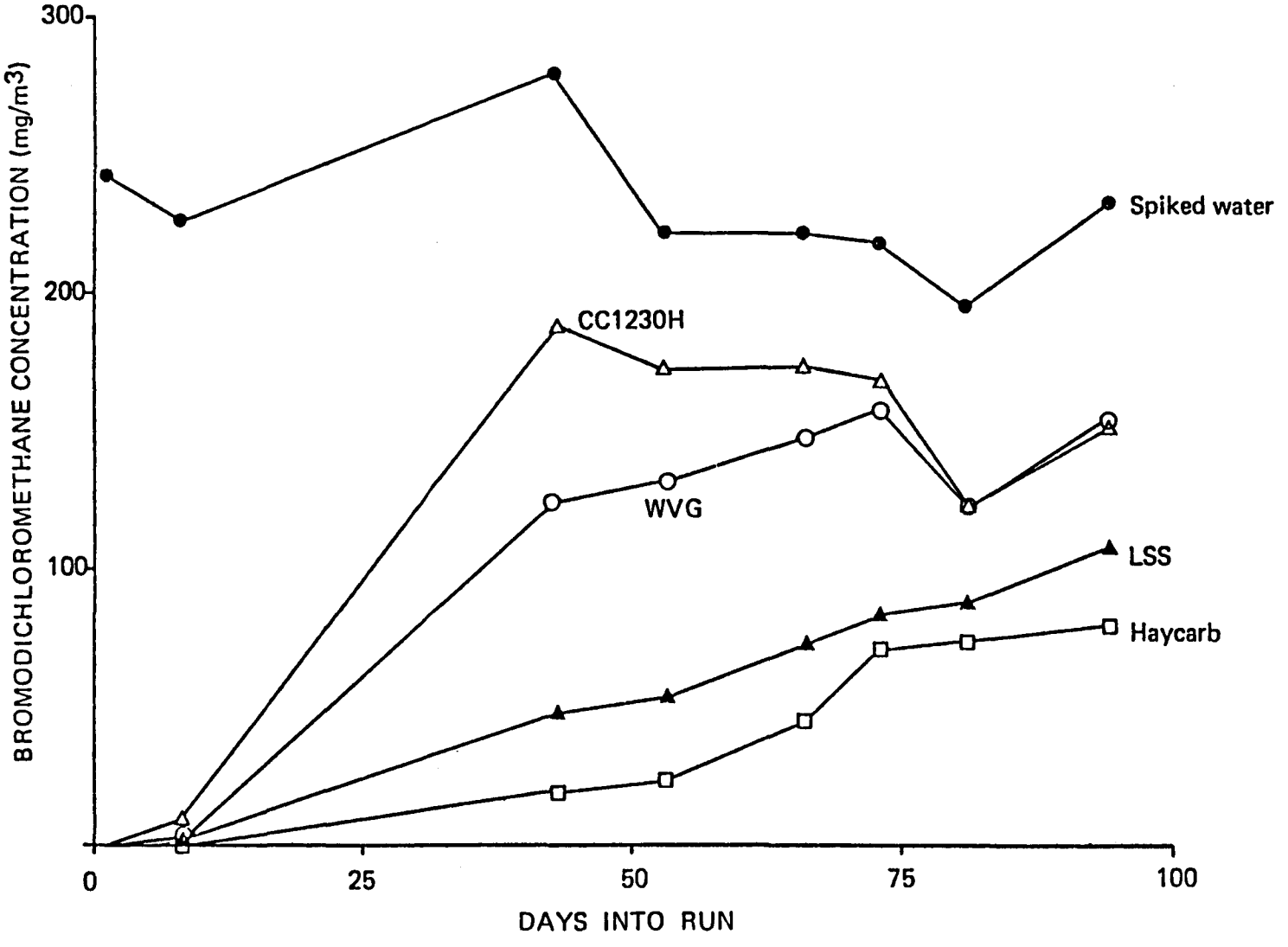

Figure 6. Comparison of Granular Activated Carbons for Bromodichloromethane Removal

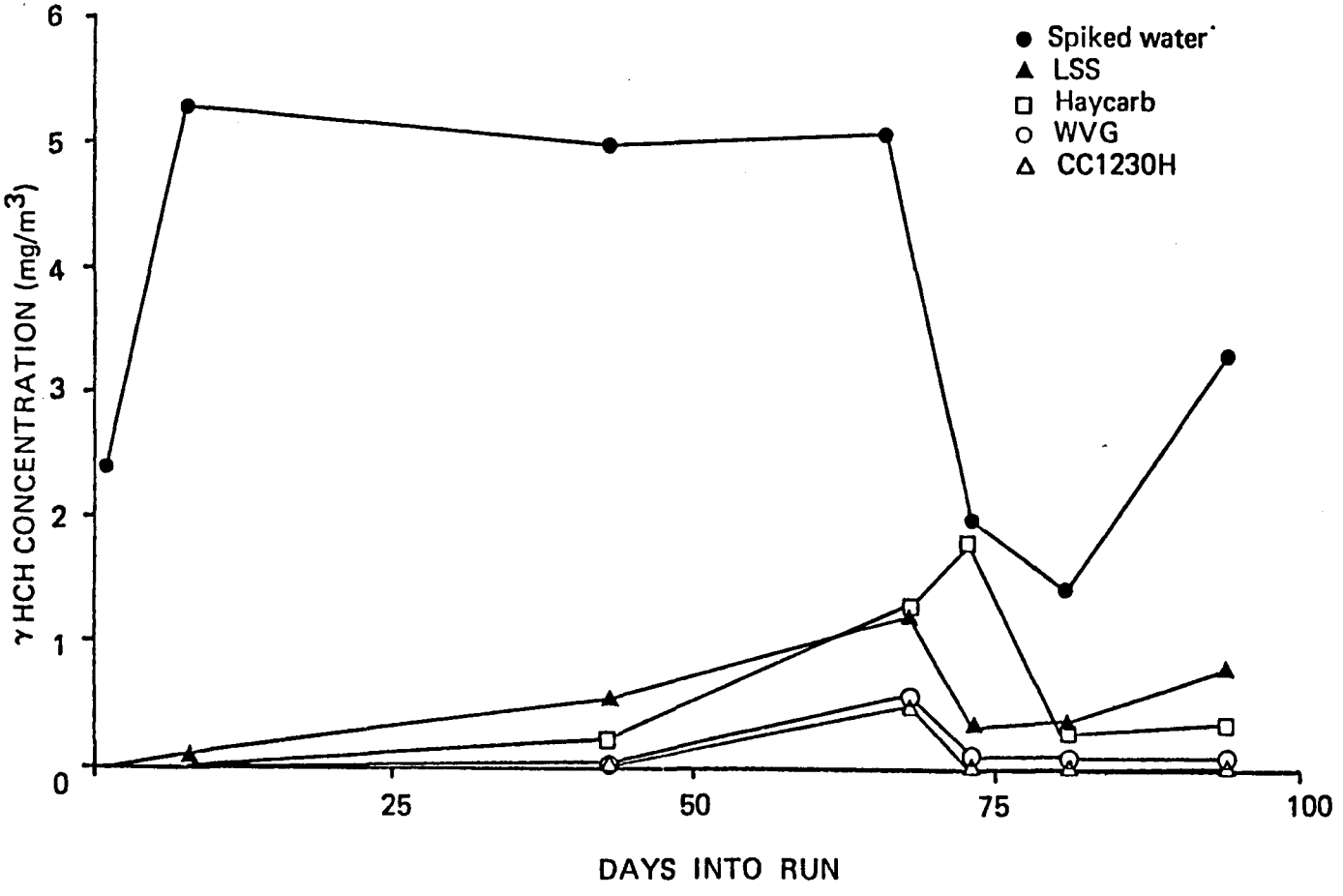

Figure 7. Comparison of Granular Activated Carbons for Hexachlorocyclohexane (HCH) Removal

The Water Research Center is embarking on a study to assess the implications on the United Kingdom water industry if legislation, such as that proposed by the United States Environmental Protection Agency (8), is brought into force.

Research work is continuing within the water supply industry and by the Water Research Center where comparisons of a wider range of adsorbents will be made. The removal of other groups of compounds such as aliphatic, aromatic and polyaromatic hydrocarbons, phenols, and chlorinated phenols will be studied.

ACKNOWLEDGEMENTS

The authors wish to thank the Director for permission to publish this paper. They would also like to thank all those members of staff from the Anglian, Severn Trent, and Welsh Water Authorities, the East Surrey Water Company, and the Water Research Center who helped in collecting the information reported.

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DESIGN CRITERIA AND PROCESS SCHEMES FOR GAC FILTERS - GERMAN EXPERIENCES

Prof. Dr. Heinrich Sontheimer

Since 1975, when a special conference was held in Karlsruhe, Germany,* on practical experiences with the use of activated carbon in drinking water treatment in Germany, research has continued at an accelerated pace. The German Ministry of Research and Development has subsidized investigations on the optimization of carbon use and regeneration, on biological treatment in activated carbon filters, and on macroreticular resins for humic acid removal, to name just a few recent projects. Many of these studies were conducted on-site at water treatment plants focusing on the practical aspects of activated carbon use. More specialized studies on process design parameters for sorption processes sponsored by the Deutsche Forschungsgemeinschaft, were undertaken at the University of Karlsruhe.

To provide a better understanding of the problems connected with activated carbon treatment in Germany, this paper describes its historical development and the resulting design criteria and process schemes for GAC filters. Defining the purpose and aim of the carbon treatment in itself poses a problem. It is said that different waters need different types of treatment, and this means different control methods and design criteria for GAC as well. In addition, many open-ended questions on activated carbon treatment still await further research.

GAC TREATMENT IN GERMANY

In surveying the development of the use of activated carbon in Germany, it must first be noted that powdered carbon is used infrequently. Many waterworks store this type of carbon for use in the event of environmental accidents, but fortunately such accidents are rare. By contrast, granular activated carbon filters have been used in water treatment for the past 50 years.

Table 1 shows the development of the use of activated carbon filters in Germany. Carbon filters have been used for dechlorination since 1930, especially where high chlorine dosages are

*The proceedings of this conference were published by the Engler-Bunte Institute, available in English as EPA-600/9-76-030 (Dec. 1976).

are needed for ammonia removal and where carbon treatment is required before infiltration into the ground. In Germany, taste and odor problems are largely associated with the use of Rhine River water. The most extensive studies on the removal of taste and odor with activated carbon filters were made in 1955, in Dusseldorf. One of the reasons for this study was that the waterworks was reluctant to install an additional pumping station that would have been needed in order to use powdered carbon. When it was later discovered that with ozone pretreatment, less carbon was needed for taste and odor removal, the additional pumping station was still needed, but this application was felt to be more efficient.

TABLE 1

Development of the Use of
Activated Carbon Filters in Germany

APPLICATION	DATE
Dechlorination	1930
Taste and Odor Removal	1955
Organics removal	1970
Biological activated carbon	1976

The grades of carbon used for taste and odor removal had to have good phenol values, but required no high activity for other substances. Therefore, the carbons had only small pores and a small surface area. When in 1970 the removal of organics became increasingly important, new types of carbon with a higher activity and surface area had be to used. For these more expensive carbons, regeneration was an economic necessity. Since on-site regeneration, if done properly, is cheaper in most instances than off-site regeneration at the carbon-producing company, the first carbon regeneration installations at the waterworks were constructed and are now in operation.

The use of a higher quality carbon led to observations on biological activity in carbon filters, especially at the waterworks on the Rhine River where preozonation is used. From these findings, data were obtained in 1976 on the practical use of this process, which combines the economy of biological oxidation with the safe operation of granular activated carbon treatment.

DESIGN CRITERIA FOR GAC FILTERS

Table 2 describes the design criteria of dechlorination, taste and odor removal, organics removal, and biological activated carbon. The development of these treatment processes reduced high filtration velocities to fairly low velocities and, at the same time, increased the height of the filter beds. Thus the empty bed retention times increased considerably, as did the investment costs for activated carbon filters. Concurrently, on-site regeneration provided a better margin of safety for the removal of organics and also reduced operating costs, as did biological activity in the filters.

TABLE 2

Design Criteria for GAC Filters in Germany

	Filtration velocity m / h	Bed height m	Empty bed retention time min.	Throughput ratio before regeneration m^3/m^3
Dechlorination	25 – 35	2	2 – 4	> 1000 000
Taste and odor removal	20 – 30	2 – 3	6 – 10	~ 100 000
Organics removal	10 – 15	2 – 3	8 – 15	~ 25 000
Biol. activated carbon	8 – 12	2 – 4	15 – 25	~ 100 000

Today, biological oxidation is critical to the economical operation of the carbon filters. Table 3 describes the median reduction of removal efficiency in carbon filters, using data from the Mülheim treatment plant for filters 2.5m in height and

10m/hr in filtration velocity, having a 15-min empty bed retention time. The decline in DOC removal with time, resulting from the reduction in biological oxidation and from increased loading onto the carbon of nonbiodegradable organics, indicates that the oxidation process used here was not sufficiently effective to convert more substances into biodegradable matter. However, the median data shown in the tables are still fairly good.

TABLE 3

Reduction of Removal Efficiency
in Carbon Filters (RWW Dohne)

Throughput m^3/m^3 GAC	DOC-Removal g DOC/m^3d	Biological DOC-Oxidation g DOC/m^3 d	Biologically Oxidized %	Loading of Carbon as DOC g/kg
0—18000	135	101	71	39
18000—39000	77	64	80	58
39000—59000	26	22	82	61
0—59000	78	61	78	61

PROCESS SCHEMES FOR GAC FILTERS

The data on the Mülheim treatment plant emphasize the importance of using the correct means of oxidation and the optimum process scheme. The most important types of treatment processes are shown in Figure 1. The optimum process for treating river water usually includes two-stage ozonation. The first dose is applied before flocculation. After sedimentation and before filtration, a second dose is applied. This type of treatment enhances efficient flocculation, and if the correct dosage is used, the conversion of nonbiodegradable into biodegradable substances is also aided. In this scheme, carbon filters are used for the adsorption of hazardous substances and provide a site for biological oxidation of organics.

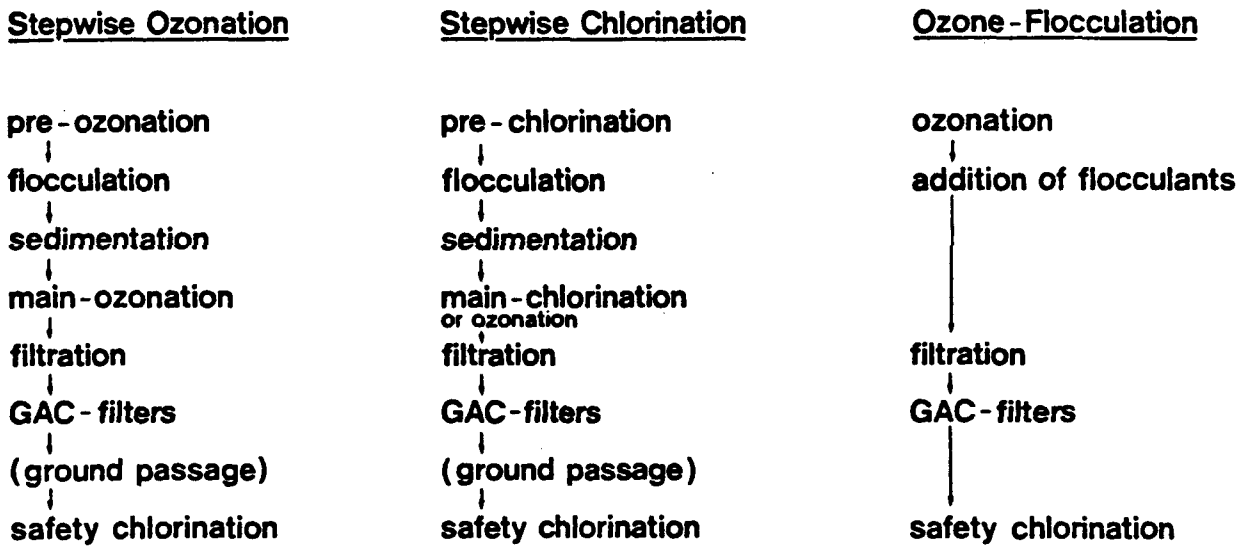

Figure 1. Oxidation and GAC Filters Process Schemes

This combined treatment scheme extends the operating time period between GAC regenerations by three to ten times. If suspended or colloidal substances are present in low concentrations, flocculation or sedimentation are not needed, and ozone-induced flocculation in the filters is all that is necessary. These modifications do not, however, negate the general process principles. These remain in effect even if chlorine is applied in small dosages instead of ozone.

Thus sufficient experience has been obtained for this combined biological adsorptive treatment and also enough design criteria to decide on the empty bed retention time and the type of pretreatment for each type of water. How to operate a pilot plant to gather more data on the special design of treatment facilities for a particular type of water also is known. However, it is often difficult to choose among the many available alternatives for control of activated carbon filters. Figure 2 lists a number of the possible control methods for activated carbon filters that are currently in use.

1) **Carbon loading on the top and the bottom layer of the filter**

a) **DMF-extract**
b) **Dioxane-extract**
c) **Loading with organic chlorine**
d) **Loading with nonpolar chlorine**
e) **Loading with specific compounds**

2) **O_2 consumption for biodegradation**
Measurement with two or more filter velocities

3) **Breakthrough behaviour:**

a) **For sum-and group parameters of organic substances:**
e.g. DOC, UV, DOCl, DOCIN
Taste and Odor, Aromatic Amines etc.

b) **For defined substances:**
e.g. $CHCl_3$, C_2HCl_3, Chlorobenzenes etc.

Figure 2. Possibilities for Activated Carbon Filter Control

METHODS OF CONTROLLING ACTIVATED CARBON FILTERS

Control of the filter efficiency and the carbon activity is achieved by three processes. The first process was developed to measure the different carbon loadings, either by extraction using dimethylformamide to obtain all the organics, or by using dioxane or similar solvents to measure nonpolar organics. When extraction is employed, it is important to look for group parameters such as nonpolar organic chlorine compounds, or for specific substances like chlorobenzenes that are especially significant for monitoring the carbon filter efficiency for Rhine River water.

Besides extraction, group parameters such as organic chlorine can be measured through direct pyrolysis of the carbon, saving time and permitting easier control. However, these methods have the disadvantage that loading in itself does not provide specific data on the breakthrough behavior of a filter. This is true to some extent for the measurement of oxygen consumption. The data in Figure 3 show that oxygen consumption declines with time. Additional information is needed on the filter breakthrough behavior and on the significance of these measurements.

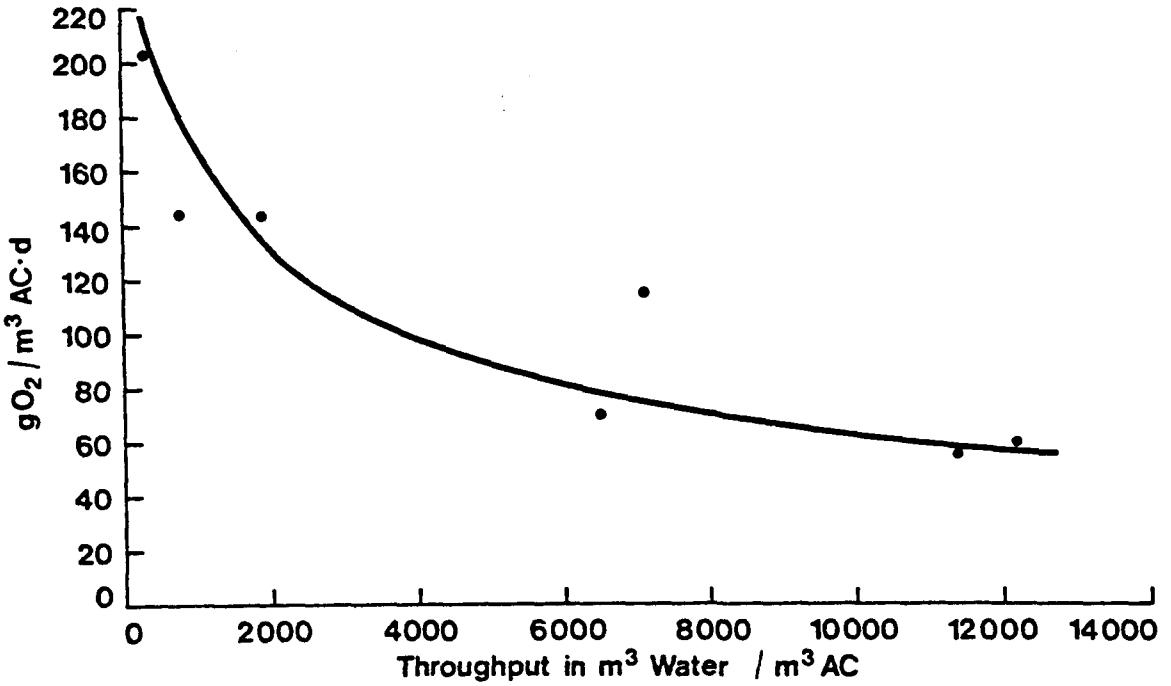

Figure 3. Oxygen Consumption in an Activated Carbon Filter as a Function of Water Throughput (Düsseldorf)

The problems related to breakthrough measurements are well illustrated by measurements for four different parameters on two large filters in the Düsseldorf waterworks. At Düsseldorf, two different types of carbon have been used along with the same pretreatment. The breakthrough behavior for the different water quality parameters is shown in Figure 4. The dimensionless concentrations (c/c_0) are given as a function of the throughput ratio in volume per volume for the last half of the operational period and for one of the two filters. A UV reduction of 50 percent was achieved for this filter after a throughput of 8000 m^3 of water per m^3 of activated carbon in the filter. Although the DOC reduction is not as good, the two curves run parallel and therefore the UV measurements can be used for information on the DOC values. The data show that the DOCl reduction lies in between the values for DOC and for UV removal. The problem requires further study. More data are needed for organic sulfur, organic acids, and other group parameters like the corrosion inhibition factor, which may become more significant in the future.

CHOOSING THE CORRECT CONTROL PARAMETER AND TYPE OF CARBON

However, the more parameters and criteria are measured, the more difficulties will be encountered in choosing the correct parameter for optimum control. For example, in Figure 4 the breakthrough behavior of chloroform shows that higher concentrations are found in the effluent than in the influent to the filter. On the other hand, a very good filter efficiency was achieved for all the other volatile nonpolar organic chlorine compounds, tri- and tetrachloroethylene being the most important. Although the influent concentrations of all substances were very low in this test, which was performed at a high water flow in the river, the difference in the behavior of the organic chlorocompounds remains very high. Thus the question as to which of the two parameters should be used here to control the filter efficiency is unresolved.

The same difficulty arises when two different carbons are compared. One possibilty would be to examine the breakthrough behavior for the UV-absorbing organics, an example of which is shown in Figure 5. Filter 8 has a lower efficiency at first, than the other carbon in filter 4. This remains true for UV-absorbing organics, but for organic chlorine compounds there is little difference, although filter 8 tends to be more efficient. Isotherm data can provide simlar results, but the test method used in Figure 5 is preferred for assessing activated carbon quality.

Figure 6 shows the isotherms measured by using the same water that was to be treated with the activated carbon filters. The isotherms indicate that the activated carbon in filter 4 has a somewhat higher capacity than that in filter 8 with respect to overall organic substances in water (OSW), as measured here by UV absorbance. Moreover the same effect occurs for a substance like p-nitrophenol (PNP), and similar effects can be expected for substances such as trichloroethylene. Nevertheless, the differences remain quite minimal in this test, the results of which correlate quite well with the breakthrough behavior in the full scale filter plant.

However, the close comparison between the equilibrium test and the large filter breakthrough behavior does not really indicate which parameter should be used for control and which method might be preferable. For this information the many different possibilities for controlling activated carbon filters have to be reexamined (Figure 2).

In Germany the breakthrough behavior for a certain organic pollutant will seldom supply sufficient information to control activated carbon filter efficiency. Only for some groundwaters with tri- and tetrachloroethylene, can this type of control be used advantageously.

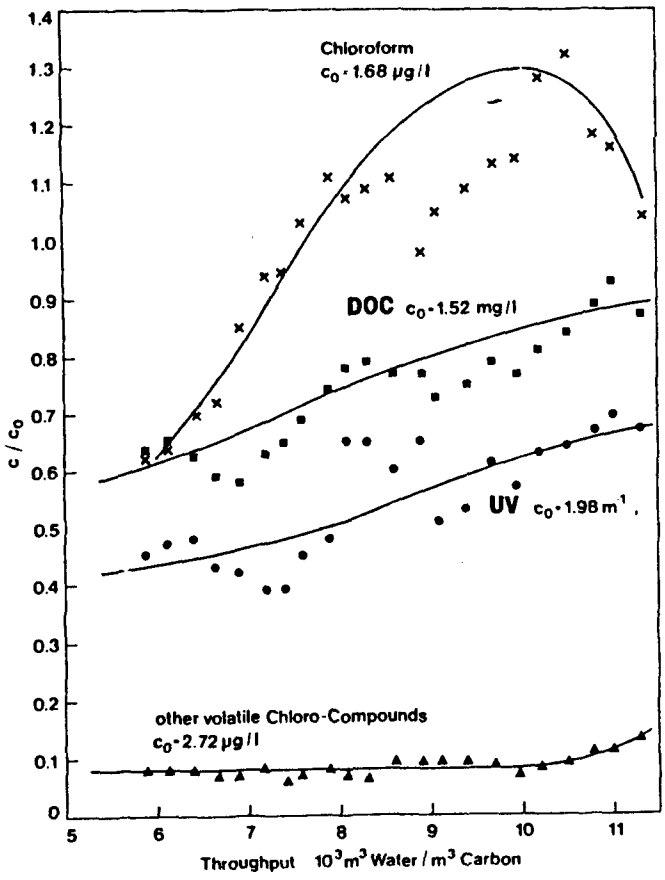

Figure 4. Breakthrough Curves for Four Parameters

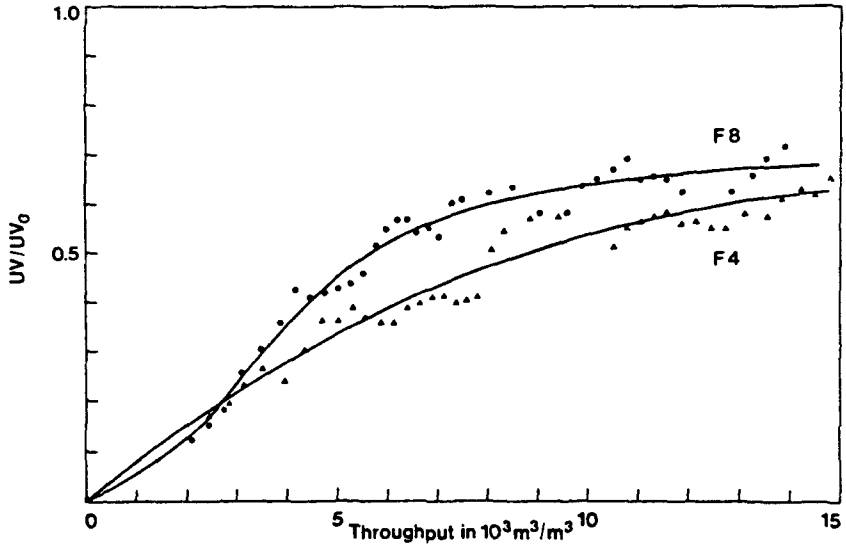

Figure 5. Breakthrough Behavior of UV-Absorbing Substances for Filters with Different Carbon Grades

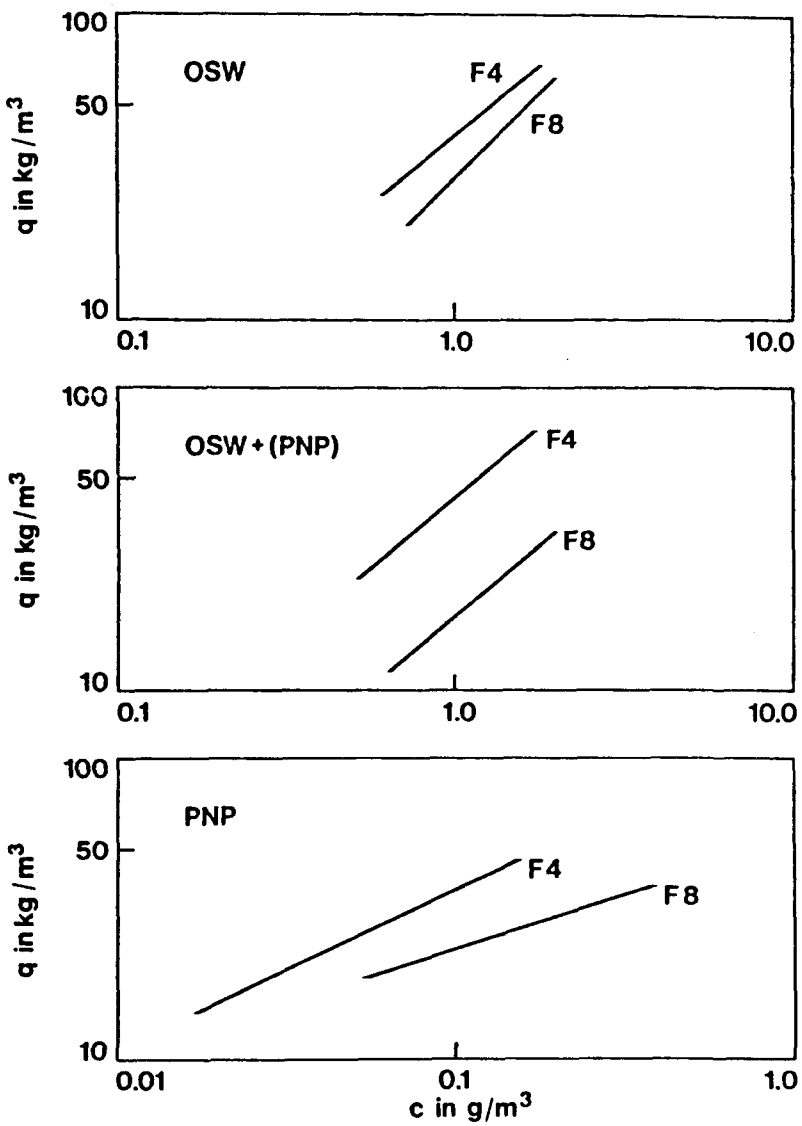

Figure 6. Comparison of Equilibrium Data for Two Different Activated Carbons

When surface water is being treated, especially the water from the heavily polluted Rhine River, it is usually not known in advance which type of chemical pollutant will be most serious at any given time. This determination can be attempted by special analytical methods, but these methods usually require so much time that the particular type of pollution may have changed in the meantime. Thus it is generally not practical to use the breakthrough behavior of specific organics as a means of control.

In practice, the waterworks has to be certain at all times that the carbon filter has enough capacity for sudden high concentrations of unknown pollutants. This can be accomplished either by studying the carbon loading at different filter heights or by observing the overall removal efficiency for organics. UV absorbance measurements are taken for the latter purpose since these can be obtained easily and correspond to DOC measurements.

When UV absorbance measurements indicate the need for parallel tests, results very similar to those from carbon loadings can be obtained by controlling the oxygen consumption of biological regeneration of the carbon in the filter. If parallel tests are made for some time, and for different process conditions, comparing the proposed simple testing methods (e.g., UV absorbance) with more sophisticated analytical measurements will provide enough information to decide when regeneration should be done.

In Düsseldorf, for example, it is known from practical experience that taste and odor problems will occur in the farthest parts of the distribution system if a 50 percent reduction in UV absorbance is not achieved. Since chromatographic enrichment of chloroform is going on at the same time, some other organic substances responsible for the renewed formation of taste and odor may also be breaking through.

Thus, many problems in the use of carbon filters remain to be solved. Further research is needed, particularly on sorption analysis for water with unknown organics; on the prediction of breakthrough behavior in sorption filters; on the mechanism of biological treatment in carbon filters; on the combination of flocculation, filtration, and adsorption; and on control means for carbon filters. In the future, waterworks should be able to predict carbon filter performance by laboratory tests because this will be the only way to optimize the production and regeneration of carbon for this particular purpose. Better information will be needed on the mechanisms influencing the efficiency of biological treatment in carbon filters, and other combined treatment effects will have to be studied intensively.

SUMMARY AND RECOMMENDATIONS

The use of activated carbon filters for drinking water treatment will become increasingly widespread in the future. Carbon filters will be primarily a safety factor similar to safety chlorination. Most chemical pollutants that are hazardous to human health can be removed with a carbon filter if the right design is selected and the adsorption efficiency is control led. Only with this treatment will the problems, arising from unknown organics in river water and in many groundwaters as well, be resolved.

If, on the other hand, carbon filters are used chiefly for safety purposes, they can still be applied for the removal of other organics. This application will permit an easier control because the overall adsorption capacity can be monitored and thereby the safety factor will be maintained for unknown substances as well.

The use of activated carbon filters for safety purposes implies that the adsorptive quality be adapted to the change in the possible pollutants; for example, by using sorbent mixtures.

Some questions still remain regarding the application of activated carbon treatment to drinking water. Exchange of information on an international level can ensure progress toward safer, cleaner drinking water.

Q UNIDENTIFIED QUESTIONER: I wonder whether you could comment on the extent to which you get removal of heavy trace metals.

A PROF. DR. SONTHEIMER: I must say we are very happy in our country that we do not have problems with heavy metals. All along the Rhine there is a low heavy metal concentration, even lower than drinking water standards permit. Furthermore, we achieve good removal in treatment. Removal efficiency depends on the concentration of heavy metals, but generally lies in the range of 50 to 90 percent. The removal efficiency varies widely, but we are not concerned because the concentrations in the Rhine River are low. The concentrations in solution are especially low, so heavy metal pollution does not pose a real problem.

Q DR. ANDREW BENEDEK, McMaster University: Professor Sontheimer, I am interested in your data on oxygen uptake. As you know, oxygen is taken up by fresh activated carbon and you showed a decline. Is that over and beyond the chemical uptake, or do you feel that the chemical uptake is negligible in that particular case?

A PROF. DR. SONTHEIMER: We do not distinguish between the two: chemical and biological. We know that in the first 2 days chemical uptake is appreciable, but I can't see any reason why chemical uptake would continue for months and there are no data to support that hypothesis. Why should the activated carbon surface become available for chemical oxidation after the surface is loaded with adsorbed material?

Q DR. ANDREW BENEDEK: Have you attempted to find out what types of organics are being oxidized, particularly by measuring changes in ultraviolet spectra?

A PROF. DR. SONTHEIMER: Yes, I think it is the same in all countries. The bulk of the organic material consists of humic substances. And most of the organics oxidized are humics. We have data on metals, change of polarity, and change of the molecular weights of the humic materials during oxidation; those

data correlate exactly with the amount of oxidation and the effect of oxidation within the carbon. Hence, we are certain that the changes we measure are mostly governed by the oxidation of the organics. It's a very important problem, because on one hand we shouldn't have too high of an organic content, because then we need too much chlorine for disinfection purposes. It is my opinion that we should reduce the total organic carbon concentration to approximately 1 mg per liter or less before chlorination; less than 10 µg/l of THM's should then be produced by safety chlorination.

Q DR. COTRUVO, EPA: I would like to ask a practical question for the engineers and water plant operators. The necessity of reactivating carbon is an additional workload placed upon the plant operation. Undoubtedly, there would be some practical limits to reactivation. In your country, what do you feel would be a practical minimum time interval between reactivations for carbon?

A PROF. DR. SONTHEIMER: I would say it should be in the range of 3 months. If you are using the right combination of pretreatment in the right way, then you will be able in most cases to reprocess in 3 months. We are now happy about our situation in the Rhine river because it is no longer heavily polluted. We reactivate every 4 or 5 months, but I think we should be able to reduce that to 3 months.

Q PAUL ROBERTS, Stanford University: The U. S. EPA has proposed a carbon treatment standard that would entail 50 percent removal of total organic carbon and allow a maximum rise of 1/2 mg/l of Total Organic Carbon (TOC). Would it be possible to cite experience from Europe that would show conditions under which that standard could be satisfied, and if so, what would be the combination of empty bed contact times and reactivation frequencies that would permit that standard to be fulfilled.

A PROF. DR. SONTHEIMER: I shouldn't comment on EPA's recommended standards, but I must say I don't agree entirely. That's my personal opinion. However, I think the general idea behind it is excellent. A collective parameter must be chosen. There's no doubt TOC is very easy to measure and a parameter that might be considered. We use ultraviolet absorption, yet I couldn't say if UV is possible everywhere. We measure TOC as well, and usually find a relatively constant relation between UV and TOC, but we think it's more important to remove the most dangerous substances. I would never propose to use activated carbon after breakpoint chlorination because I think that it is a waste of money. Breakpoint chlorination can be applied, but after 2-3 or 6 weeks of operation, you achieve the same results without it. Omitting breakpoint chlorination results in lower chemical costs and gives you the same, or much better, water quality.

I must say I honor the general idea behind these regulations, but I do reserve comment because Germany is a country small enough not to need such regulations. I have a close working relationship with most of our waterworks people and we can discuss our problems in person. We can discuss the best way for each water utility to operate. I'm very satisfied with this relationship, because this gives us a possibility of finding economic solutions to achieve good drinking water quality. I also agree with Dr. Schalekamp's statement that we really should attain the same water quality from surface water supplies that we are accustomed to in the very best ground water. This is achievable and economically feasible. I am convinced that, in treating most surface water supplies to assure good finished water quality, we need activated carbon for most cases. But it is impossible for me to establish a general figure or set standards which must be met. I must say that I am not familiar with all the factors in the U.S.A., so I cannot comment on this. In Germany, we are glad that we do not need formal standards.

Q PROF. MICHAEL SEMMENS, University of Minnesota: I have two questions for Dr. Sontheimer or anyone else who would like to respond. The first is concerned with the ozonation process used as a pretreatment step before coagulation-flocculation. Could you give me some idea of the dosages of ozone that you use in that process?

A PROF. DR. SONTHEIMER: Yes, the ozone dose is in the range of 0.1 to 0.4 mg/l per liter; in other words, very low dosages, but nonetheless very beneficial. There is, normally, a very well-defined optimum in the range of 0.2 to 0.3 mg/l per liter.

Q PROF. SEMMENS: If you exceed that range, do you see a deterioration in the effectiveness of coagulation?

A PROF. DR. SONTHEIMER: No, you see it in the removal of organics. You must add some ozone to get better flocculation, but not too much or you will reduce its effectiveness.

Q PROF. SEMMENS: The second question relates to the coagulation process itself. Historically, coagulation and flocculation have been used to reduce the turbidity of the water prior to filtration. If your objective is to reduce the organic content of the water, do you still use turbidity removal as the control or means of determining the best coagulant dose? Or do you use organics removal?

A PROF. DR. SONTHEIMER: We use both. I think we have to use both. Turbidity removal is very important, especially for virus removal and for other reasons related to disinfection. So, we should really have low turbidity levels. I tell the German water supply specialists that they should achieve 0.1 turbidity units, but the other important objective is to remove the organics. This is one problem that remains. We save money and minimize sludge problems with activated carbon, but it also takes out organics that may be corrosion inhibitors. So I think a very important research project for the future will be to optimize flocculation, not only for turbidity removal, but also for organic removal. I think that optimized flocculation, in combination with some preoxidation has a real future.

Q BRIAN TOMLINSON, Fluor Northwest, Fairbanks, Alaska: We have problems in the north where as much as 6 to 8 feet of ice accumulates on our lakes. There is no dissolved oxygen in the water. You indicated 78 percent average reduction of organics by aerobic biological oxidation. What has been your experience on anaerobiosis and how do you treat it, by pretreatment or scavenger chemical or something like that?

A PROF. DR. SONTHEIMER: Biological treatment has been widely used for hundreds of years in Germany and in most European countries. We do not have any German waterworks for surface water that do not use biological treatment. The effect of ground filtration is achieved quite easily. The filters contain activated carbon and, if properly designed, are very similar. We use activated carbon instead of sand filters or ground infiltration. It's only a matter of money and space that determines the practicality of using activated carbon. It's not a general proposal, you can obtain the same data by ground filtration, so we don't make an issue of these things. But I think biological treatment is so inexpensive and so easy to use in combination with the right pretreatment, that I recommend it.

Q MR. TOMLINSON: Maybe I misunderstand your presentation. Are you performing biological treatment within the activated carbon column?

A PROF. DR. SONTHEIMER: Yes sir.

Q MR. TOMLINSON: And it's strictly aerobic?

A PROF. DR. SONTHEIMER: It is strictly aerobic. We are very sure about this. We must have greater than 5 mg/l of oxygen outside the carbon. The oxidation kinetics and the diffusion coefficient shows that the oxygen concentration inside the carbon is higher than zero.

Q MR. TOMLINSON: Therefore, you have had no experience with anaerobic biological reduction of organics?

A PROF. DR. SONTHEIMER: Yes we have, with nitrates and so on, but it wasn't a special study. I should say we have received unexpected experience.

Q GERALD SPEITEL, University of North Carolina: I wanted to follow up on the question about pretreatment organics removal. What kind of experiences do you have in terms of percentage removal of TOC?

A PROF. DR. SONTHEIMER: The removal of TOC in pretreatment is 35 to 40 percent. Although not very high, it is still significant.

Q MR. SPEITEL: Do you feel that coagulants or pH ranges greatly influence the pretreatment conditions?

A PROF. DR. SONTHEIMER: Oh yes, we pay attention to that, but on the other hand, it would be uneconomic to optimize flocculation by means of two or more stages.

Q MR. SPEITEL: Does the optimum for organics removal differ greatly from the turbidity optimum?

A PROF. DR. SONTHEIMER: To some extent, yes. We studied this and found there are waters that should be flocculated at different pH values for optimum organic removal and optimum turbidity removal.

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DESIGN CRITERIA FOR ACTIVATED CARBON ADSORBERS

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PREDICTION OF MULTICOMPONENT ADSORPTION BEHAVIOR IN ACTIVATED CARBON ADSORBERS: KINETIC ASPECTS

Werner Merk

INTRODUCTION

A major problem in the design of adsorption beds for water treatment is the prediction of breakthrough behavior in multi-component mixtures. The objective of this research is to formulate the kinetic models needed and to verify the results with experimental data.

Experimental data of three multi-component systems are shown. In the first bi-solute system, p-nitrophenol/p-chlorophenol, both solutes have a similarly high affinity for activated carbon; in the second bi-solute system, p-nitrophenol/phenol, both solutes have different equilibrium behavior, and in the three-solute system, p-nitrophenol/p-chlorophenol/propionic acid, propionic acid has a much lower affinity to activated carbon than p-nitrophenol or p-chlorophenol(1). In all experiments, the activated carbon Bayer C 10 II* was used (apparent particle density ρ_K=0.59 g/cm^3, equivalent particle radius R=0.66 mm.).

Design of fixed-bed adsorbers requires, in addition to rate parameters, information about adsorption equilibria. Adsorption equilibria of bi-solute systems are predicted from single solute data using the ideal-adsorbed-solution (IAS) theory (2,3), while the single-solute equilibria are represented by Freundlich isotherms (1,4,5).

EXPERIMENTAL

To investigate adsorption kinetics, two different experimental methods were used (Figure 1). In a batch reactor test (left part of Figure 1), at time t=0, a known quantity of carbon granules S was added to the aqueous solution with the initial concentration c_{i0} of solute i. The concentration profile, $c_i(t)$ decreasing with the time t, was measured.

*Manufacturer: Lurgi, Frankfurt, Germany.

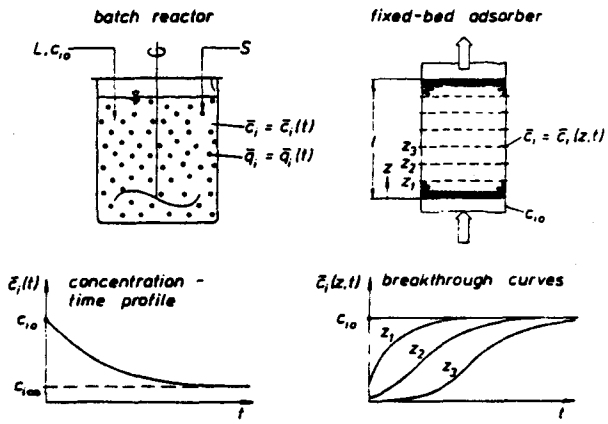

Figure 1. Concentration Profiles in an Activated Carbon Particle "Film-Diffusion Model"

In a column experiment (right part of Figure 1), the aqueous solution with the influent concentration $c_{i,0}$ flows from the bottom to the top of the bed. The variation of the concentration c_i in the water phase with time t was measured at different bed lengths z.

Both concentration-time profiles from batch measurements and breakthrough curves from column experiments were used for testing model predictions. Moreover, from the batch measurements, the required rate parameters for design of multi-solute fixed bed systems were determined.

KINETIC MODELS

Adsorption kinetic models require an assumption about rate controlling steps. In the systems investigated in this work, the adsorption kinetics may be controlled by: diffusion of solute molecules through the external film, in the following called film diffusion; and by diffusion within the particle, in the following called internal diffusion.

Multi-solute adsorption is more complicated than single-solute adsorption, owing to solute-solute interactions during the diffusion process and to competition between the different species for available sites on the surface of the adsorbent.

As a first approximation, it is assumed that the several solutes diffuse independently of one another. Thus competitive effects are taken into account only through the adsorption isotherm.

FILM-DIFFUSION MODEL

If mass transfer is governed only by external resistance, there are no concentration gradients within the particle of diameter 2R (Figure 2).

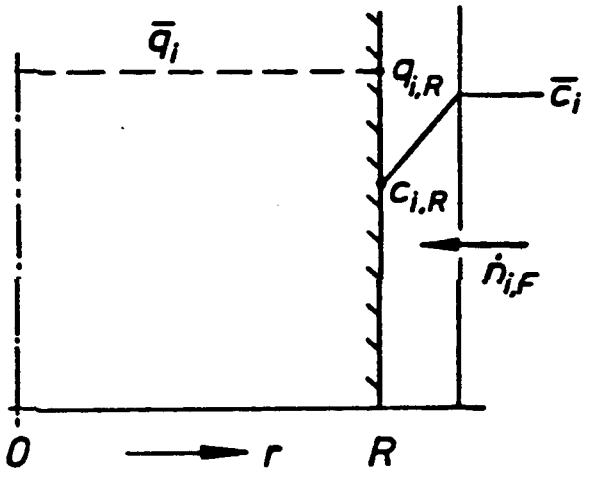

Figure 2. Concentration Profiles in an Activated Carbon Particle "Film-Diffusion Model"

The diffusion of solute molecules through the external film may be expressed by the following rate equation for each component:

$$\dot{n}_{i,F} = \beta_{i,F}(\bar{c}_i - c_{i,R}) \qquad (1)$$

where $\bar{c}_i$ is the bulk liquid concentration; $c_{i,R}$ is the liquid concentration at the outer surface of the particle; and $\beta_{i,F}$ is the external mass transfer coefficient for component i. It is assumed that equilibrium is achieved at the outer surface of the particle, between the concentration in the liquid $c_{i,R}$ and the concentration in the adsorbed phase $q_{i,R} = \bar{q}_i$. The concentration gradient $\dot{n}_{i,F}$, which is the driving force for mass transfer, is in the liquid phase.

$\beta_{i,F}$ can be predicted by the general correlation for heat and mass transfer in fixed beds (1,6). The Sherwood-number, Sh_i, of component i, is given by:

$$Sh_i = \frac{\beta_{i,F} \; 2R}{D_{i,L}} \qquad (2)$$

where $D_{i,L}$ is the diffusion coefficient in the bulk liquid. Sh_i can be calculated using the following equations:

$$Sh_{i,\text{Packed Bed}} \cong [1+1.5(1-\varepsilon)]Sh_{i,\text{ Single Particle}} \quad (3)$$

$$Sh_{i,\text{Single Particle}} = \min Sh_i + F\,(Sc_i)^{1/3}(Re)^{1/2} \quad (4)$$

$$\min Sh_i = 2 \text{ for spheres}$$

$$F = 0.664\left[1+\frac{0.0557Re^{0.3}\,Sc_i^{2/3}}{1+2.44(Sc_i^{2/3}-1)Re^{-0.1}}\right]^{1/2} \quad (5)$$

where Re, Sc_i, and Pe_i are the Reynolds-, Schmidt-, and Peclet-numbers (1), respectively.

These equations can be used, if $Sc_i > 0.6$ and $Pe_i = Re \cdot Sc_i > 1000$.

The diffusion of solute molecules through the external film is the only rate determining step for low concentrations and for solutes having a very favorable isotherm (1,4,7,8). In Figure 3, results are shown for the bi-solute system p-nitrophenol/p-chlorophenol. The influent concentration of both solutes was 0.1 mmol/l. The fluid phase concentration x_i, expressed relative to the influent concentration of p-chlorophenol in the liquid phase, can in this case increase up to 50 percent above the influent concentration. The enrichment of the weaker adsorber, p-chlorophenol, in the liquid phase can be explained by displacement effects.

The experimental breakthrough curves of both solutes are accurately described by the "film-diffusion model." The agreement is remarkable, considering that no adjustable parameter is used in the calculation. The only information used from experimental results is the single solute equilibrium for each component. The assumption of equilibrium at the outer surface of the carbon particle and the hypothesis that there is no interaction between the diffusing molecules in the liquid phase seems to be confirmed, or at least cannot be refuted.

At higher influent concentrations, deviations are observed between measured breakthrough curves and those calculated from the "film-diffusion model." The deviations are caused by the internal mass-transfer resistance which becomes significant at higher concentrations.

Internal diffusion can occur either by pore or by surface diffusion, or by both simultaneously. The increasing influence

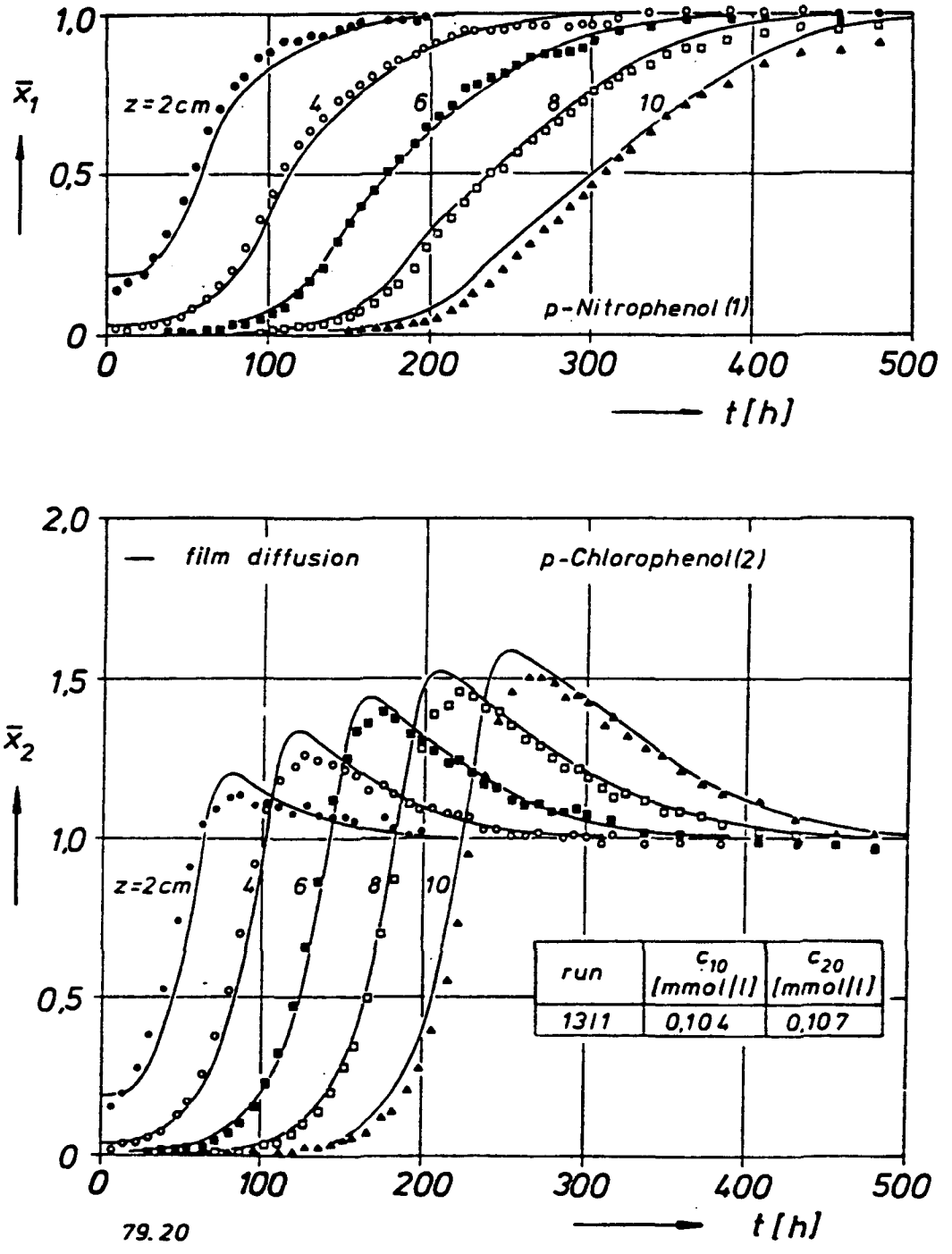

Figure 3. Calculated and Measured Breakthrough Curves of the Bi-Solute System p-nitrophenol/p-chlorophenol (bed density ρ_B = 0.39 g/cm^3, interstitial fluid velocity u = 5.65 m/h, external mass transfer coefficient $\beta_{1,F} = \beta_{2,F} = 1.7 \quad 10^{-5}$ m/s, as in all column experiments presented in this paper.) Equilibrium represented by IAS-method.

of internal mass transfer resistance, observed in this work, indicates that diffusion within the carbon particle occurs predominantly in the adsorbed phase. Recent literature data (9, 10, 11, 12, 13) also favor the "surface diffusion model." With the assumption that accumulation of adsorbate within the pores can be neglected, the frequently used "film-surface diffusion model" gives the same result as the "film-homogeneous diffusion model."

Film-Homogeneous Diffusion Model

The "film-homogeneous diffusion model" assumes adsorption of solute molecules at the outer surface, which can be described by an equilibrium model, followed by diffusion within the particle (Figure 4). The flux $\dot{n}_{i,F}$ is described by Equation (1) and the flux $\dot{n}_{i,K}$ of each component within the particle can be described by Fick's first law.

$$\dot{n}_{i,K} = \rho_K D_{i,K} \frac{\partial q_i}{\partial r} \qquad (6)$$

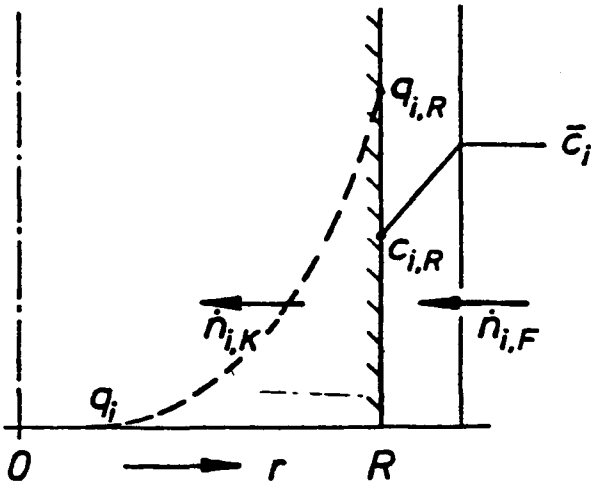

Figure 4. Concentration Profiles in an Activated Carbon Particle: "Film-Homogeneous Diffusion Model"

The diffusion coefficient, $D_{i,K}$, which describes the mobility of solute i in the particle, is obtained from single-solute batch reactor tests by comparing experimental and theoretical data at $\bar{q}_i/q_{i,\infty} = 2/3$.

Figure 5 shows the estimated diffusion coefficients $D_{1,K}$ of the single solutes p-nitrophenol, p-chlorophenol, phenol and propionic acid. Although the diffusion coefficients $D_{1,K}$

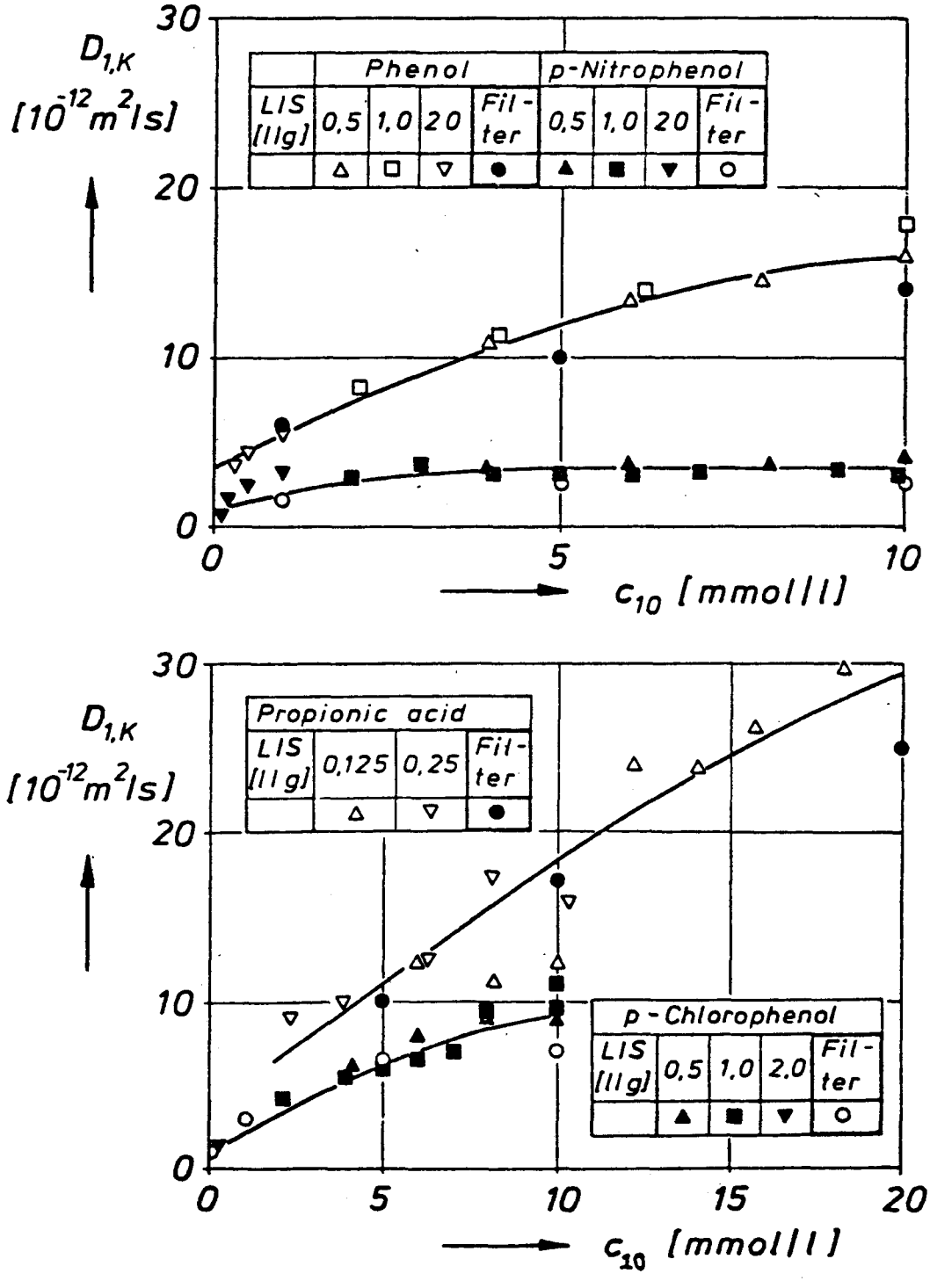

Figure 5. Diffusion Coefficients of the "Film-Homogeneous Diffusion Model" $D_{1,K}$ versus initial (influent) Concentration

depend on the initial concentration, they are in good agreement with those estimated from equivalent column experiments. This leads to the following conclusion for the prediction of breakthrough curves:

The average diffusion coefficient $D_{i,K}$ can be estimated from a batch experiment with an initial concentration identical to the influent concentration of the column experiment.

These coefficients can be used to predict breakthrough curves of bi-solute systems, if one assumes that there is no mutual interaction between the diffusing molecules.

Figure 6 shows measured breakthrough curves of the bisolute system p-nitrophenol/phenol. The influent concentration c_{10} of p-nitrophenol is 1 mmol/l and the influent concentration c_{20} of phenol is 5 mmol/l. Good agreement for all column lengths is obtained between measured breakthrough curves and those calculated from the "film-homogeneous diffusion model." The calculations were performed using only single solute equilibrium data and rate parameters, determined from batch experiments with the single-solute systems. However, the "film-homogeneous diffusion model," using only single solute data, has limitations, as indicated in Figure 7. This figure shows experimental results for the same mixture as in Figure 6, but now the influent concentrations of both components are 5 mmol/l. An increasing deviation can be seen as bed length increases. The breakthrough curves predicted by the "film-homogeneous diffusion model" show a later breakthrough for the stronger adsorber p-nitrophenol, an earlier one for the weaker adsorber phenol, and for both components a faster approach to equilibrium than that observed. These deviations occur in all experiments with mixed solutes if there is a dominating internal resistance and marked displacement inside the carbon particle.

A better understanding of the deviations described above is shown in Figure 8. This figure illustrates the fluxes of both solutes on a single particle, depending on time and bed length, according to run 12/3 (Figure 7). The length of the arrows is a measure of the fluxes and the area of the segments is a measure of the amount adsorbed. For solute 1, the flux only changes its quantity with the time, whereas for solute 2, there is a change in quantity and direction.

As Figure 8 indicates, only a little phenol will be adsorbed in the presence of p-nitrophenol, the component with the higher affinity to activated carbon. Therefore, for short operating times, p-nitrophenol will be predominantly adsorbed at the beginning of the column and phenol will be adsorbed further along the bed length. After longer operating times, as p-nitrophenol migrates down the bed, phenol is displaced by p-nitrophenol. With displacement occurring, phenol must diffuse out of the

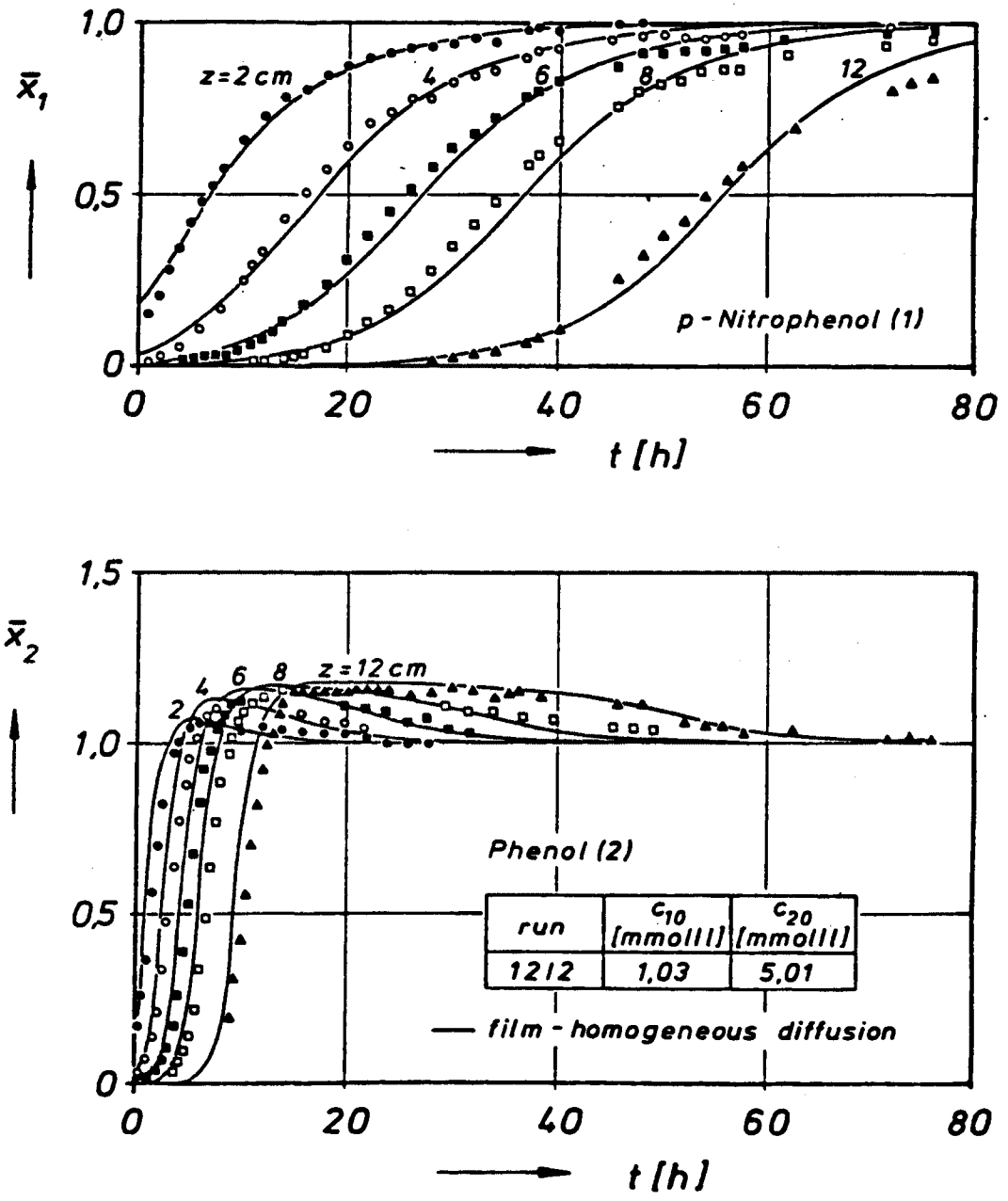

Figure 6. Calculated and Measured Breakthrough Curves of the Bi-Solute System p-nitrophenol/phenol. Equilibrium represented by IAS-Method.

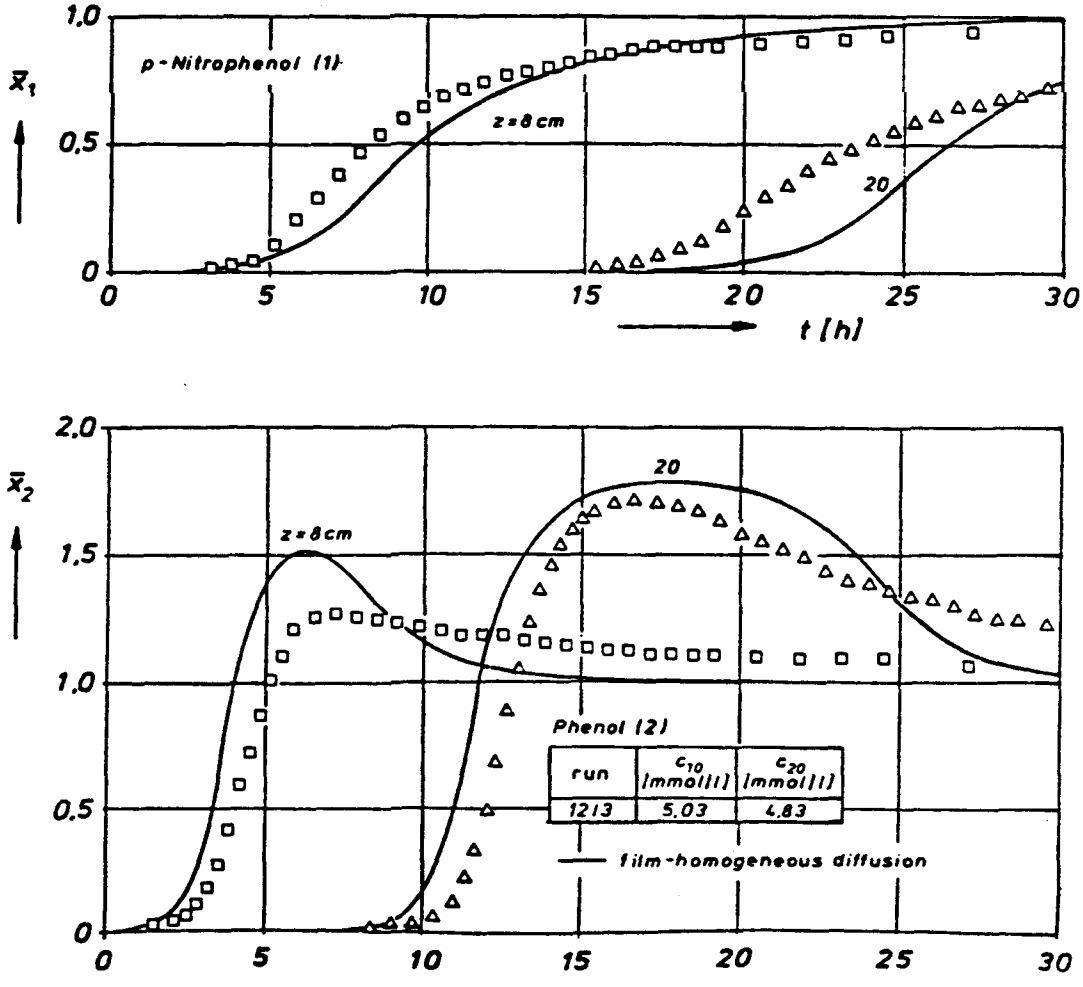

Figure 7. Calculated and Measured Breakthrough Curves of the Bi-Solute System p-nitrophenol/phenol. Equilibrium represented by IAS-Method.

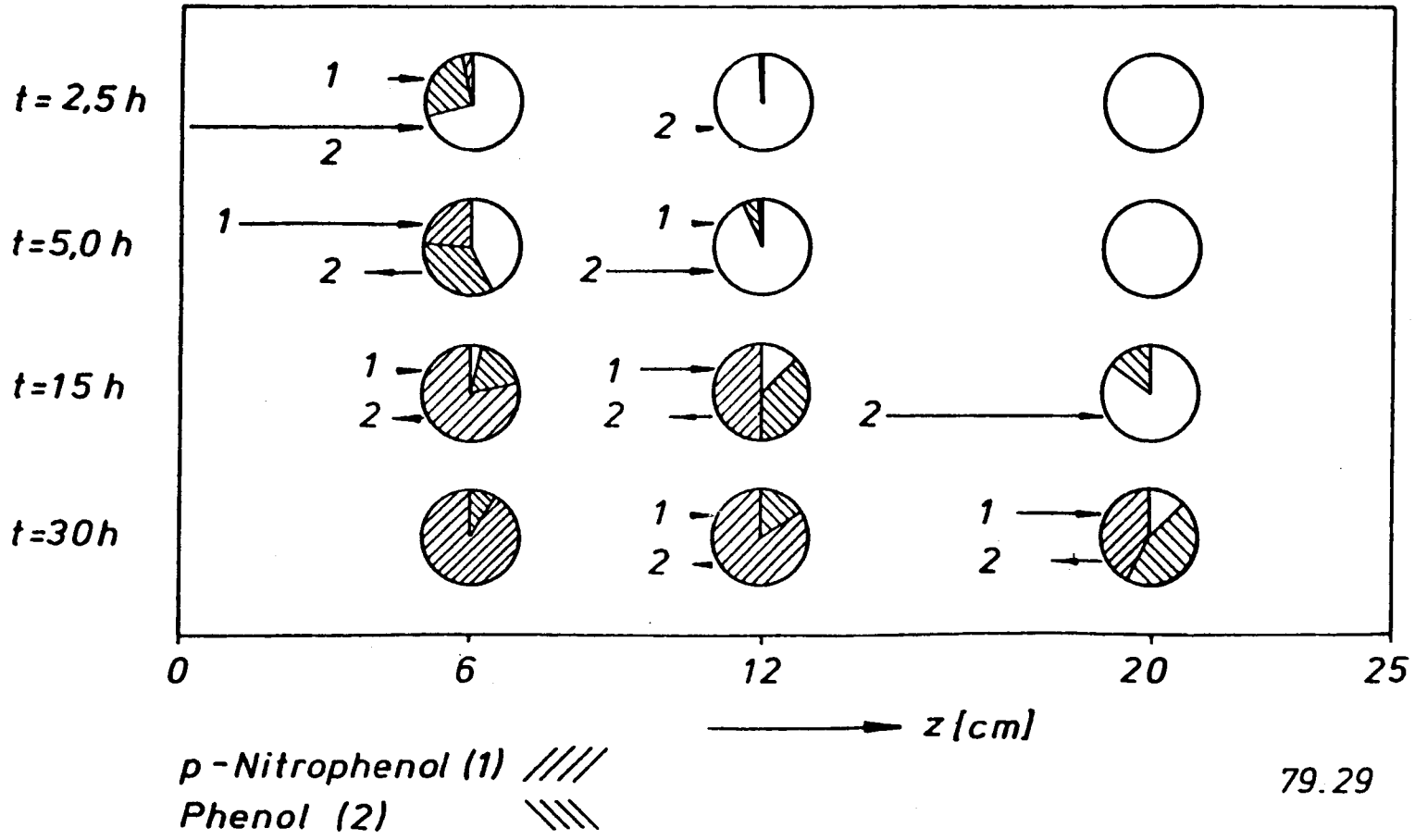

Figure 8. Fluxes into Activated Carbon Particles at Different Times and Bedlengths (Compare Run 12/3, Figure 7)

carbon while p-nitrophenol diffuses in. This counter-diffusion could explain the deviations between calculated and experimental results in this experiment.

For further investigation of this possibility, experiments with preloaded columns were performed. Results of one experimental run are shown in Figure 9. Prior to the experiment, the bed was in equilibrium with a solution of 5 mmol/l phenol. The experiment was carried out with a bi-solute solution of p-nitrophenol and phenol with equal influent concentrations of 5 mmol/l. After the bi-solute system is introduced, there is continuous displacement of phenol by p-nitrophenol. Therefore all phenol concentrations, determined experimentally, exceed the influent concentration. During the entire experiment, there is counter-diffusion inside the carbon particles. Large deviations can be seen between measured breakthrough curves and those calculated from the "film-homogeneous diffusion model" using only single solute data. The deviations are caused by a much higher mass-transfer resistance in this experiment than expected from single solute data.

Extended Film-Homogeneous Diffusion Model

In order to include diffusional interference, the "film-homogeneous diffusion model" has to be extended:

$$\dot{n}_{1,K} = D_{11,K}\,\rho_K\,\frac{\partial q_1}{\partial r} + D_{12,K}\,\rho_K\,\frac{\partial q_2}{\partial r} \qquad (7)$$

$$\dot{n}_{2,K} = D_{21,K}\,\rho_K\,\frac{\partial q_1}{\partial r} + D_{22,K}\,\rho_K\,\frac{\partial q_2}{\partial r} \qquad (8)$$

Thus, the flux of solute 1, $\dot{n}_{1,K}$, depends on the driving forces of solute 1 and solute 2. The same is valid for the flux of solute 2, $\dot{n}_{2,K}$. That means that for a bi-solute system, four coefficients must be determined from mixture data. These coefficients can also be determined in batch reactor tests. But now, two batch reactor tests with the bi-solute system are necessary, the first with fresh carbon and the second with preloaded carbon (1,8). Coefficients from these batch tests were used for predicting breakthrough curves in Figure 10, which are compared with experimental curves already shown in Figure 7. It can be seen that for both solutes, the agreement between measured and predicted values is much better than before, when mutual interference was neglected.

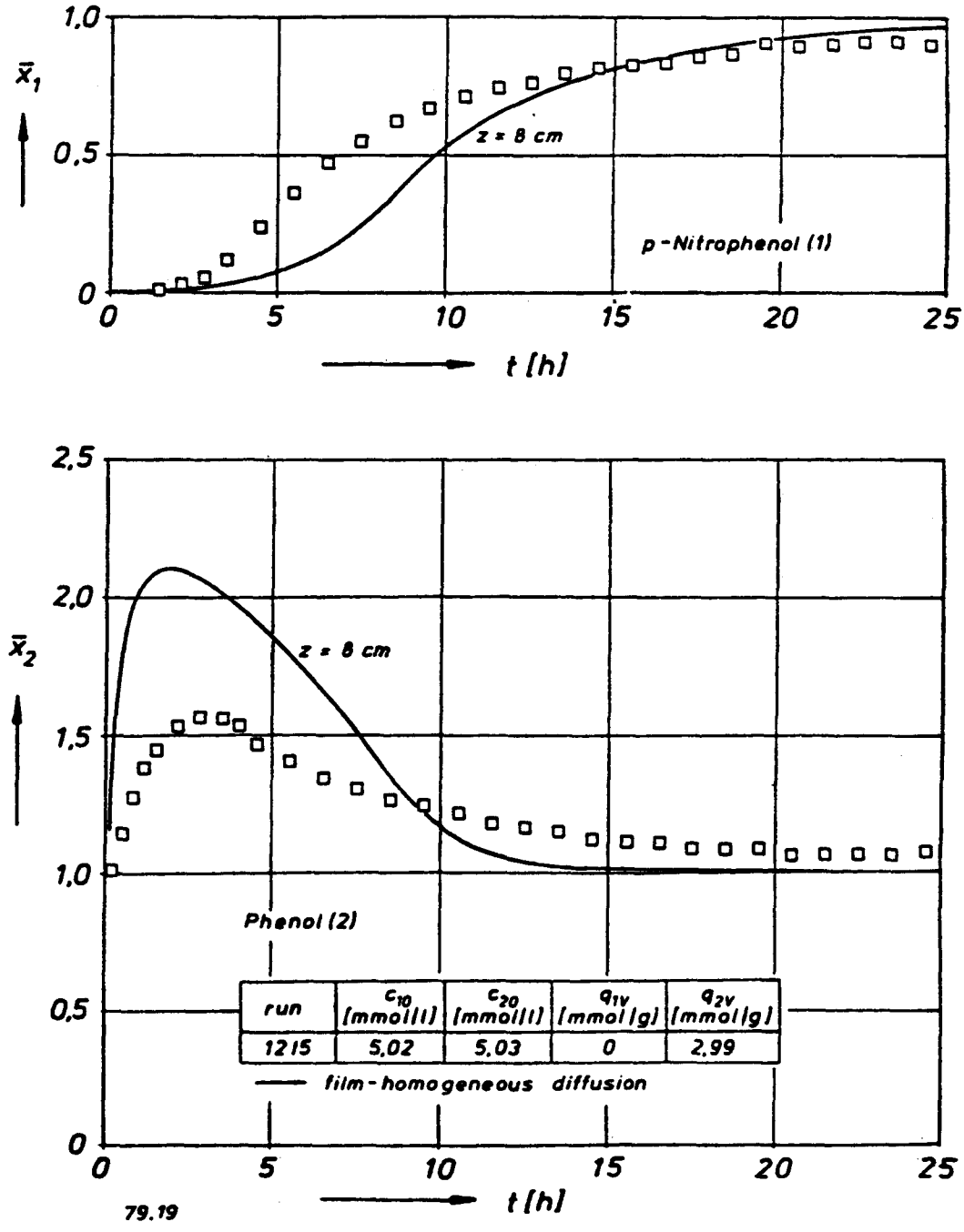

Figure 9. Calculated and Measured Breakthrough Curves of the Bi-Solute System p-nitrophenol/phenol. Activated Carbon Initially Preloaded with Phenol

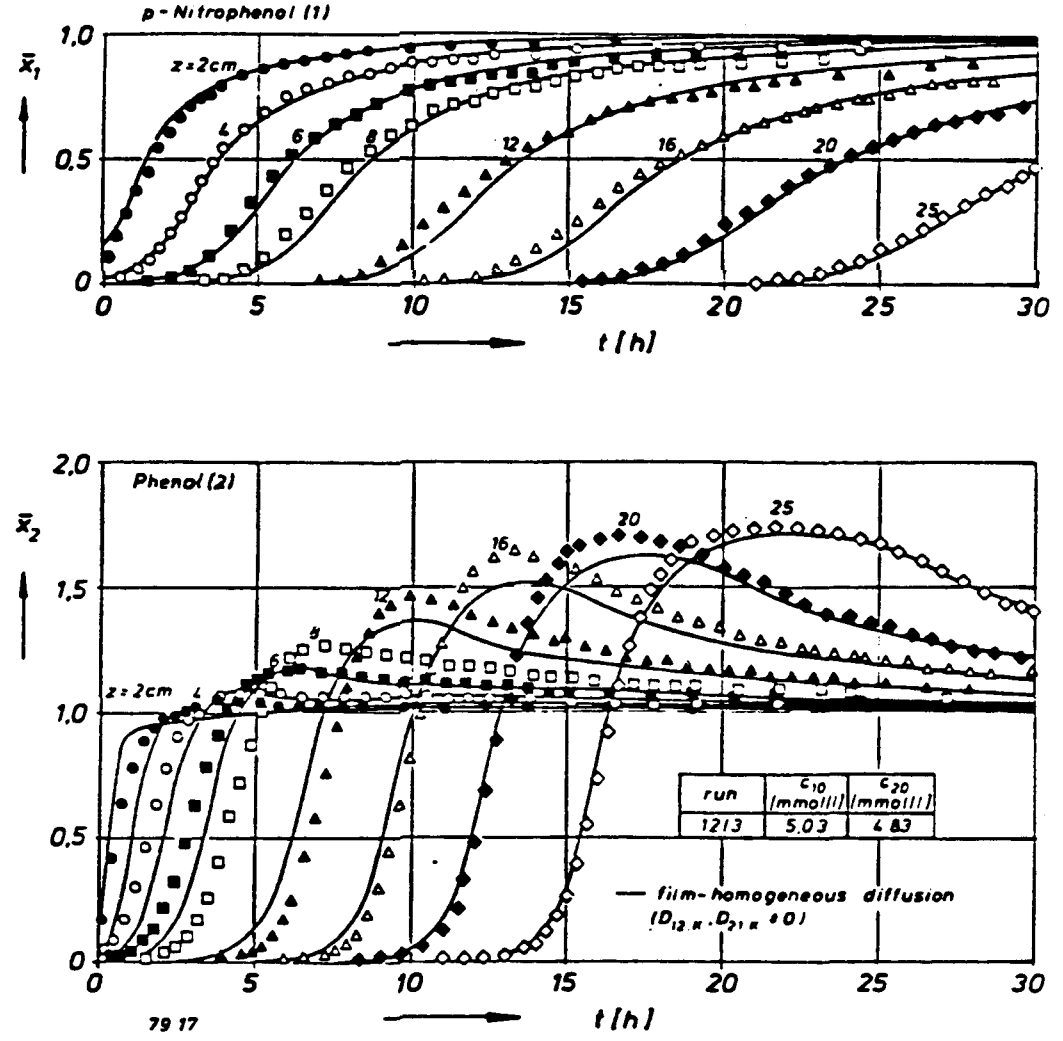

Figure 10. Predicted and Measured Breakthrough Curves of the Bi-Solute System p-nitrophenol/phenol

($D_{11,K} = 2.5 \cdot 10^{-2} m^2/s$; $D_{12,K} = 1.5 \cdot 10^{-12} m^2/s$;

$D_{21,K} = 1.0 \cdot 10^{-2} m^2/s$; $D_{22,K} = 2.0 \cdot 10^{-12} m^2/s$)

Equilibrium Represented by IAS-Method

SIMPLIFIED CALCULATION OF BREAKTHROUGH CURVES

To simulate a more practical case, the problem now is how to handle the calculation of breakthrough curves for a mixture in which one solute has a much higher concentration than the others. This is illustrated with the bi-solute system p-nitrophenol/p-chlorophenol in Figure 11. The bed was saturated with p-chlorophenol after 20 hours. During this time, p-nitrophenol occupies only a negligible capacity of the bed because of its comparatively low concentration. Thus, p-chlorophenol is adsorbed nearly undisturbed by p-nitrophenol.

Although the presence of p-chlorophenol has a strong effect on the adsorption of p-nitrophenol, its breakthrough curves can also be calculated like a single-solute system. Actually, for this case, p-nitrophenol diffuses into the carbon which is already in equilibrium with an aqueous solution containing 5 mmol/l of p-chlorophenol. In order to calculate the breakthrough curves of p-nitrophenol, assuming a single-solute system, equilibrium data and rate parameters have to be estimated from batch experiments using carbon which was already in equilibrium with an aqueous solution containing 5 mmol/l of p-chlorophenol.

The breakthrough curves of p-nitrophenol and p-chlorophenol, in the three-solute system p-nitrophenol/p-chlorophenol/propionic acid, are predicted using the same simplification that was pointed out in the previous example. P-nitrophenol and p-chlorophenol are adsorbed on activated carbon, which is already in equilibrium with the water/propionic acid solution. Thus, equilibrium data and rate parameters of p-nitrophenol and p-chlorophenol have to be estimated from batch tests using activated carbon already in equilibrium with the water/propionic acid solution. With these data, breakthrough curves of p-nitrophenol and p-chlorophenol in the three-solute system are calculated like a bi-solute system. Results are shown in Figure 12. The agreement between measured breakthrough curves and those calculated from the "film-homogeneous diffusion model" is good.

The method used in these two examples can be generalized. If one knows which solute should be removed from water, two estimations have to be made:

- Solutes which are present in very small concentrations compared to the solute to be removed, and/or which have a small affinity to activated carbon, do not disturb the adsorption of the specific solute one is interested in and thus may be neglected.

- Solutes which are present in very high concentrations compared to the solute to be removed, and/or which have a high internal diffusion resistance, may be added to the water phase.

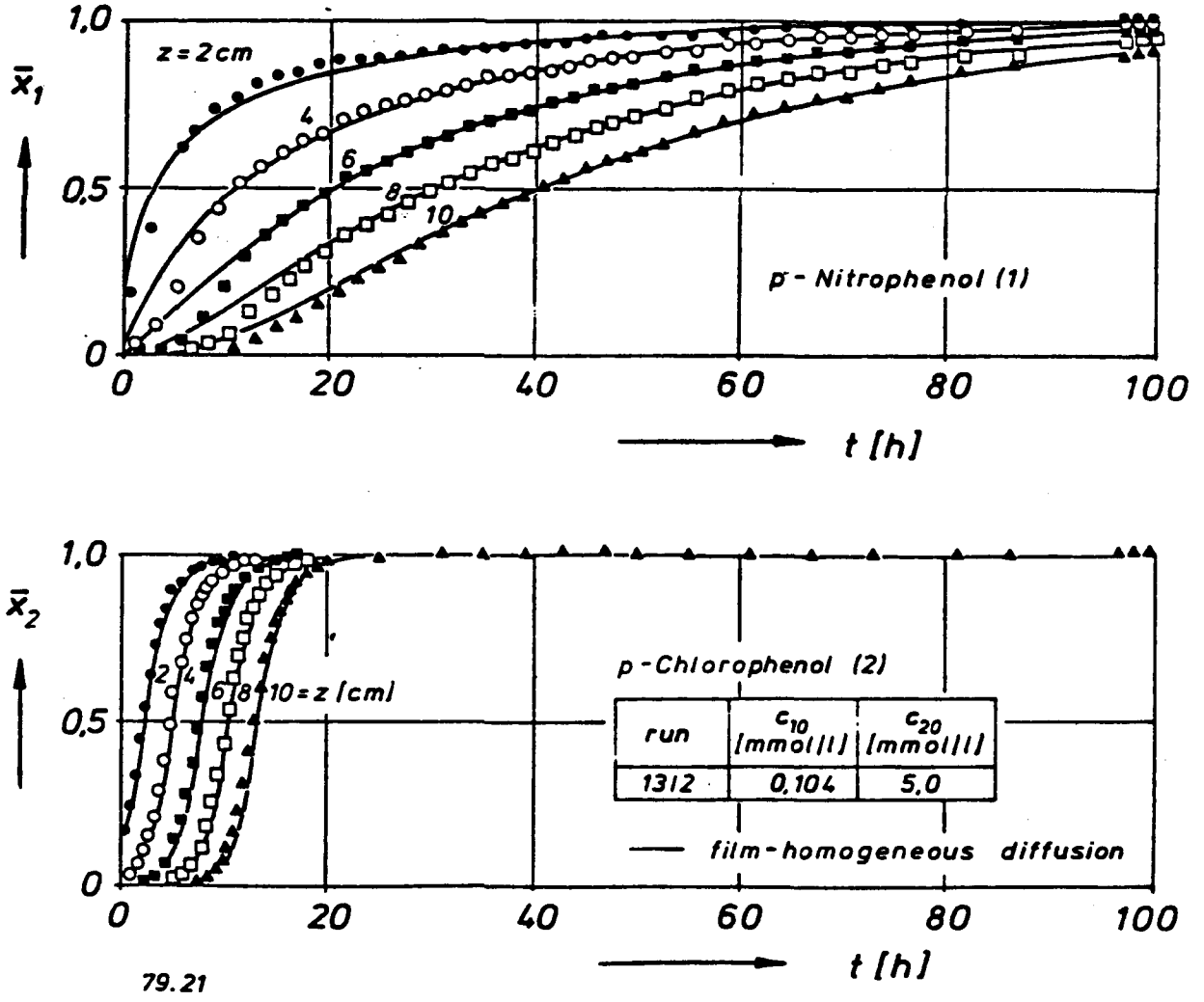

Figure 11. Calculated and Measured Breakthrough Curves of the Bi-Solute System p-nitrophenol/p-chlorophenol. The Curves of Both Solutes Are Calculated Assuming, in Each Case, a Single Solute System.

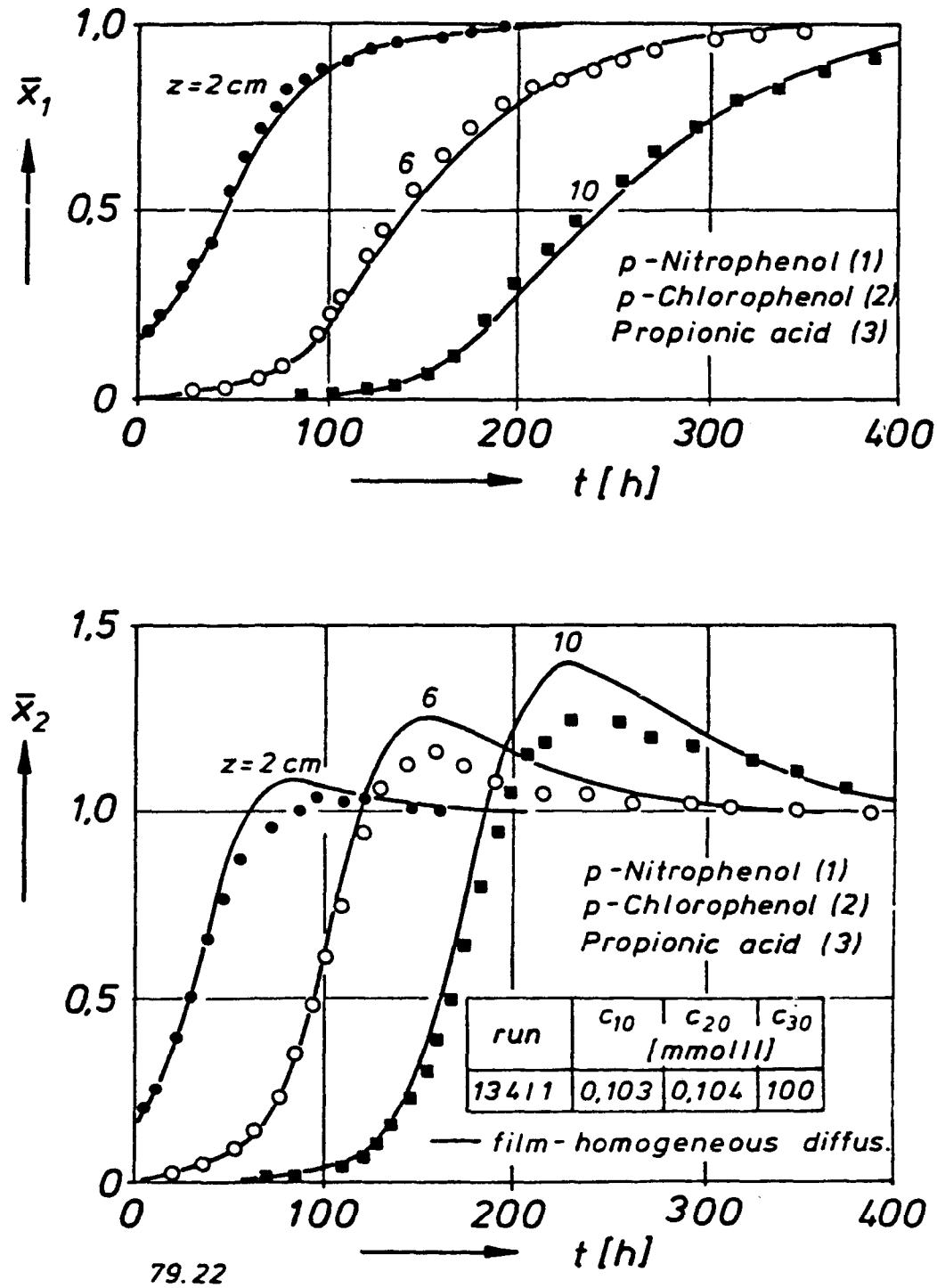

Figure 12. Calculated and Measured Breakthrough Curves of p-nitrophenol/p-chlorophenol in a Water/Propionic Acid Solution

SUMMARY

Although the concentrations of solutes are very low in water treatment, it cannot be expected that the "film-diffusion model" predicts breakthrough behavior satisfactorily because, in general:

> most of the solutes have less favorable isotherms than p-nitrophenol or p-chlorophenol; many solutes are much larger molecules and hence have a much higher internal diffusion resistance than p-nitrophenol or p-chlorophenol; displacement effects cause a much higher internal resistance than expected from single-solute data.

Therefore, internal diffusion resistance has to be incorporated into the "film-homogeneous diffusion model." All parameters needed in this model can be obtained from batch reactor tests.

Multi-solute systems may be regarded as a single-solute system or a bi-solute system, respectively, if all solutes except one or two are present in very different concentrations; and/or have a comparatively small affinity to activated carbon; and/or have a comparatively small internal diffusion coefficient.

NOTATION

c	fluid-phase concentration	mmol l^{-1}
D	diffusivity	m^2 s^{-1}
L	volume	liter
l	total length of packed bed	cm
$\dot{n}$	flux	mmol s^{-1} cm^{-2}
q	concentration of adsorbate	mmol g^{-1}
R	radius of particle	mm
r	radial coordinate	mm
S	mass of carbon	g
t	time	s
$\bar{u}$	interstitial fluid velocity in packed beds	m h^{-1}
x	normalized fluid phase concentration ($=c/c_0$)	-
y	normalized concentration of adsorbate ($=q/q_0$)	-
z	axial distance coordinate in column	cm

GREEK SYMBOLS

β	mass transfer coefficient	ms^{-1}
ε	void fraction ($=1-V_s/V_t$)	-
ν	kinematic viscosity	m^2 s^{-1}
ρ_K	density of dry particle	g cm^{-3}

NOTATION

Pe = Peclet-number (=Re.Sc)

Re = Reynolds-number ($\bar{u}2R/\nu_L$)

Sc = Schmidt-number ($=\nu_L/D_L$)

Sh = Sherwood-number ($=\beta_F 2R/D_L$)

SUBSCRIPTS

F in the film

i solute i

K in the particle

L in the bulk liquid

R at the outer surface of the particle

s solid

t total

V preloaded

0 initial value

∞ final value

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PREDICTION OF MULTICOMPONENT ADSORPTION BEHAVIOR: EQUILBRIUM ASPECTS

Bernd Frick

INTRODUCTION

The knowledge of adsorption equilibria, and the ability to describe them, is essential to determining the breakthrough behavior of organics in GAC filters. When dealing with multi-solute systems, for instance in water treatment, it is necessary to use an adsorption model which can predict competitive adsorption. In many cases, competitive adsorption will be very important in the treatment of water supplies containing anthropogenic organics in addition to large amounts of natural substances. For the prediction method to be useful, the mathematical structure of the equilibrium model has to be simple and only single-solute data should be necessary.

A number of competitive adsorption models more or less fulfill these provisions (1,2), but they all have advantages as well as disadvantages. For the prediction of competitive adsorption equilibria, the author used the Simplified Competitive Adsorption Model (SCAM) proposed by Baldauf, et al. (3,4).

All these models can be applied successfully only to defined systems with a limited number of components. However, the waters used in practice are mixtures of thousands of components, of which only a few percent can be identified. Because of the lack of information on the composition of water, it seems impossible to predict the adsorption behavior of such an undefined system.

It is the aim of this paper to show that, despite this fact, there are possibilities to use such a model for solving the practical problems of activated carbon adsorption. Based on the discussion of the adsorption behavior of multi-solute mixtures and on the explanation of the observed effects by means of model calculations, a method will be proposed which allows the prediction of adsorption equilibria in unknown mixtures. Results obtained by this method will be shown for a mixture of practical interest.

ADSORPTION BEHAVIOR OF MULTI-SOLUTE MIXTURES

The collection of equilibrium data is an important part in the design of a GAC adsorber. This is done by measuring adsorption isotherms. In most cases, the organics are measured collectively by group parameters such as DOC or UV absorbance. Therefore, the resulting isotherms represent the adsorption behavior of all adsorbable and non-adsorbable substances. DOC seems to be the most suitable because it covers all the organics. Figure 1 shows DOC isotherms of two actual waters and of two single solutes. It is striking that the isotherms of the river water and of the humic acid are relatively steep while the single-solute isotherms of p-nitrophenol and phenol-4-sulfonic acid are flat. All the isotherms can be fitted by the Freundlich equation. This is appropriate for the two single solutes, but it is not so with the others because they are multi-solute mixtures. By treating them as single-solutes, valuable information will be lost, especially with regard to the competitive adsorption behavior. From Figure 2 it can be seen that the description of a mixture by a single-solute equation is a gross simplification. The data in Figure 2 are for the same humic acid as shown in Figure 1. By increasing the carbon dosage, however, lower concentrations can be achieved; in this range, the isotherm shows a totally different shape. This indicates that we have to deal with a multi-solute mixture.

In most cases, smaller carbon dosages are used and only the steep part of such isotherms can be observed. It is therefore interesting to look for the reasons for such steep isotherms.

There are two main questions:

1. What are the conditions for steep isotherms?

2. Is it possible to describe the adsorption behavior of such mixtures by a model?

For this purpose, a number of model calculations have been carried out and some examples of these calculations are shown in Figure 3. It can be seen that the slope of the isotherms is a function of the single-solute data of the components and of their initial concentrations. In the case of very different single-solute behavior, the isotherm slope increases when the concentration of the weaker-adsorbed component is increased. (Figure 3, left-hand side). For constant initial concentrations of the two components the isotherm slope is a function of their adsorbability. For similar single-solute data, the isotherm slope of the mixture is almost identical to that of the single solutes. But when there is a large difference in single-solute behavior, the isotherm slope reaches values which are four- to six times larger than those of the single-solute isotherms.

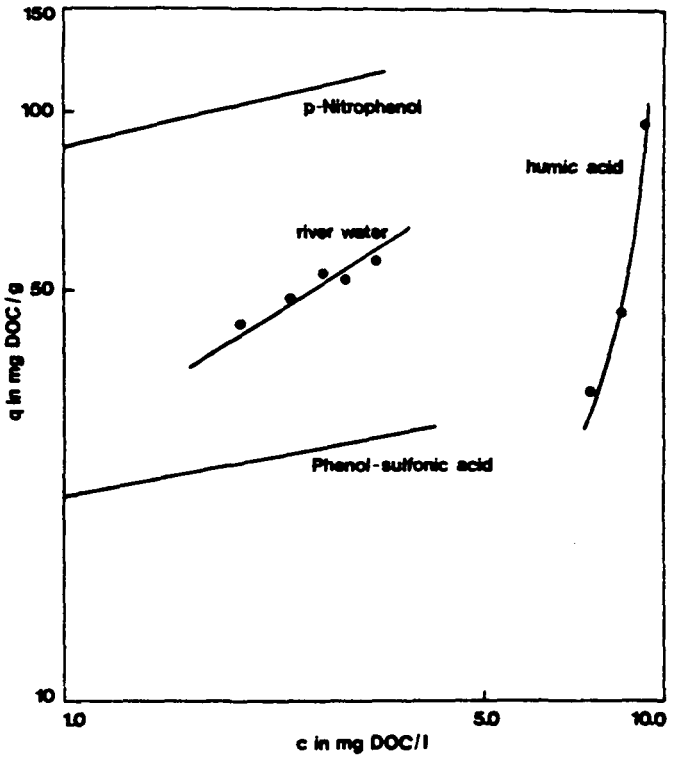

Figure 1. DOC-Isotherms of Single Solutes and Multi-Component Mixtures

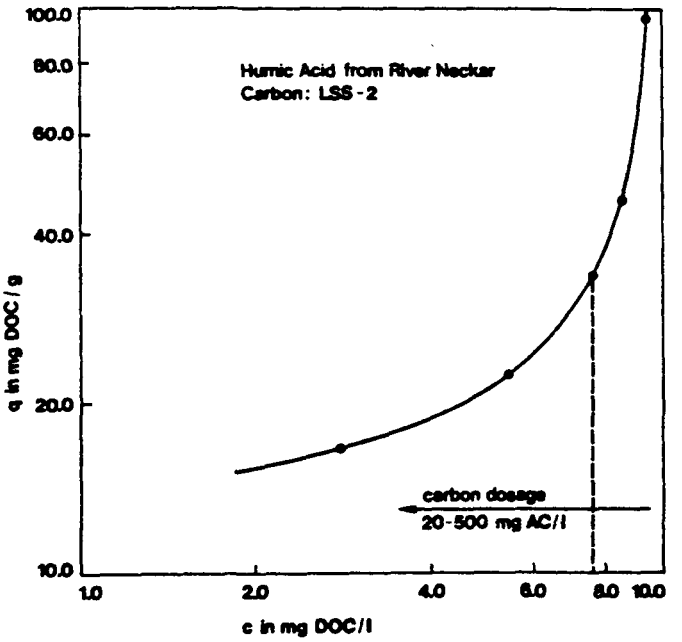

Figure 2. DOC-Isotherms of a Chlorinated Humic Acid (after Sander)

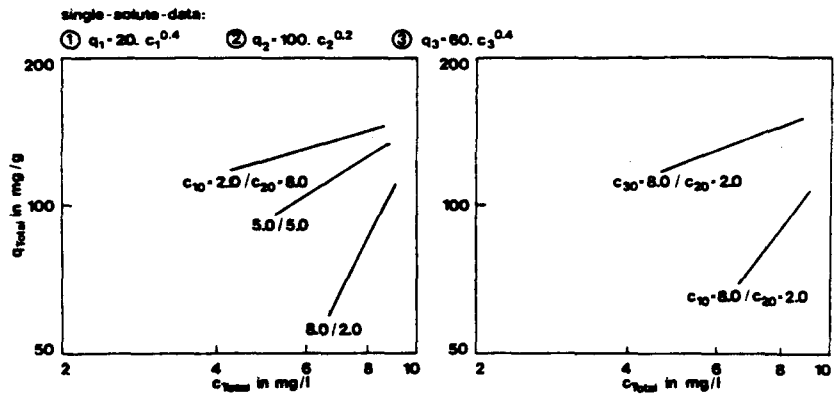

Figure 3. Influence of Single Solute Data and Concentration on the Total Adsorption Behavior

These findings were confirmed experimentally with a defined ternary system. This mixture consists of phenol-4-sulfonic acid, 4-hydroxybenzoic acid (HBA), and 4-nitrophenol (PNP). The sulfonic acid is the weakest-adsorbed substance, while HBA and PNP are strongly-adsorbed compounds. Figure 4 shows the DOC isotherms of this mixture with different initial concentrations of the three components. The greater the amount of the weaker-adsorbed component, the greater is the isotherm slope of the overall isotherm.

To show that the competitive adsorption model used in this report can predict the adsorption of multi-solute systems, Figure 5 presents a comparison between experimental and predicted results for the mixture containing the largest amount of phenol-4-sulfonic acid.

It can be summarized that the isotherms of mixtures strongly depend on the single-solute behavior of the components and on their concentration distribution. When this interaction is recognized, it is possible to predict the behavior of the mixture using the single-solute data of the components. Nonetheless, the description of such a mixture as a pseudo-single solute is an oversimplification. It may be adequate for a qualitative evaluation, but it is quite insufficient for the prediction of competitive adsorption effects.

To overcome the drawback of missing information on the composition of the mixture, research was directed towards the development of a combined laboratory- and calculation procedure

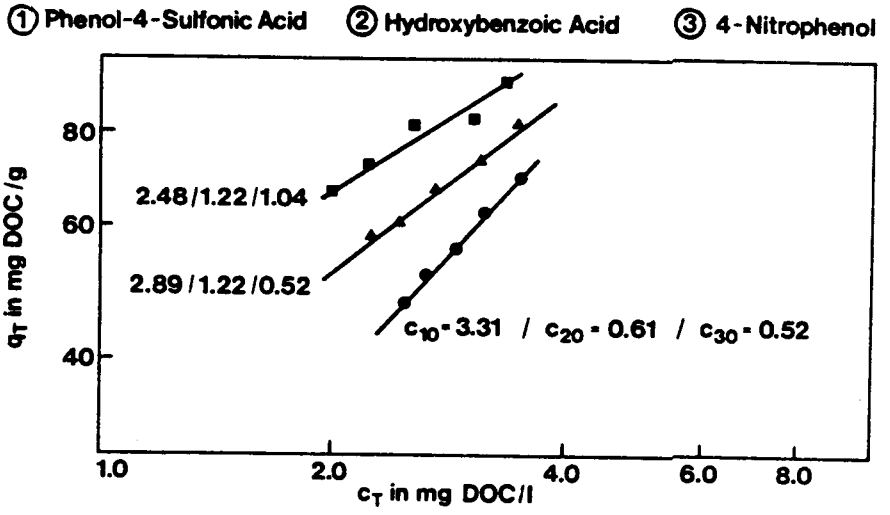

Figure 4. Influence of Initial Concentrations on the DOC-Isotherms of a Three-Component Mixture

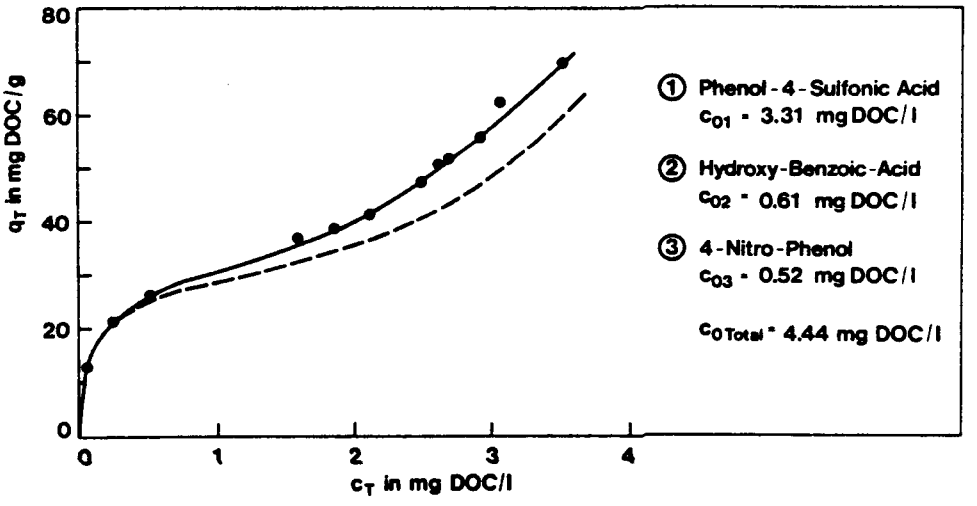

Figure 5. DOC-Isotherm of a Three-Component Mixture

which allows the prediction of mixture adsorption by reducing the mixture to a binary or ternary system.

PREDICTION OF MULTI-SOLUTE ADSORPTION OF UNDEFINED MIXTURES

From a chemical point of view, raw water is a mixture of many different substances with specific structures affecting the quality of the final water. From the engineering point of view, the raw water is a mixture of compounds with different adsorbability. In contrast to the chemical viewpoint, it can be assumed that fewer components need to be considered if only the adsorption behavior is regarded, because it is possible that in spite of the different chemical structures, there are similarities in adsorption behavior. It will be necessary, however, to reduce the number of components by introducing key components which represent a specific range of adsorption behavior. This is supported by the following assumption:

The overall adsorption is determined by the organic background of the fulvic , humic , and lignin-sulfonic acids. This behavior can be described by regarding the unknown mixture as a system of two or three key components with different adsorbabilities. The effects of competitive adsorption with regard to the behavior of trace organics can be predicted by using the single-solute data of the key components and the data of those organics which are of interest.

CHARACTERIZATION OF ADSORPTION BY SPLITTING INTO KEY COMPONENTS

The splitting procedure is based on the competitive adsorption model which needs only single-solute data for the prediction of competition. This model, strictly valid only for defined systems, can be applied to unknown mixtures when converting this mixture into a semi-defined system. This can be achieved by adding a specific amount of a defined substance to the mixture. By watching the adsorption behavior of the added compound (tracer substance) in the presence of the unknown organics, it is possible to obtain information on the single-solute data and on the concentrations of the key components. Figure 6 shows the flow sheet of the procedure.

For this purpose the SCAM model was modified for application to three and four component mixtures, respectively.

When considering the unknown mixture as a system of two key components, there are six independent variable parameters to describe the adsorption behavior of the unknown organics and their influence on the adsorption behaviour of the tracer substance. The parameters are the initial concentrations of the two key components C_{io} and the constants K_i and n_i describing the single-solute behavior of the key components, expressed by the Freundlich equation $a_i = K_i C_i^{n_i}$

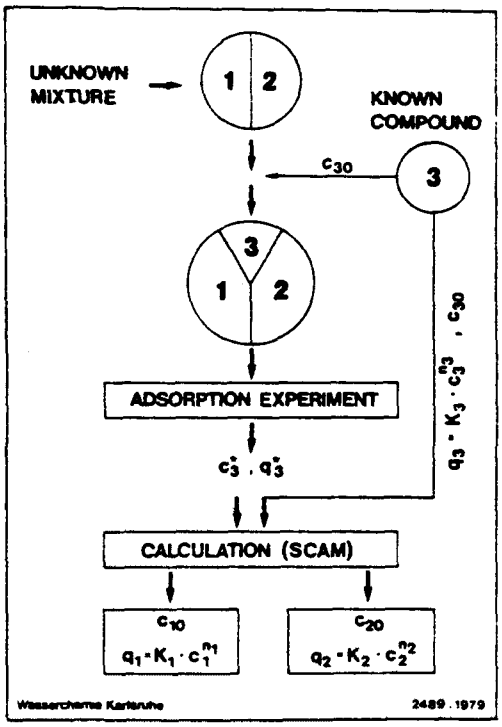

Figure 6. Flowsheet of Splitting Procedure

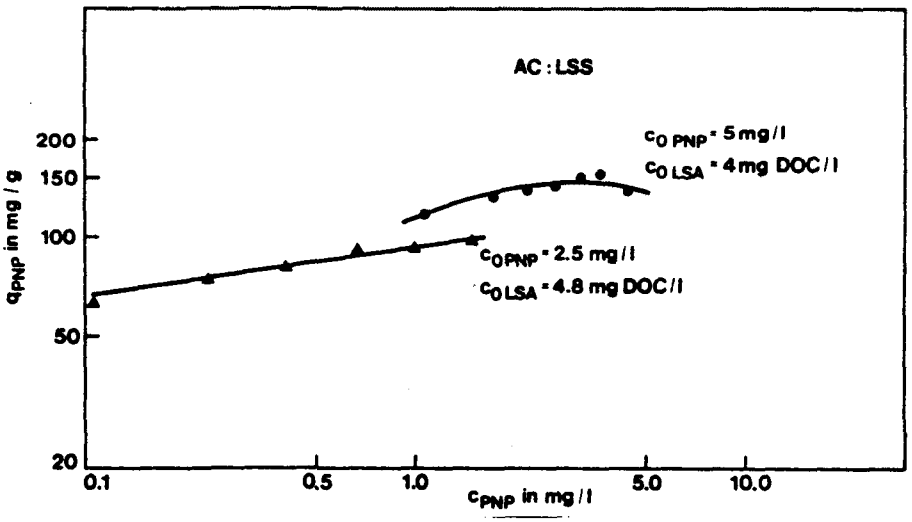

Figure 7. PNP-Isotherms in the Presence of Two Different Lignin Sulfonic Acids

The number of parameters has to be reduced due to a simplification of the fitting procedure. The initial concentrations of the key components can be coupled with the total initial concentration of the mixture

$$C_{T0} = C_{10} + C_{20}$$

The adsorption behavior of the single solutes can be formulated arbitrarily or by using the adsorption behavior of defined compounds representing good or poor adsorbability.

A more precise way of making inferences regarding the single-solute behavior is to interpret the adsorption behavior of the tracer substance and of the overall isotherm of the mixture. The adsorption behavior of the tracer component gives valuable information on the strongly-adsorbed compounds in the mixture when using a tracer substance known as a well-adsorbing substance.

Figure 7 shows the PNP isotherms in two different mixtures of lignin sulfonic acids. While the lower isotherm is shown as a straight line in the log-log plot, the other isotherm shows curvature. This is the result of a better adsorption behavior of a certain part of the lignin sulfonic acid. When observing such an effect, we can better infer the adsorption behavior of the key component representing the strongly-adsorbed part of the unknown mixture (5,6).

Information on the adsorption of the weaker-adsorbed component can be obtained from the overall isotherms for lower concentrations. There, the isotherm is almost identical with the single-solute data of the weakest-adsorbed compound in the mixture. As an example, Figure 8 shows the total isotherm in a log-log plot of the mixture described in Figures 4 and 5. In the concentration range where the overall isotherm is nearly identical with that of phenol-4-sulfonic acid, the only compound remaining in the solution is the sulfonic acid.

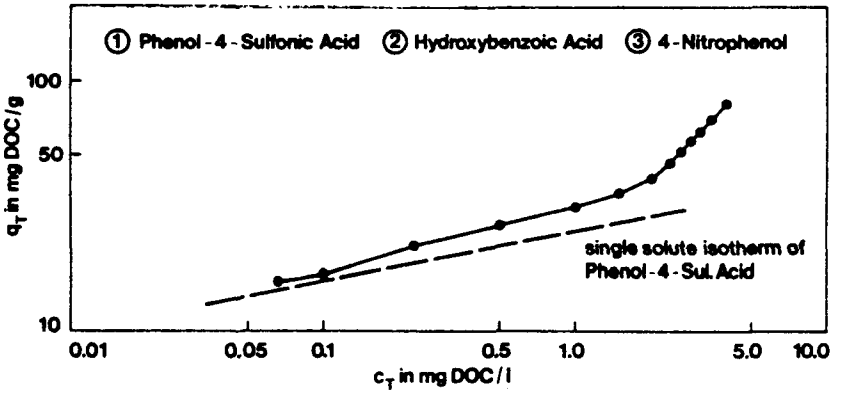

Figure 8. DOC-Isotherm of a Three-Component Mixture

The evaluation of the single-solute behavior by means of overall isotherms and the shape of the tracer isotherm is an important step for calculating the concentration distribution of the key components. The definition of fixed adsorption behavior seems to be advantageous, especially if the characterization of the adsorption is carried out with more than two components. The whole range of adsorbability can then be divided into intervals with defined adsorption data.

In the case of characterization by two key components it is advantageous to define the adsorption data of one component only and to vary the other data in order to get a better description of the adsorption behavior. This way it is possible to obtain a number of solutions; i.e., combinations of initial concentrations and single-solute adsorption data. All these combinations can predict the competition of the key components with the tracer substance.

To be able to decide which of the combinations will produce the best description of the adsorption behavior of the mixture, an additional criterion is necessary. There are two criteria which can be used for this purpose. One is the DOC isotherm of the unknown mixture without the tracer substance, and the other the DOC isotherm in the presence of the tracer substance. That combination which agrees best with the two criteria should be used for the characterization of the mixture.

RESULTS OF THE CHARACTERIZATION METHOD

For demonstrating the proposed method, a lignin sulfonic acid (LSA) solution was used. After flocculation of a commercial product to separate high-molecular-weight compounds, the overall adsorption behavior can be compared to that of an actual raw water of the Rhine River (5). The aim of the characterization method is the description of the entire adsorption by two key components. For this purpose, three adsorption experiments are necessary to evaluate the following:

1. The single-solute isotherm of the tracer substance (p-nitrophenol = PNP);

2. The overall isotherm of the LSA;

3. The isotherms of the lignin sulfonic acid as well as those of the PNP in the mixture. The concentration of PNP can be measured independently of DOC by UV absorbance at 317 nm.

Figure 9 shows the experimental results. Curve 1 represents the LSA isotherm and curve 2 the LSA isotherm in the presence of 1 mg/l PNP. The curvature of the second isotherm is

a good indication for the presence of a larger amount of weakly-adsorbed substances. The isotherm of PNP in the presence of LSA shows no curvature.

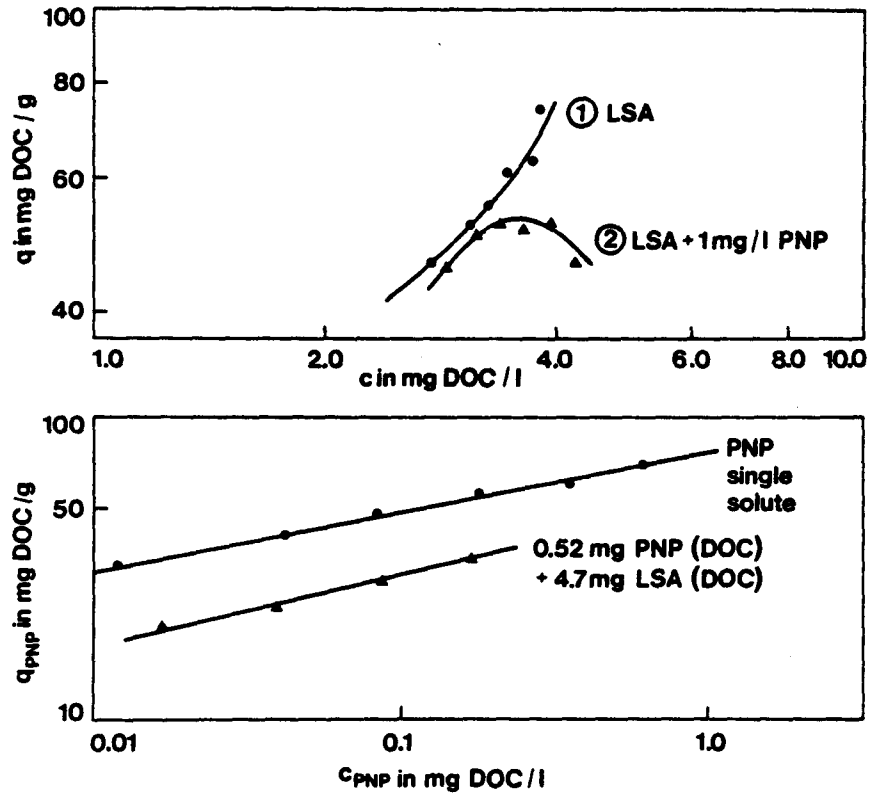

Figure 9. LSA and PNP Isotherms as Single Solutes and in Admixture

Therefore, the single-solute isotherm of the component representing the strongly-adsorbed substances was assumed to be only 90 percent of that of the tracer substance. The single-solute data of the second component were varied. By means of the proposed equilibrium model, a number of combinations were calculated and compared to the two LSA isotherms.

Figure 10 gives a comparison between experiment and calculation for the best fitting combination. There is reasonable agreement between the forms of the measured and the predicted LSA isotherm. The single-solute data used for the calculation

are shown at the top of the figure. Curve number 3 is the measured LSA isotherm in the presence of PNP;curve number 4 the corresponding isotherm, predicted with the same data as for curve number 2. In this case the agreement is less satisfactory, but the effects of strong competition are evident.

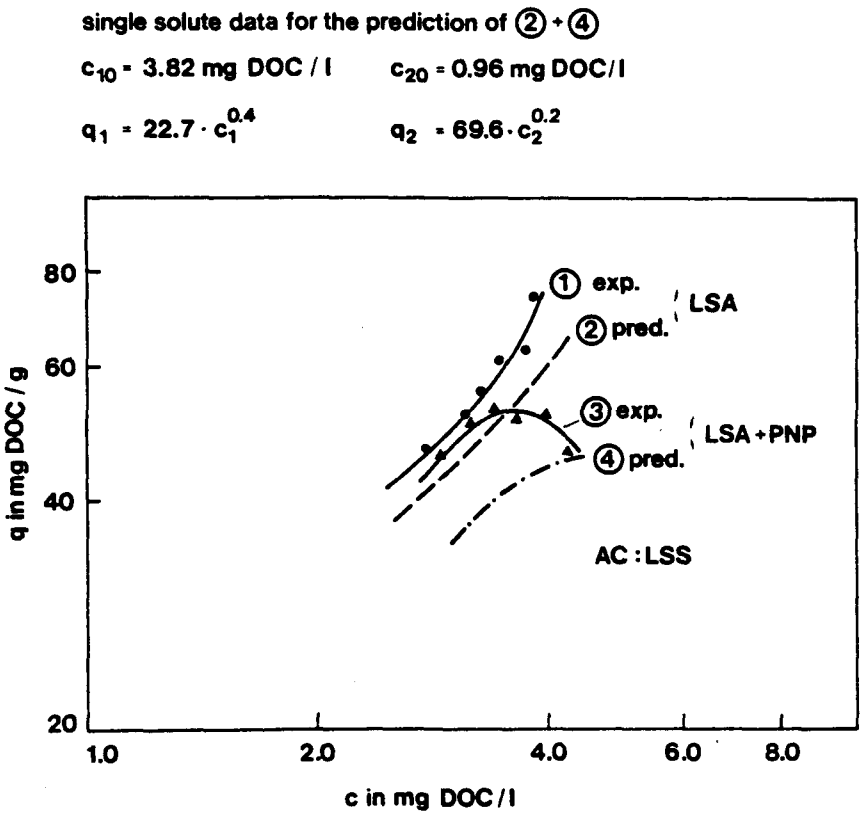

Figure 10. Comparison of Measured and Predicted DOC-Isotherms for Lignin Sulfonic Acid (LSA)

Similar results were obtained by using another type of activated carbon with the same LSA (Figure 11). The prediction is not met as well as it is in Figure 10.

One of the reasons for the deviations between experimental and predicted curves may be the simplification or reduction to a two-component system. It can be assumed that the characterization by three or four components improves the quality of description. The other reason is an experimental one. Unfortunately, DOC measurement is less exact than 5 percent. This can result in deviations as large as 30 percent in the carbon loading, and therefore to an apparent larger deviation between calculation and experiment.

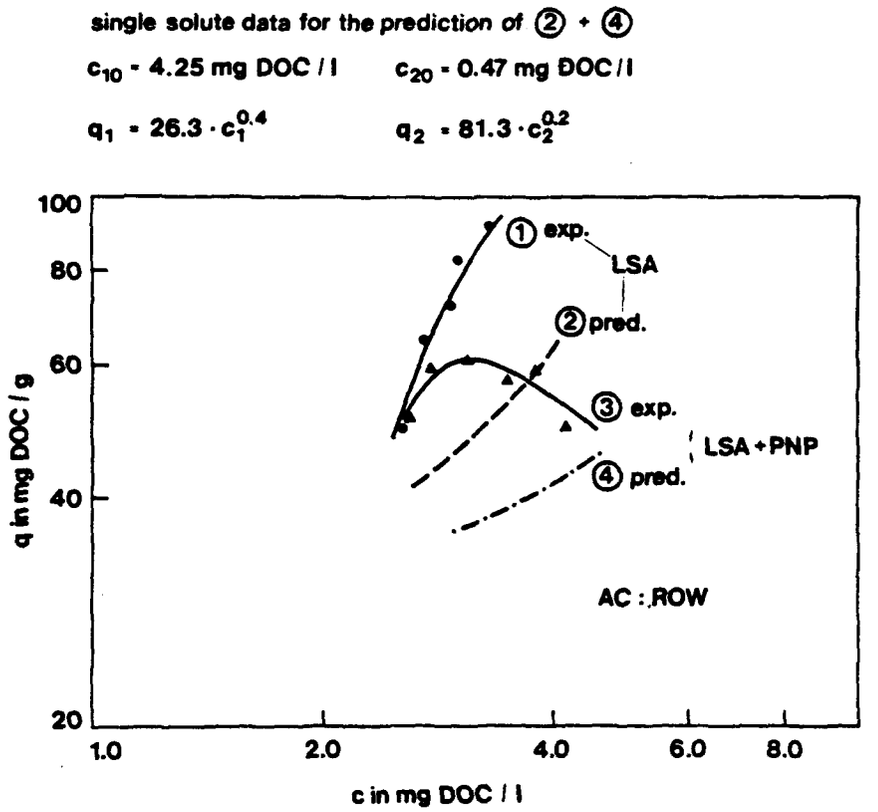

Figure 11. Comparison of Measured and Predicted DOC-Isotherms for Lignin Sulfonic Acid (LSA)

Nevertheless, this kind of treatment for an unknown mixture will improve the prediction of adsorption behavior, especially in regard to competitive adsorption. While it is possible to describe the competition between the key components and organics of interest by the proposed adsorption model, it has proved impossible when regarding the unknown mixture as a single solute. This is shown by Baldauf (3), using the proposed characterization method for the prediction of GAC filter performance.

CONCLUSIONS

It has been shown that the adsorption behavior of actual waters or similar solutes is determined by the adsorption behavior of the single solutes and their concentrations. The main effects of mixture adsorption can be predicted using a competitive adsorption model.

The application of such a model to unknown systems requires knowledge of the single-solute behavior. This was investigated by using a combined experimental- and calculation procedure, splitting up the unknown mixture into two key components of defined quasi-single-solute behavior. With the aid of these two hypothetical components, it is possible to describe the adsorption behavior of the mixture as well as the competitive effects when additional solutes are present.

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LABORATORY ACTIVATED CARBON TEST METHODS FOR WATER UTILITIES

Gerd Hölzel

Many different types of activated carbon are offered for water-treatment purposes by various producers. In order to find the most suitable and most economic product for a particular application (1,2), it is necessary to have specific test methods.

OVERVIEW OF TEST METHODS

Table 1 gives a summary of tests which, in our opinion, are helpful for evaluating activated carbon products for use in water utilities. As a first step, it is necessary to get a representative sample of the carbon. Because this is often difficult, it is important to come to an agreement with the producer over sampling.

The mechanical test methods yield information on apparent density, necessary to determine carbon quantities, and on particle size distribution. A good evaluation of the sieve analysis is the method accepted by the German Materials Standards Institute (DIN) (3). This analysis gives two parameters: a characteristic particle diameter, and the particle size distribution.

Another important mechanical property of granular activated carbon is abrasion resistance. A weak carbon may produce large losses in the filter operation, and the fine particles may cause complications in the distribution system.

The physical and chemical parameters are easy to guarantee by the producer. In the case of impurities, this guarantee is of hygienic and toxicologic importance; but we never have measured significant concentrations of those substances in activated carbons used by the German waterworks.

The pore volume of the carbon, especially the pore volume distribution [4,11] give information for equilibrium and kinetic properties. However, it seems to be more convenient for

Table 1

Test Methods for Activated Carbons

1. SAMPLING

2. MECHANICAL TEST METHODS
   - 2.1 Apparent Density
   - 2.2 Particle Size Distribution
   - 2.3 Abrasion Resistance

3. PHYSICAL AND CHEMICAL PARAMETERS
   - 3.1 Moisture
   - 3.2 Impurities

4. PORE VOLUME
   - 4.1 Densities
   - 4.2 Pore Size Distribution

5. COMPETITIVE ADSORPTION TEST

6. KINETIC TEST METHODS
   - 6.1 External Mass Transfer
   - 6.2 Effective Diffusion Coefficients

7. THERMOANALYTICAL TEST METHODS FOR SPENT CARBONS

the user to measure both properties directly by sorption tests (i.e., the competitive adsorption test and the kinetic test). These test methods will be discussed in detail later in this paper.

Finally, to characterize spent carbons, we find it suitable to use thermoanalytical test methods to determine significant parameters, not only for the characterization of the loading of spent carbons, but also for a subsequent regeneration.

For the adsorption behavior, several test methods were evaluated. Some of them, such as iodine number or molasses number, are described in the AWWA [5], ASTM [6], or the German DIN [7] standards. But, to get direct information about the adsorption capacity (e.g. m^3 water treatable with 1 m^3 of granular activated carbon), it was necessary to develop new methods beyond the known empirical ones. This new concept of testing granular activated carbon is presented in this paper.

TESTING ADSORPTION BEHAVIOR

From filter measurements, it is well known that weakly adsorbed substances are replaced by more strongly adsorbable substances. This effect was considered in the proposed method for a competitive adsorption test. Figure 1 shows the experimental results of such a test. Here, the loading of the carbons is plotted vs. the equilibrium concentration. The dashed lines represent the Freundlich isotherms of organic substances in natural water which enters the GAC filters. The carbon manufactured by Norit, indicated by the thick dashed line, has clear advantages over carbon NK 12, represented by the thinner dashed line.

The competitive conditions in a real filter are simulated by adding 1 mg/l p-nitrophenol (PNP) to the water under investigation. This admixture causes an evident change: the loading of organic substances in water (OSW) on Norit carbon decreases considerably, as shown by the thick solid line that represents the isotherm of OSW with the admixture of PNP, whereas the loading of OSW on NK 12 changes to a much lesser extent, as shown by the thin solid line. The adsorption of PNP from the same solution mixture is also different for both carbons: the NK 12 shows better adsorption characteristics than the Norit carbon.

Frick (9) explained how these equilibrium isotherms could be used to describe the adsorption behavior of multicomponent mixtures. Now it will be shown how the same data can be used to get representative information on the adsorption capacity of the carbons.

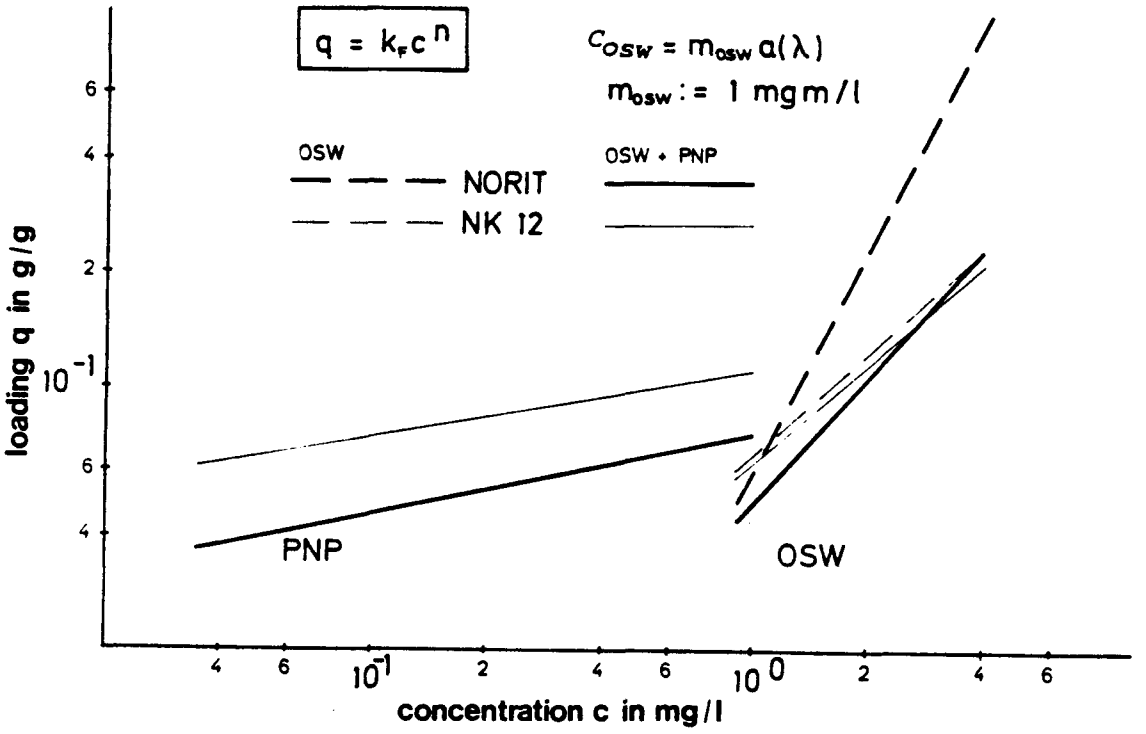

FIGURE 1

Comparison of the Equilibrium Isotherms of Two Different Activated Carbons.
PNP = p-nitrophenol, OSW = organic substance in water.

A practical evaluation method was developed by Martin, et al. (10). In this method, filter breakthrough behavior is predicted based on a model assumed of a total mixed reactor; therefore, only the filter influent concentration and two parameters of the Freundlich isotherm, K_F and n, are needed.

In Figure 2, the dimensionless concentration, c, is divided by the constant influent concentration, c_o, and is plotted vs. the throughput V_v, expressed as 10^3 m^3 water treated by one m^3 GAC. For a given throughput, an actual filter effluent concentration, as indicated by the upper line in the figure, is obtained. In treatment plants, filters with different carbon qualities, different operation times, and therefore different effluent concentrations normally work in parallel. The effluent of all these filters then is blended. To characterize the carbon under investigation for such a filter plant it is assumed that all the effluent from that given carbon filter is collected in the same tank. The concentration in this tank, which is the integral filter effluent concentration, is given by the lower curve. For comparison of different carbons, it is helpful to define a criterion for terminating a filter run; for example, a throughput where the integral filter effluent reaches a certain concentration. This parameter may differ for different treatment plants. Here, a purification of 75 percent, or a remaining concentration of 25 percent of the influent concentration is assumed as the significant test value, V_v*.

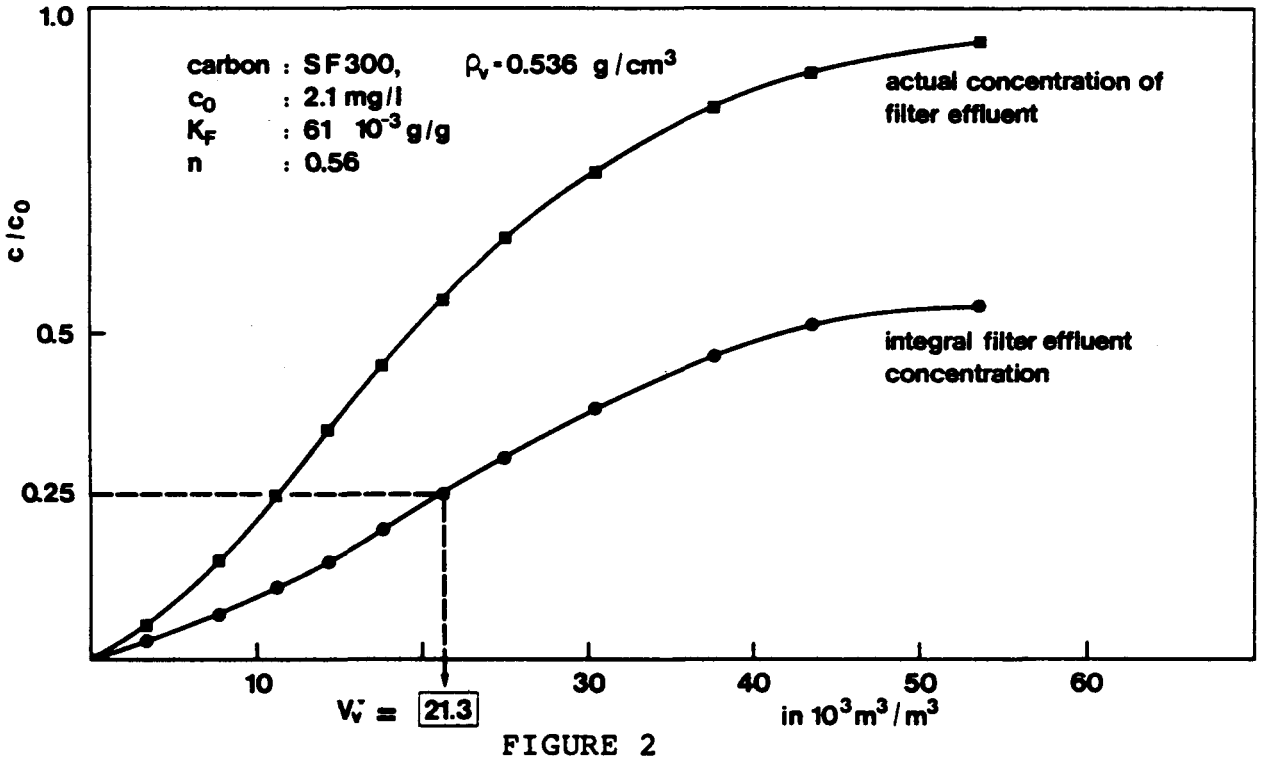

FIGURE 2

Determination of the Competitive Adsorption Test Data

The test method not only allows the comparison of virgin granular activated carbons, but also reactivated ones.

In Table 2, there are collected different test values for the OSW and PNP equilibrium data obtained by the competitive adsorption test and by the former explained procedure. In the first section of Table 2, four carbons of the same type, but reactivated in different reactivation plants, are compared with SF 300. There are no significant differences in the V_v^*-OSW throughput values, but there are in the V_v^*-PNP data. It seems that the V_v^*-PNP test values are of great importance for reactivation control. This will be illustrated later in this paper.

To make the competitive adsorption test useful for the producer and to make comparison possible for water utilities, we have tried to find a substance that represents the organics in the waters to be treated. After a long series of experiments we obtained good results with flocculated lignin sulfonic acid (LSA). In the second section of Table 2, where those values are listed, slight differences are found between the V_v^*-values for LSA but significant differences are found in the values for PNP.

In the last section of Table 2 the test values of various virgin GAC's are given in order to demonstrate the possible range of the test results. Those values differ for LSA between 45×10^3 m^3 treated water per m^3 GAC for the best carbon, down to 11×10^3 m^3/m^3 for a less effective one. It is also possible to distinguish between the different selectivities of the carbons. The LSS 1.5 seems to be especially effective for removing PNP.

It is obvious that good reactivation is possible. The data from the reactivated carbons in the second section of Table 2 do not differ significantly from those of the virgin carbons in the last section.

As mentioned earlier, a smaller V_v^*-PNP value implies a lesser suitability for water-treatment purposes. For more information about this effect, we have analyzed the pore structure of various types of GAC. The Freundlich coefficient, K_F of PNP, the K_F of crystal violet (KV) dye stuff, and the iodine number were correlated with the microporous volumes of those carbons. These microporous volumes are defined by an upper pore radius. The results are shown in Figure 3, in which the K_F values and the iodine numbers are plotted vs. the pore volume expressed in mm^3 per g GAC. It is obvious that a small K_F or a small iodine number is due to a small pore volume. Hence, it follows that it is important in the activation of virgin carbons and the reactivation of spent carbons to choose the conditions for reactivation in such a way that the microporous volume is in the desired range.

Table 2

Competitive Adsorption Test Data

A. CARBON	WATER	V^*_{VOSW} $10^3 m^3/m^3$	V^*_{VPNP} $10^3 m^3/m^3$
SF 300	OSW - BENRATH + PNP	21	54
R 6		19	24
R 7		19	22
R 8		16	26
R 16		26	39
SF 300	LSA + PNP	16	52
R 6		21	23
R 7		17	11
R 8		18	23
R 16		17	45
LSS 3	LSA + PNP	11	25
LSS 1.5		13	60
NORIT SM		21	22
NK 12		20	34
CHEM 5		45	30

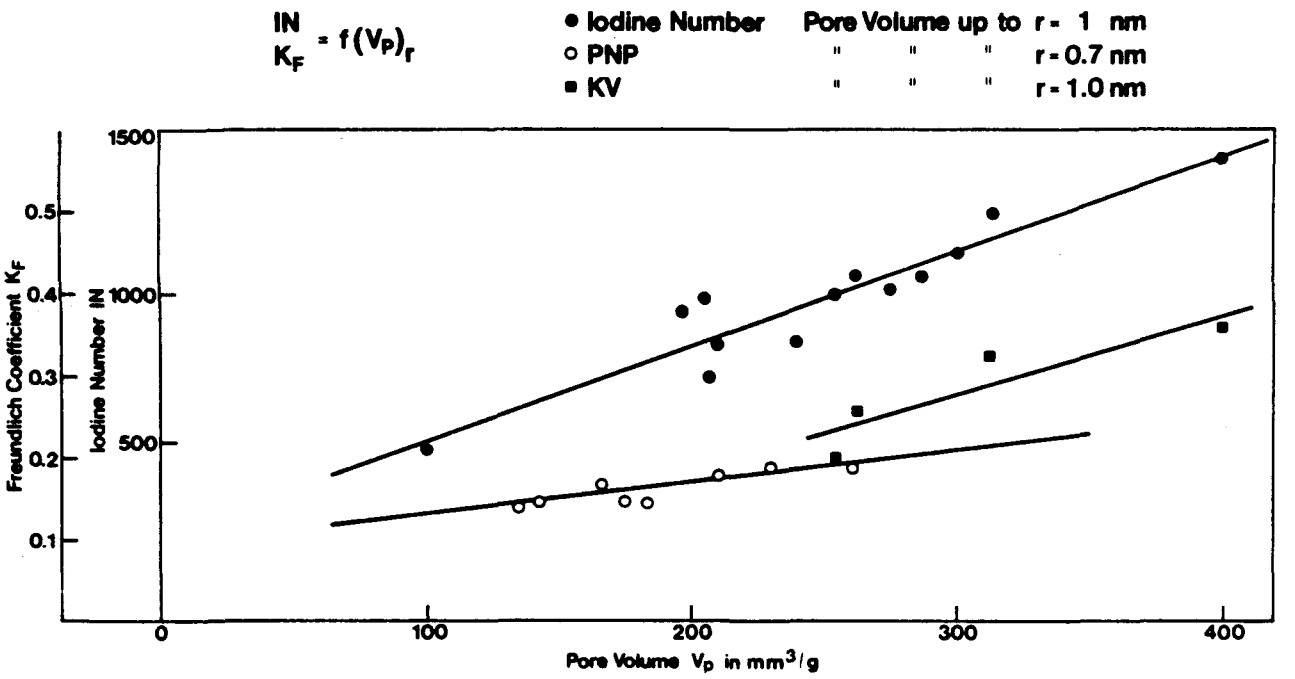

FIGURE 3

Correlation Between Micropore Volume and Freundlich Coefficient or Iodine Number

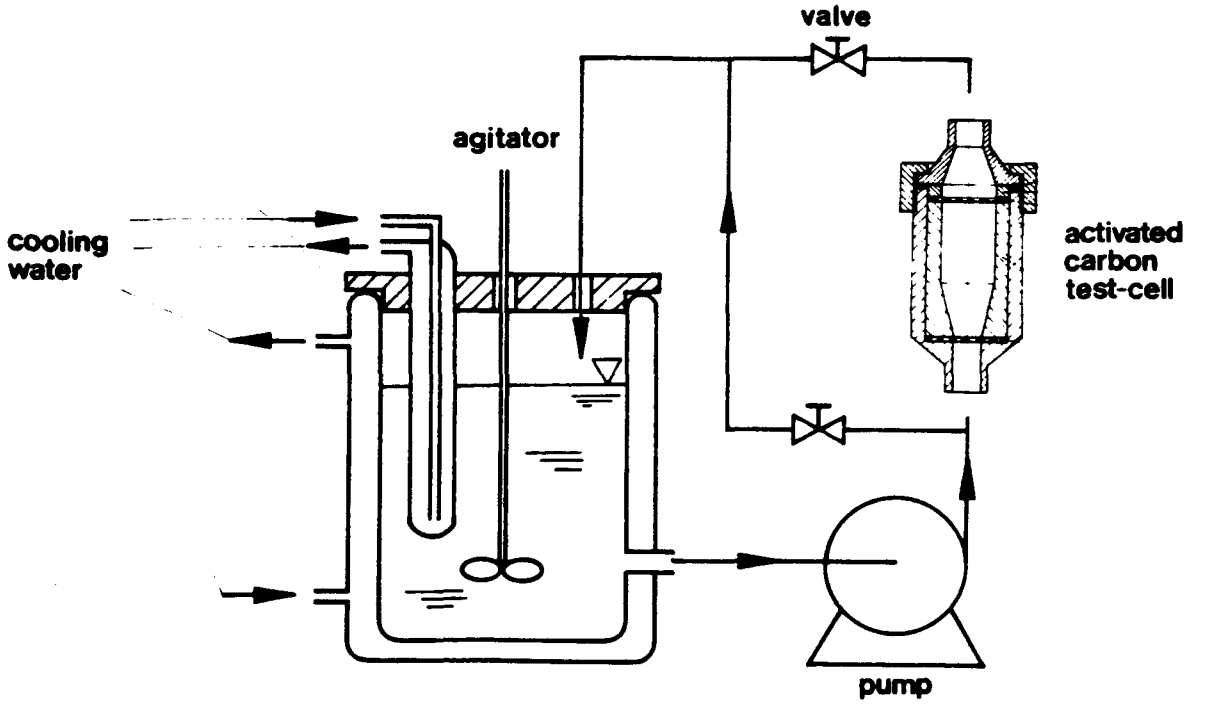

FIGURE 4

Apparatus for Kinetic Tests

In many cases, not only the equilibrium characteristics of a carbon, but also the kinetic behavior are of considerable importance. The apparatus shown in Figure 4 was developed for a kinetic test which would supply data that can be used for filter breakthrough behavior prediction. Therefore, the test solution is pumped from a double-walled tempered breaker through the activated carbon test cell, in which the thin layer of carbon is fixed to avoid abrasion.

For kinetic measurements, it is possible to distinguish between two rate-limiting steps in GAC treatment, namely:

1. The transport of organics from the bulk solution through a boundary layer to the carbon particle (external mass transfer), and

2. The diffusion of adsorbed substances within the carbon.

We have studied the external mass transfer resistance for various types of GAC and different substances. Figure 5 presents the results for PNP. Here, the measured mass transfer

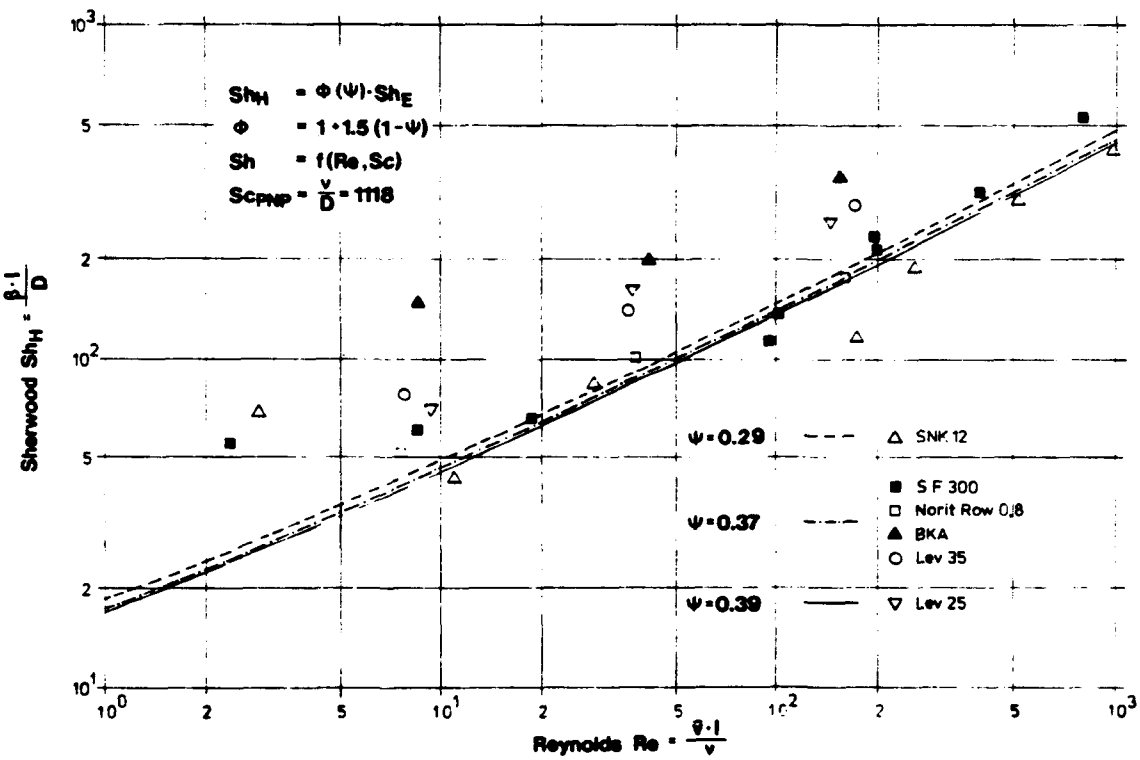

FIGURE 5

Sherwood Numbers for Different Carbons Compared with Gnielinski's Correlation

coefficients, designated as β, are expressed by dimensionless Sherwood numbers, and the fluid velocity within the test cell is expressed by Reynolds numbers. The dashed and solid lines are calculated for different bed porosities from Gnielinski's (14) correlation. This correlation for heat and mass transfer in packed beds has been verified for many similar chemical engineering problems. It is obvious that the Sherwood numbers for our experiments are higher than the values predicted by the correlation. This leads us to the idea to take into consideration an additional surface which originates from the outer pores of the activated carbon particle and to correct the measured mass transfer coefficients to account for these areas.

The effective surface area can be determined by an independent experiment based on mercury porosimetry or by a rapid kinetic test with a substance of known diffusivity in the bulk liquid. Thus, it becomes possible to predict the mass transfer coefficients for different fluid velocities and different GAC types.

Besides the external mass transfer, the transport within the carbon particle is also of importance for the adsorption kinetics as shown by Baldauf (13). This overall mass transfer can be described by the homogeneous diffusion model as explained by Merk (8). In this model, there is only one adjustable parameter, the effective diffusion coefficient, D_{eff}. This effective coefficient is another significant kinetic test value in this concept.

In Figure 6, the dimensionless concentration is plotted vs. time. The points are the measured concentrations, and the solid line was calculated with the homogeneous diffusion model. The effective diffusion coefficient was evaluated for the best fit. In the tabulation included in Figure 6, the diffusion coefficients, as determined by this kinetic test, are given for four different carbons. Three of them were reactivated samples. The obtained values vary from 3.3×10^{-15} m^2/sec to 6.1×10^{-15} m^2/sec.

With these three test methods, it is possible to predict filter breakthrough curves for substances if their diffusivities in the bulk liquid are known; it is important to have this capability. In practice, however, we are not concerned with single-solute solutions, of which we know the bulk liquid diffusivity, but rather with unknown multicomponent systems of indefinite composition. Before further calculations are possible, the effective diffusivities of the mixture components must be known or a mean diffusion coefficient has to be estimated. This

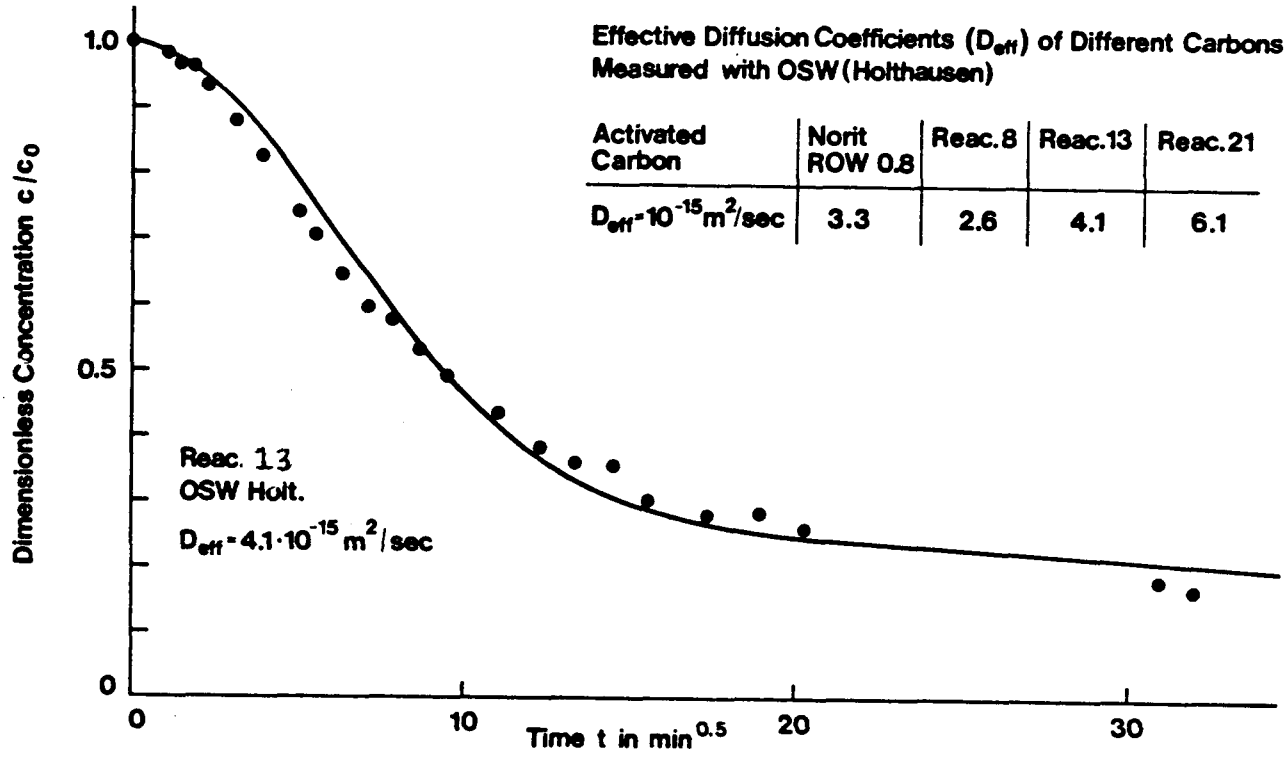

FIGURE 6

Determination of the Surface Diffusion Coefficient

becomes possible together with the above mentioned correlation of Gnielinski, if carbon properties are known. Table 3 illustrates that a given water, analyzed with different GACs, is characterized in all tests by the same bulk diffusivity, D_{-10}, for the organics. The mean value was in this case 1.0 x 10^{-10} m^2/sec. On the other hand, we measured different diffusion characteristics for different waters using the same carbon. The analyzed waters were taken from carbon filter influents from Langenau, Mulheim, and Stuttgart.

With this method, it also becomes possible to determine the influence of water treatment on the mean bulk diffusion coefficient of the remaining organics. In the lower part of Table 3, it is shown that significant differences exist between the raw water and the water after ozonization and filtration. There is a considerable improvement in view of the adsorption kinetics expressed by the bulk diffusivity of the organics in treated waters from different Dusseldorf treatment plants. The bulk diffusion coefficient increases from 1.0 x 10^{-10} to 5.1 x 10^{-10} m^2/sec at the Flehe treatment plant, and from 0.9 x 10^{-10} to 3.9 x 10^{-10} m^2/sec for the Holthausen plant.

TABLE 3

Diffusion Coefficient (D_L) of Different Organics in Water

Water	Activated Carbon Norit ROW	Reac.8	Reac.21	Reac.13	Mean Value
Holt.	1.0	1.2	0.9	0.9	1.0
Lang.	2.9				
Mül.	0.6				
Stutt.	0.5				

INFLUENCE OF TREATMENT ON THE DIFFUSION COEFFICIENT

Water	Raw Water	after Ozonation and Filtration
Flehe	1.0	5.1
Holt.	0.9	3.6

$[D_L] = 10^{-10} m^2/sec$

All the significant parameters which are necessary to describe the adsorption behavior of granular activated carbons have been discussed. Figure 7 is a schematic diagram of the proposed test concept.

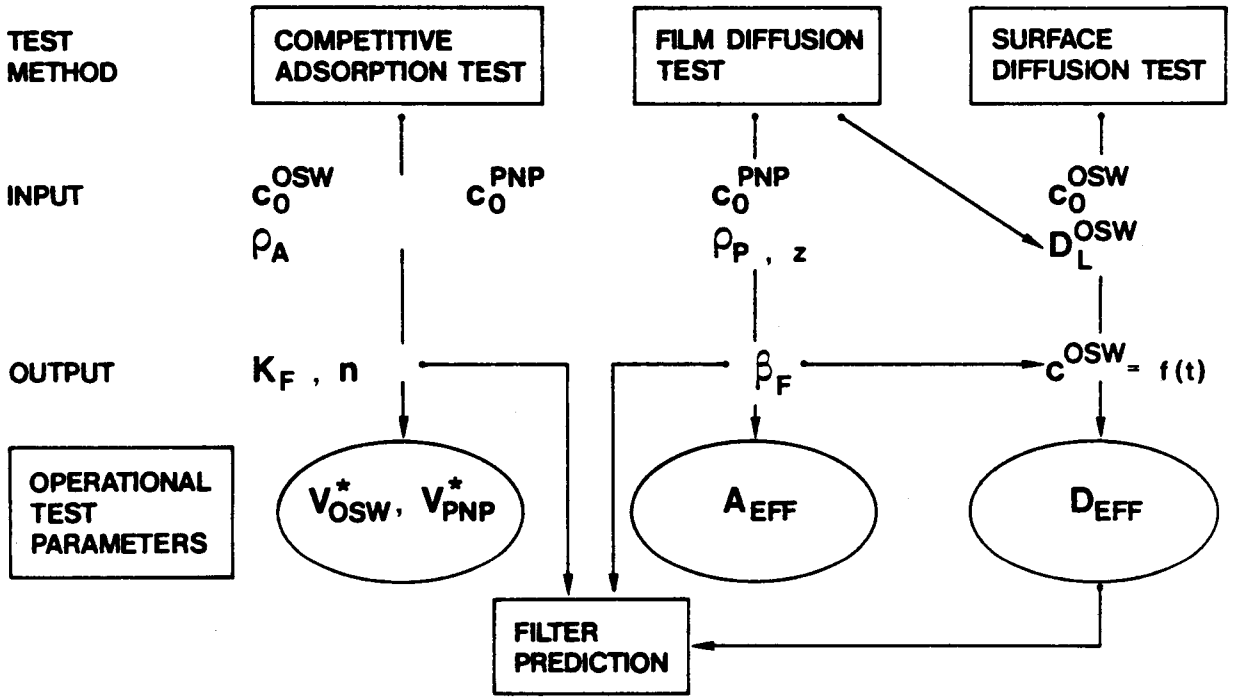

FIGURE 7

Test of Adsorption Behavior of Activated Carbon

First, we have to evaluate the equilibrium parameters, K_F and n. Frick (9) has shown how to determine those parameters for multicomponent solutions. For comparison and classification of different carbons, we can calculate the V_V^*-OSW and the V_V^*-PNP values corresponding to m^3 water treated per m^3 GAC. Secondly, we can determine a mass transfer coefficient with the film diffusion test and evaluate an effective external surface area A_{eff}. Finally, we can measure an effective diffusion coefficient as a characteristic value for the internal kinetic behavior of the carbon under investigation.

With the results of the granular activated carbon tests and the diffusion characteristics of the organics in the bulk liquid, it is possible to predict filter breakthrough curves of unknown multicomponent solutions, as discussed by Baldauf (13).

ACKNOWLEDGEMENT

I would like to express my thanks to the waterworks of Düsseldorf, Wuppertal, and Cologne, and to the Ministry of Research and Technology of the German Federal Republic for their support in this work.

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PREDICTION OF BREAKTHROUGH PATTERNS OF ORGANICS FROM LABORATORY TESTS

Dr. Günther Baldauf

The papers by Merk, Frick, and Holzel presented different aspects of dealing with the problem of multicomponent mixtures of organics in waters to be treated for drinking water purposes. The following views are widely accepted:

1. The efficiency of granular activated carbon filters can be predicted for mixtures containing two or three single components, using equilibrium and kinetic data for the single components only.

2. Multicomponent mixtures of organics as they are found in our natural waters can be described as a mixture of two or three single groups of organics, each group representing a range of adsorption behavior.

3. While this division into groups is possible for the equilibrium data, we have also been able to determine adsorption kinetic data for multicomponent mixtures.

By using this knowledge, we can predict the breakthrough behavior of waterworks filters.

LABORATORY TESTS

To study these problems, special filter tests have been made in Karlsruhe. They allow a comparison between experimental data and precalculated concentration profiles, thus showing whether the methods discussed so far are worthwhile when applied in practice. Two different types of activated carbon were used for the experiments. The adsorption isotherms are shown on a log-log scale in Figure 1.

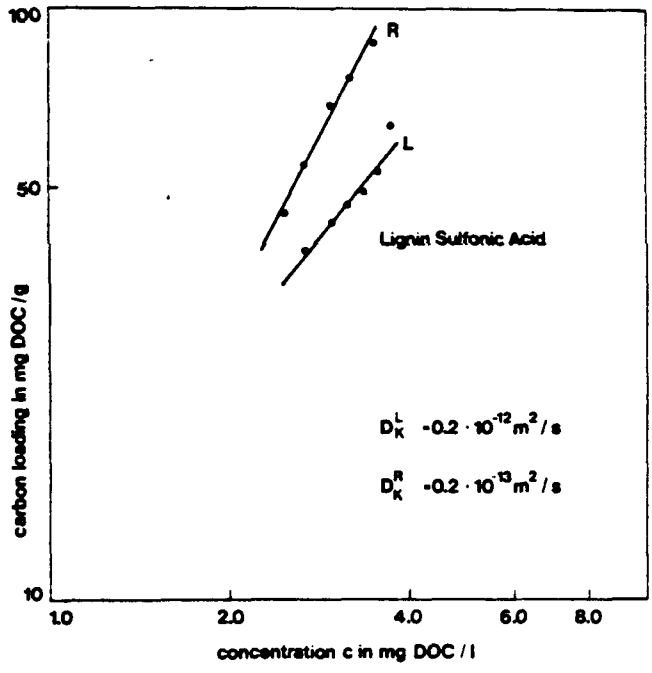

Figure 1. DOC-Isotherms of LSA for Two Activated Carbons

A lignin sulfonic acid solution (LSA) from which the high-molecular components were removed by flocculation was used in these experiments. As indicated by Hölzel (1), this mixture of lignin derivatives behaves similarly to organic substances in Rhine-water during adsorption. Two types of activated carbon were studied. One can see from Figure 1 that of the two carbon types, the adsorption capacity of the carbon R is considerably better. Therefore, this carbon should produce the better results in an activated carbon filter. If one compares the two internal diffusion coefficients, which are also shown in Figure 1, one can see that the carbon L, which adsorbs less strongly as evidenced by the equilibrium isotherms, has a much better kinetic behavior than the carbon R. Exactly the same tendencies are found if UV absorption is used as a measure for concentration instead of dissolved organic carbon (DOC). As a consequence, the isotherms are less steep, and according to Frick (2), mainly those substances which behave as a single solute will be covered by UV absorption, as far as adsorption is concerned. To learn how the two activated carbons behave in an activated carbon filter, experiments were made with a pilot-plant filter.

A plexiglass column with an inner diameter of 52 mm and a height of 1.50 m was used. The depth of the carbon layer was 1 m. Sampling tubes were installed at intervals of 10, 30, 50, 70 and 90 cm. The filter velocity was 10 m/h. A lignin

sulfonic acid solution containing 4 mg DOC/l was fed to the filter. The concentration of lignin sulfonic acid was analyzed spectrophotometrically at 280 nm. Parallel to this, the DOC value of all samples was measured.

In Figure 2 the experimental UV breakthrough curves of the two activated carbon filters are shown. In the ordinate of this diagram the UV values for two bed heights related to the UV values of the influent are plotted above the period of operation of the filter. One can see that the UV-active substances in the filter containing the carbon with poorer kinetics but a better equilibrium behavior will produce an earlier breakthrough. This example shows clearly that it is important to observe the adsorption kinetics for the adsorption in the fixed-bed adsorbers. For a comparison of carbons of different kinetic behavior, it is not enough to use equilibrium data only for the characterization of activated-carbon quality. To check whether the adsorption process in the column is film-diffusion controlled, the breakthrough curves were calculated using the film diffusion model. This model was used because Merk (3) had shown that the adsorption of low-molecular weight substances is film-diffusion controlled.

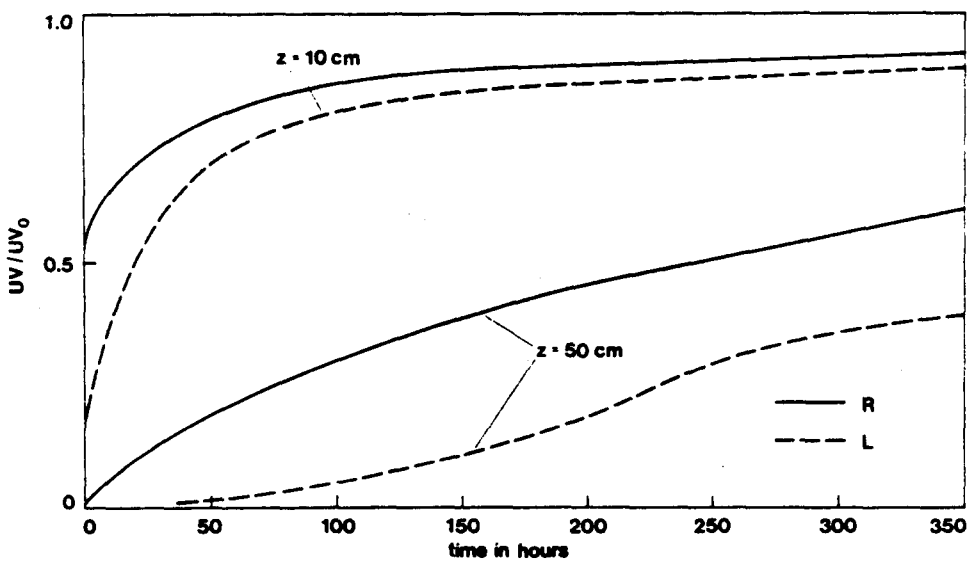

Figure 2. UV-Breakthrough Curves for Two Activated Carbons

In Figure 3 the calculated concentration profiles at different bed heights are plotted. Beside the calculated curves, the measured points are also shown. Apart from the initial period, the UV-active substances in the filter have a quicker breakthrough than would be expected from the

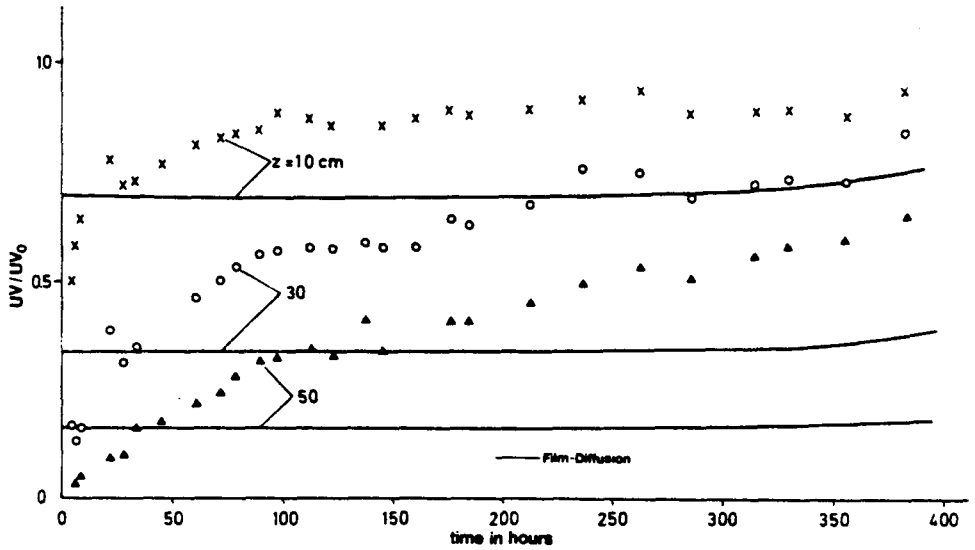

Figure 3. UV-Breakthrough Curves for Lignin-Sulfonic-Acid (Activated Carbon R). Experimental data are compared with curves calculated by the film diffusion model [3]. The parameter--10,30, and 50 cm--refers to the sampling depth in the activated carbon bed.

calculation. This earlier breakthrough can be explained by an additional solute transport resistance within the carbon grains.

Whereas with the simple film diffusion model it is assumed that the entire transport resistance takes place within the film covering the carbon particle, the film homogeneous diffusion model takes into consideration an additional transport resistance within the grain. Despite the low overall concentration, the transport resistance has to be taken into account because of the relatively high molecular weight of the sorbing substances. For the calculation of the breakthrough curves according to the film homogeneous diffusion model the diffusion coefficient D_K within the carbon particle must be known. This can be obtained simply from the reaction- and time-curve.

In Figure 4, the curves calculated with this model are plotted in addition to the measured points. Taking into account the internal mass transport resistance within the carbon particle, a good description of the experimental results can be obtained.

So far, the lignin sulfonic acid has been regarded as a single-solute substance. This simplifying assumption is

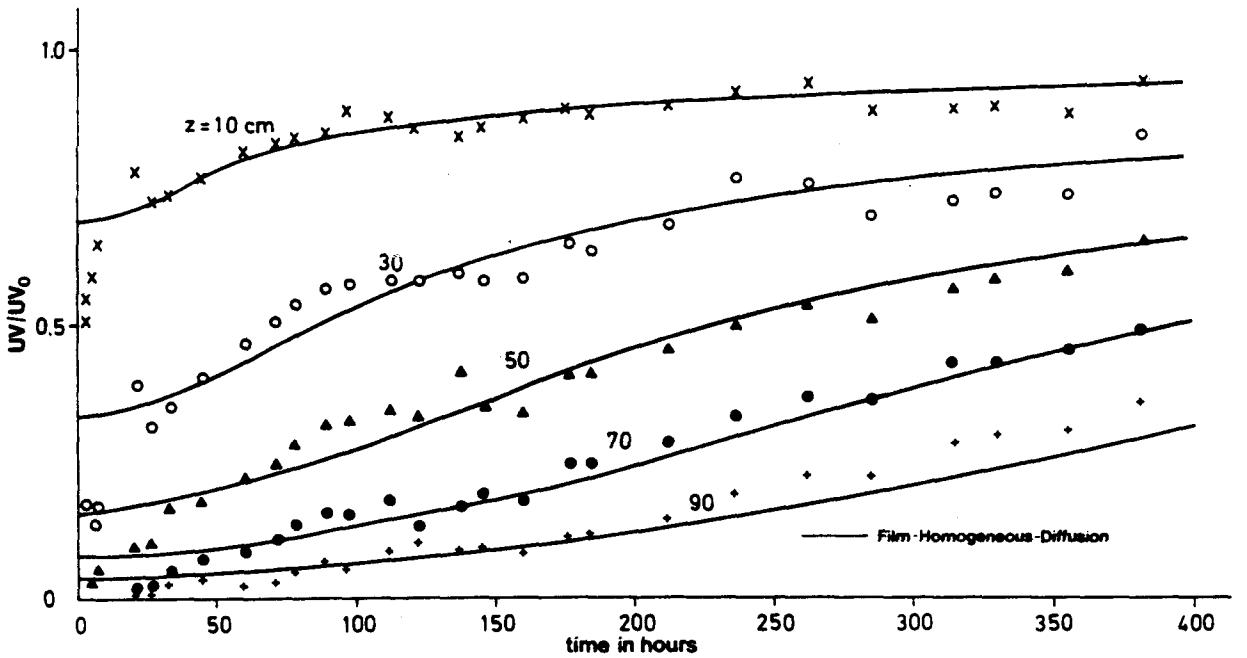

Figure 4. UV-Breakthrough Curves for Lignin-Sulfonic-Acid in a Pilot Plant (Activated Carbon R). The parameter—10, 30, 50, 70, and 90 cm—refers to the sampling depth in the activated carbon bed. Experimental data are compared with curves calculated by the film-homogeneous diffusion model (3).

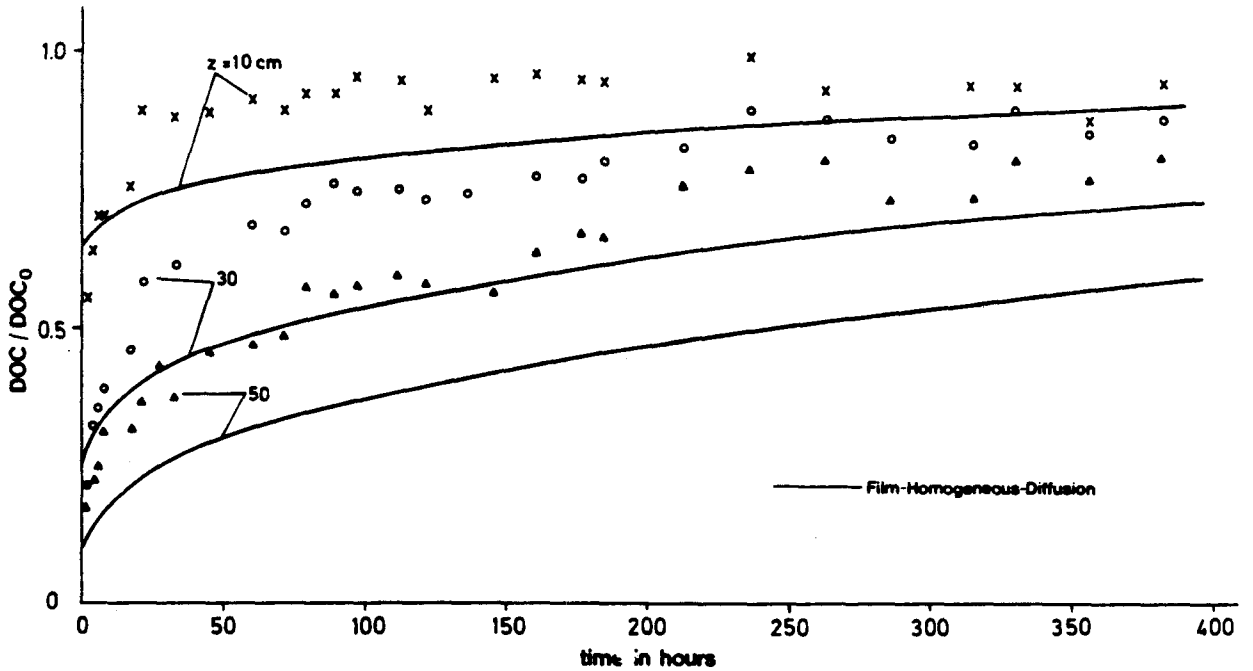

Figure 5. DOC-Breakthrough Curves for Lignin-Sulfonic-Acid in a Pilot Plant (Activated Carbon R). The parameter—10, 30, and 50 cm—refers to the sampling depth in the activated carbon bed.

justified here since a mere fraction of the total substance can be detected spectrophotometrically. These compounds differ only slightly from each other. If the DOC value instead of UV adsorption is used as a measure for the concentration, systematic deviations between measured values and those calculated from the film homogeneous diffusion model will result. This can be seen in Figure 5.

The DOC breakthrough predicted by the film homogeneous diffusion model are plotted together with the experimental data. The earlier breakthrough in the pilot plant filter may be explained by assuming that only part of the components that are detected by DOC measurement are easily adsorbed, whereas compounds more difficult to absorb cannot be retained in the filter. For this reason, the lignin sulfonic acid was divided into fractions which are easy or difficult to absorb, in accordance with the method suggested by Frick [2]. Figure 6 indicates the breakthrough curves calculated by using the film homogeneous diffusion model, assuming such a two-component mixture.

The good agreement with the measured points in Figure 6 shows that the description of the DOC breakthrough curves is also possible for complex mixtures of substances if they are divided into two groups.

Apart from the high-molecular-weight compounds, represented here in the form of lignin sulfonic acid, the undesired and in some cases toxic low-molecular-weight compounds must also be removed in an activated carbon filter. The following is a demonstration of how these species, mostly present in low concentrations only, behave. P-nitrophenol was selected as a model substance for these low-molecular compounds because it can be analyzed quickly and exactly, and because its properties are similar to the aromatic chlorinated compounds which are of particular importance in the Rhine River.

Filter tests were made in the pilot plant with a mixture consisting of lignin sulfonic acid with a DOC concentration of 4 mg DOC/l and 1 mg/l of p-nitrophenol. The DOC concentration and the UV absorption were measured at the inlet and at several sampling points along the column.

With these data the concentration of both substances can be calculated. The breakthrough patterns of p-nitrophenol are plotted in Figure 7. Assuming that there is no mutual influence between the two substances in the adsorbed phase, the breakthrough curve No. 1 is calculated. A comparison with the measured points shows that this simplified assumption does not hold, because the p-nitrophenol breaks through much earlier. On the other hand, by regarding p-nitrophenol as a single-solute substance, which is adsorbed from an aqueous lignin sulfonic

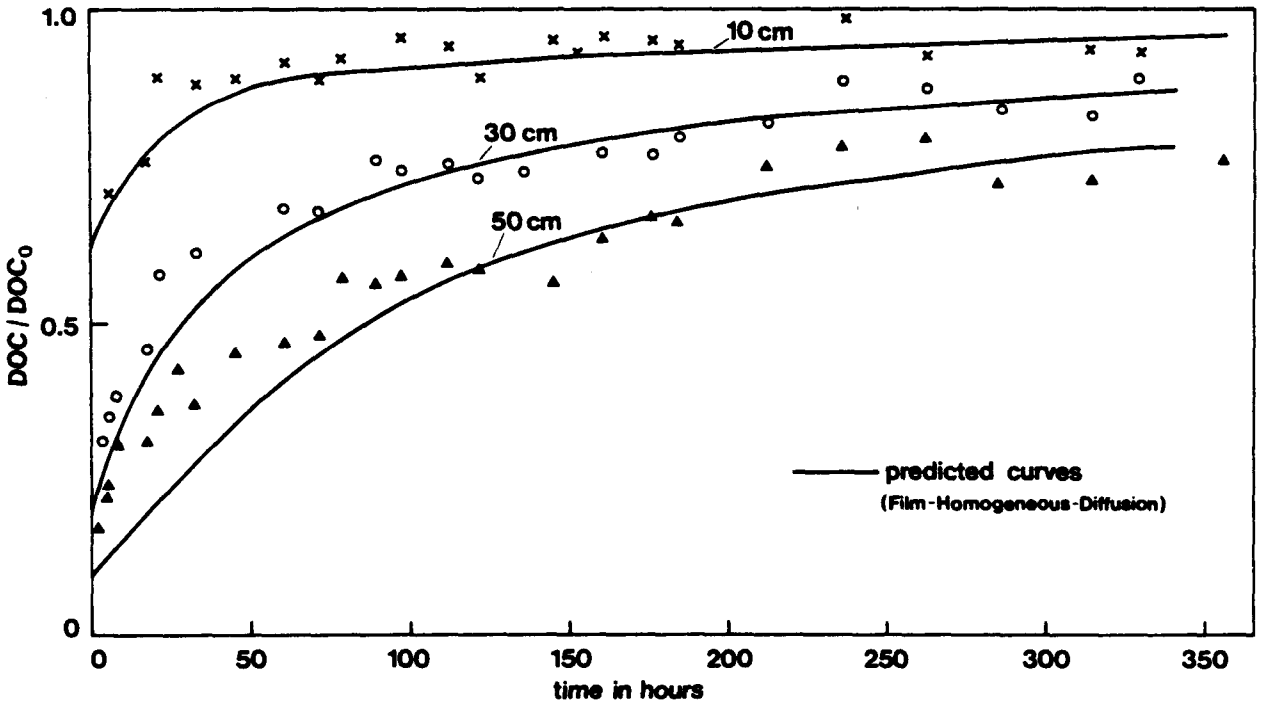

Figure 6. DOC-Breakthrough Curves for Lignin-Sulfonic-Acid in a Pilot Plant (Activated Carbon R).

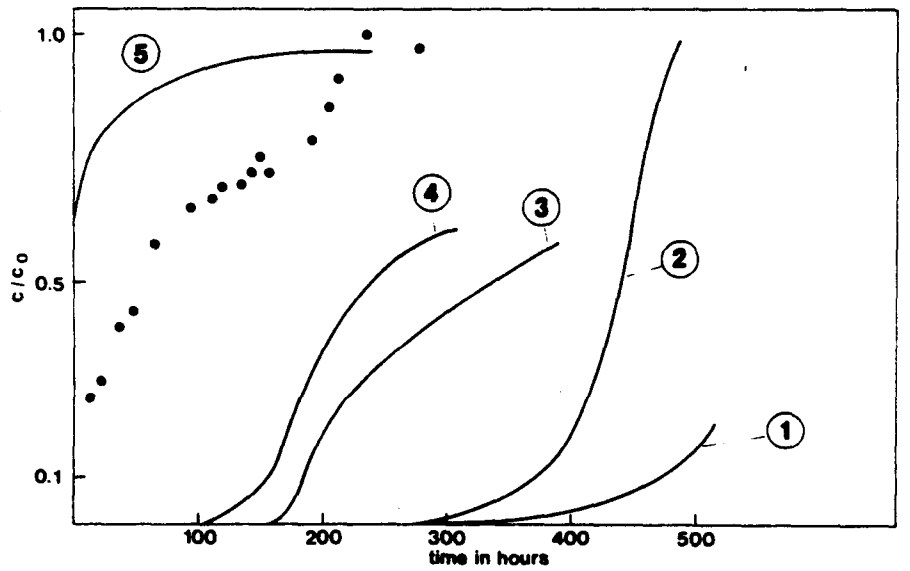

Figure 7. Breakthrough Curves for p-nitrophenol (PNP) in Presence of Lignin-Sulfonic-Acid (LSA) By Activated Carbon R . Closed circles are experimental data. Calculated curves: 1) no interaction between solutes, 2) regarding PNP as a single solute in aqueous LSA solution, 3) considering competition between PNP and LSA, 4) considering competition between PNP and the better adsorbable portion of LNA, and 5) considering competition between PNP and both portions of LSA.

acid solution, curve No. 2 will result. Nevertheless, this curve also shows a large deviation from the data. The third possibility is to calculate the concentration profiles of the lignin sulfonic acid and of p-nitrophenol as a two-component mixture with the film homogeneous diffusion model, taking into account a mutual competition in the activated carbon filter, with the result shown in curve No. 3; the results obtained are still unsatisfactory. The reason why it was not possible in cases 1, 2, and 3 to describe the measured concentration profiles is that the lignin sulfonic acid was treated as a single-solute substance. However, the fact that this simplification is not permissible has also been shown by the results obtained with the pure lignin sulfonic acid. For this reason the lignin sulfonic acid will subsequently be treated as a two-component system, consisting of a well- and a poorly-adsorbable portion.

If the better-adsorbable component of the lignin sulfonic acid only determines the breakthrough behavior of p-nitrophenol, then curve No. 4 in Figure 7 will result. It is shown that the better-adsorbable part of the lignin sulfonic acid, amounting to about 10 percent of the total substance, contributes decisively to the early breakthrough of p-nitrophenol. The deviations, arising even here, seem to indicate that the less-adsorbable part of the lignin sulfonic acid, amounting to about 90 percent, also competes with the p-nitrophenol. A precalculation of the measured concentration profiles will be possible only if the less-adsorbable component is also taken into account.

The precalculation of three-component mixtures is relatively complicated. Therefore, the attempt was made to regard, mathematically, the three-component- as a two-component mixture. As the less-adsorbable portion of the lignin sulfonic acid is insufficiently retained in the filter, it can be assumed that for p-nitrophenol and for the better adsorbable component of the lignin sulfonic acid, the activated carbon will be in equilibrium with the concentration of the poorly-adsorbable component of the lignin sulfonic acid. A comparison of the calculated curve No. 5 with the measured points shows that with this kind of calculation an earlier breakthrough is achieved. In this connection it must be mentioned that in calculating the p-nitrophenol breakthrough shown in Figure 7 the very low diffusion coefficient of the lignin sulfonic acid was used. On the other hand, by applying the diffusion coefficient of p-nitrophenol in the presence of lignin sulfonic acid for the calculation of the concentration profiles, a better adjustment of the experimental data can be obtained.

The UV breakthrough curves of the lignin sulfonic acid in the presence of p-nitrophenol, shown in Figure 8, were calculated by using the single-solute isotherms only. The good agreement with the measured points can be explained by the fact

that the lignin sulfonic acid is only slightly displaced by p-nitrophenol.

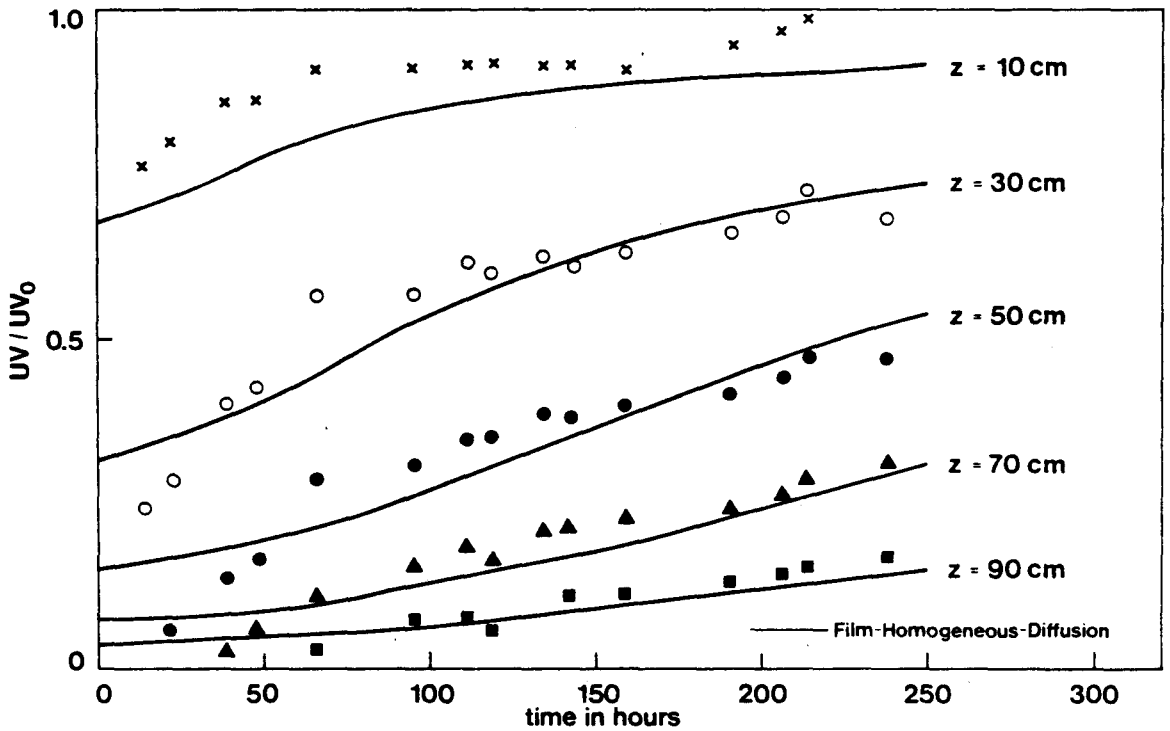

Figure 8. UV-Breakthrough Curves for Lignin-Sulfonic-Acid in Presence of p-nitrophenol (Activated Carbon R).

SUMMARY AND CONCLUSIONS

The investigations have shown that it is possible to predict the breakthrough behavior of complex mixtures in a pilot-plant filter. The aim of future studies will be to predict the breakthrough behavior of waterworks filters in the same way as discussed here. This seems to be fairly simple if the filters are working with adsorption only. If, in addition, biological processes occur in a filter (as is generally observed), these processes have to be taken into account because an additional mechanism exists for removal of organic substances in the activated carbon filter. Investigations in a new research program will also need to consider the influence of ozone on biodegradation.

Use of the methods already discussed, can help to optimize existing plants, as well as a proper control of the efficiency of the regeneration processes.

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PREDICTION OF FULL SCALE PLANT PERFORMANCE FROM PILOT COLUMNS

Jack DeMarco
and
Noel Brodtmann

INTRODUCTION

The purpose of this paper is to compare pilot granular activated carbon (GAC) column data with full scale activated carbon bed data from a field investigation sponsored by the U.S. Environmental Protection Agency. The literature does not contain reports of a very large data base that shows the results of parallel operation of pilot and full scale activated carbon beds for removal of a variety of organic substances. This paper describes an effort to compare pilot and full scale activated carbon beds for removing a variety of organics with the objective of providing the needed data for ultimate full scale design.

ANALYSES AND SYSTEM DESCRIPTIONS

Analyses were performed for purgeable halogenated organics collected by purge and trap techniques and for substances described by general parameters such as Total Organic Carbon (TOC) and Trihalomethane Formation Potential (THMFP) [1]. For research purposes, several criteria for comparison were selected that compare the effluent quality of the activated carbon systems at different points of the resultant breakthrough curves. Data presented include concentrations of:

1. Total Organic Carbon (TOC)
2. Trihalomethane Formation Potential (THMFP)
3. Chloroform
4. 1,2-Dichloroethane

These were the substances that occurred most frequently and at the highest concentrations. The granular activated carbon units, located at Jefferson Parish, Louisiana, are being studied by personnel at the water treatment plant.

Figure 1 is a flow diagram showing the full scale unit processes at the study site. The water source is the Mississippi River. The raw water is pumped to the plant site where potassium permanganate is added for taste and odor control. Next a cationic polymer is added as the primary coagulant. As the water enters the flash mixing chamber, a low dosage of lime is added for pH adjustment and a ferrous salt used at times for alkalinity control. The water then passes through an upflow precipitation process for removal of floc and lime precipitated hardness. The water is then disinfected during transport to the sand filters by addition of chlorine and ammonia as shown. Only chloramine disinfection is practiced, which accounts for the generally low trihalomethane (THM) concentrations present in the finished water. Sand filtered water passes through the clearwell and is either pumped directly to the distribution system or to on-site reservoirs.

The 30 in (76 cm) of filter sand was removed from one existing sand filter and replaced with 30 in (76 cm) of WVG 12 x 40 mesh granular activated carbon (GAC). The bed received coagulated, settled, and disinfected water and is referred to in this paper as a filter/adsorber (sand replacement system) because it performs both the filtration and adsorption process.

Two other existing sand filters were connected in series operation. The 30 in (76 cm) of filter sand was removed from the second bed in series and the sand was replaced with 30 in (76 cm) of WVG 12 x 40 mesh GAC. This activated carbon bed received water that was coagulated, settled, disinfected, and sand filtered. The activated carbon bed is referred to in this paper as an adsorber (post-filter adsorber) because it primarily performs the adsorption function and does not serve the purpose of filtration. Samples for the full scale beds were routinely analyzed at the sample points shown in Figure 1.

Figure 2 shows a schematic configuration of the pilot granular activated carbon column system and full scale activated carbon beds studied during the phase of the project completed in January, 1979. The pilot adsorber and pilot filter/adsorber received the same influent water as their full scale counterparts. The activated carbon bed depths were the same as the full scale systems on initiation of the study. The objective was to attempt to match the empty bed contact time

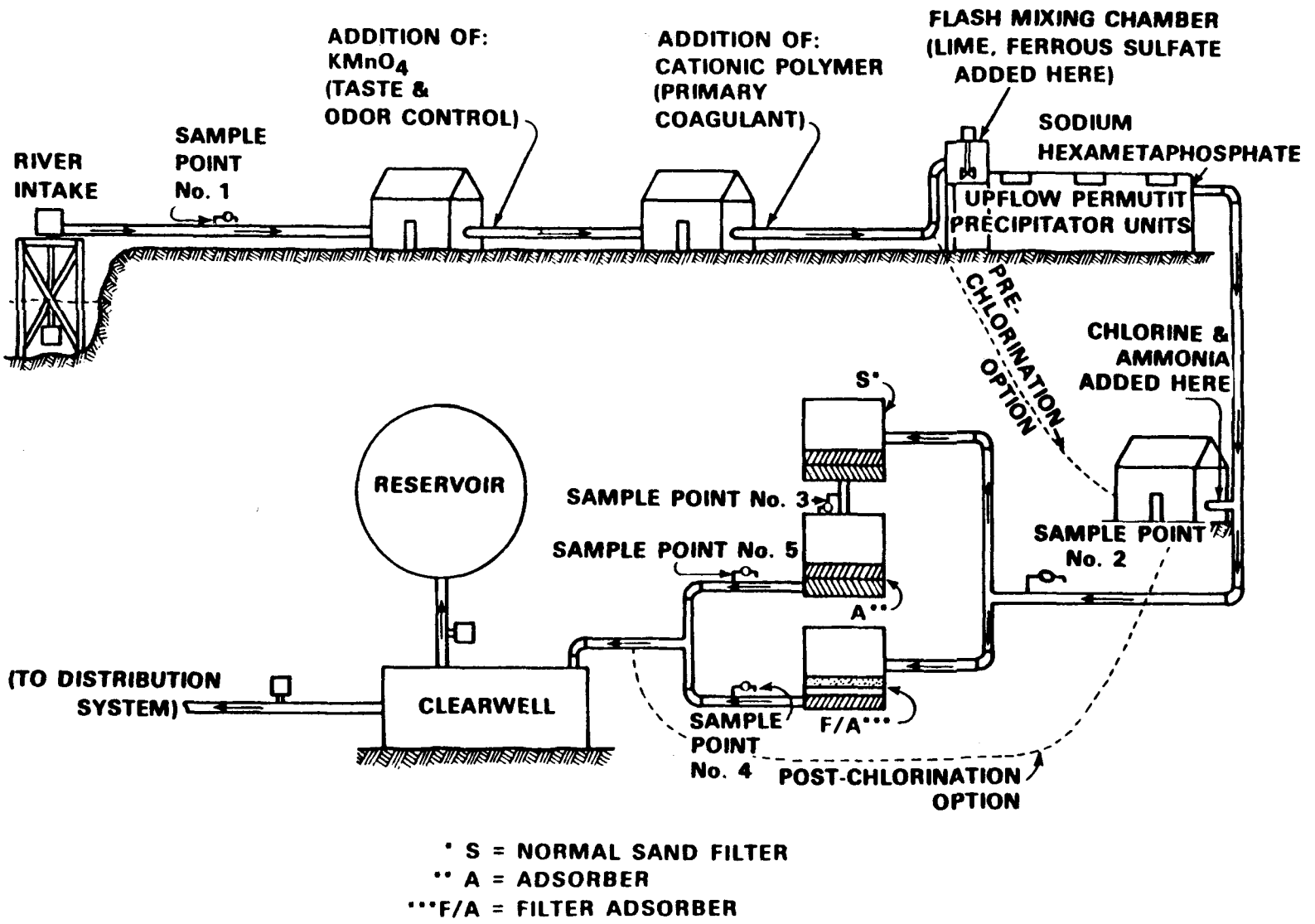

Figure 1. Plant Flow Chart, EPA-JPWD Organic Removal Study

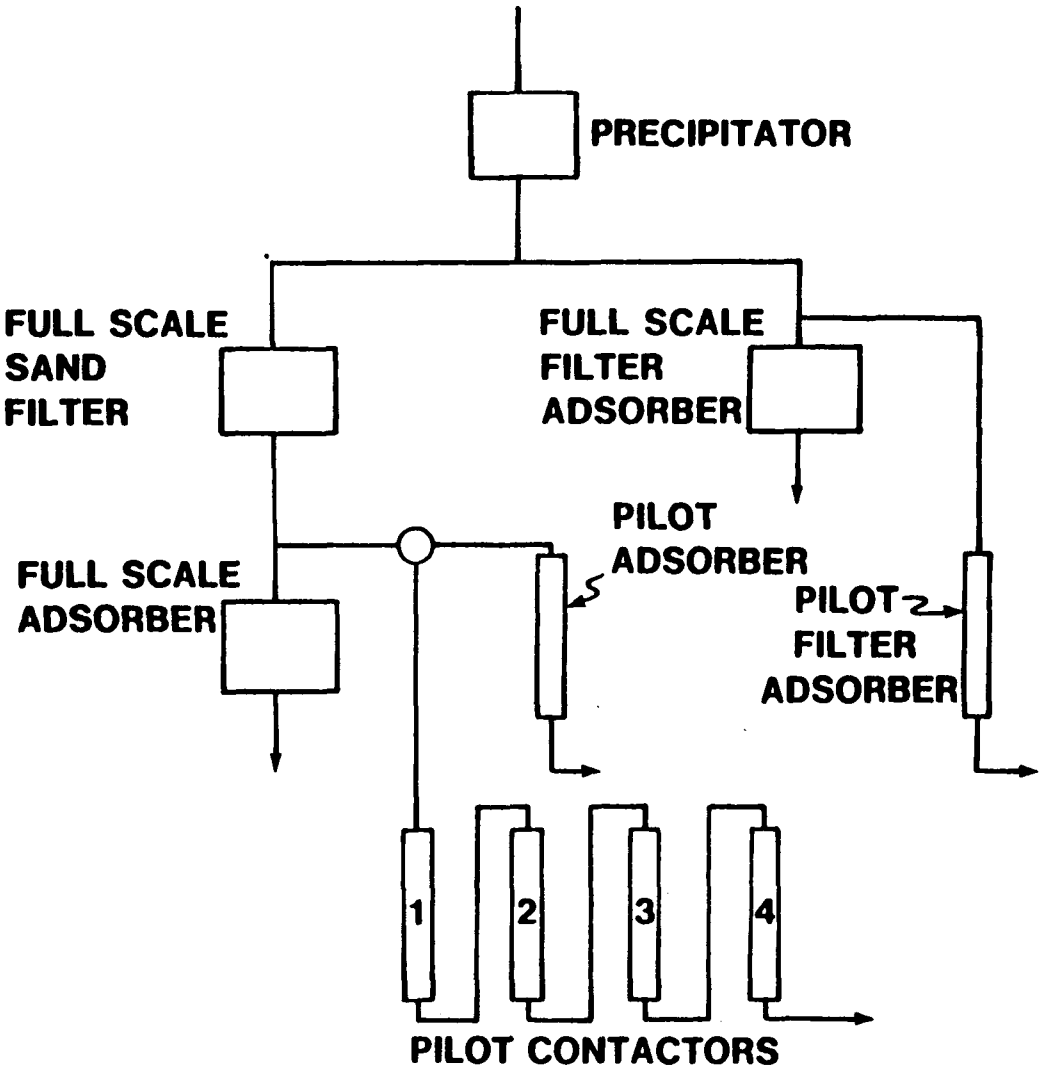

Figure 2. Schematic of Carbon Units

(EBCT), hydraulic loading rates, and operation of each set of pilot columns with their respective full scale system.

A set of pilot columns connected in series was also operated to provide a range of empty bed contact times and show the influence of contact time on effluent quality for various parameters.

Table 1 includes background data on the activated carbon systems used. The full scale carbon beds started with a 2.5 ft (0.8 meter) activated carbon depth. Carbon losses during the 180 days of operation, however, resulted in an average bed depth of 2.4 ft (0.7 meter) for the adsorber and 2.1 ft (0.6 meter) for the filter/adsorber. The average contact time for the full scale units are shown in Table 1. The pilot adsorber and filter/adsorber are 3 in (8 cm) diameter glass columns and the pilot contactors are 4 in (10 cm) in diameter.

Table 1
Background Data

System	Area		Ave. Carbon Depth		Ave. Flow		Ave. EBCT
	ft^2	m^2	ft	m	gpd	m^3/day	Minutes
Adsorber	381.2	35.4	2.4	0.7	0.6×10^6	2271	17.5
Filter Adsorber	381.2	35.4	2.1	0.6	0.64×10^6	2422	13.6
Pilot Adsorber	0.05	0.005	2.5	0.8	70.5	0.267	21.4
Pilot Filter Adsorber	0.05	0.005	2.5	0.8	80.3	0.307	16.3
Pilot Contactors							
Col. 1	0.09	0.008	3	0.9	271	1.027	10.9
Col. 2	0.09	0.008	3	0.9	271	1.027	10.9
Col. 3	0.09	0.008	3	0.9	271	1.027	10.9
Col. 4	0.09	0.008	3	0.9	271	1.027	10.9

RESULTS

Contact Time

The contact time for the pilot adsorber was approximately 22 percent longer than the contact time in the full scale adsorber that it was to simulate. Also the contact time for the pilot filter adsorber was about 24 percent longer than the contact time in the full scale filter/adsorber that it paralleled. This must be kept in mind when comparing the results of the pilot systems to full scale bed comparisons. The longer contact times in the pilot systems would theoretically be expected to produce better effluent quality results if removal of the given substance increases with increasing contact time. The results in Figures 3 to 6 show that the pilot contactor data generally support the theoretical expectations for TOC, THMFP, chloroform, and 1,2-dichloroethane. The rate of rise of effluent concentration is lower for longer contact times (EBCT). In Figures 3 to 6, the values of EBCT are estimated by summing the values for the individual contactors in series; the corresponding values are 10.9, 21.8, 32.7, and 43.6 minutes for contactors 1, 2, 3, and 4, respectively.

The TOC data shown on Figure 3 indicate the same pattern reported by other investigators (2). The TOC data appear to be less affected by contact time beyond about 21.8 minutes (contactor 2 effluent). Also the lack of equilibrium conditions (influent concentration equals effluent concentration) for TOC has been frequently observed in many investigations and reported as the effects of biodegradation. Although this is likely true, the continued difference between the influent and effluent concentrations is also likely to be caused by the removal of a component of the TOC that is comprised of strongly adsorbed substances that are totally removed for very long time periods.

The pilot contactor data for THMFP was the most variable, which may partly be explained by the analytical procedures used to quantify this organic fraction. Further studies will be conducted to investigate the high THMFP variation during the first 60 days of data collection. The TOC and specific organics data show the influence of contact time more clearly.

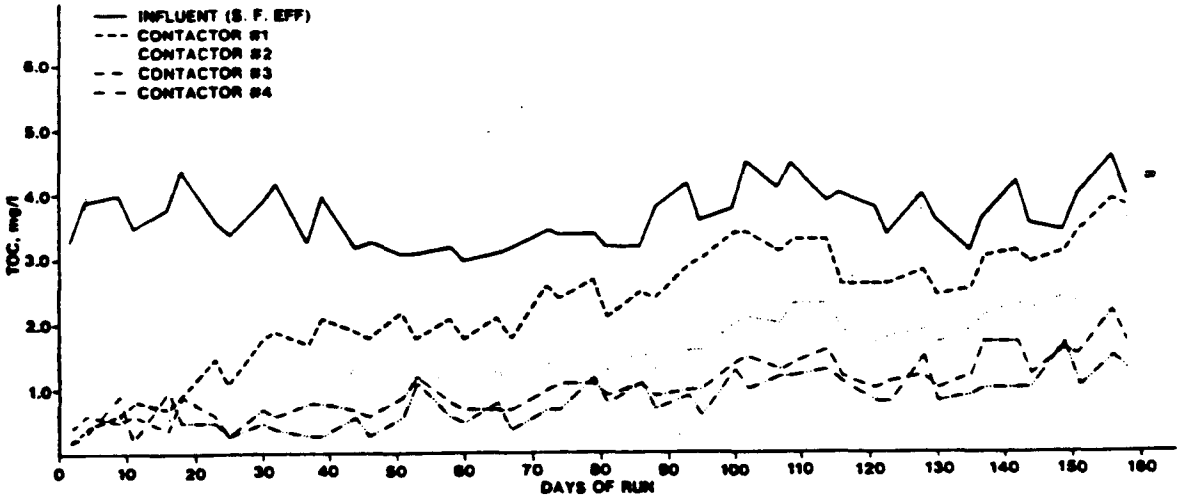

Figure 3. Effect of Contact Time on TOC Removal

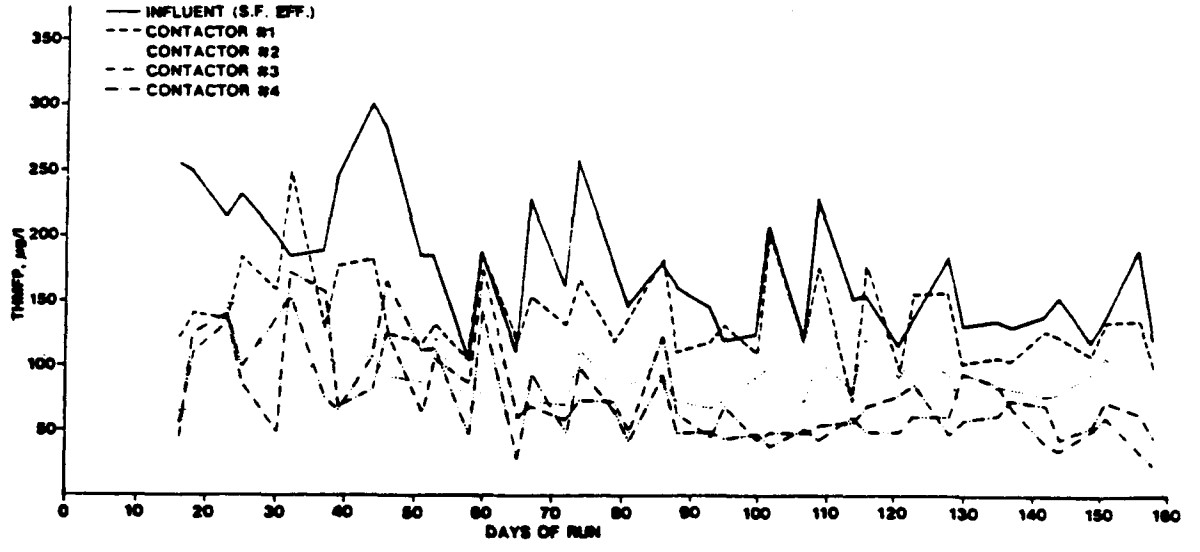

Figure 4. Effect of Contact Time on THMFP Removal

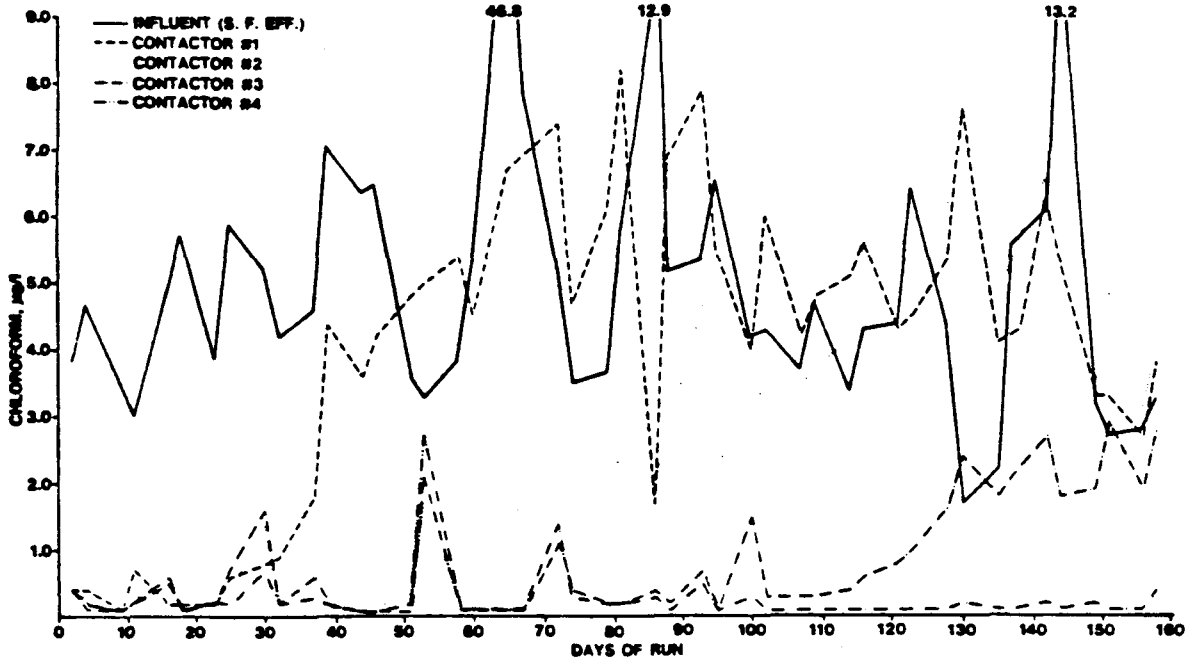

Figure 5. Effect of Contact Time on Chloroform Removal

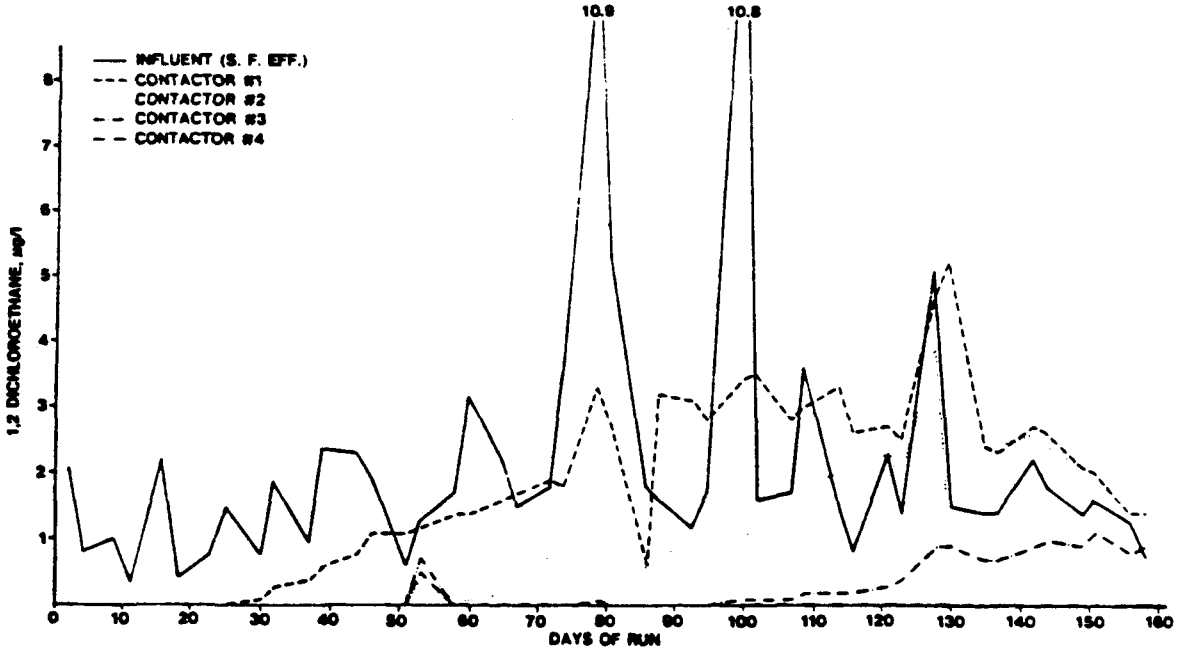

Figure 6. Effect of Contact Time on 1,2 Dichloroethane Removal

Pilot Adsorber (Post-Filter Adsorber) and Full Scale Adsorber (Post-Filter Adsorber) Comparisons

Total Organic Carbon (TOC)--

The pilot system appears to produce a better quality effluent than the full scale system using TOC data (Figure 7). As cited previously, the pilot carbon adsorber column had about 22 percent longer contact time than did the full scale carbon adsorber. Using an effluent TOC criterion of $\leq$ 1 mg/l in the effluent would result in an observed allowable operating time of 28 days in the full scale system compared to 53 days in the pilot system, or about 89 percent more service time. The resulting effect would be that about 25 days less service time would be achieved in the full scale system than would be predicted by the pilot system.

An effluent criterion of 2 mg/l TOC in the effluent would not be reached for about 88 days in the full-scale system and 95 days in the pilot system. This results in 7 days less service time for the adsorber than would be predicted by the pilot adsorber. Thus, the comparisons of differences in service time varied between 7 to 25 days depending on the criterion selected. Further study will include attempts to reduce the difference in empty bed contact time to evaluate whether this caused the differences in predicted service time in this instance.

Trihalomethane Formation Potential (THMFP)--

A consistent pattern of improvement of effluent quality did not occur in the pilot system that had the longer contact time mentioned previously. Detailed evaluation of the erratic results of Figure 4 may indicate that small changes in contact time are not as significant for removal of THMFP beyond about 20 min EBCT as compared to the other parameters tested for these waters. This may partially explain the results shown in Figure 8. Repeat testing is planned to further evaluate the preliminary results obtained.

Chloroform and 1,2-Dichloroethane

The results shown in Figures 9 and 10 present a different pattern than indicated for TOC in Figure 7. Figures 9 and 10 indicate that no practical differences occurred between the effluent quality of the full scale adsorber and pilot adsorber, even though a longer contact time existed in the pilot system.

An effluent quality $\leq$ 1 µg/l chloroform would be maintained for about 45 days and $\leq$ 2 µg/l chloroform would be maintained for about 62 days in both systems. Equilibrium between the effluent and influent chloroform concentrations occurred in approximately 110 days.

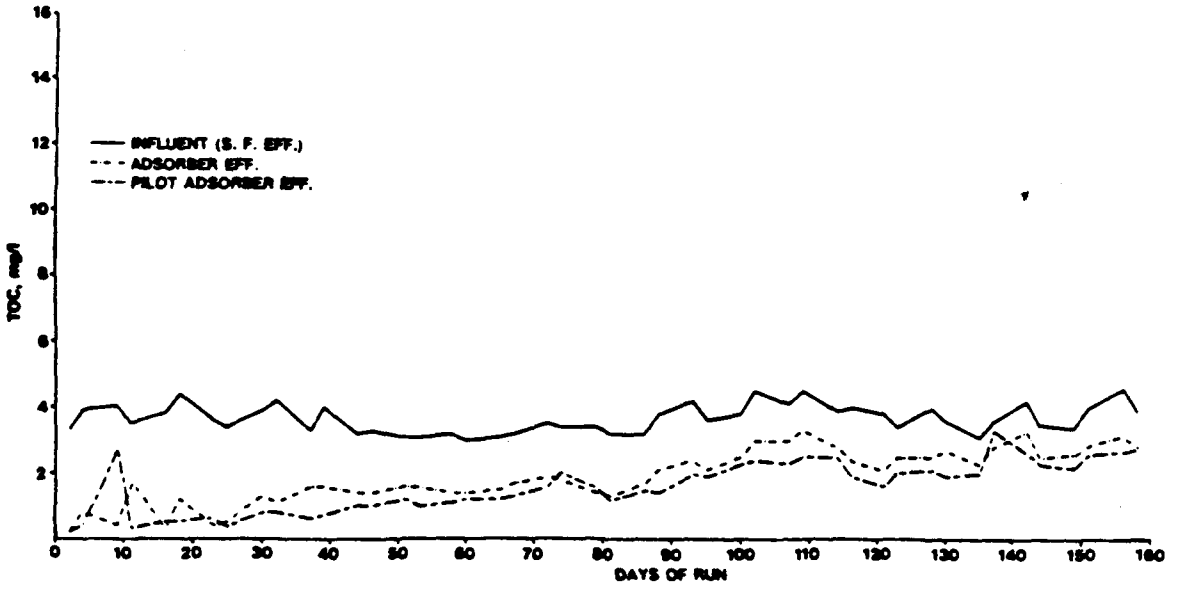

Figure 7. Adsorber and Pilot Adsorber Comparison--TOC Removal

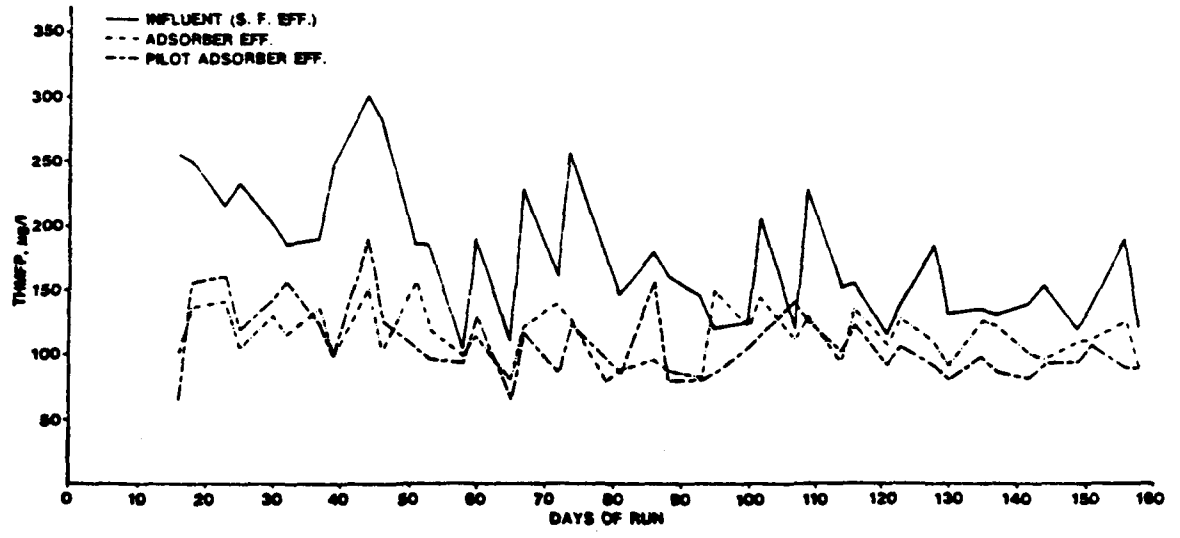

Figure 8. Adsorber and Pilot Adsorber Comparison--THMFP Removal

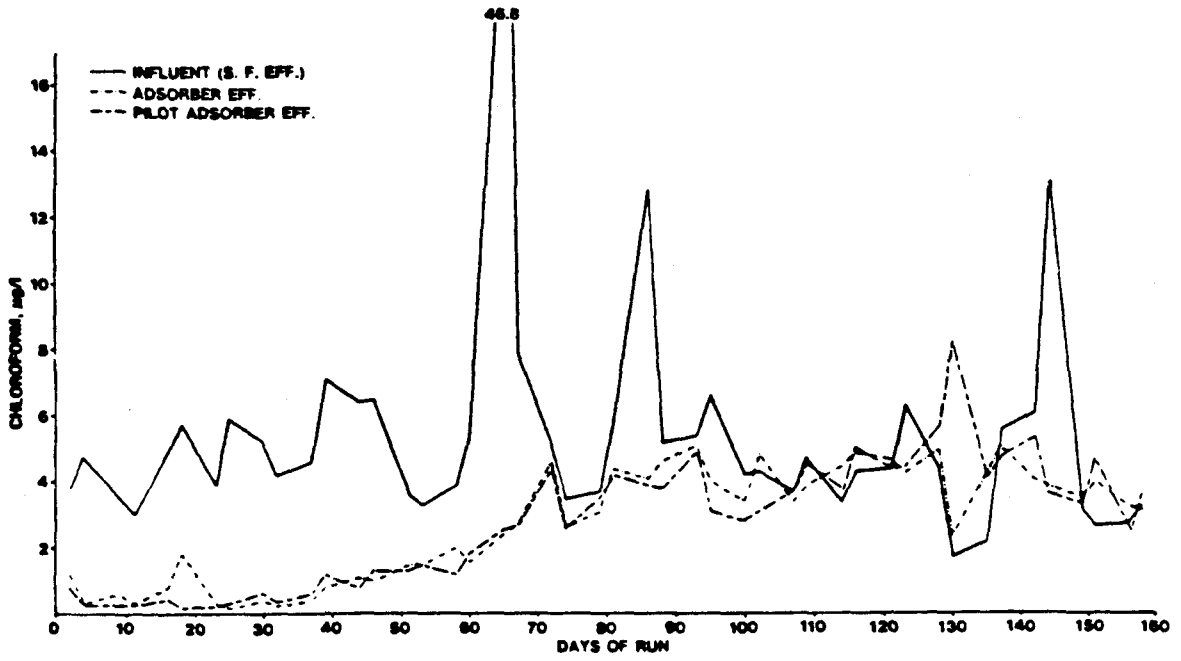

Figure 9. Adsorber and Pilot Adsorber Comparison--Chloroform Removal

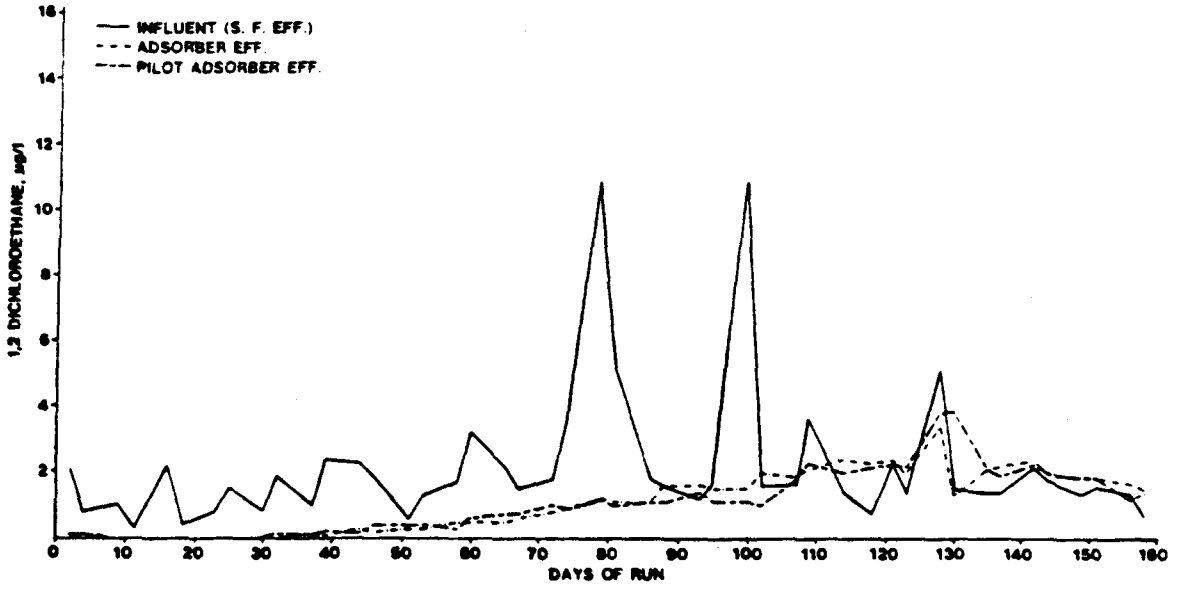

Figure 10. Adsorber and Pilot Adsorber Comparison--
1,2 Dichloroethane Removal

Similar results were achieved for 1,2-dichloroethane. Using an effluent criterion of 1 µg/l would result in a service time of about 80 days for the full-scale and pilot adsorber. Also equilibrium with the influent 1,2-dichloroethane concentration occurred in the effluent betwen 90 and 110 days. Both figures show the variable influent conditions that existed in the influent water and the ability of the granular activated carbon systems to reduce the concentrations of organics even when considerably higher influent conditions were present.

Pilot Filter/Adsorber (Sand Replacement) and Full Scale Filter/Adsorber (Sand Replacement) Comparisons

Total Organic Carbon

Using TOC data, the pilot system seems to provide a better effluent quality than the full scale system (Figure 11). For these systems the pilot filter/adsorber has about 24 percent longer contact time than the full scale filter/adsorber. An effluent concentration $\leq$ 1 mg/l TOC was maintained for only 3 days in the full scale system compared to about 25 days in the pilot system. This results in about 22 days less service time for the full scale bed than predicted by the pilot system. Using an effluent TOC criterion of $\leq$ 2 mg/l resulted in a difference of about 23 days between the full scale and pilot system.

If the contact times had been equal, the breakthrough curves and predicted service times for TOC might have been more equal. These TOC results show a similar trend to those results observed for the adsorber system data shown in Figure 7.

Trihalomethane Formation Potential (THMFP)

Figure 12 shows erratic results similar to Figure 4 and Figure 8 for precursor (THMFP) removal and further evaluation of these results will be performed through repeat testing and investigation of the analytic techniques. The lack of a clear-cut difference in quality of effluent may be caused in part by the lack of a large impact in contact time beyond 20 minutes, EBCT, see Figure 4.

Chloroform and 1,2-Dichloroethane

The results shown in Figure 13 and 14 for the filter/adsorber systems indicated that a slightly better effluent was consistently achieved by the pilot filter/adsorber system. The difference in quality between the pilot and full scale adsorber effluents is more pronounced for the chloroform data than for the 1,2-dichloroethane data. The respective average influent concentrations were about 5 µg/l for chloroform and about 2 µg/l for 1,2-dichloroethane. Equilibrium with the respective influent concentrations occurred at about 110 days for chloroform and 88 days for 1,2-dichloroethane. Without the occurrence of

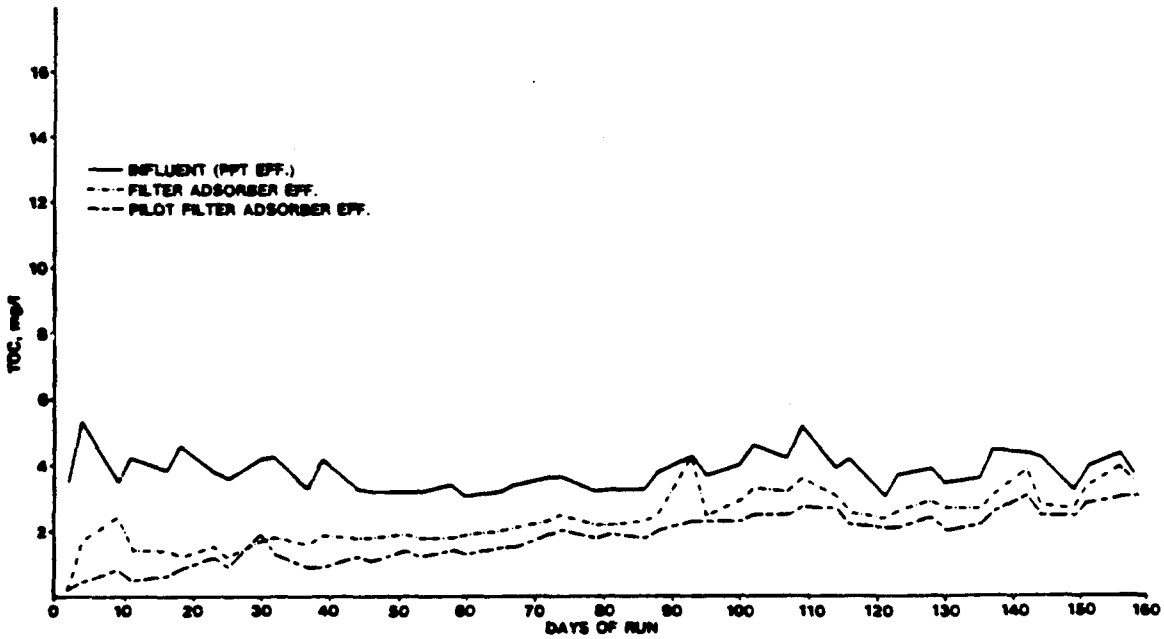

Figure 11. Filter Adsorber and Pilot Filter Adsorber Comparison--TOC Removal

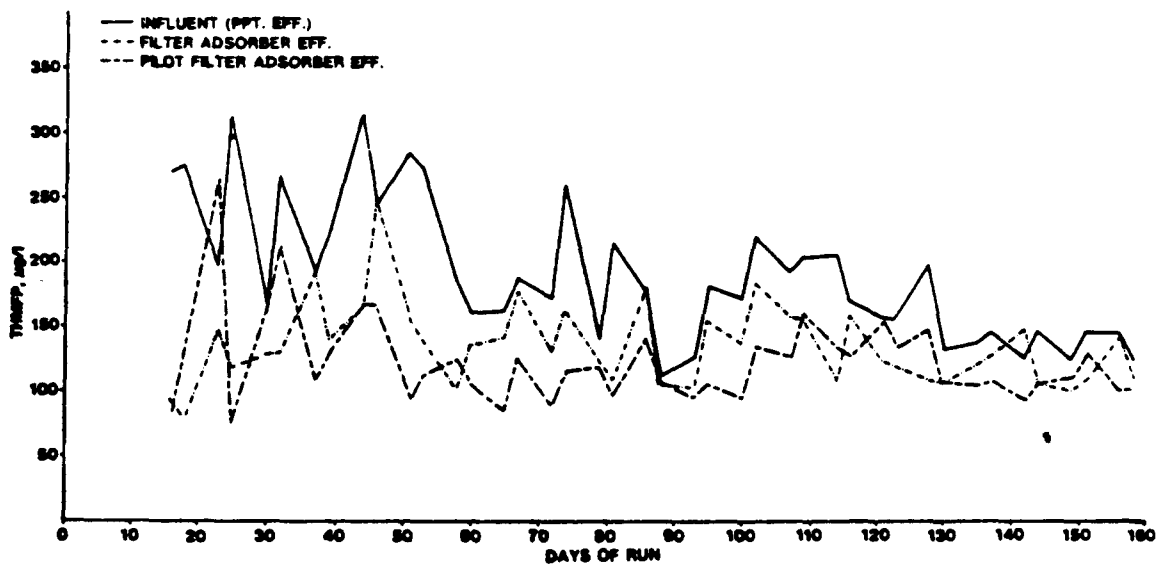

Figure 12. Filter Adsorber and Pilot Filter Adsorber Comparison--THMFP Removal

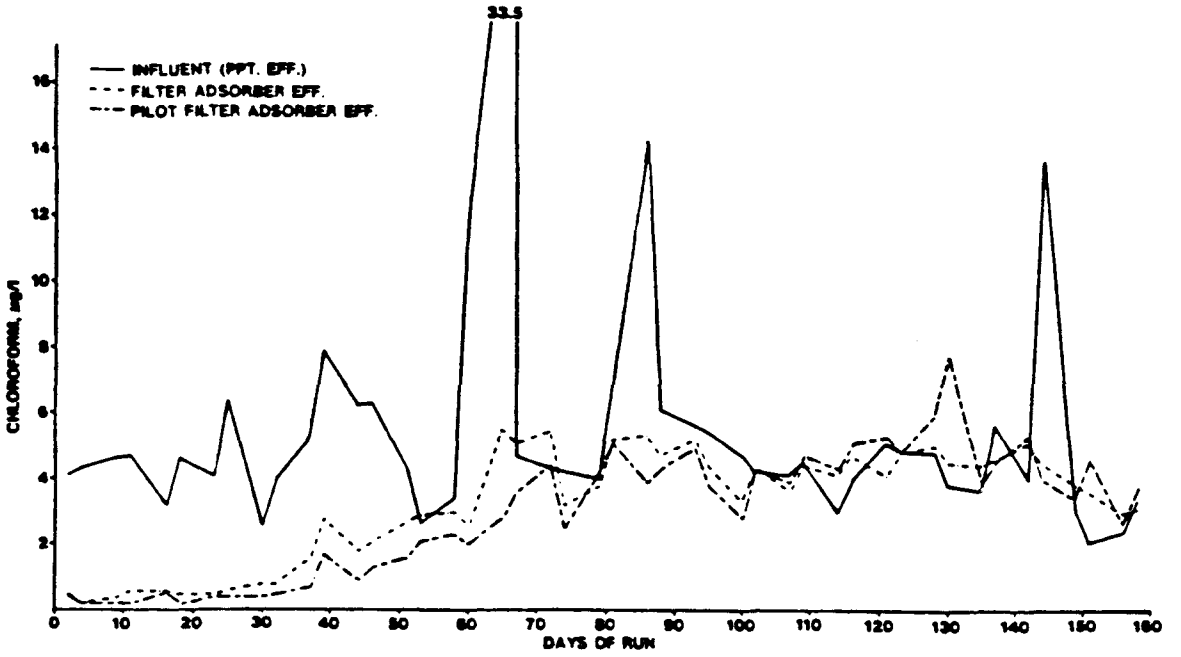

Figure 13. Filter Adsorber and Pilot Filter Adsorber Comparison--Chloroform Removal

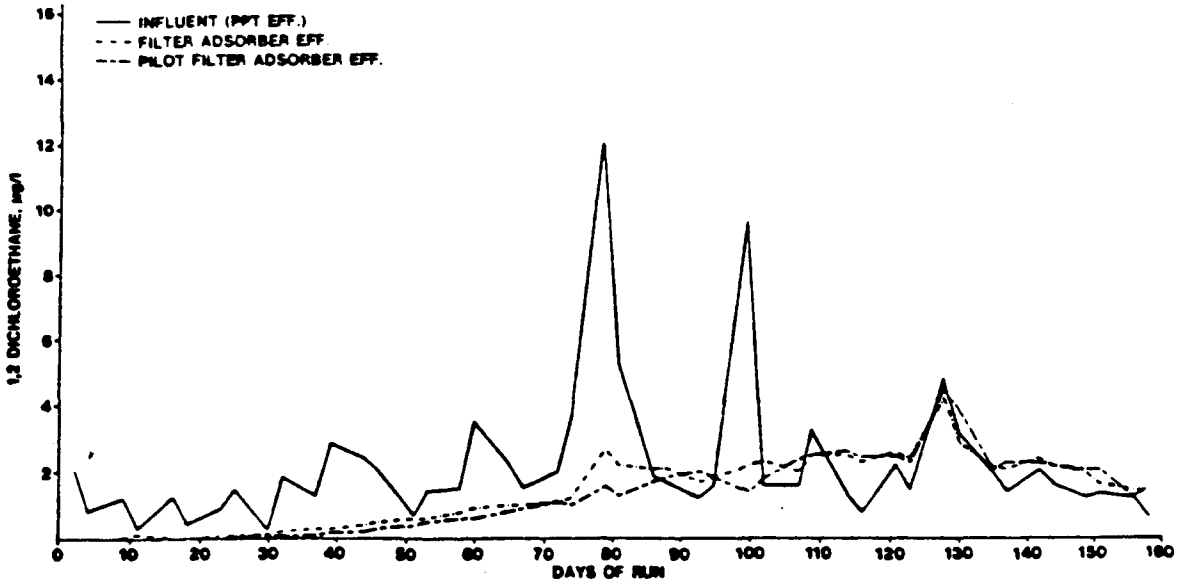

Figure 14. Filter Adsorber and Pilot Filter Adsorber Comparison--1,2 Dichloroethane Removal

periodic high influent concentrations the systems could also be judged to be at equilibrium as early as 70 days for chloroform and about 85 days for 1,2-dichloroethane. The plateaus for the breakthrough curves appear to start at about this time period.

Using a criterion of $\leq$ 1 µg/l of chloroform in the effluents would result in a predicted service time of 32 days for the full scale system compared to 38 days for the pilot system data shown in Figure 13. Figure 14, however, shows that an effluent concentration of $\leq$ 1 µg/l of 1,2-dichloroethane would be maintained for about 74 days by both the pilot and full scale filter/adsorber.

DISCUSSION

The series pilot contactor system data (Figures 3 to 6) show that increased empty bed contact time would generally increase the service time allowed using a selected criterion. Comparisons of the chloroform results for the adsorber and filter/adsorber systems shown in Table 2 do not consistently agree with the series pilot contactor results.

Table 2
Comparisons of Adsorber and Filter Adsorber Systems for Chloroform

System	Ave. EBCT (minutes)	Service Time (days) At < 1 µg/L	Service Time (days) At < 2 µg/L
Filter/Adsorber	13.6	32	45
Pilot Filt./Adsorber	16.8	38	60
Adsorber	17.5	45	62
Pilot Adsorber	21.4	45	62

The systems in Table 2 have been listed by increasing average empty bed contact times. The data show that the filter/adsorber and its pilot system have different service times for each criterion whereas the adsorber systems do not. The contact times in each pilot system were longer than the respective full scale systems. Although the filter/adsorber systems show a relationship with increased contact time, the adsorber systems, which were backwashed less frequently and also received a different quality water, did not.

The pilot filter/adsorber and full scale filter/adsorber comparisons were more consistent; for example both the total organic carbon data(Fig. 11) and the chloroform data (Fig. 13) showed increased service times for the pilot system. This is consistent with the general expectation of longer service time with increased contact time. This was not as apparent, however, when 1,2-dichloroethane data (Fig. 14) were used to evaluate the pilot and full scale filter/adsorbers.

The pilot adsorber and full scale adsorber showed expected longer service times only for the general parameter of TOC. An increase in service time with increased contact time did not occur when the pilot and full scale adsorber were compared using chloroform and 1,2-dichloroethane.

The results are unexplained to date (May, 1979) but further evaluation of all data will be performed.

Statistical Comparisons

Judgement of whether a difference did or did not exist in the effluent quality of each pilot adsorber column and its full scale counterpart is sometimes made subjectively. Little debate usually exists for breakthrough curves that are "widely separated" and judged different, even if some scatter exists. Likewise curves that are "very close" to one another and judged to show no difference are not generally debated. Evaluations that rely on these subjective approaches leave room for improvement. Applying effluent quality criteria such as was previously done is a method of providing practical evaluations of the significance of any difference.

To improve this situation a statistical aid to judging differences in the data has been tested. Efforts to date consist of developing an equation or model for each breakthrough curve, and then using a log transformation of the data to develop a best fit least squares regression line. This straight line plot is then used to determine the slopes and intercepts of each line.

The hypotheses that the slopes are or are not equal is then tested at the 0.05 significance level and the same method is used to test the intercepts. The concept is similar to that suggested by Cairo and coworkers (3). Chloroform and 1,2-dichloroethane data for the pilot and full scale adsorber have been used with both the percent breakthrough approach described in their paper and our model, which used influent and effluent concentrations.

Both approaches indicate that no statistical difference existed in either the slopes or intercepts of the transformed lines. Thus, these results agree with a visual subjective evaluation and the effluent quality criteria tests applied. Additional work will be done with breakthrough curves having varying degrees of separation, to assess the overall usefulness of the statistical tools.

Summary

The first attempt to provide a data base for comparing a pilot and full scale system for various organics produced results that require further investigation.

Although both of the pilot systems had longer average contact times than their respective full scale systems, a uniform pattern of longer service time for the different substances evaluated did not occur. These results may not be consistent with the data collected using pilot contactors in series to observe the effect of contact time.

The series pilot contactor system provided data that show the effect of varying empty bed contact time on the removal of the organic substances studied. Improved effluent quality was generally achieved with increased contact time. A pilot series system similar to the one used is considered essential in collecting and interpreting design data.

A method of statistical interpretation of the results was developed that shows promise for use in evaluating pilot column results.

Further evaluation is required to assess that all pertinent factors were properly controlled during the investigation. Also, repeat testing will be conducted, attempting to control more closely the contact times between the pilot and full scale systems. The comparative granular activated carbon particle sizes also will be more closely examined.

Although pilot to full-scale comparisons have been successfully performed for single parameters, the results for multiple organics have not been previously reported. Such a data base, if properly collected, will provide invaluable background in assessing what types of design safety factors are required when using pilot column data to predict full scale results for a naturally occurring mixture of organic substances.

ACKNOWLEDGEMENTS

The co-authors wish to express their thanks for the assistance provided for the development of statistical tests

by Michael Pence and Pat Cairo of the Philadelphia Water Department, and to Robert Clark and Michael Laugle of the Drinking Water Research Division of the U.S. Environmental Protection Agency. Also Wayne Koffskey of the Jefferson Parish Water Department provided assistance in the analytical data evaluations used in this paper.

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THE MÜLHEIM PROCESS FOR TREATING RUHR RIVER WATER

Ewald Heilker

Granular activated carbon filters are widely used in Germany. The process design criteria differ depending on whether the carbon filters are used for chlorine removal or in a combined adsorption and biological treatment. Besides the process design criteria, many other design problems occur in practice as demonstrated by the history of the use of granular activated carbon filters for treating the Ruhr River water at the Rheinisch-Westfälische Waterworks Association at Mülheim.

In order to meet the peak demand for water in the Ruhr area, the waterworks has depended on the Ruhr River surface water since the beginning of industrial development because only a small amount of groundwater occurs in the gravel layers of the river valleys. The treatment of the Ruhr water in slow sand filter basins and ground passage has been the classical and most favored treatment in nearly all the waterworks along the Ruhr for many decades. After a 1- to 3-day retention time in the aquifer (which is about 12- to 20-m thick), the water is collected in a series of wells parallel to the slow sand filter basins, disinfected, and pumped into the distribution system.

The Rheinisch-Westfälische Waterworks Association supplies about 1 million people in the western part of the Ruhr area, as well as the Ruhr industries, with water from three rivers. It has had difficulty in meeting the demand in the drought years of 1959 and 1964. With an increasing amount of nutrient material in the Ruhr, algae blooms have occurred in early summer and autumn, reducing the hydraulic capacity of the sand filters.

Geohydrological considerations and the density of population in the nearby Ruhr valley make it impossible to augment the water supply by building new filter basins or wells. The first approach to the problem was to install rapid filters in two waterworks. However, all the colloidal dissolved iron in the Ruhr water could not be satisfactorily removed despite the use of different granular media combinations in the filters. The dosage of aluminum sulfate before filtering caused post-flocculation at the basin surface and in the injection wells,

leading to a considerable decrease in the infiltration rate within 3 months.

After pilot plant tests for about one year with several pollution loads of the Ruhr water, flocculators were built in two of the waterworks, and the water was treated in a conventional way with superchlorination, flocculation, sedimentation, and filtration.

The ammonia content of the raw water made a 10-15 mg/l dosage of chlorine necessary for breakpoint chlorination. The filter effluent was seeped into the slow sand filter basins and injected into the ground as before, producing high infiltration rates of 3 m^3/m^2/day and slow sand filter runs of 6 months. As a result of the relatively high chlorine excess of 1 mg/l, algae did not develop significantly on the basins. However, the biological decomposition of taste- and odor-causing substances decreased considerably because of the chlorine in the slow sand filters and in the ground passage. Therefore, filtration with activated carbon was initiated, primarily in order to eliminate the excess chlorine, but also to reduce the organic load.

After the startup of the activated carbon filters, the water quality greatly improved. The taste of the carbon filtrate was no longer impaired and the organic load at the beginning of the filter run was reduced. It was believed that the ground passage step could be eliminated and the carbon filtrate could be pumped directly into the distribution system. Virological tests demonstrated that the flocculator outlet was virus-free despite the high virus counts in the Ruhr water. Because of the organic load, however, consumers could not be provided with water that had not passed through the ground. The breakthrough of taste and odor substances indicated that the activated carbon was exhausted after a 4 month run.

The effectiveness of dechlorination with carbon made it possible to obtain a satisfactory final purification of the water by biological processes in the slow sand filters and in the ground passage. Considering the anticipated future demand, a treatment process without ground passage had to be developed.

THE MÜLHEIM PROCESS

The effectiveness of the different treatment processes is shown in Table 1. The data were obtained by the Mülheim Waterworks and by the Engler-Bunte-Institut of the University of Karlsruhe. The high prechlorination caused the formation of organic chlorinated compounds which could not be reduced to a tolerable degree either by activated carbon or by ground passage. At the time the data were compiled the activated carbon was highly loaded and had spent most of its adsorptive capacity. Because these results were confirmed by tests performed in a

Table 1. Organochloro Compounds after Breakpoint Chlorination Treatment

Source of Sample	DOCl* µg/l	DOCl N* µg/l
Raw Water (Ruhr)	17	5
After Breakpoint Chlorination flocculation and filtration	203	30
After GAC-filters	151	17
After Ground Passage and Safety Chlorination	92	18

*DOCl signifies dissolved organic chlorine; N signifies nonpolar

pilot plant with different kinds of activated carbon, it was decided to abandon breakpoint chlorination in the development of a new treatment system. The removal of ammonia was to be achieved by biological oxidation. This approach had been tested at other plants, which found that nitrification was effective in removing ammonia and that the negative effects of breakpoint chlorination could thus be avoided.

Figure 1 shows the general Mülheim process scheme and Figure 2 illustrates the composition of the filter media. The raw water is taken out of the impounded Ruhr navigation canal and pumped into the mixing basin (1.8 by 1.8 by 5.2 m) where, instead of chlorine, off-gases from the ozonation basin are drawn back into the flash mixing basin by a high speed aspirating turbine and injected into the raw water. Additional fresh ozone can then be added directly to the mixing chamber. The amount of ozone added, averaging 1-1.5 mg/l, depends mainly on the degree of turbidity of the raw water. The water is dosed with 4-6 mg/l polyaluminum chloride and mixed thoroughly by the turbine. The pretreated water is pumped into the flocculator through perforated pipes on the bottom of the pulsator basin. After 90 minutes of clarification, nearly all the particulate materials are settled, and water with a turbidity less than 1 FTU flows into the ozonation basin. Fresh ozone is injected through porous ceramic pipes. Residual small flocs are subsequently removed in the rapid sand filters. Figures 3 through 9 show construction details of the GAC treatment installation.

Since a biological process requires a longer retention time than a purely adsorptive process, the GAC bed depth was increased from 2 to 4 m, increasing the empty bed contact time from 5 to 10 min.

In the activated carbon filters, a temperature-dependent interaction was observed between adsorption and biological oxidation behavior. At low temperatures, non-decomposable, as well as decomposable, substances are concentrated by adsorption. At

increasing temperatures, an efficient microbial population develops and the previously adsorbed biodegradable compounds are biologically oxidized, increasing the filter rate. At the same time, the nitrification activity in the activated carbon filters led to a nearly complete oxidation of the ammonia to nitrate, despite the extremely low winter temperatures (0.5°C). Pure oxygen is injected before the filter pumps so that a sufficient amount of oxygen (7-8 mg/l) is present in the carbon filtrate.

The bacterial investigations of the carbon filtrate also produced satisfactory data, although in the summer of 1978 a population explosion of nematodes was observed in the rapid sand and carbon filters. Clearly, nematode development was caused by long backwashing intervals of more than a week. The nematodes disappeared when these intervals were reduced to 3 days (the reproduction cycle of this genus of nematodes).

Backwashing in the gravel filters is accomplished by a mixture of air and water at a rate of 25 m/hr. The GAC contactor columns are backwashed, first with air to loosen the material, and then water is pumped through at a rate of about 40 to 50 m/hr.

Table 2 compares the process data of the conventional treatment (with breakpoint chlorination) with the new treatment including adsorptive and biological granular activated carbon filters. In essence, the breakpoint chlorination was replaced by a two-stage ozonation and the retention time of the carbon filters was lengthened, resulting in an increase of the biological capacity of the filters.

The treatment plants in the Dohne waterworks have been operating for more than 1-1/2 years using the revised process. The drinking water quality has significantly improved without incurring higher treatment costs. The Dohne plant is less susceptible to disturbance and can thus be operated with half of the former staff size. The activated carbon filter runs are three to five times longer than before. The other waterworks of the Rheinisch-Westfälische Waterworks Association are being rebuilt to accommodate the Mülheim process.

FILTER CONSTRUCTION AND CORROSION INHIBITION

Some aspects of the construction and technical equipment of filters have been particularly important.

Steel filters were selected because they were better suited for the overall process design and easier to work with in modifying existing treatment plants. However, it was found that corrosion problems caused high repair costs.

Table 2. Changes in Water Treatment Processes at the Dohne Plant

Treatment Step	Classic Treatment	New Treatment
Preoxidation Dosing Power Input	10-50 mg/l Cl_2 4-6 mg/l Al_2O_3 0.1 kW/m^3 Retention time 0.5 min.	1 mg/l O_3 4-6 mg/l Al_2O_3 2.5 kW/m^3 Retention time 0.5 min
Flocculation Sedimentation	5-15 mg/l $Ca(OH)_2$ Retention time 1.5 hr.	5-15 mg/l $Ca(OH)_2$ Retention time 1.5 hr.
Ozonation	—	2 mg/l O_3 Retention time 5 min.
Filtration	Filter Velocity v = 10.7 m/hr	Filter Velocity v = 10.7 m/hr
Activated carbon filter Bed height	v = 22 m/hr h = 2 m	v = 22-11 m/hr h = 4 m
Ground Passage	Retention time 12-50 hr.	Retention time 12-50 hr.
Safety Chlorination	0.4-0.8 mg/l Cl_2	0.2-0.3 mg/l Cl_2

After 10 years of testing different filters having additional cathodic corrosion protection, a method has been found that offers nearly complete protection. Twelve double-stage filters are being modified to prevent corrosion: all interior welded seams are being straightened and ground; rust is being removed with sand blasters; condensate is being prevented by aeration during coating; solvent-free epoxy resin, which is resistant to abrasion and ozone, is being used; a 450 to 500-µm poreless coating is being applied and is being tested with 1.5 to 2 kV.

Further experiments have determined that the interior filter surface and all installations can be completely protected if combined cathodic protection with sacrificial anodes is used and the electric power supply is transmitted over platinum-covered titanium anodes.

The costs for all corrosion protection devices being applied to the carbon filters amount to approximately 10 percent of the total plant modification.

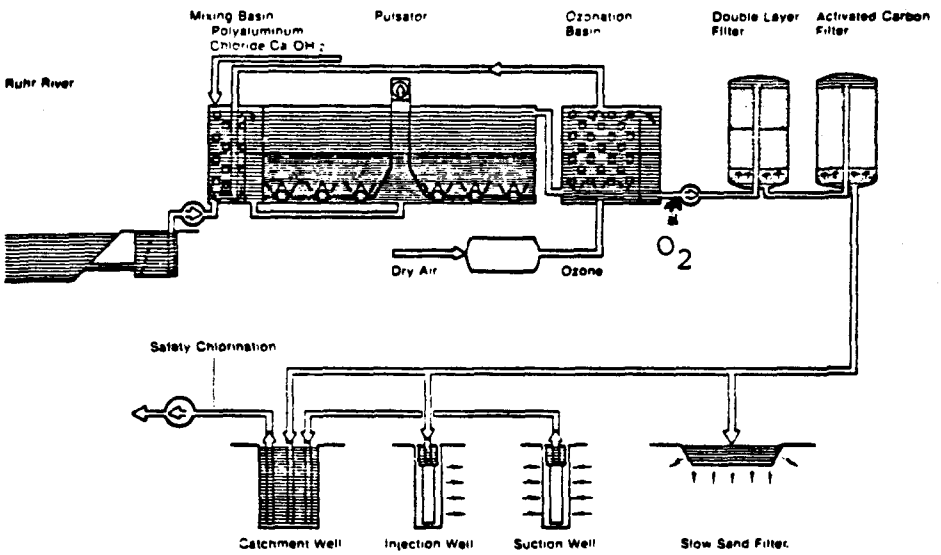


Figure 1. Process Scheme at Mülheim

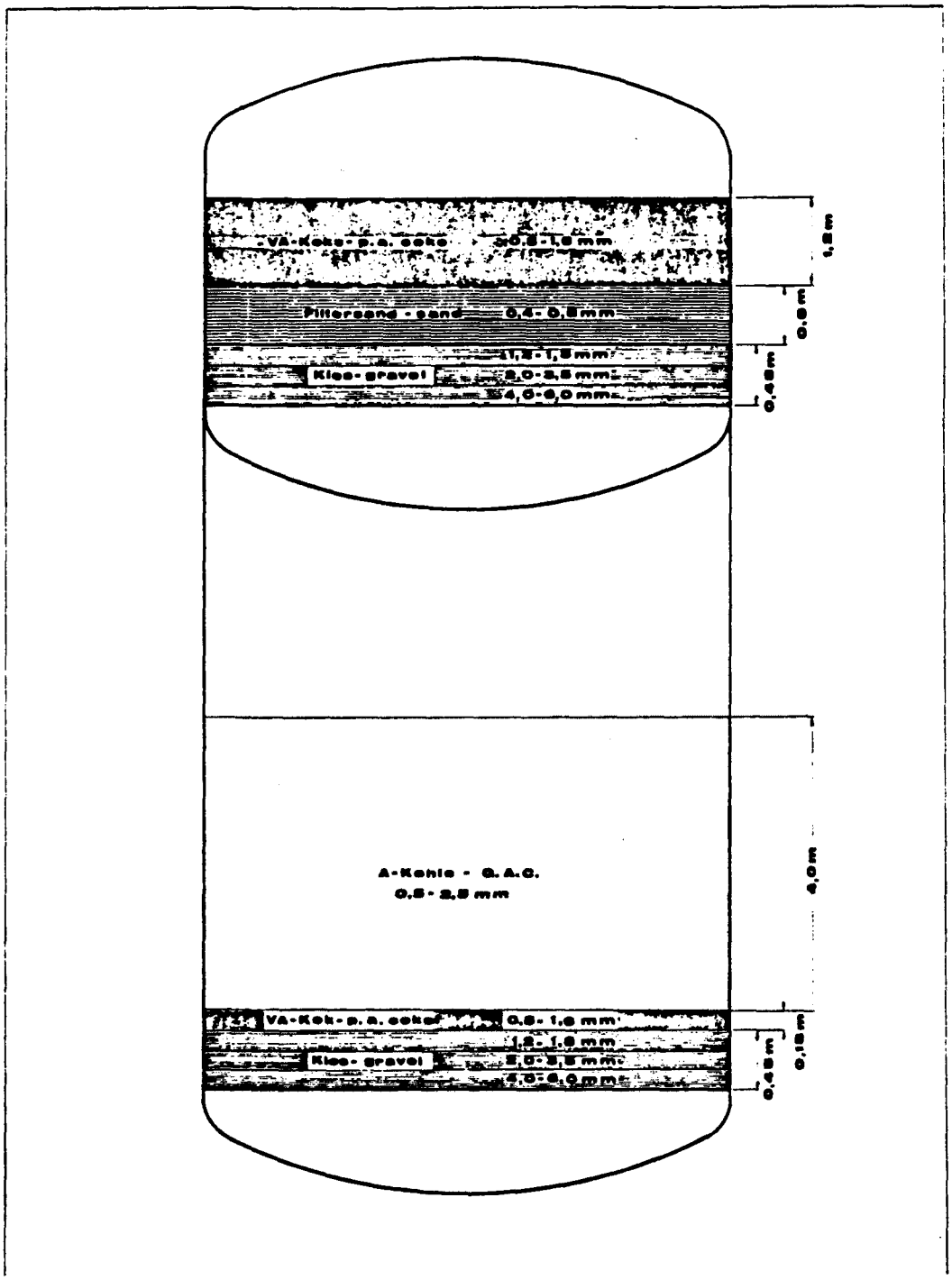


Figure 2. Composition of Filter Media

The double-layer filter and activated carbon filter, shown separately in the schematic diagram (Fig. 1), are combined in a single vessel as shown here.

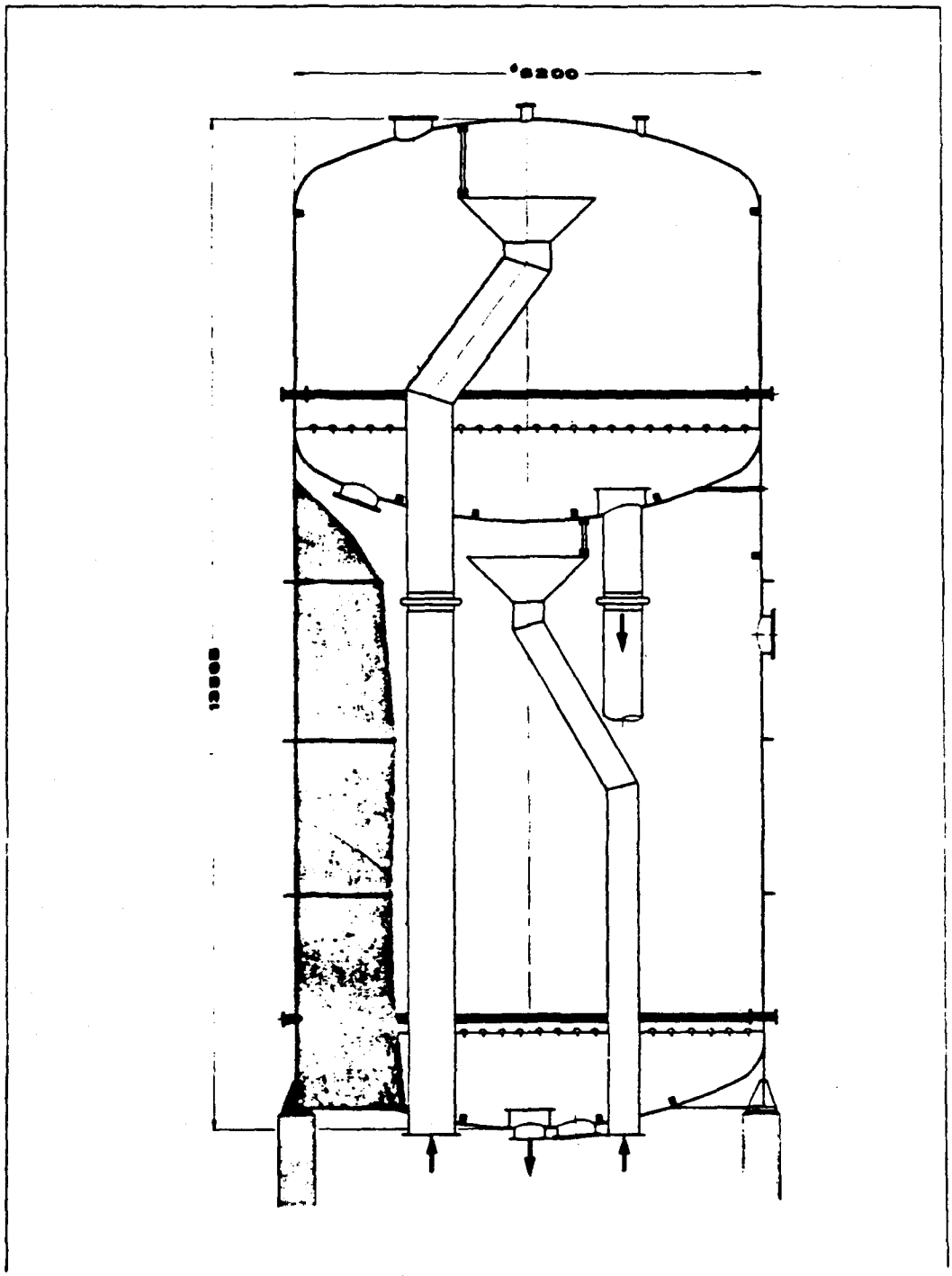


Figure 3. Cross Section through a Double-Stage-Filter, Upper Stage with Multi-Layer-Filter, below the GAC-Filter. Dimensions are in mm.

The upper filter bottom is to avoid clogging of the filter nozzles during backwash.

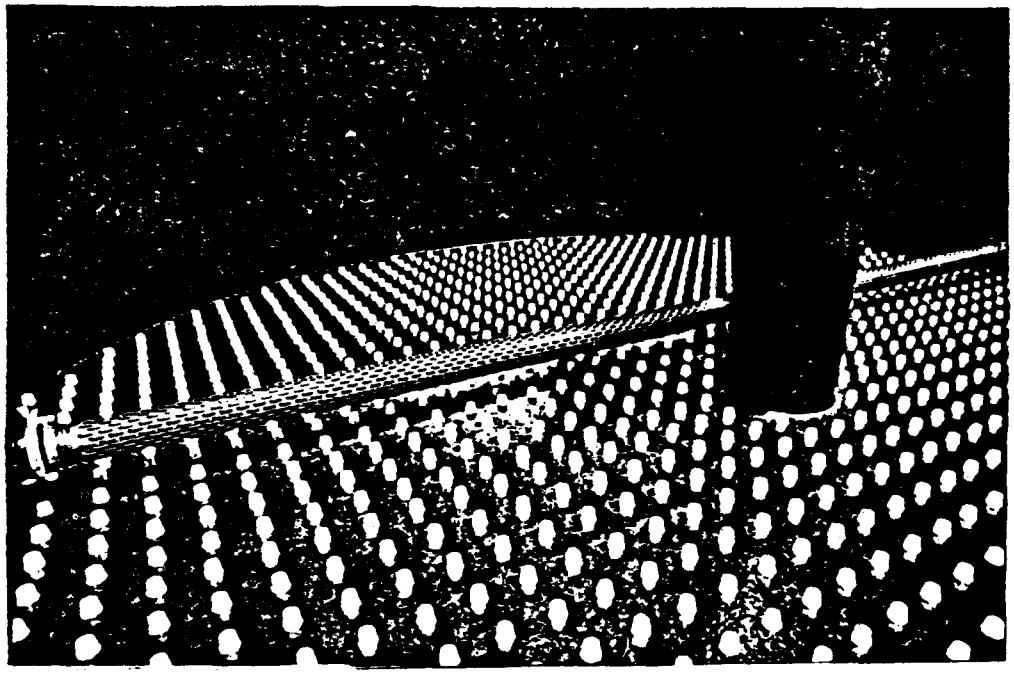


Figure 4. Nozzle Bottom with Filterpipe as Protection for the Anode Wires

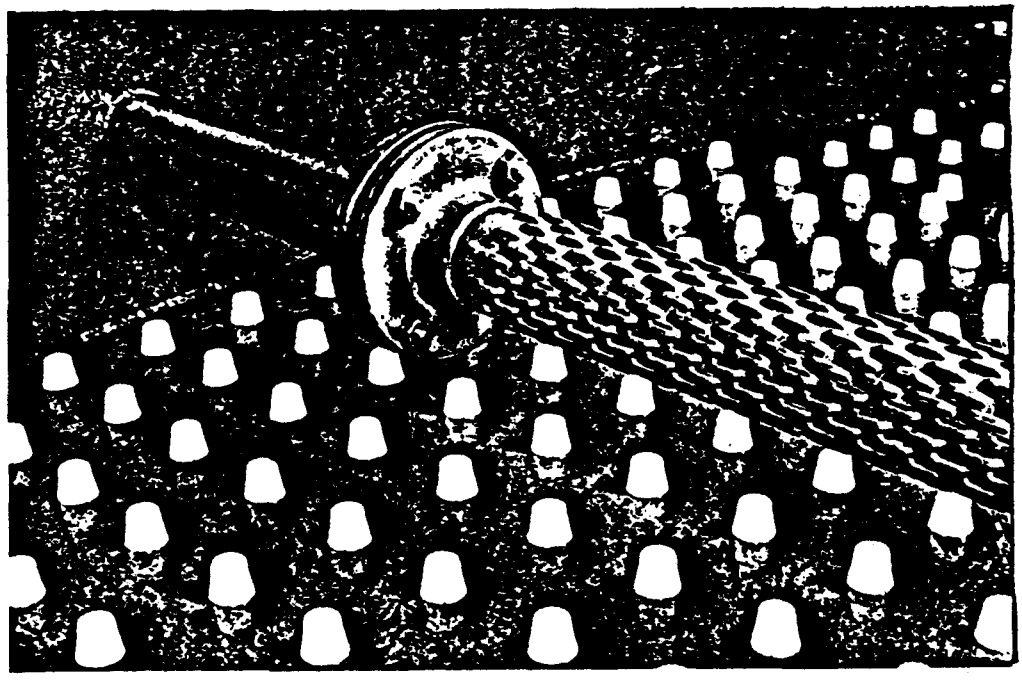


Figure 5. Detail of the Previous Picture

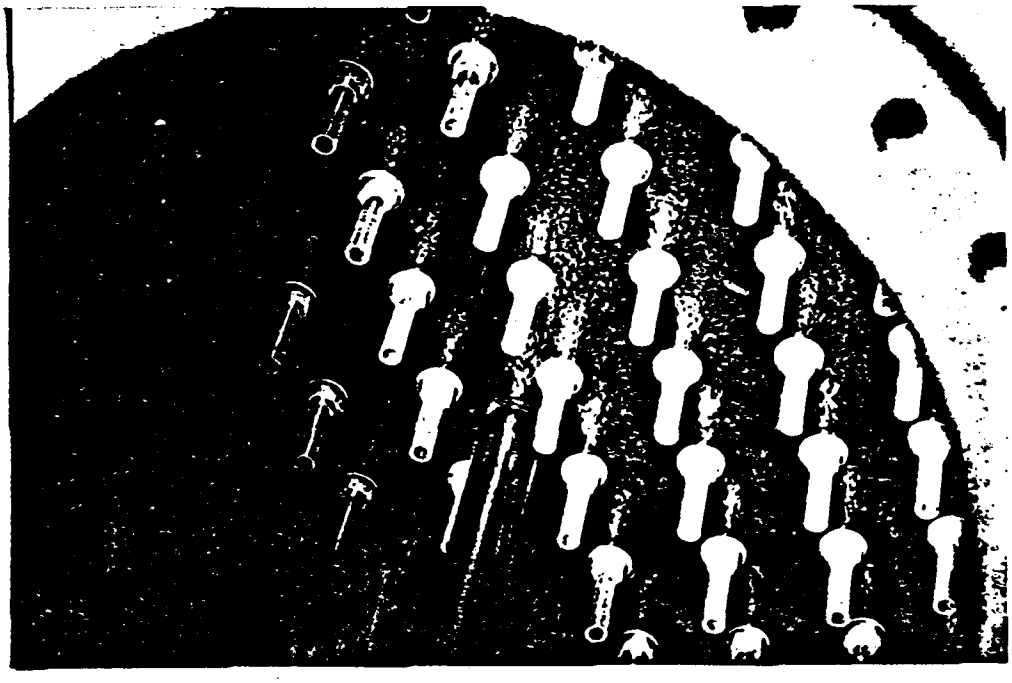


Figure 6. View of the Nozzle Bottom from Below

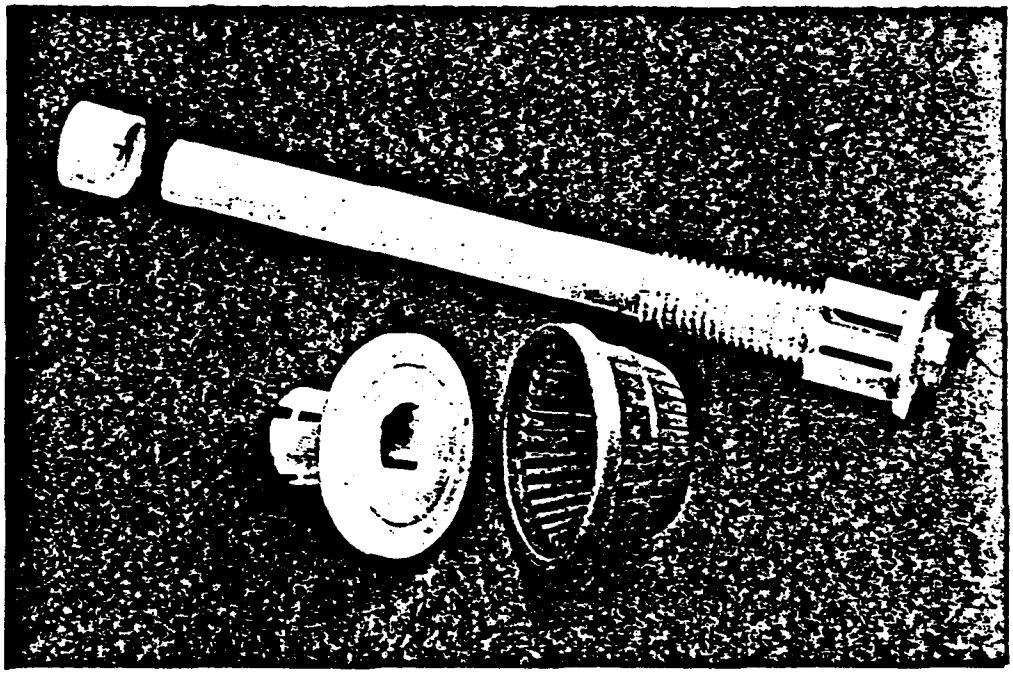


Figure 7. Details of the Nozzles; nozzles with long shafts are used for the backwash with air and water.

Figure 8. Filter Hall

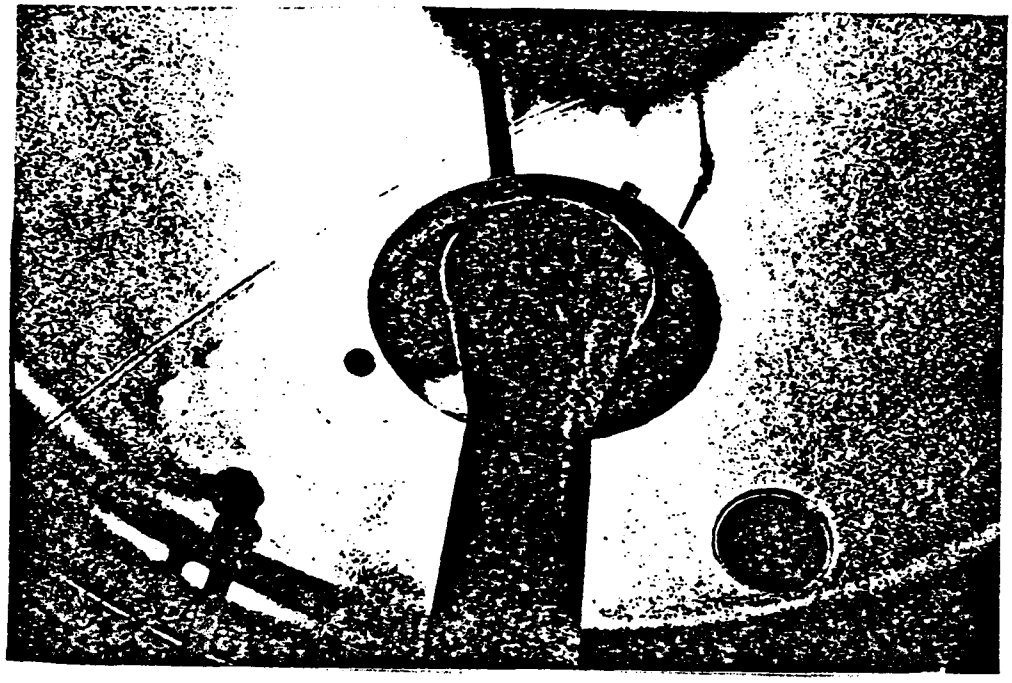


Figure 9. Raw Water Inlet, Also Used as Backwash Water Outlet

DISCUSSION

TUESDAY, MAY 1
MORNING SESSION

Q HAROLD PEARSON, Metropolitan Water District, Southern California: I'd like to ask about the relationship between water temperature and your biologically activated carbon operations. I noticed your rates of flow were from 22 down to 11 m^3/h. Do you correlate that with the temperature and the biological activity so that you get maximum efficiency in the removal of the organics?

A PROF. DR. SONTHEIMER: No, not exactly. This can be easily explained. Normally in winter, water use declines, enabling us to reduce the throughput. If the temperature increases, we have more biological activity and more biological regeneration of the carbon. It is very clear that biological activity in activated carbon depends on temperature; you must pay careful attention to this, especially if there are very low temperatures in winter, as in Germany. This past winter we had 6 or 8 weeks with temperatures below 1°C.

Q UNIDENTIFIED QUESTIONER: Mr. DeMarco, you indicated that everyone had different criteria for regenerating carbon, and depending upon the criteria, different regeneration times would apply. The regeneration costs and facilities are very important. One criterion in the proposed regulations states that when the effluent COD or TOC increases 0.5 mg/l above that for freshly regenerated carbon, then one should regenerate. In looking at your data, I had difficulty telling when that might be; depending upon how you look at it, it may be from 1 to 20 days. I wonder, as a representative of EPA, if you would interpret that data in view of that criterion.

A MR. DeMARCO: All you really need to know would basically be what the breakthrough concentration was at startup. About 0.5 mg/l came through very quickly, and this was not based on a 3-day running average. What I attempted was to interpret the unadjusted data and say when it exceeded a given criterion: in a state above that criterion, that's what I did my comparison on. You could probably get a rough estimate of when you might have to regenerate, according to the proposed regulations, by looking at the 1 mg/l effluent concentrations that I talked about for TOC.

Q PROF. PERRY McCARTY: Using 1 mg/l? Would you suggest using a 3-day running average? Are you just picking that number?

A PROF. PAUL ROBERTS: I have a suggestion along that line. It seems to me, if you recognize that in most large installations there will be many of these adsorbers operated in parallel, and that the concentration of interest is really an average over those many filters, then what you ought to look at would be a cumulative average of the effluent concentration rather than the instantaneous value. One of the speakers from Karlsruhe presented a graph in which he showed a curve of effluent concentrations and another that he called "integrated effluent concentration." I suggest that the integrated effluent concentration would be appropriate for a multi-adsorber installation. That would do two things for you: one, it would be approached more slowly; and secondly, it would tend to iron out a lot of the daily variability in the data.

A MR. DeMARCO: That's a good comment. I think it ties in, somewhat, with some of the comments made the other day about compositing, which I firmly believe in. I think the answer is a combination of compositing and integrating for our research work. What we intend to do at one of our full-scale locations where we have more discreet contactors, such as in Cincinnati, is to study the combined effluent of a series that will be a staged operation, just as you would do in a full-scale plant. We couldn't do it in the original test, because we didn't have a staged operation in the plant. When we do have that staged operation, we will look at the composite quality that comes out of the parallel operation of three beds at different stages of operation. In addition, we will be able to compare the effluent quality of the staged operation with one unit to determine the differences. I do think that we will see some smoothing out, as you suggest.

Q RICHARD WOODHALL, Connecticut State Health Department. I would like to ask the gentleman from Germany exactly what is meant by soil passage treatment. What kind of soil and how many feet of it?

A PROF. DR. SONTHEIMER: Soil passage means that we have a slow sand filter. We introduce the water into the ground, which is mostly sand, approximately 12 meters thick. There are wells approximately 50 meters from the infiltration basin, and the water passes through the ground to the wells. This varies from one waterworks to another, since some have sufficient space and some have not. In some cases, the underground residence time is only 10 or 12 hours, whereas in other treatment works operated by the same companies the residence time in the ground is 50 days, so it depends on local conditions. Ground passage means

introducing the water into the ground, where it is mixed with natural ground water as it moves to the wells and is removed after some time.

Q STAN SMITH, Georgia Tech: Mention was made in the last paper about a pre-activated carbon, which is used as filter material. I'm wondering about the fate of that. Is that material actually taken out and activated to useful carbon, or is it perhaps added as a makeup to the regeneration cycles?

A PROF. DR. SONTHEIMER: No, it's made from pyrolysis of carbon. It's made out of coal; the coal is ground and coke is produced. It must have a very rough surface; this is the most important factor for filtration efficiency. It's like anthracite coal, but it's a type of coke.

Q MR. SMITH: I am curious to know if it was actually removed and made into activated carbon later.

A PROF. DR. SONTHEIMER: No, it's actually made from coal and it's an intermediate step in the fabrication of activated carbon.

Q MR. SMITH: It's used as a matter of convenience?

A PROF. DR. SONTHEIMER: No, it's a very good filter material. It's sold as a filter material, like other available filter materials.

Q MR. SMITH: I had another question on an earlier paper about a parameter that was used as a test criterion, called OSW. Is there a speaker still here who could explain this?

A PROF. DR. SONTHEIMER: Yes, OSW means Organic Substances in the Water. It's only an acronym, nothing else.

DR. SYMONS: You see, they're learning from us to confuse people with initials.

Q DR. RIP RICE, Jacobs Engineering: For Herr Heilker please; you have been operating your new process with the 4 m GAC column since November 1977, a period of a year and a half. Have you regenerated the carbon yet? And if you do, or when you do, what will be the regeneration criteria?

A PROF. DR. SONTHEIMER: That is a difficult question that I tried to answer yesterday. I think it is very clear in this case. The carbon has to be regenerated immediately because oxygen uptake is very low.

Q PROF. DAVE HENDRICKS, Colorado State University: A question that's been bothering me for several years has been referred to here by a number of people, concerning the fortuitous benefit of biological treatment in conjunction with activated carbon adsorption. It seems that there's a trade-off between the lessening of the adsorption capacity because of the bacteria occupying the adsorption area, and also, possibly, the lowering of the transfer coefficients because the access to the carbon pores may be blocked. Logically, there appears to be a trade-off, but I've never seen this articulated. I wonder if it's been considered by people who observe this and by those who wish to promote the synergistic features of biodegradation and adsorption.

A PROF. SONTHEIMER: I understand your concern, but our data show that there is no real difference in adsorption capacity. That means that the bacteria on the carbon do not have any significant influence on the adsorption capacity of the carbon. Our data show that the mass transfer rates are not really changed by the presence of bacteria, but this has only been done with very low concentrations of organics. Mass transfer considerations may limit the amount of bacteria desired on the carbon. There are some data, I believe, that show some changes in the mass transfer criteria. This may occur, but we didn't find it under the conditions that we investigated.

OPERATIONAL EXPERIENCES WITH ACTIVATED CARBON ADSORBERS

EPA
NATO
OTAN
CDSM
CCMS
NATO – CCMS

OPERATIONAL EXPERIENCES WITH THE CARBON ADSORPTION PLANT AT CHURCH WILNE

D.J. Osborne and C.A. Kennett

The Church Wilne Works are of a conventional clarification filtration type, taking water from the River Derwent and producing a potable supply for part of the City of Nottingham. They were commissioned in 1970 with a flow of 45,500 m^3/day and have now been doubled in size as part of a possible final extension to 180,000 m^3/day. The subject of this paper is the granular activated carbon adsorption plant of 91,000 m^3/day (24×10^6 US gal/day) capacity built as an extension to the works in 1973.

The works intake is located 16 km (10 miles) downstream of the large industrial town of Derby. The combined industrial and municipal sewage of Derby is treated to a conventional standard in a large modern sewage works and discharged to the river, where it is diluted between 4 and 20 times, depending on the river flow. The sewage undergoes further self-purification before a portion is removed for treatment at Church Wilne (Figure 1).

It was known that the quality of this water was near the limit of that considered acceptable as a potable supply source; consequently, a pilot plant study on treatment methods was undertaken for several years prior to and during construction of the main plant.

The treatment process decided upon was as follows:

(i) Long reservoir storage, minimum 30 days

(ii) Flocculation and clarification using chlorinated ferrous sulphate. The chlorine added is controlled to give a level of 0.8 mg/l free chlorine at entry to the final contact tank.

(iii) Powdered activated carbon dosing.

(iv) Rapid gravity sand filtration.

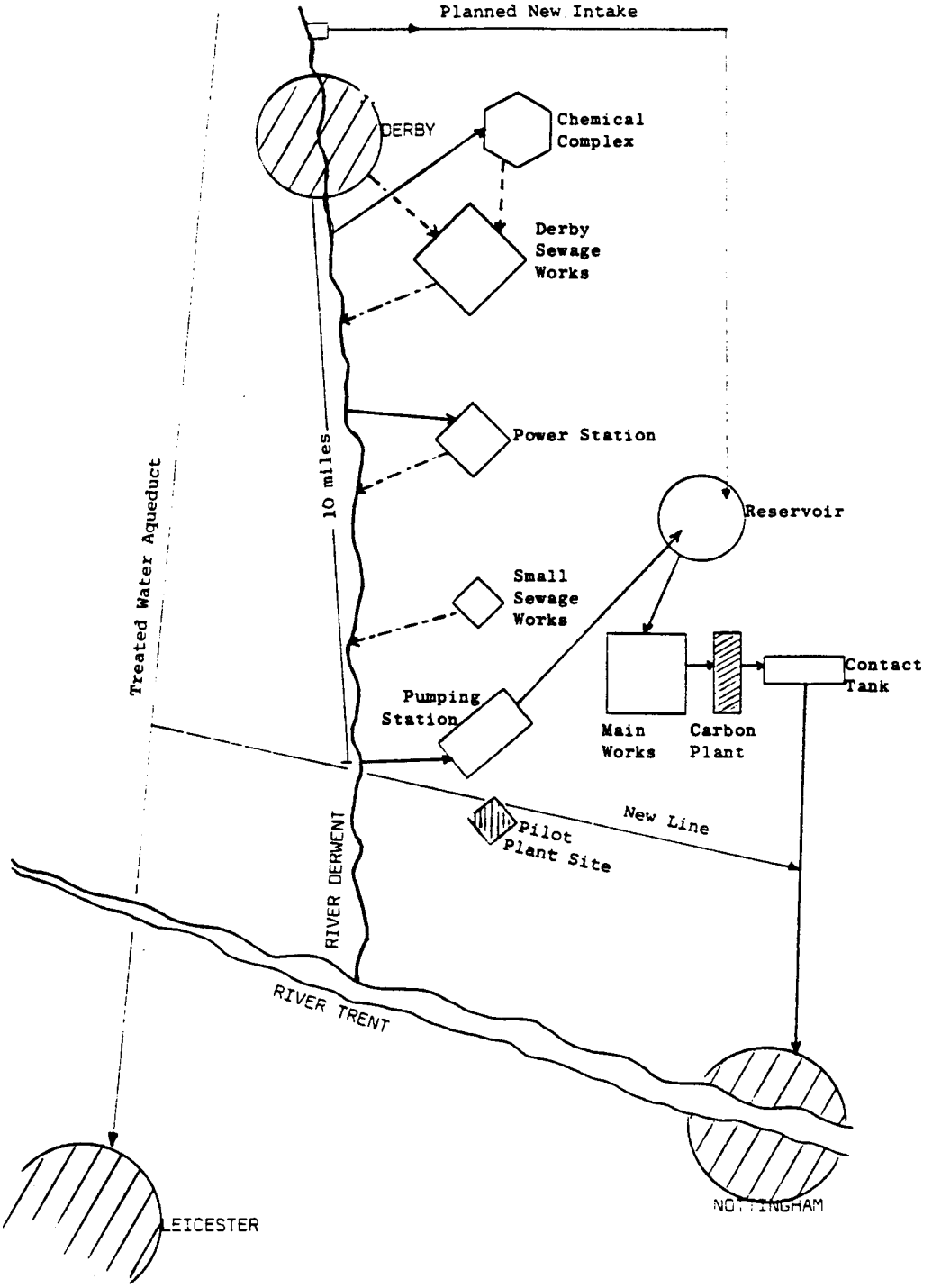


Figure 1. Plant Location

(v) Residual chlorine adjustment with sulphur dioxide to give 0.3 mg/l going into supply after 12 hours residence in the contact tank.

PILOT PLANT

The bankside pilot plant (Figure 2) was a replica of the proposed works.

In the first year's operation of the pilot plant, taste and odor control became difficult. Powdered carbon dosages for complete taste and odor removal averaged 40 mg/l and peaked at 90 mg/l. At this time, studies with potassium permanganate, ozone, chlorine dioxide, and superchlorination all produced no noticeable odor removal. A 30 cm (1 ft.) dia. single stage granular activated carbon column experiment did, however, give complete odor removal. At this stage, Humphreys and Glasgow, Ltd., and Chemviron (Calgon Corp. in the USA) suggested a trial in the summer of 1970 using a test rig comprised of four 10 cm (4 inch) diameter columns with F200 carbon. Contact times per column, which were placed in series, were 1.5, 1.8, 1.8, and 1.8 minutes. Taste and odor results from this unit are shown in Figure 3. Measurements were also made of phenol values, anionic detergents, and TOC using an early-model instrument with a detection limit of approximately 2 mg/l (Figure 4). By that autumn, sufficient data had been accumulated to enable inquiry documents for a granular activated carbon plant to be prepared.

While this pilot plant work was going on, the main works had started up and a high, and consequently expensive, usage of powdered carbon had become a regular necessity. The most effective way of dosing the powdered carbon was found to be a special air-mixed precontact tank with a 20 minute residence time ahead of the clarifiers. Some air stripping of volatiles probably occurred in this tank. Moreover, the carbon was not influenced by coagulation chemicals, as it was when added to the clarifiers. The high dosage rate precluded addition solely at a point before the filters, since otherwise unacceptably short filter runs would have resulted.

BID SPECIFICATION AND CONTRACT

The design requirement was that the equivalent carbon dose rate would be 20 mg/l. This was based on the assumption that if the powder dose rate were 40 mg/l, as in the summers of 1969 and 1970, then the granular dose rate would be 20 mg/l, and that the reservoir storage of 4 to 8 weeks would not give any improvement or deterioration in water quality. The contractor was given freedom of choice over the bed contact time to use in

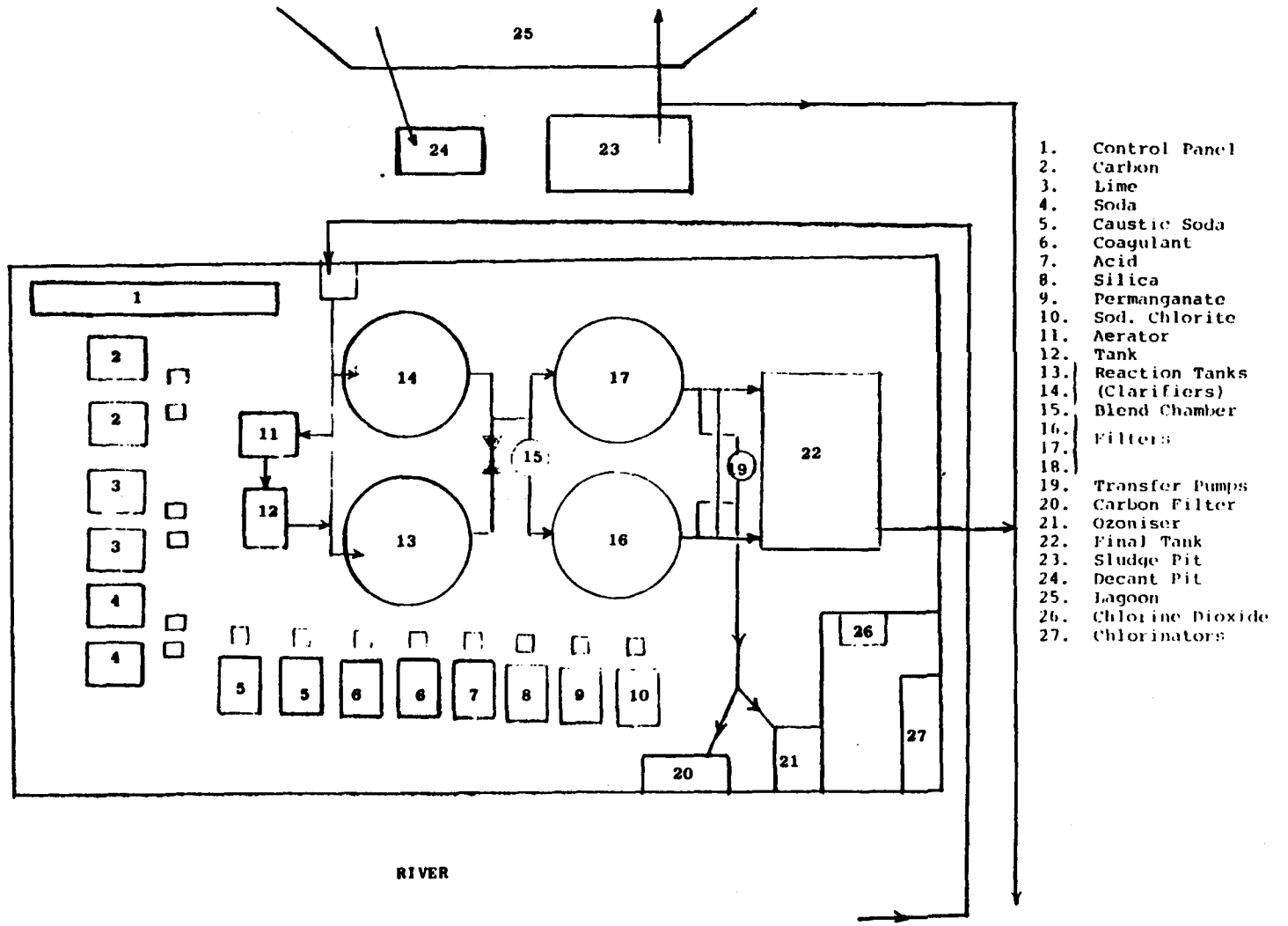


Figure 2. Bankside Pilot Plant

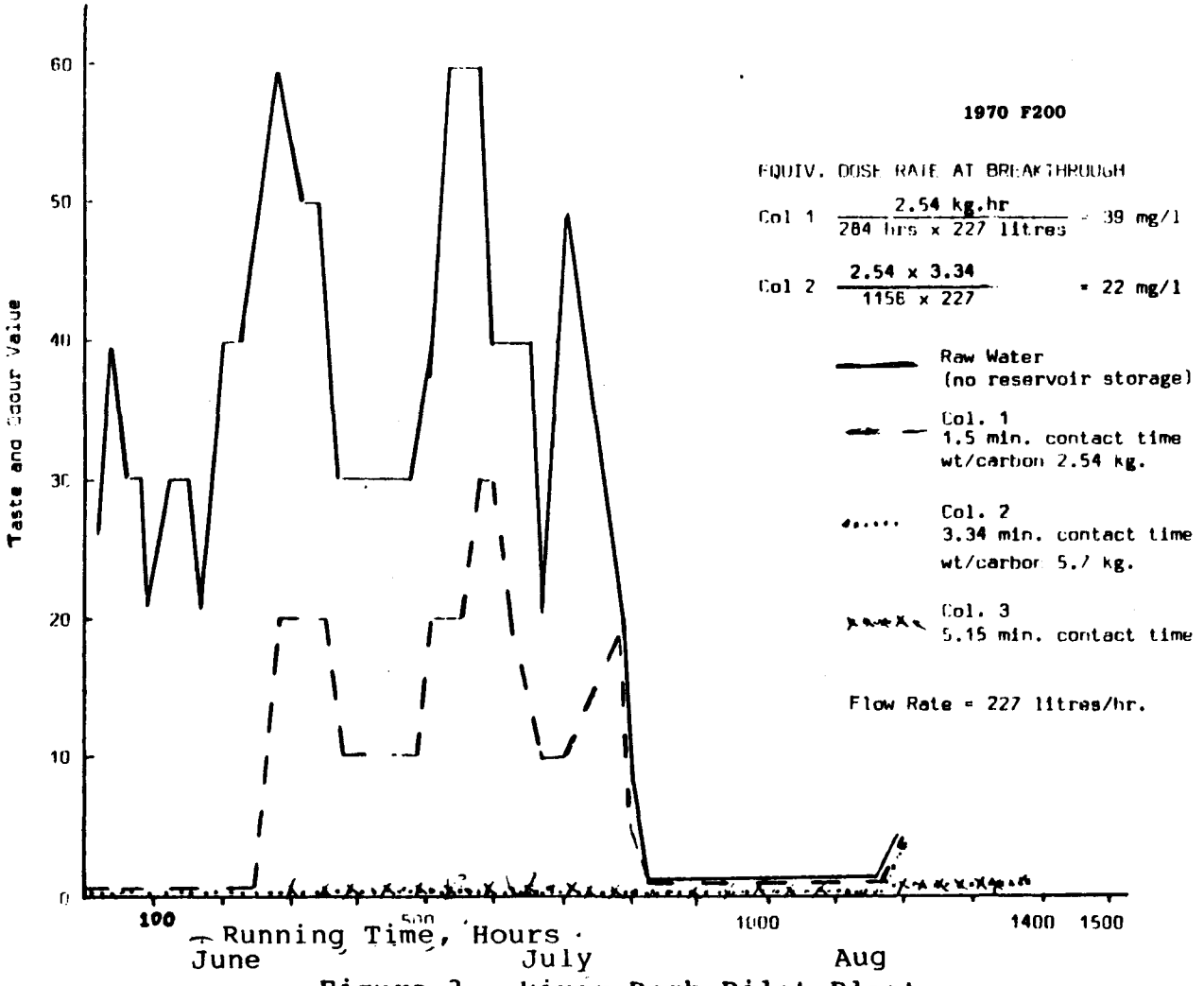


Figure 3. River Bank Pilot Plant

Note: Contact times are cumulative from each preceding column in series; e.g., the contact time for column 3 represents the contact time for columns 1,2, and 3 in series. Column 4 results were below detection limits.

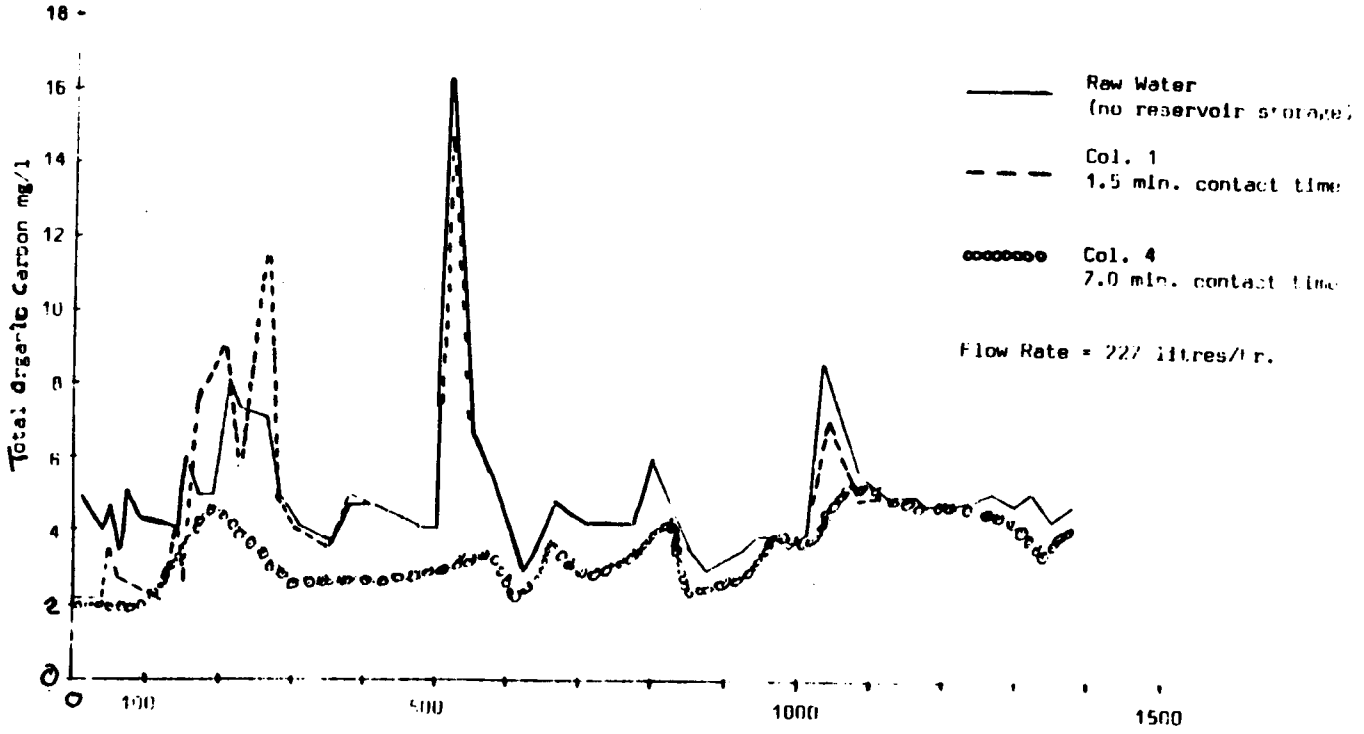


Figure 4. River Bank Pilot Plant
1970 F200

his bid. The specification also called for the following guarantees, regarding:

> complete taste and odour removal at the full scale plant when operating under raw water quality conditions not worse than those encountered by the water treated by the pilot plant; maximum total quantity of carbon required to be regenerated for any particular annual throughput; and the costs of on-site regeneration per ton of carbon regenerated in terms of annual costs. These guarantees were for a two year period. The contractor was required to pay for any losses above 7 percent of the regeneration furnace throughput as part of this guarantee.

The specification did not state that regeneration of the carbon had to be on site; it could be transported to the manufacturer's works for regeneration if this were economic.

CARBON ADSORBERS

The overall flow scheme for adsorption, regeneration, and carbon transfer is shown in Figure 5. The 12 carbon adsorber vessels are arranged in a rectangle of 3 rows of 4 vessels. There are 2 main inlet and outlet headers running between rows 1 and 2 and beyond row 3. The first serves the vessels of rows 1 and 2, the second the 4 vessels of row 2. There are similar headers for inlet and dirty backwash water.

Each carbon vessel is 4.1 m dia by 3.75 m on the straight side. There is an allowance for a carbon bed depth of 2.3 m supported on a 457 mm gravel layer. The carbon depth of the initial charge was 1.6 m, allowing a 4 min contract time. Water is distributed across the top surface by a cross-shaped distributor and collected within the gravel bed by a special slotted pipe/nozzle system. The vessels are painted internally with a 7 mm thick Wailes Dove Bituros enamel paint, applied hot in the vessel fabricator's works. The carbon vessels were built taller than necessary with sufficient sidewall for an extra 763 mm depth of carbon to be added at a later date if required. All pressure loss and other calculations were made assuming the extra carbon depth was in place.

The plant hydraulic design assumption allow for flow surges up to 119,000 m^3 per day at the sand filter plant upstream. This consideration also allows daily output to be maintained while one carbon adsorber is temporarily out of service for bed replacement and another being backwashed.

Carbon is transported throughout the plant as a water slurry of about 1 kg of carbon per 7 litres of water. It is important for minimum attrition of carbon particles that they experience no high shear forces. In the wet carbon system, no

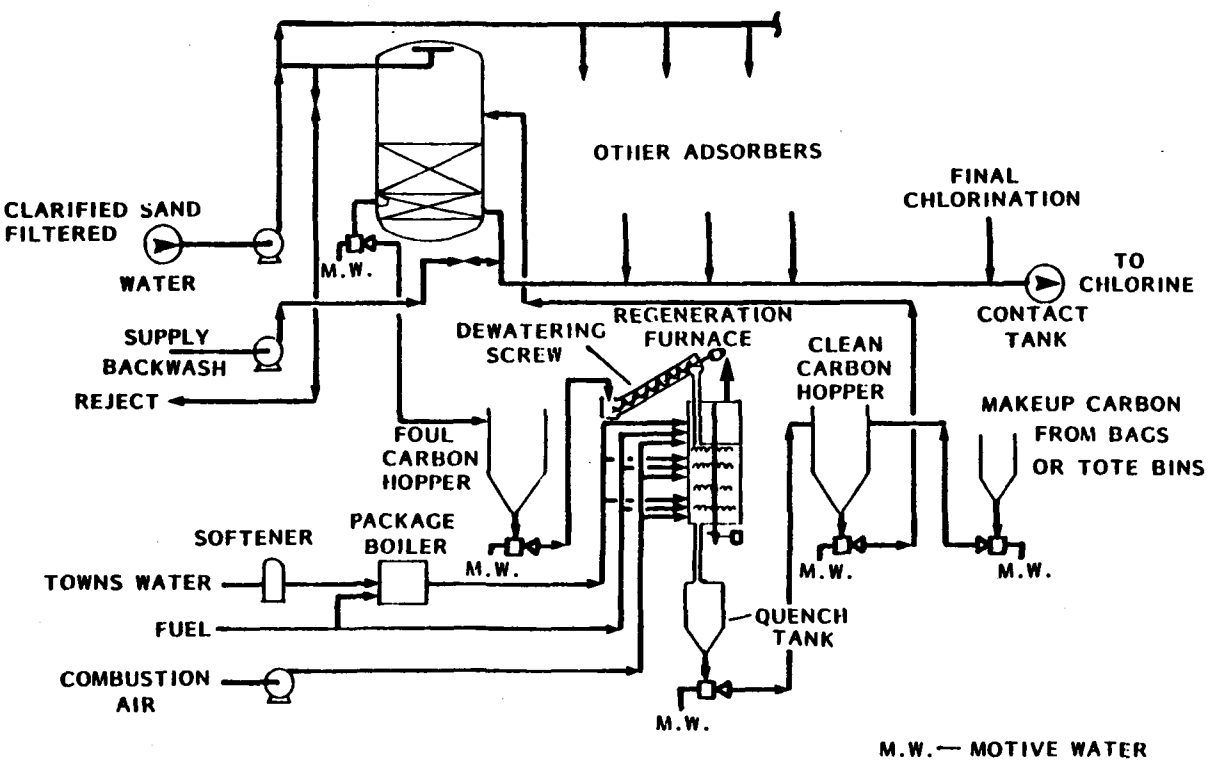


Figure 5. GAC Regeneration System

pumps are used, only water operated jet eductors. There is one large 3-inch eductor per pair of adsorbers, six in all, three smaller 1-inch and 1.5-inch eductors associated with the carbon regeneration furnance and one 3-inch eductor at the clean carbon hopper.

The plant has two large open-top carbon storage hoppers for storage of spent ("foul") and regenerated ("clean") carbon (Figure 5). When a carbon adsorber charge requires regeneration it is transferred to the foul carbon hopper and a fresh charge of regenerated carbon is transferred into the adsorber from the clean carbon hopper. Each operation can be easily completed in two eight-hour shifts. The regeneration of the carbon is then carried out at a slow, controlled rate over the next several days, carbon being taken from the foul hopper, regenerated, and returned to the clean hopper.

COMMISSIONING - ADSORBER SECTION

Construction of the adsorber section was completed in August 1975, and loading of the gravel layers and carbon was completed that September. The initial carbon charge was supplied in 30 kg bags. These were loaded into the carbon makeup hopper. This was designed to take later deliveries of carbon in standard 1 ton tote-bins. For initial loading, a temporary plastic-sided structure and platform with water sprays was erected to keep dust from dry carbon to a minimum. The carbon was educted from the makeup hopper to the clean carbon hopper to ensure good wetting of the particles and from there to each adsorber in turn. In all, 135 tons of carbon (13-1/4 adsorber charges) was loaded in two weeks. This left 1-1/4 charges in the clean hopper after all adsorbers were filled. Each adsorber was backwashed for about 45 minutes to stratify the carbon, leaving smaller granules on top, larger below, and to thoroughly wash fines from the beds. Some difficulty was encountered with air removal from the pipework around the plant. This resulted in unpredictable flows until the full pressure of the low lift pumps was supplied by fully closing the interrupter/bypass valve at the plant inlet/outlet. The predicted plant pressure drops were borne out in practice to within 100 mm (Hg), measured at the top liquid level in the adsorbers.

The second phase of commissioning was a 1-month training period for the operators, during which charges of carbon were moved out of each adsorber into the foul carbon hopper and replaced from the clean hopper. A temporary connection was made from the foul hopper to the clean hopper to bypass the furnance. Each operator shift had about three carbon transfers to handle. All 12 adsorbers were emptied at some time. The emptying technique for the flat-bottom adsorber beds was developed by trial-and-error applications of backwash water, while educting the carbon from an exit point at one side of the adsorber. It is

not possible to empty the adsorbers fully; some 100 mm to 150 mm of carbon always remain above the gravel. There were some fears that this may, at some future date, need to be removed if the same carbon remains at each regeneration; as yet, no problem appears to have been attributed to this. Manual entry with a portable eductor would be necessary to remove this carbon. At the older plant at Gothenburg (converted from an open top gravity sand filter), a rotating gravel-removal screen was installed at the foul carbon hopper when this emptying method was used, to remove any small gravel sucked up with the carbon.

WATER QUALITY

Taste and Odour

Experience with taste and odour removal has been excellent (Figure 6). Before the granular carbon plant was completed and only the powdered system was in use, the complaint level from 80,000 consumers ran at around 10 to 12 per week, but this dropped to 1 per month when the adsorbers were put on line.

One supply area, previously on an ultra-pure sandstone borehole water, and then switched to the river supply, did produce a number of complaints at a time when the carbon adsorbers were nearing exhaustion. Since final disinfection was changed to chlorine dioxide in 1977, no complaint of taste and odour from consumers has been made.

Results from the interlaboratory studies of Taste and Odour Numbers vary widely. One sample of very poor raw water was split four ways and sent to different labs; each recorded intra-laboratory repeatable result is indicated in Table 1.

Table 1

Interlaboratory Comparison of Taste and Odour Numbers

	Taste and Odour Numbers
Works Laboratory	90
Local Industrial Laboratory	80
Trent River Authority	420
W.R.C. Medmenham	600

The last two numbers were determined under very strict air cleanliness research conditions using a panel of samplers and are much higher than the results determined under routine methods in the Works Laboratory.

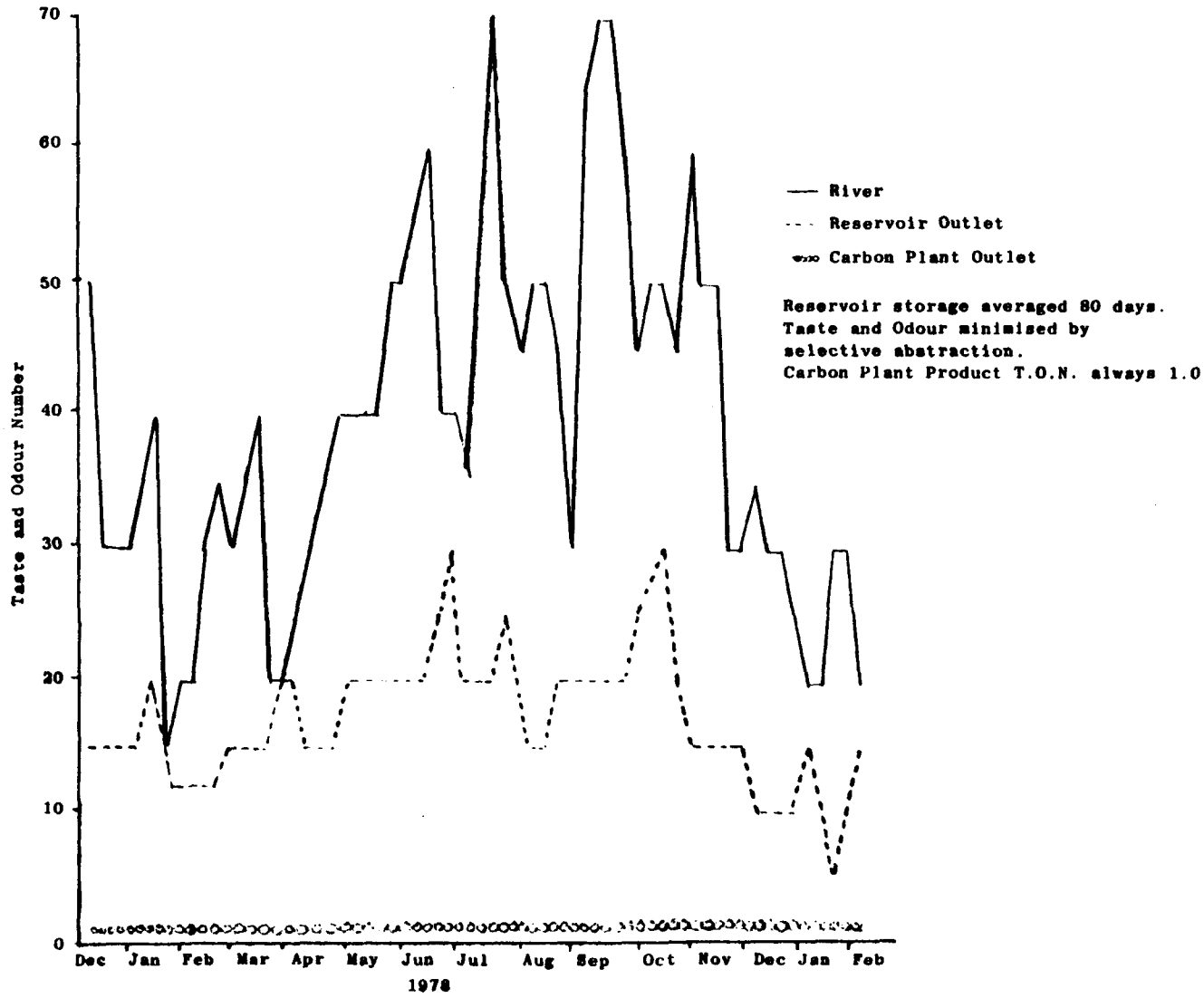


Figure 6. Taste and Odor Removal at Church Wilne Works

Microbiological

One problem mentioned by other carbon bed users is a proliferation of microbiological growth within the bed. This has never been a problem at Church Wilne. The water at the plant inlet contains 0.8 mg/l of free chlorine and the dechlorination reaction within the beds has never taken the concentration below 0.05 mg/l (normally 0.1 mg/l) at the outlet, even at a 15 minute contact time. One UK plant reported a severe outbreak of Nais worms when dechlorinated water was fed to carbon beds.

At one period in the pilot plant study an outbreak of the algae anabaena was incompletely stopped by the sand filters and decomposition of these within the carbon bed produced a strong "chloroform" type odor at the plant outlet. This occurred to a lesser extent at the main plant, but a more rigorous backwashing, particularly of any idle adsorbers, cured the problem.

Total Organic Carbon

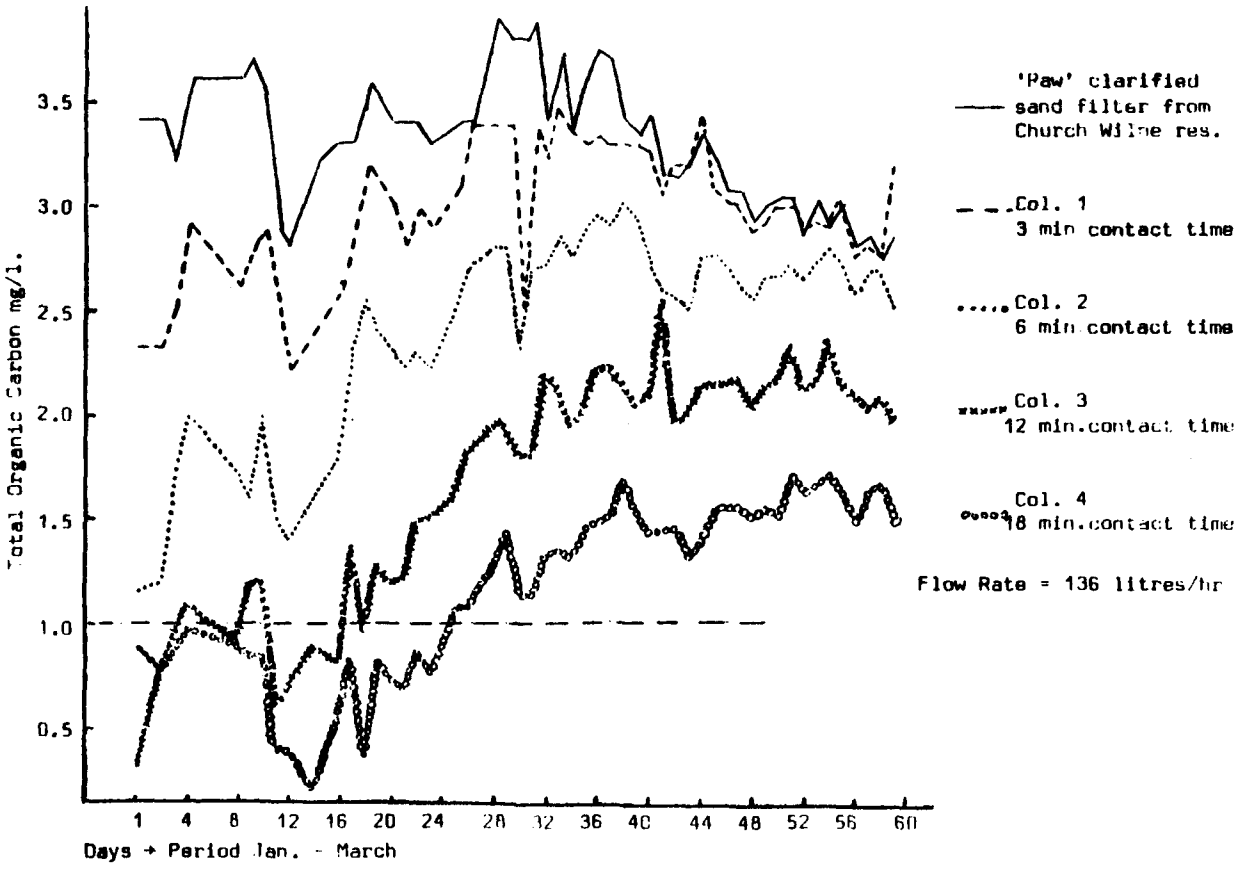
Removal of TOC was not a criterion for the plant design using F200 carbon. In a pilot column test a contact time of 4 minutes with new carbon gave a reduction to 40 percent of the influent TOC level of about 3 to 5 mg/l for 5 to 6 days. This then rapidly rose to 95 percent of the raw water level. In fact, TOC's higher than the influent levels are often recorded. This is probably due to a selective leaching effect or possibly some sinking movement of heavier exhausted grains to the bottom of the bed.

The pilot four column unit was initially used in parallel with the main plant for guarantee purposes. Later, when these initial objectives had been met, it was used for research on TOC removals at long contact times using F400 carbon. At this time, accurate TOC measurements were possible at low levels using a CO_2/CH_4 converting, GLC type, TOC instrument (Figure 7).

If a 1 mg/l TOC standard were set, a carbon bed with 12 and 18 minute contact times would be exhausted in 17 days and 24 days, with equivalent dose rates of 196 mg/l and 218 mg/l, respectively.

HALOFORMS

Haloform levels produced by chlorination are not significantly reduced by activated carbon beds when free chlorine is present throughout the bed (Table 2). Levels are reduced if chlorine is absent, but other operational problems of a microbiological nature can result. One advantage of the use of ClO_2 for the distribution residual is that no further increase of haloforms is found in the supply network.



Running Time, Days

Figure 7. TOC Removal in a Column Test With F400

Table 2

Typical Haloform Concentrations, mg/m^3

	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
River Water	3.0	0.3	0.5	2.4
Before Carbon Plant	14.8	20.2	19.6	2.4
After Carbon Plant	10.4	14.4	9.8	2.4

Detergents

Removal of anionic detergents, although not expected to be significant at the low contact times with F200, was in fact quite good. The low influent levels of 0.08 to 0.10 mg/l were reduced by 90 to 100 percent for 34 days, followed by a gradual rise to the input level.

OPERATION

Some difficulties occurred in the summer during plant restart after shut-down periods. In normal operation, no growth of organisms in the beds is apparent. During one period, after a shut-down of only 4 hours, a bloom of a bright green discoidal diatom ("Cyclotella") caused clogging of the beds and a long backwash was necessary to restore forward flow. The first backwash water contained thousands of cells per ml.

It is now normal practice to give the adsorbers a short, easing backwash before restart after any shutdown. Otherwise, problems such as air blinding, gas bubble generation within the beds, bed compaction, or biological growths invariably cause high bed pressure drops.

Winterization

The plant is one of the first in the UK designed to conform to normal outside petrochemical plant practice, but operation in severe winter conditions of -1 to -10°C has still caused operational difficulties. A fairly extensive program of preventive measures against freezing was devised, but has proven too onerous on the operators, especially when the furnace is not operating. The furnace area has now been enclosed in a light weatherproof building and some of the adsorber valves, notably the backwash drain valves where the butterfly discs were often frozen to their seats, have been trace heated.

Normal Backwashing

The adsorber valves are all electrically operated butterfly types. They can be set to any position between fully open and fully closed, either locally by hand, by local control of the motors, or automatically in the control room. This facility, coupled with the display of flowrate from magnetic flow meters on each adsorber, enables the total flow to be equally divided among the adsorbers in service.

The backwash velocity for a given bed expansion is a function of the density difference between the bed media and water at the operating temperature (Figure 8). This density difference is smaller for GAC/water than sand/water. This means that in GAC adsorbers, a greater expansion can be produced by a given flow than in similar sand filters. However, with the adsorber, the expansion, and hence cleaning and stratification, efficiency is influenced to a greater extent by water temperature and a higher backwash rate is needed in summer than in winter. The temperature of the water is displayed on the control panel to allow an appropriate rate to be set. Some difficulty arose when two adsorbers were loaded with a 2.3 m (7.5 ft) bed depth, as some carbon was generally carried over with the backwash water. This may have been due to poor adherence to the precise instructions or possibly to a slight biological film on the top of the bed making clumps of carbon granules less dense than normal granules, thus enabling them to be washed out during backwash.

LATEST OPERATION

In 1976-7, new analytical procedures allowed the detection of a series of organic compounds of industrial origin in the final water at trace levels of 20 microgram/litre (µg/l). These were not causing taste and odor problems, but Severn-Trent decided to use the plant for their removal, if possible. Thus, all the adsorbers were put on line even though the daily flow was below half the design flow at approximately 35-45,000 m^3/day. This results in a contact time of 8-10 min. as opposed to the original 4 min. The compounds in question are removed to below 1 µg/l and this level has been set as a standard for this water.

At one period, 2 years ago, two adsorbers were filled with 15 tons of F200 carbon and 15 tons of F400 carbon using the extra bed depth available, creating a 10 min. contact time. A TOC reduction from the average 3-4 mg/l inlet level to 1.5 mg/l at the outlet was seen for the F400. The F400 was no better than the F200 in removing the trace organics mentioned above.

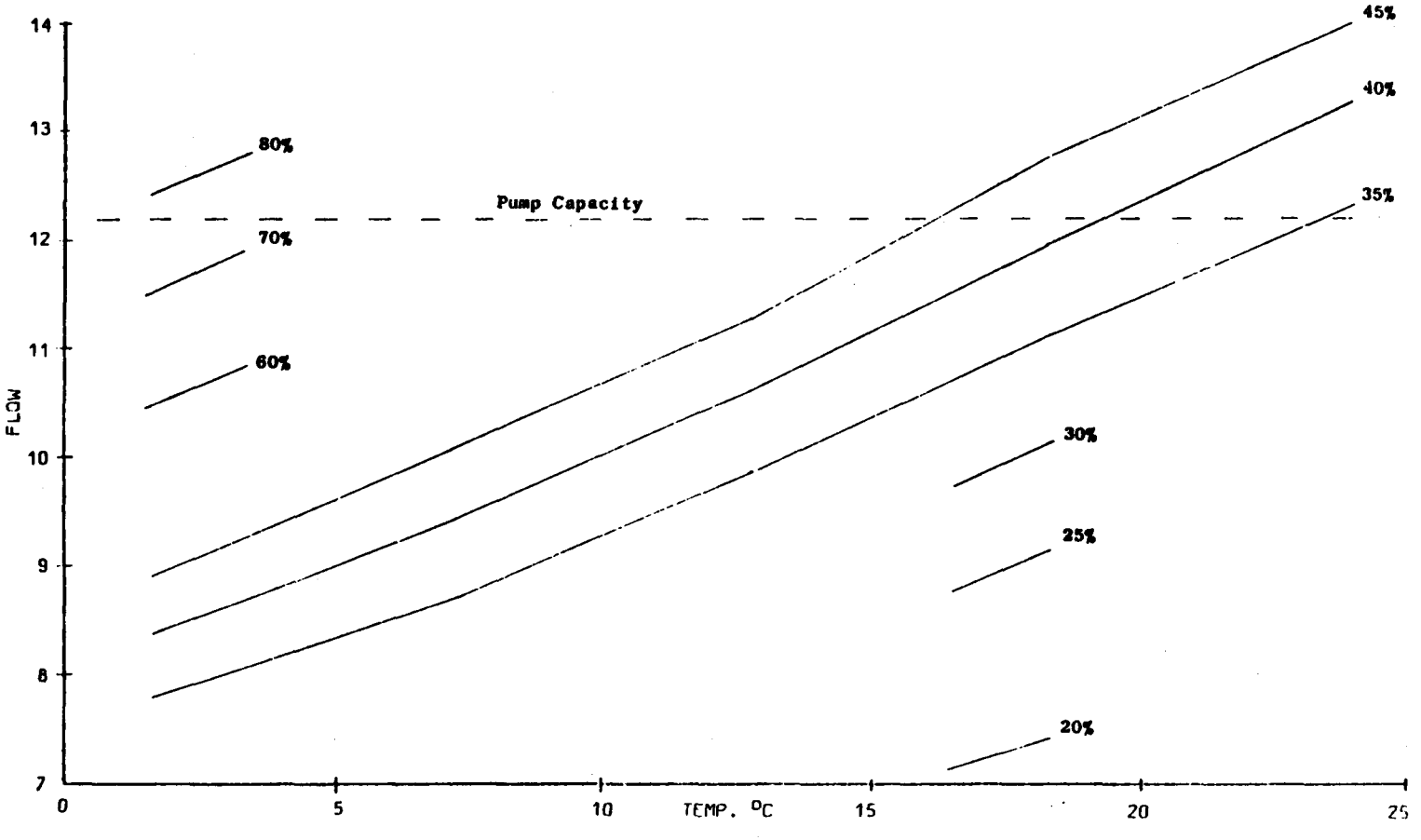


Figure 8. Bed Expansion on Backwashing

SUMMARY

The Church Wilne Works now has a carbon treatment facility that allows water from a problematic source to be supplied to part of the City of Nottingham. The difficulties with odour, from warm water, have been overcome and the originally unsuspected problem of trace organic contamination has been satisfactorily resolved. The Works has its own self-contained carbon regeneration facility, which is covered in a separate paper at this conference.

FUTURE OPERATION

The long term continued operation of the Church Wilne carbon plant is in some doubt. Since the UK water industry reorganization, a more rational use of water supplies in the region has become possible. Already, a short pipeline has been completed to a treated water aqueduct running down the Derwent Valley to Leicester.

The quantity that can be taken from this line is limited but it allows the shortfall at Church Wilne, due to the increased contact time, to be made up. A blended water is currently supplied to Nottingham.

Within the next four years, a new raw water intake upstream of Derby is due to be constructed. The adsorbers may then be allowed to fall into disuse or be retained in a minor taste and odour control role, but continued upkeep of the regeneration facilities will be in doubt.

ACKNOWLEDGEMENTS

This paper is given by kind permission of W.H. Richardson, C Eng, MICE, MI. Mun. E, MRTPI, Dip. TP, Divisional Manager Lower Trent Division of the Severn-Trent Water Authority and of Humphreys and Glasgow Limited (H&G). The authors thank the operations and scientific staff of Severn-Trent and commissioning staff of H&G, on whom the successful running and careful monitoring of the plant depended and whose work is reported in this paper. The comments made and conclusions drawn are those of the authors alone and not those of Severn-Trent W.A. or H&G.

TREATMENT OF GROUNDWATER WITH GRANULAR ACTIVATED CARBON

Paul R. Wood
and
Jack DeMarco

Introduction

Three years of research were conducted at the 23 X $10^3 m^3$/day (60-mgd) Preston water treatment plant in Hialeah, Fla. Groundwater obtained from wells 18 to 30 m (60 to 100 ft) deep, in the porous limestone aquifer, is the sole source of drinking water in southern Florida. The groundwater contains 10 mg/l total organic carbon (TOC) and the trihalomethane formation potential (THMFP) ranges from 650 to 950 µg/l. After lime softening, approximately 18 mg/l of chlorine is added for breakpoint chlorination. The water passes through a chlorine contact basin, a rapid sand filter [2 mm/s (3 gpm/sq ft)] and then into the clearwell. Finished water entering the distribution system contains 3 mg/l of free chlorine. Free chlorine drops to zero in 24 to 48 hr resulting in water at the consumer's tap containing trihalomethanes in the 300-µg/l range. The presence of other purgeable halogenated organic compounds (HOC) increases the total HOC level to the 330-µg/l range.

The results of the first 2 years of research on adsorption of HOC, TOC, and THMFP substances by granular activated carbon (GAC) and synthetic adsorbents from raw, lime softened, and finished water, have been presented in an earlier work (1). Results of the first year of research on the 3-year EPA pilot plant project for removing organic substances from drinking water were presented in periodic progress reports to EPA. This paper, covering a portion of both projects, describes the effectiveness of four types of GAC in removing organic substances from raw, lime softened, and finished water. Carbon 1* was tested in beds 0.75, 1.5, 2.25, and 3 m (2.5, 5, 7.5, and 10 ft) deep with empty bed contact times (EBCT) of 6.2,

*Filtrasorb 400, 12 by 40 mesh, Calgon Corp., Pittsburgh, Pa.

12.4, 18.6, and 24.8 min. Carbons 2**, 3***, and 4**** were tested in beds 0.75 m (2.5 ft) deep with an EBCT of 6.2 min, each.

DISCUSSION

It was found that GAC was the best adsorbent for the water tested because of its ability to remove both precursor substances, as measured by TOC and THMFP, and volatile HOC. Therefore GAC was extensively studied, as represented by the composite flow diagram in Figure 1, for all phases of the 3 years of study. The bench scale adsorption unit located in the laboratory at the Preston plant receives raw, lime softened, and finished water directly from the plant. The glass columns measured 1.5 m (5 ft) in height by 2.54 cm (1-in) inner diameter. A flow rate of 2 mm/s (3 gpm/sq ft) was maintained by rotameters. The columns were backflushed as required to maintain a given range of inlet pressure.

PURGEABLE HALOGENATED ORGANIC COMPOUNDS

The average concentration of 19 specific purgeable HOCs for the 3-year study period for raw, lime softened, and finished water at the Preston plant is shown in Table 1. The raw groundwater had a very low level of high molecular weight extractable compounds (industrial and agricultural pollutants) and a considerable concentration of purgeable HOC averaging 48 µg/l. The three major compounds in order of concentration were cis-1,2-dichloroethene, vinyl chloride, and trans-1,2-dichloroethene. The generally lower concentrations of HOC in the lime softened water versus that in raw water can be explained by the loss of compounds through volatility and adsorption on the precipitated sludge. The increase in the THM levels can be attributed to a small amount of chlorine, which was added before the lime to activate the sodium silicate used as a flocculation aid. The concentration of HOC in finished water was less for some compounds and greater for others. Finished water from the clearwell contained approximately 187 µg/l of HOC. Detailed results of changes in HOC concentrations in the overall treatment plant profile, and adsorption by adsorbents were presented in an earlier work (1). The only other observation drawn from the earlier paper is that despite a reduction in TOC from 10 mg/l in raw water to 5.4 mg/l in finished water, the adsorptive capacity of carbon 1 for cis-1,2-dichloroethene was 30

**Nuchar WVG, 12 by 40 mesh, Westvaco Corp., Covington, Va.
***Hydrodarco 1030, 10 by 30 mesh, ICI Americas, Inc., Wilmington, Del.
****Witcarb Grade 950, 12 by 30 mesh, Witco Chemical Corp., New York, N.Y.

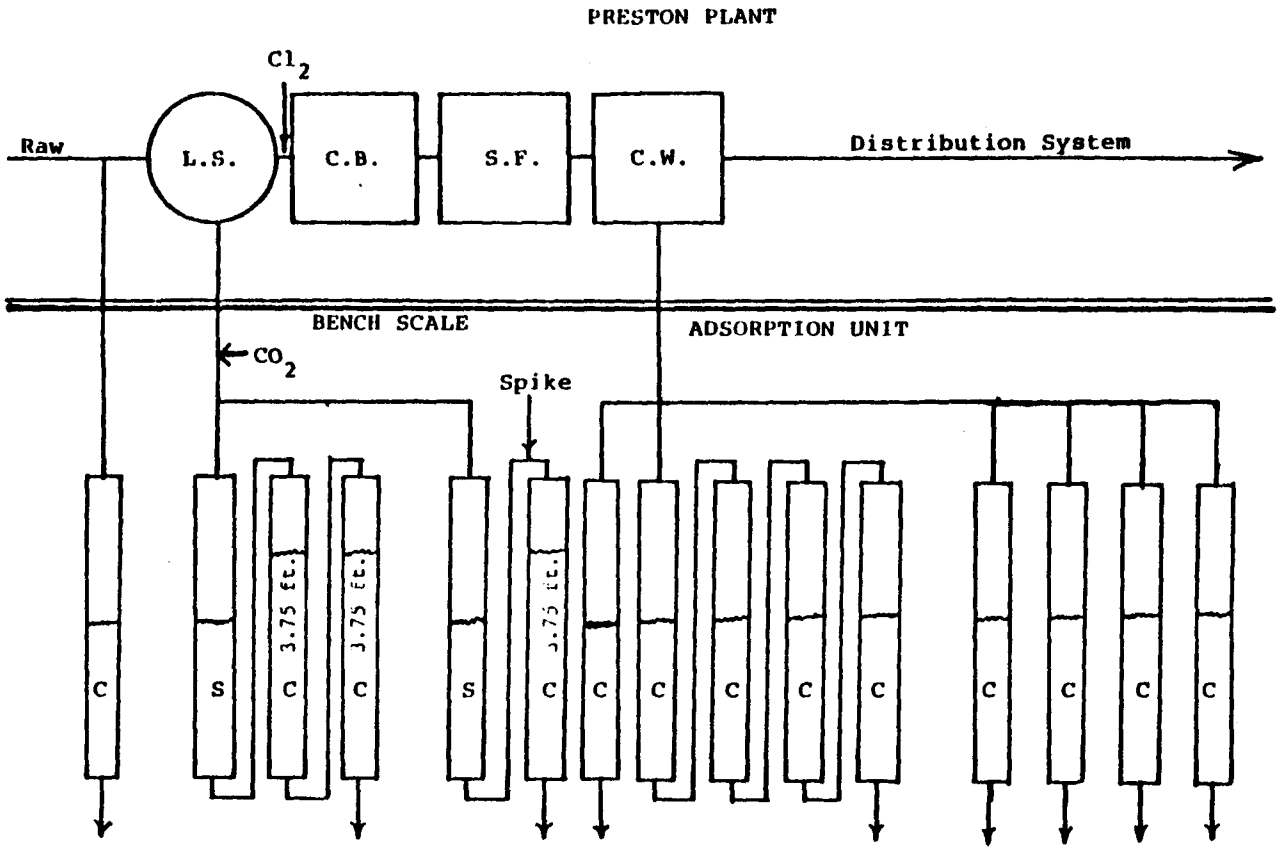


Figure 1. Composite Flow Diagram For All Phases of GAC Studies Over A Three Year Period

Table 1

Average Concentration of Nineteen Specific Purgeable Halogenated Organic Compounds in Raw, Lime Softened (L.S.), and Finished Water (F.W.) at the Preston Plant

Average Consentration
ug

	RAW	L.S.	F.W.
VINYL CHLORIDE	12.8	9.7	6.2
METHYLENE CHLORIDE	0.45	ND	ND
TRANS 1,2-DICHLOROETHENE	1.5	0.95	0.77
1,1-DICHLOROETHANE	0.58	0.45	0.4
CIS 1,2-DICHLOROETHENE	25.6	22.3	19.9
CHLOROFORM	.08	1.2	67.3
1,1,1-TRICHLOROETHANE			
1,2-DICHLOROETHANE	0.1	0.12	7.7
CARBON TETRACHLORIDE			
TRICHLOROETHYLENE	0.34	0.33	0.68
BROMODICHLOROMETHANE	N	0.35	47
TETRACHLOROETHYLENE	0.003	0.004	0.003
CHLORODIBROMOMETHANE	N	0.13	33.6
CHLOROBENZENE	1.1	0.72	0.86
BROMOFORM	N	0.007	2.6
p-CHLOROTOLUENE	0.02	0.03	0.1
m-DICHLOROBENZENE	N	N	N
p-DICHLOROBENZENE	0.51	0.28	0.21
O-DICHLOROBENZENE	0.17	0.16	0.14
TOTAL	43.25	36.73	187.36

N=Nil
ND=Not Determined

percent greater in raw water than in finished water. As observed in Table 1, the level of cis-1,2-dichloroethene compared to the total level of all 19 HOCs is 59 percent in raw water and 11 percent in finished water. The greater adsorptive capacity of GAC for cis-1,2-dichloroethene in raw water is attributed to less competitive adsorption by other HOCs, despite the larger amount of TOC present. The adsorptive capacity of GAC increases with the influent concentration of a substance. This was included in the calculations (1) and the 30 percent increase was based on equal influent concentrations.

ORGANIC REMOVAL BY FOUR TYPES OF GAC

The bench scale adsorption unit was set up, as shown in Figure 2, to study the effectiveness of four types of GAC to adsorb TOC, THMFP, and HOC from finished water. The volume and EBCT (6.2 min) were constant for all carbons.

HOC Removal

The effectiveness of the four types of GAC in removing HOC is discussed briefly; emphasis is placed on the removal of THM precursor substances. Detailed HOC removal data based on both equal volume and equal weight of GAC are reported elsewhere (2).

Chloroform breakthrough curves are presented in Figure 3. These curves are typical of the relative performance of each GAC for all the HOC monitored. The results of integrating these breakthrough curves are shown in Table 2.

Table 2

Percent of Chloroform Removal By Four Types of GAC

Type of GAC	Weight of Carbon in Grams	% Chloroform Removal By Equal Volume of GAC	% Chloroform Removal By Equal Weight of GAC (172.4 Grams)
WVG	195.6	40	36
ICI	144.1	48	57
F400	163	53	56
W950	172.4	78	78

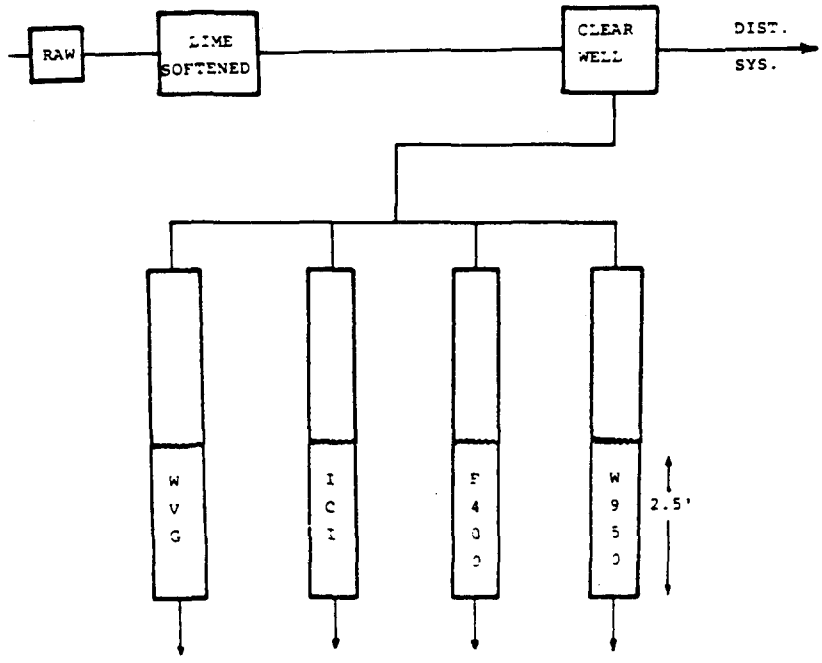


Figure 2. Bench Scale Adsorption Unit Flow Diagram for the Study of Four Types of GAC on Finished Water

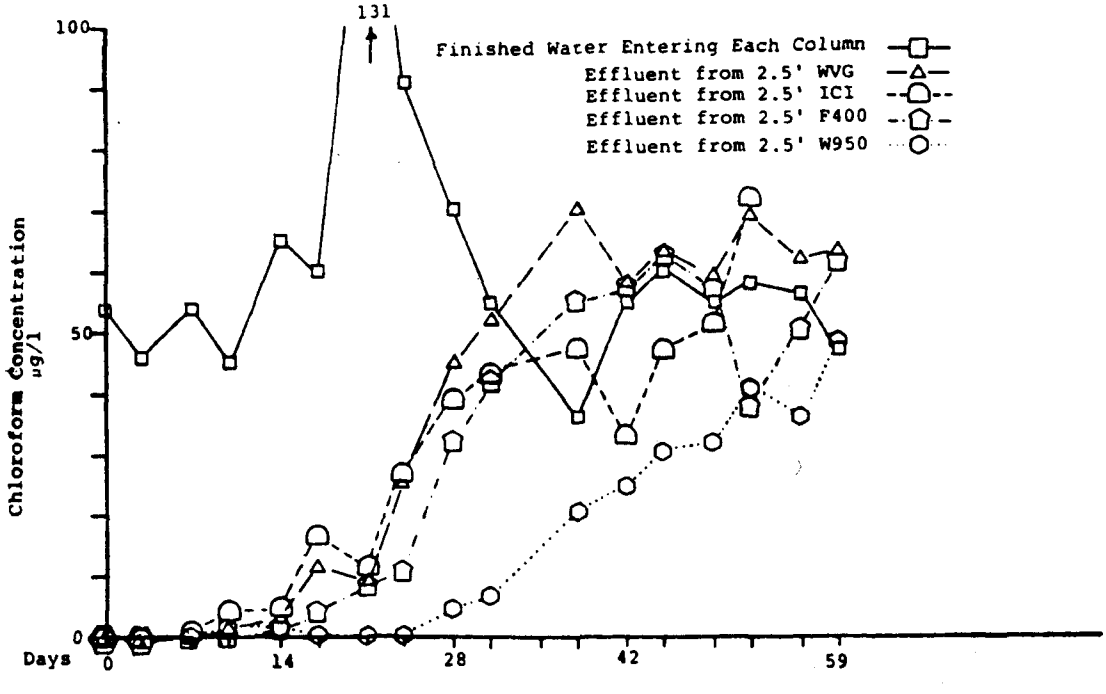


Figure 3. Chloroform Breakthrough Curves Through Four Types of GAC Columns

On an equal volume basis, W950 had the largest adsorptive capacity with 78 percent removal of chloroform, followed by carbons F400, ICI, and WVG with 53, 48, and 40 percent, respectively. The last column of data in Table 2 shows the percentage removal at equal carbon weights of 172.4 g, the weight of W950 used. Once again, W950 is superior with 78 percent removal. F400 and ICI are very similar with 56 and 57 percent removal, respectively. The removal of chloroform by WVG was 36 percent.

In Figure 3, the scale of the "Y" axis does not show that W950 allowed a continuous low level passage of chloroform before the major breakthrough at 28 days. This continuous low level passage averaging 1 µg/l is shown in Figure 4. Since the surface of this GAC (made from a hydrocarbon resin) is hydrophobic and there is a higher percentage of surface area in the small diameter pore range than in the other types of GAC, the manufacturer recommends boiling the carbon in water to deaerate it. This was not done for the initial test. Toward the end of the 59-day test period another column was placed in service using boiled W950 GAC. Low level passage of chloroform through this column is shown in Figure 4. The average passage was again 1 µg/l indicating that deaeration did not affect the level. Further study with greater bed depths of this carbon will be necessary to determine the mass transfer zone.

GAC Bed Life

In this water system, it was discovered that the most economical use of GAC is on finished water. Finished water normally leaves the plant with 3 mg/l of free chlorine and a total HOC level in the 185 µg/l range. The free chlorine reacts with precursor substances still present in the water after it leaves the plant, dropping to zero in less than 24 hr. Occasionally the decline in the amount of free chlorine will take up to 2 days. The growth of additional THM in the distribution system raises the level of total HOC at the consumer's tap to more than 300 µg/l.

If GAC were used on finished water from the clearwell before the water leaves the plant, in order to remove HOC and THMFP substances and limit the level of total THM at the consumer's tap to not more than 100 µg/l, several problems would be encountered. Carbon removes all free chlorine so that the effluent from a GAC column would have to be rechlorinated to 3 mg/l of free chlorine to meet current state requirements.* Rechlorination is also necessary because of the high bacterial

*Free chlorine levels in finished water vary according to individual state requirements.

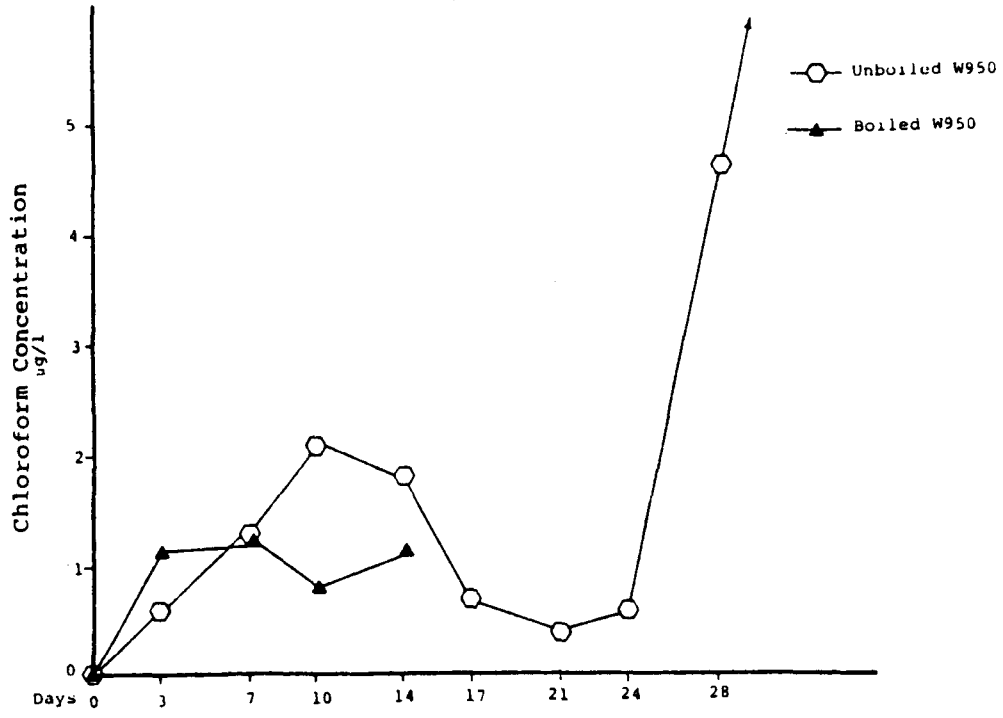


Figure 4. Low Level Passage of Chloroform Through GAC W950 Before Major Breakthrough at 28 Days

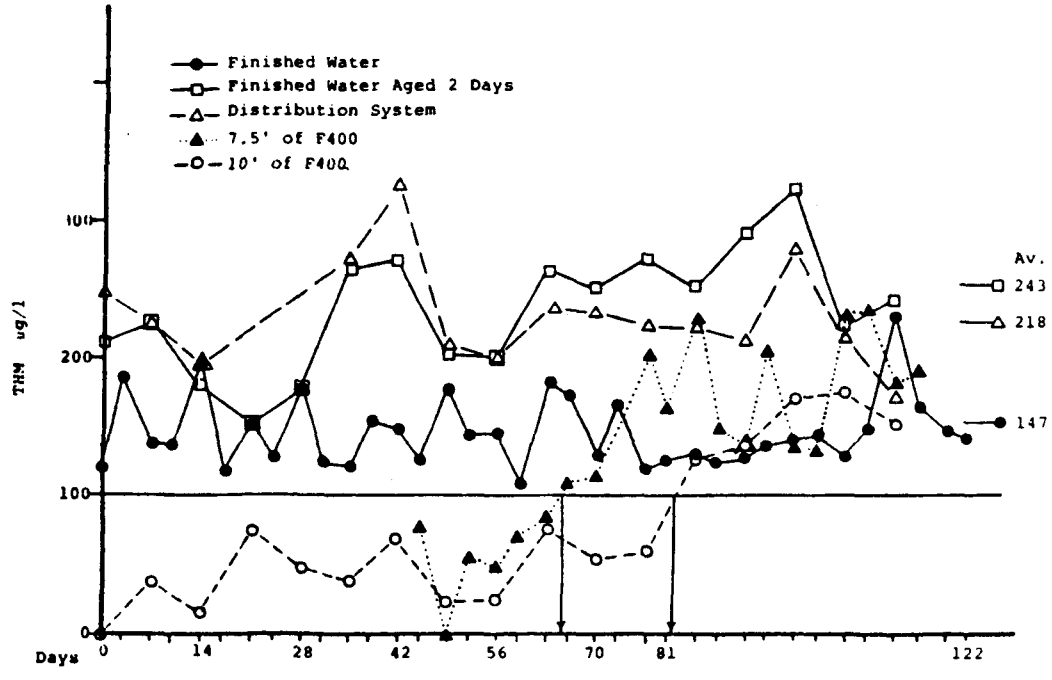


Figure 5. Bed Life of 7.5 and 10 Feet Deep Filtrasorb 400 Adsorbers

count (1) in the GAC effluent. The GAC bed life for this system was determined by using the criterion that bed exhaustion occurs when a sample of the bed effluent, rechlorinated to 3 mg/l of free chlorine and held for 2 days, reaches a THM level of 100 µg/l. Bed life for 2.25- and 3-m (7.5 and 10-ft) deep columns of carbon 1 are shown in Figure 5. The influent concentration of total THM in µg/l in the finished water entering the distribution system is shown. Values showing the total THM in finished water aged 2 days in the laboratory and having 2 days' residence in the distribution system are also shown. Rechlorinated 2-day, bottle-aged sampling was initiated on day 45 of the 122-day test period for the 2.25-m (7.5-ft) deep column. For a 7.5-ft GAC column, the 100 µg/l line was crossed at 65 days. For a 3-m (10-ft) deep column, the bed life was 81 days, which represents a carbon use rate of 10 kg/ml (80 lb/mil gal). During most of the 81 days, the level of total THM at the consumer's tap would exceed 50 µg/l.

By plotting THM breakthrough in the 2.25- and 3-m (7.5 and 10-ft) deep carbon 1 beds, as shown in Figure 6, it can be seen that even if all the THMFP were removed from finished water by the carbon, bed failure would occur (i.e., breakthrough would reach the 100 µg/l level) in 94 and 119 days, respectively. If vertical lines are drawn from the X axis at 65 and 81 days (Figure 6), which are the bed life failure days for 2.25 and 3 m (7.5 and 10 ft) of GAC in Figure 5, it is observed that at 65 and 81 days, respectively, one half and one fifth of the 100 µg/l level were a result of THM breakthrough.

In a separate phase of the work, bed life based on the above criterion was determined for a bed of carbon F400 that was 0.75 m (2.5 ft) deep (Figure 7). Curves are also presented for the concentration of total THM in the finished water entering the column, the total THM in 2-day, bottle-aged finished water (representing distribution system growth), THM breakthrough in the column effluent, and THM growth in rechlorinated 2-day aged column effluent. If the carbon removed all the THMFP, bed life would be 35 days because of THM breakthrough. However, actual bed life was only 9 to 10 days and the failure was solely a result of THMFP breakthrough.

In Figure 8, data for the THMFP in finished water and removal by 0.75 m (2.5 ft) of carbon F400 are plotted. A vertical line from 9 to 10 days meets the THMFP breakthrough curve at approximately 200 µg/l THMFP. Therefore a GAC bed 0.75 m (2.5 ft) deep fails (based on the criterion chosen above) when the THMFP breakthrough level reaches 200 µg/l. When the breakthrough curve for TOC was plotted, the value of TOC breakthrough at failure (9 to 10 days) was 3 mg/l.

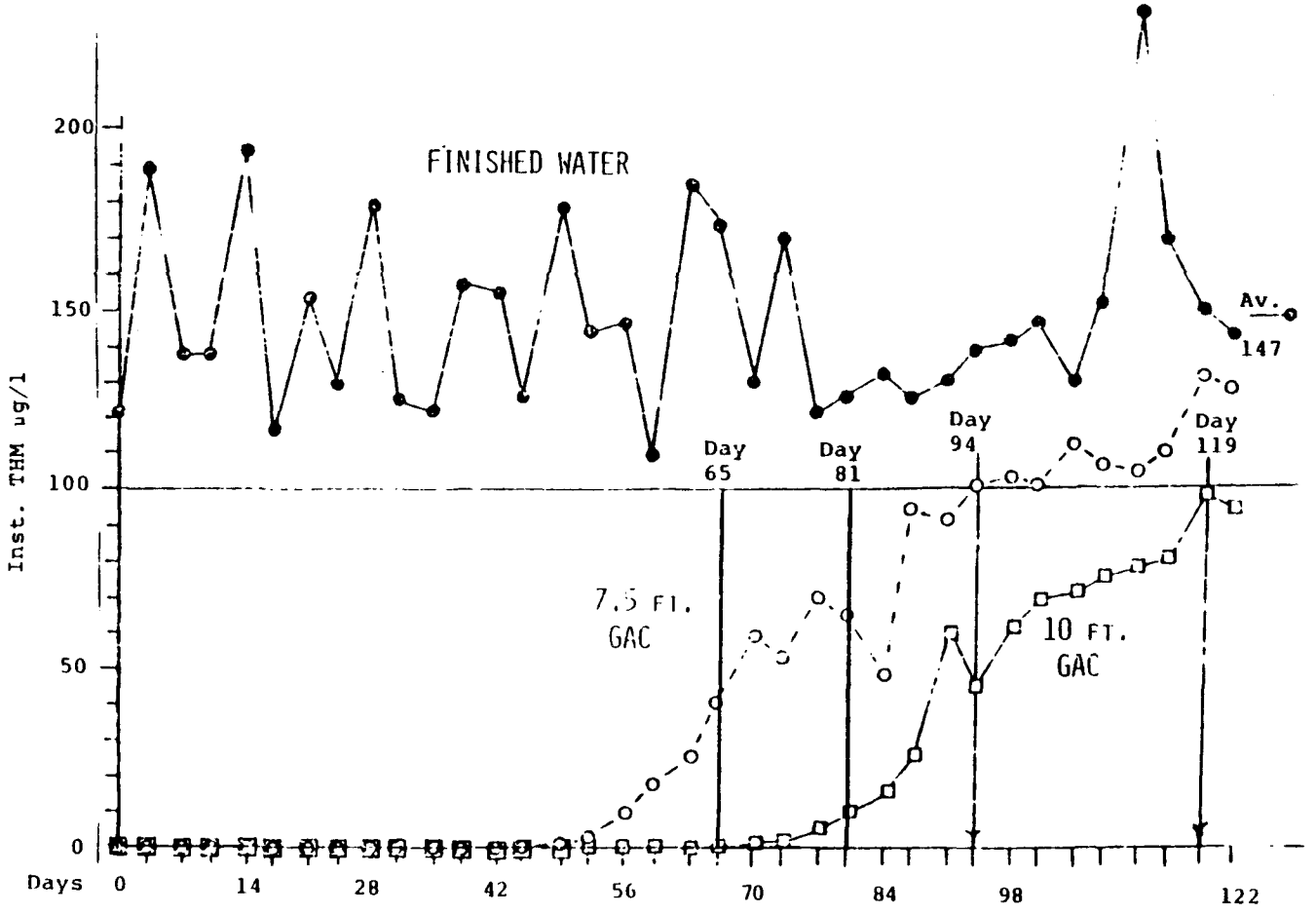


Figure 6. Trihalomethane Breakthrough Curves for 7.5 and 10 Feet of Filtrasorb 400

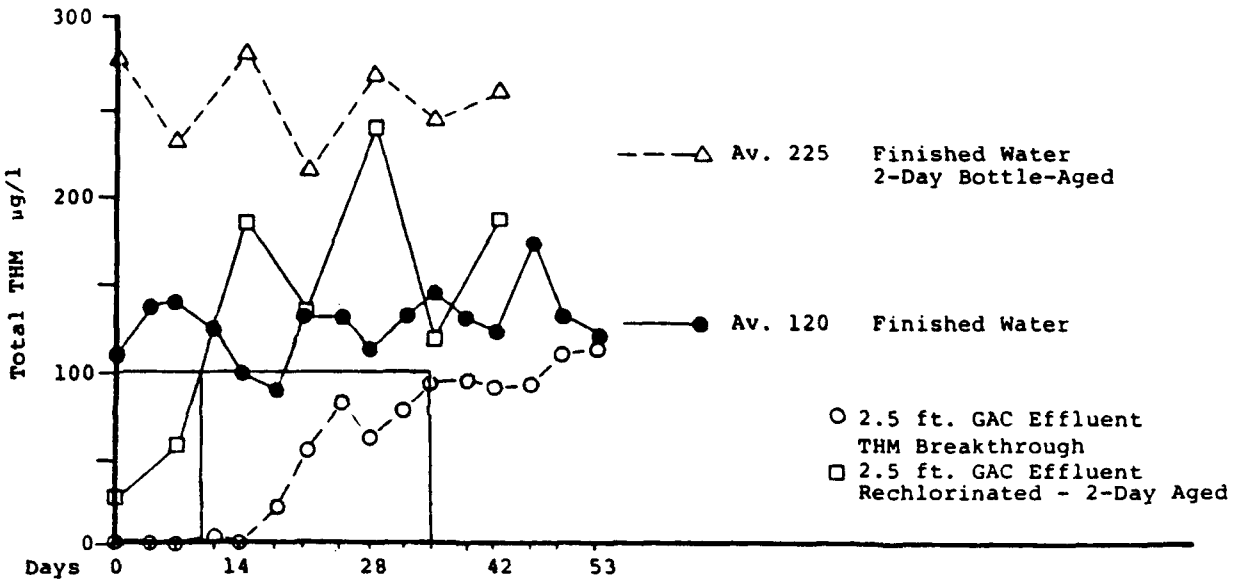


Figure 7. Bed Life of 2.5 Feet of Filtrasorb 400 and THM Breakthrough

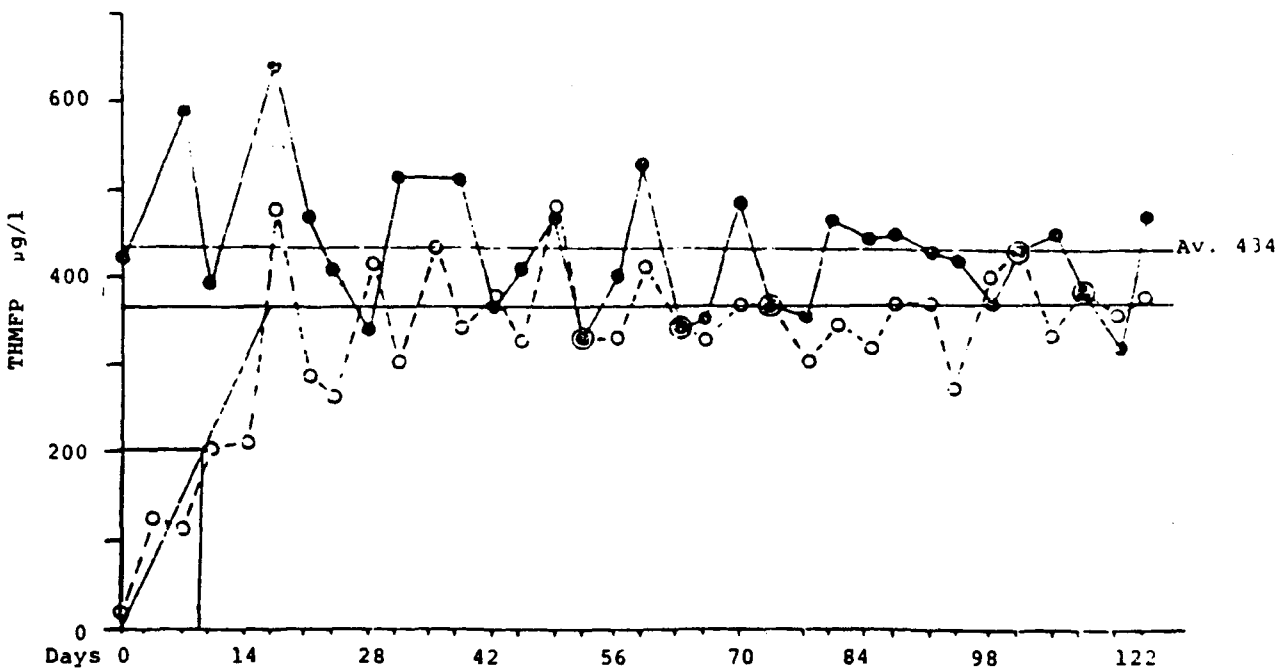


Figure 8. THMFP In Finished Water and Removal by 2.5 Feet of Filtrasorb 400

THMFP and TOC Removal

In Figure 9 the THMFP concentration in finished water entering columns containing four types of GAC and the THMFP breakthrough curves for each carbon are plotted. Adsorption by the four carbons was compared at two points. The curves were integrated at the end of the 59-day test period and at a THMFP breakthrough level of 200 µg/l, the point of bed failure for 0.75 m (2.5 ft) of GAC. At 200 µg/l breakthrough (Figure 9) the bed life for carbon F400 was 10 days, for carbon WVG, 7 days, for carbon ICI, 3 days, and for carbon W950, approximately 1-1/2 days. Although carbon 4 was the best carbon for HOC removal, it was the poorest for THMFP removal. Similar results are observed with TOC data (Figure 10) when compared at the TOC breakthrough of 3 mg/l.

Table 3 shows the amount of THMFP adsorbed by each carbon column in 59 days. This compares the carbons at equal volume and the adsorption on an equal weight basis, compared to the 163-g weight of carbon F400.

Table 3

THMFP Adsorbed by Each Carbon in 59 Days

THMFP Entering in 59 Days = 2002 milligrams (mg)

Equal Vol.	Grams (gm)	Adsorbed mg	% THMFP Removed by Equal Volume of GAC	Wt. to Adsorb as much as 163 gm F400	% THMFP Removed Equal Weight of GAC (163 grams)
F400	163	524	26		26
WVG	195.6	545	27	188 gm	23
ICI	144.1	314	16	240 gm	18
W950	172.4	160	8	565 gm	8

By the 59th day, 2,002 mg of THMFP had entered each column. The weight of each carbon is shown in Table 3. F400 (163 g) adsorbed 524 mg, WVG (195.6 g) 545 mg, ICI (144.1 g) 314 mg, and W950 (172.4 g) 160 mg. The last column of data in Table 3 shows the number of grams of each carbon required to adsorb as much as 163 g of F400. The required weight of WVG was 188 g (163 g of WVG would adsorb 454 mg). The required weights for ICI and W950 were 240 and 565 g, respectively.

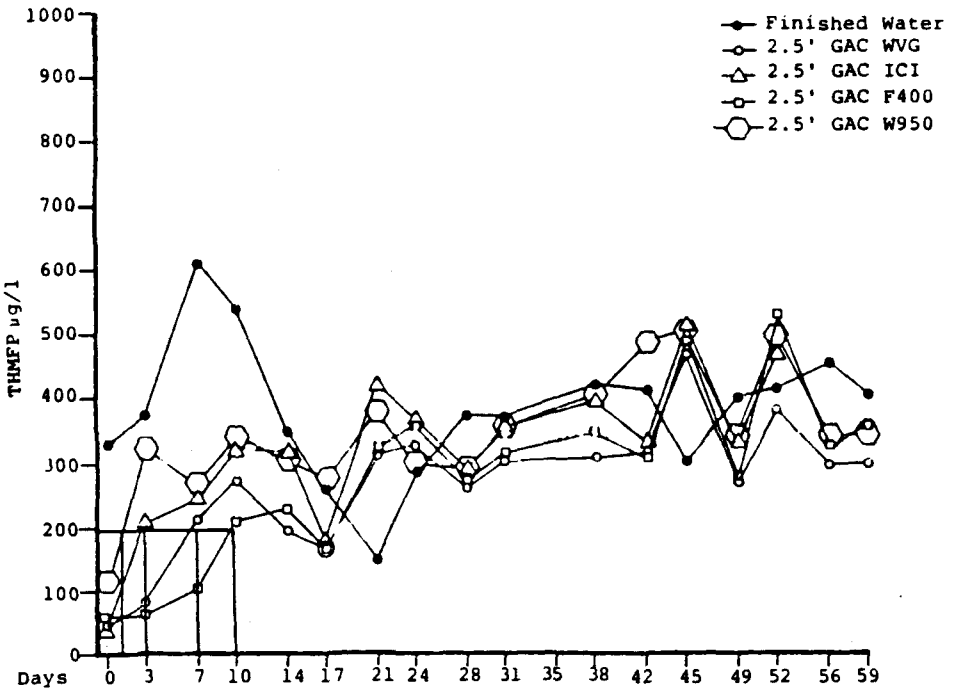


Figure 9. THMFP In Finished Water and In the Effluent From Four Types of GAC

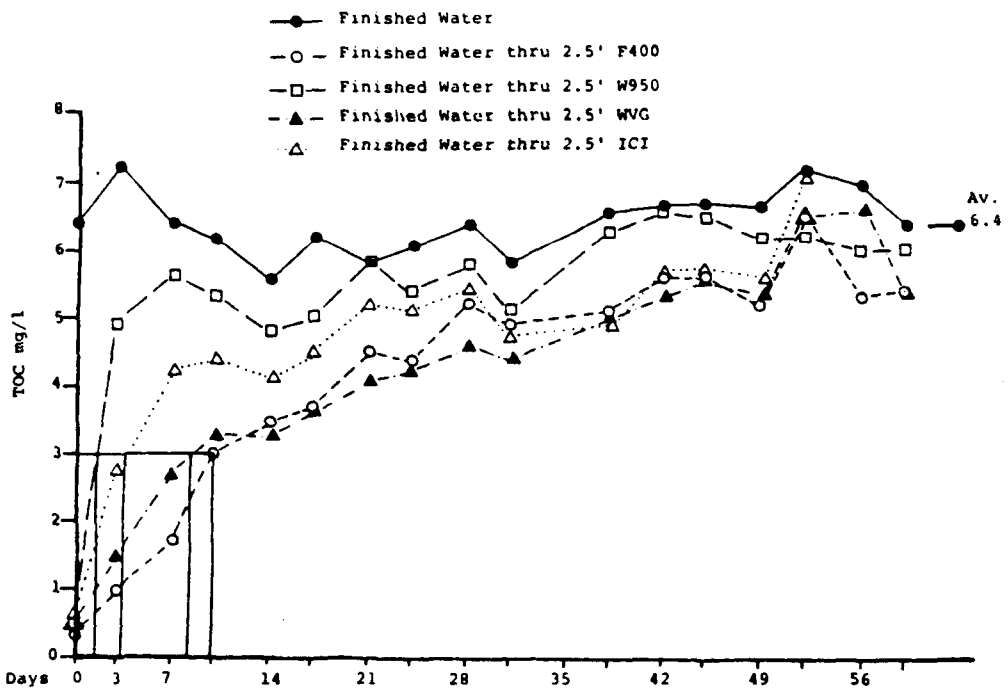


Figure 10. TOC in Finished Water and Removal by Four Types of GAC

An adsorption comparison of each carbon at approximately 10 days is made in Table 4. At this comparison point, F400 appears to adsorb better than at the 59-day comparison point. Similar data for TOC adsorption were found for the two comparison points.

Table 4

THMFP Adsorbed by Each Carbon in Approximately 10 Days

THMFP Entering in Approximately 10 Days = 172 mg

Equal Vol.	Grams (gm)	Adsorbed mg	% THMFP Removed by Equal Volume of GAC	Wt. to Adsorb as much as 163 gm F400	% THMFP Removed by Equal Weight of GAC (163 grams)
F400	163	92.6	54		54
WVG	195.6	60.3	35	300 gm	29
ICI	144.1	23.7	14	563 gm	16
W950	172.4	15.1	9	1057 gm	8

COMPARISON OF GAC ON LIME SOFTENED AND FINISHED WATER

In another phase of the study, F400 was evaluated on the lime softened water. The flow diagram of the bench scale adsorption unit for this phase is shown in Figure 11. In section A, 2.25 m (7.5 ft) of GAC was evaluated to compare the removal of organics with a similar column on finished water evaluated in a previous phase. In section B, 1.13 m (3.75 ft) of GAC was evaluated for removal of organics found in the water and for removal of high molecular weight extractable compounds (industrial and agricultural chemicals) added in the spiking unit. In this paper only two points concerning this phase of the study will be discussed: (1) THMFP breakthrough in section A, and (2) removal of spiked compounds in section B.

THMFP and TOC Breakthrough

The influent concentration of THMFP to the 2.25-m (7.5-ft) GAC column is shown in Figure 12. The THMFP breakthrough for the 2.25-m (7.5 ft) of GAC on lime softened water in this phase and for finished water from a previous phase is also shown. The average influent THMFP concentration on lime softened and

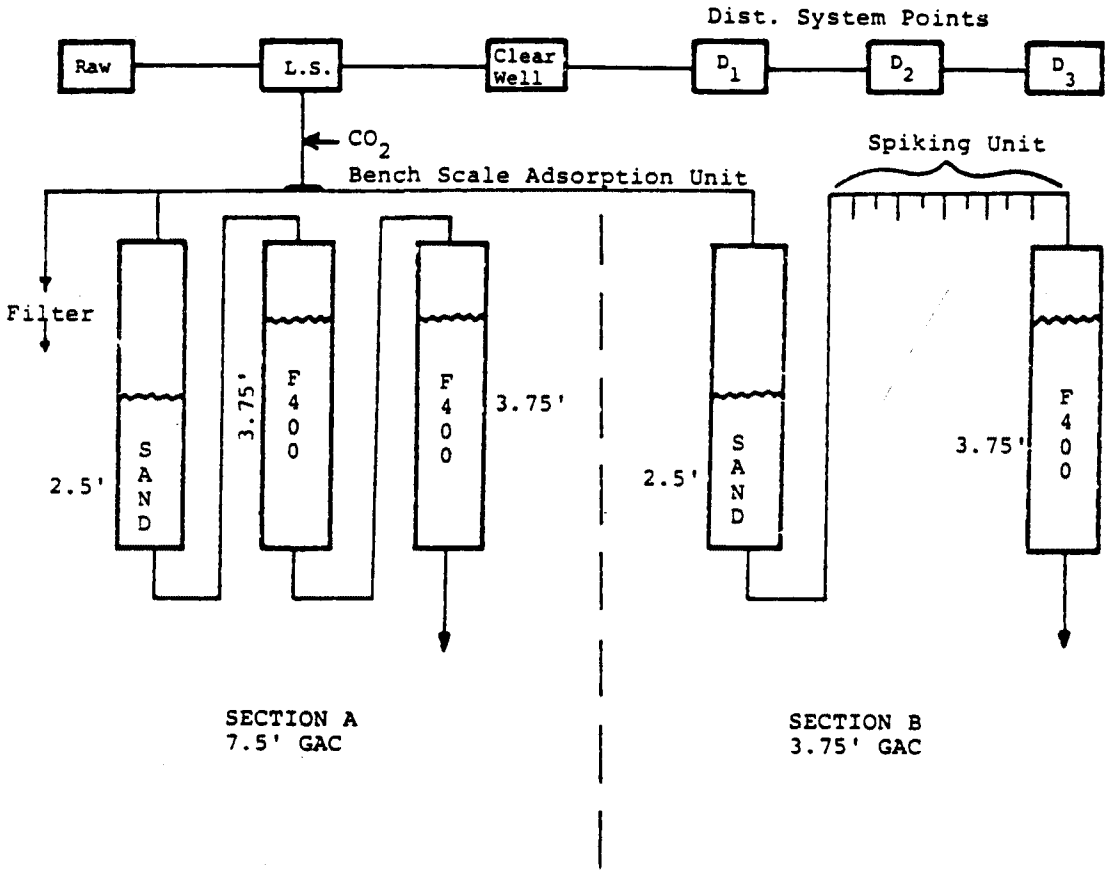


Figure 11. Flow Diagram for Evaluation of Filtrasorb 400 on Lime Softened Water

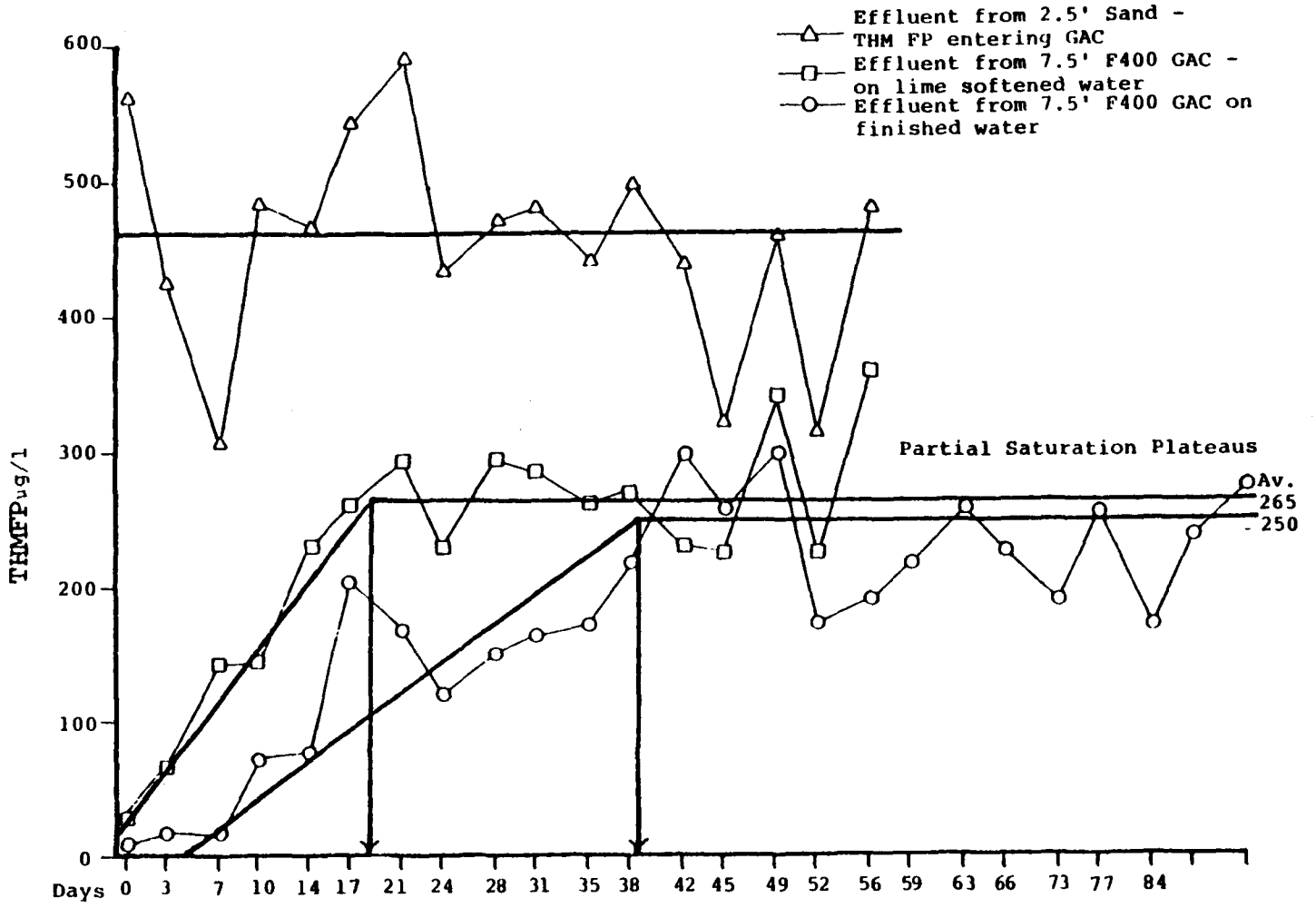


Figure 12. THMFP Breakthrough Data for 7.5 Feet of Filtrasorb 400 on Lime Softened and Finished Water

finished water feeds were 463 and 434 µg/l, respectively. Corresponding partial saturation plateau levels (1) were 265 and 250 µg/l. With the average influent concentration of THMFP in the lime softened (463 µg/l) and finished water (434 µg/l) phases so close to each other, it is surprising that the saturation time needed to achieve almost equal partial saturation plateau levels is so different—approximately 19 and 39 days, respectively. The explanation may be found in a plot of TOC data for the two phases in Figure 13. The average influent concentrations of TOC in the lime softened and finished water test periods were 6.5 and 5.4 mg/l. This is a difference of 17 percent (5.4/6.5 X 100) compared to a 6 percent difference (434/463 X 100) for the THMFP levels in Figure 12. In Figure 13 the 59-day test period is too short to determine the partial saturation plateau level. The average plateau level shown for finished water was achieved in 122 days of testing. However, if the two TOC breakthrough curves are considered at a common level of 3 mg/l, it is seen that the time to reach this level is 21 days for lime softened water and 39 days for finished water. The higher TOC level on the lime softened run resulting in earlier saturation might explain the similar results found with THMFP data despite the closeness of the THMFP.

Removal of Spiked High Molecular Weight Extractables

Since the raw groundwater entering the Preston plant is low in higher molecular weight extractable compounds from industrial and agricultural sources, section B of the bench scale adsorption unit (Figure 11) was used to spike some of these compounds. Figures 14, 15, and 16 show the results with chlorinated pesticides. The spiked influent levels are shown. In all six examples some breakthrough occurs even on initial startup. The zero-day sample was taken 30 min after water flow was begun. The percent breakthrough at each sample point is given. Overall the carbon removed more than 90 percent of the high molecular weight extractables. The results with industrial chemicals are shown in Figures 17, 18, and 19. In Figure 17 breakthrough was observed at 14 days for 2-nitrotoluene. This was followed by a period of complete removal and further breakthrough. Ethyl benzoate was completely removed up to day 42. In Figure 18 all of the naphthalene was removed except for some breakthrough on day 3, all of the 1-chloro-2-nitrobenzene was removed up to day 42. In Figure 19 all the dimethylphthalate was removed until test day 10. After test day 10 varying amounts of this compound were observed in the blank and it was necessary to abandon tracing of this compound. Di-isobutylphthalate showed early breakthrough with high levels of breakthrough occurring after day 14. This was followed by a period of low level breakthrough. The results of the studies on the removal of spiked high molecular weight compounds are in the

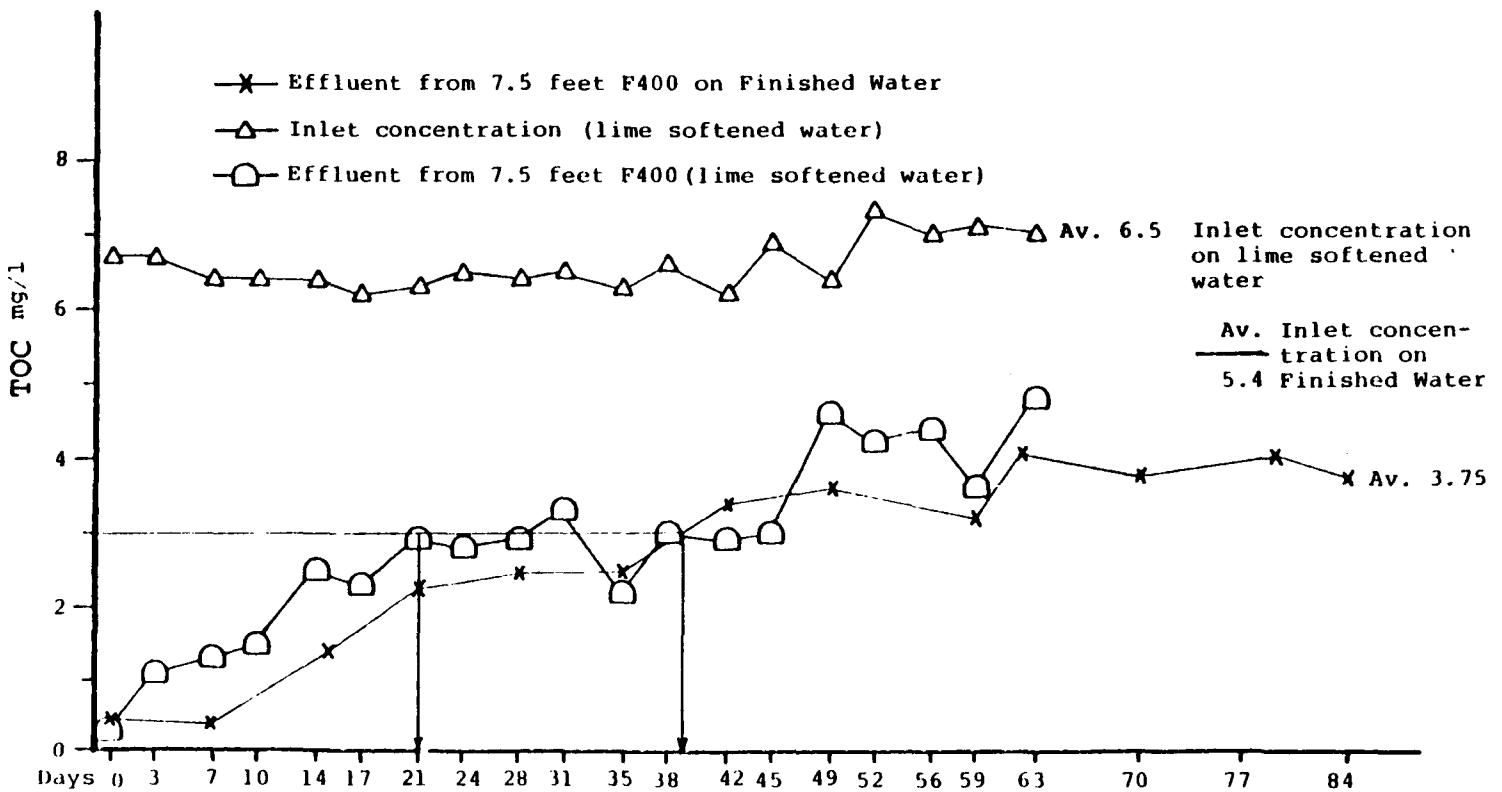


Figure 13. TOC Breakthrough Data for 7.5 Feet of Filtrasorb 400 on Lime Softened and Finished Water

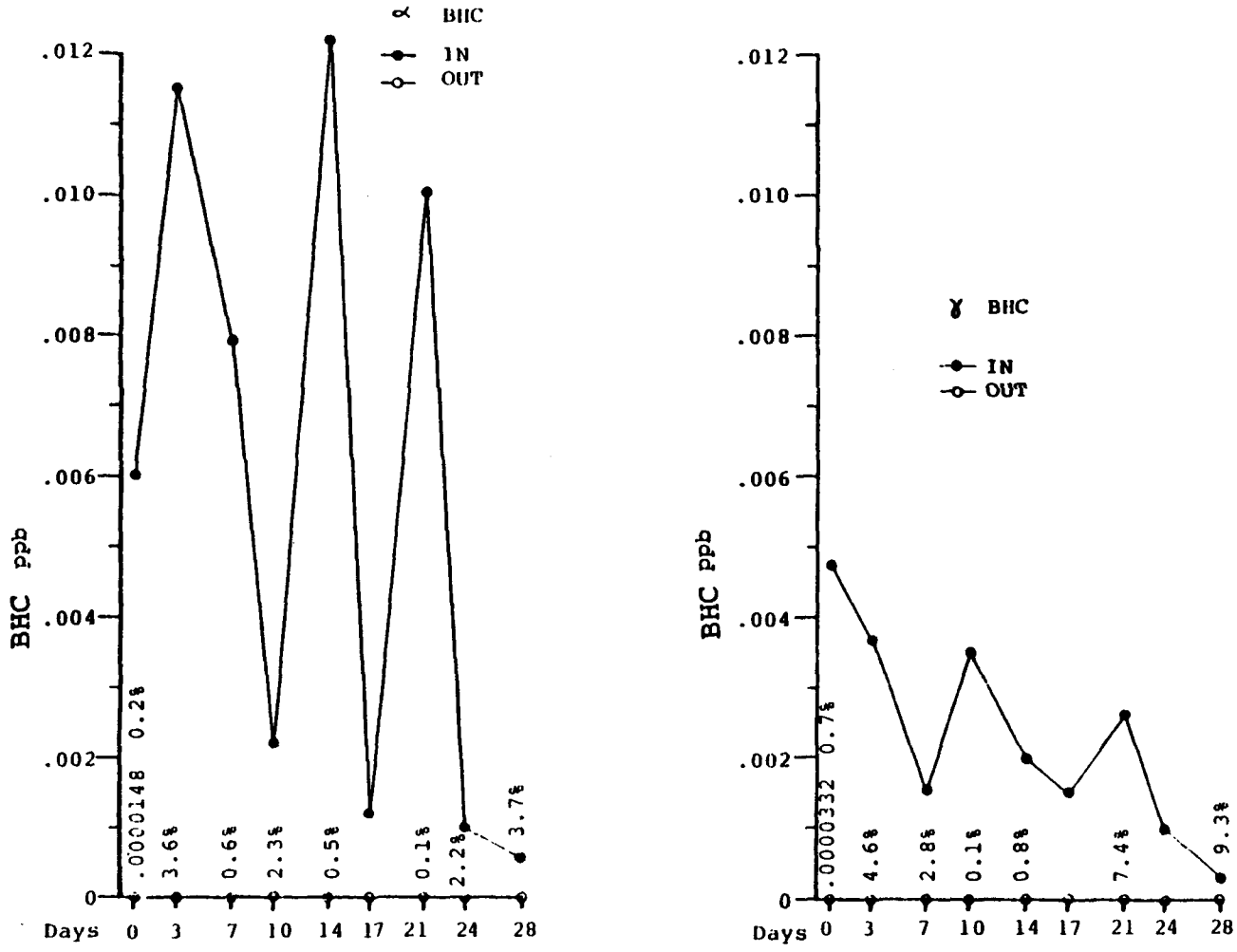


Figure 14. Concentration of Spiked Compounds In and Out of 3.75 Feet of GAC

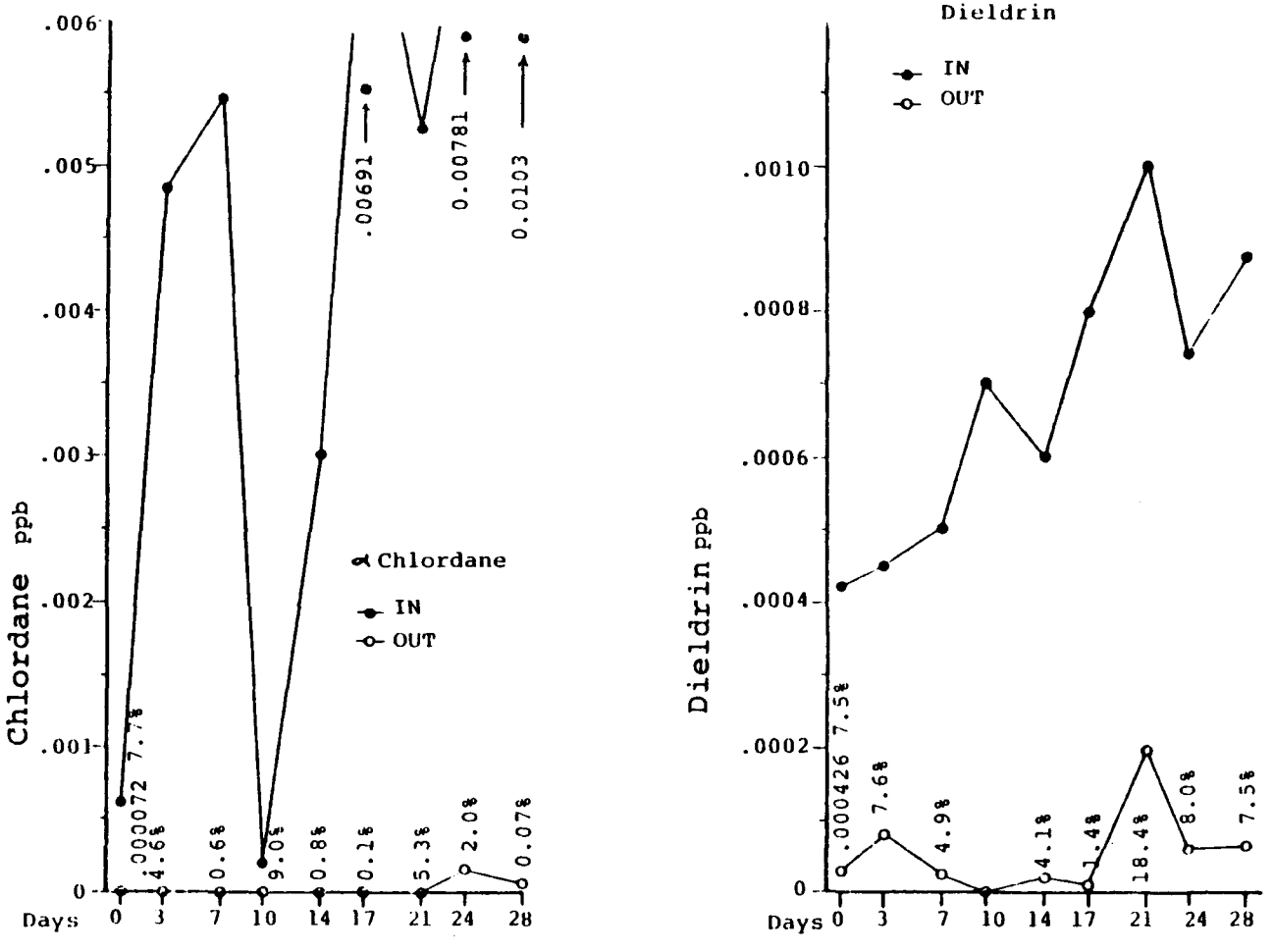


Figure 15. Concentration of Spiked Compounds In and Out of 3.75 Feet of GAC

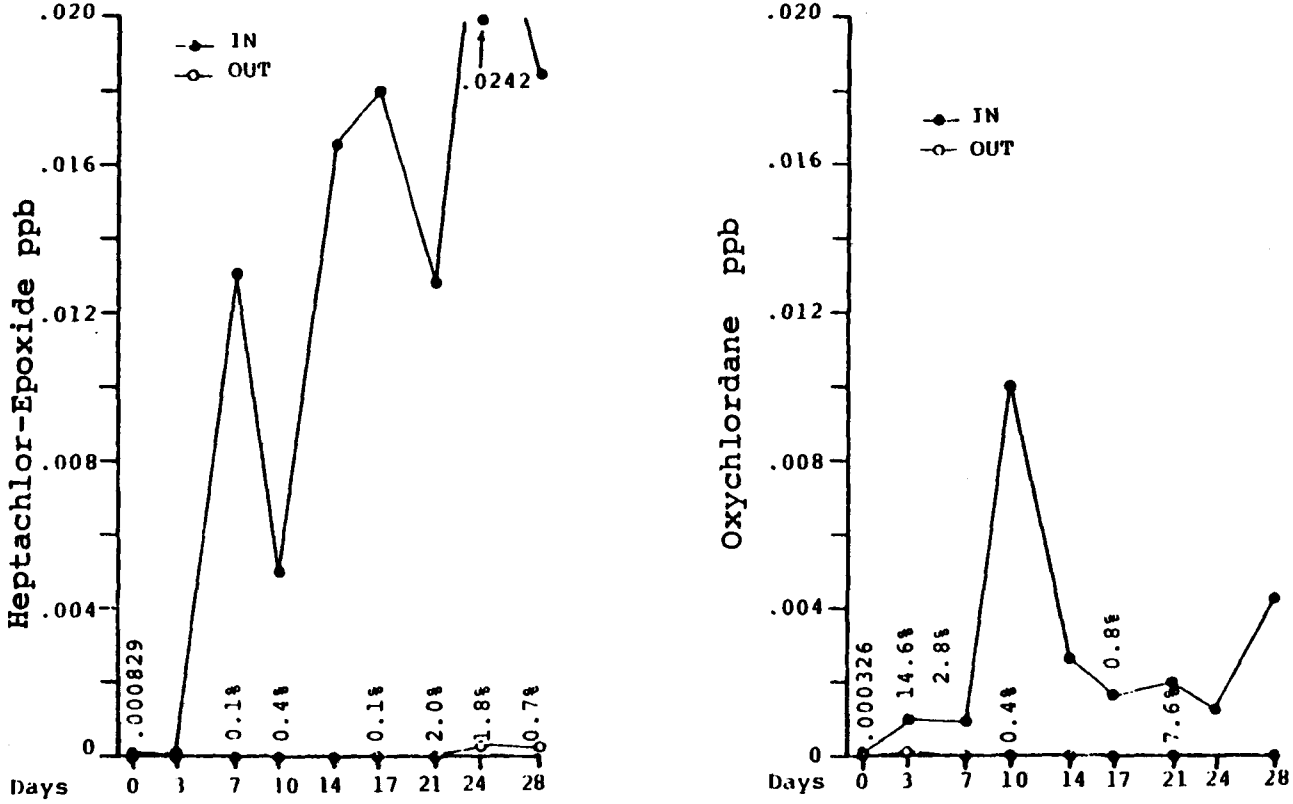


Figure 16. Concentration of Spiked Compounds In and Out of 3.75 Feet of GAC

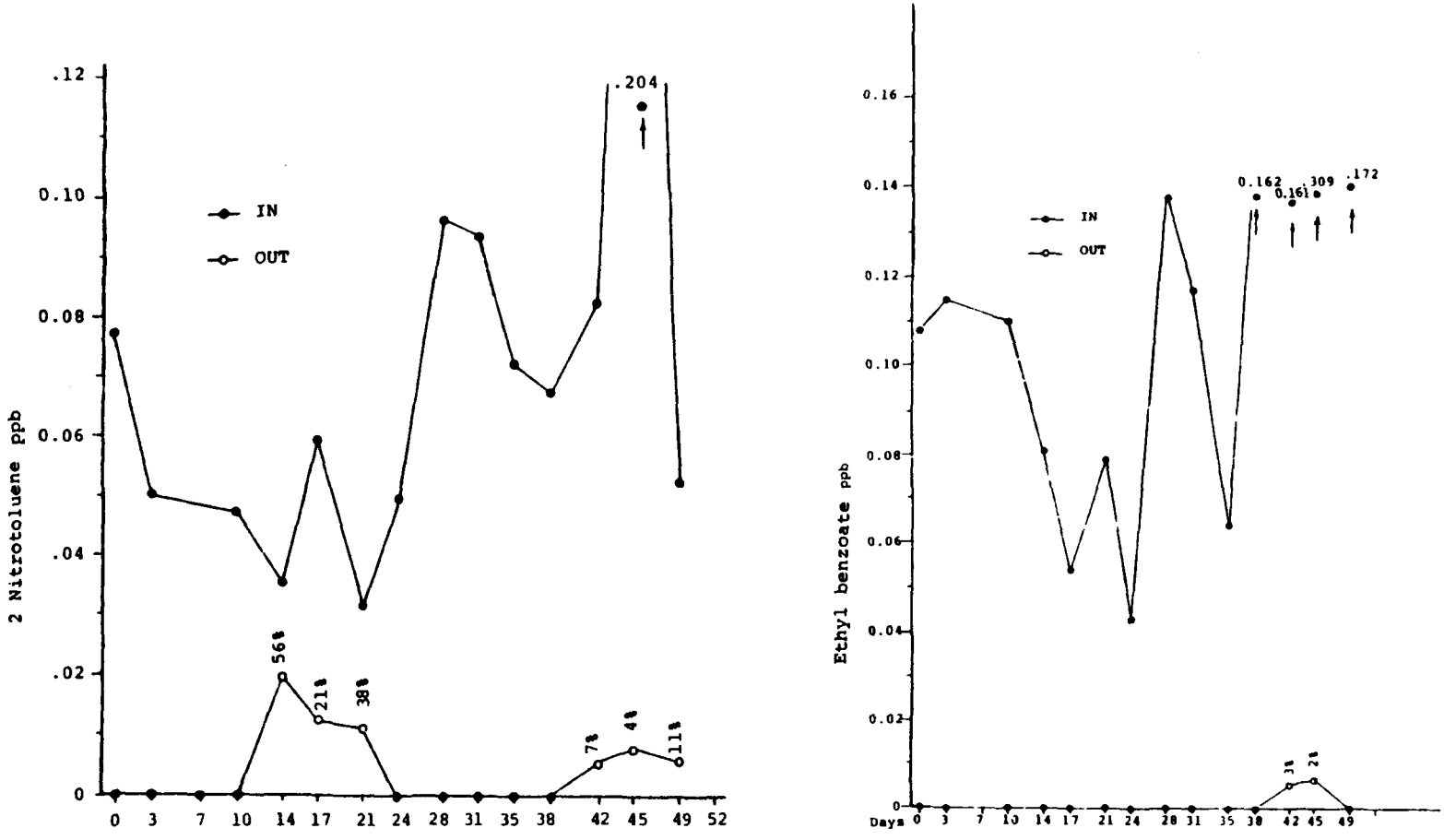


Figure 17. Concentration of Spiked Compounds In and Out of 3.75 Feet of GAC

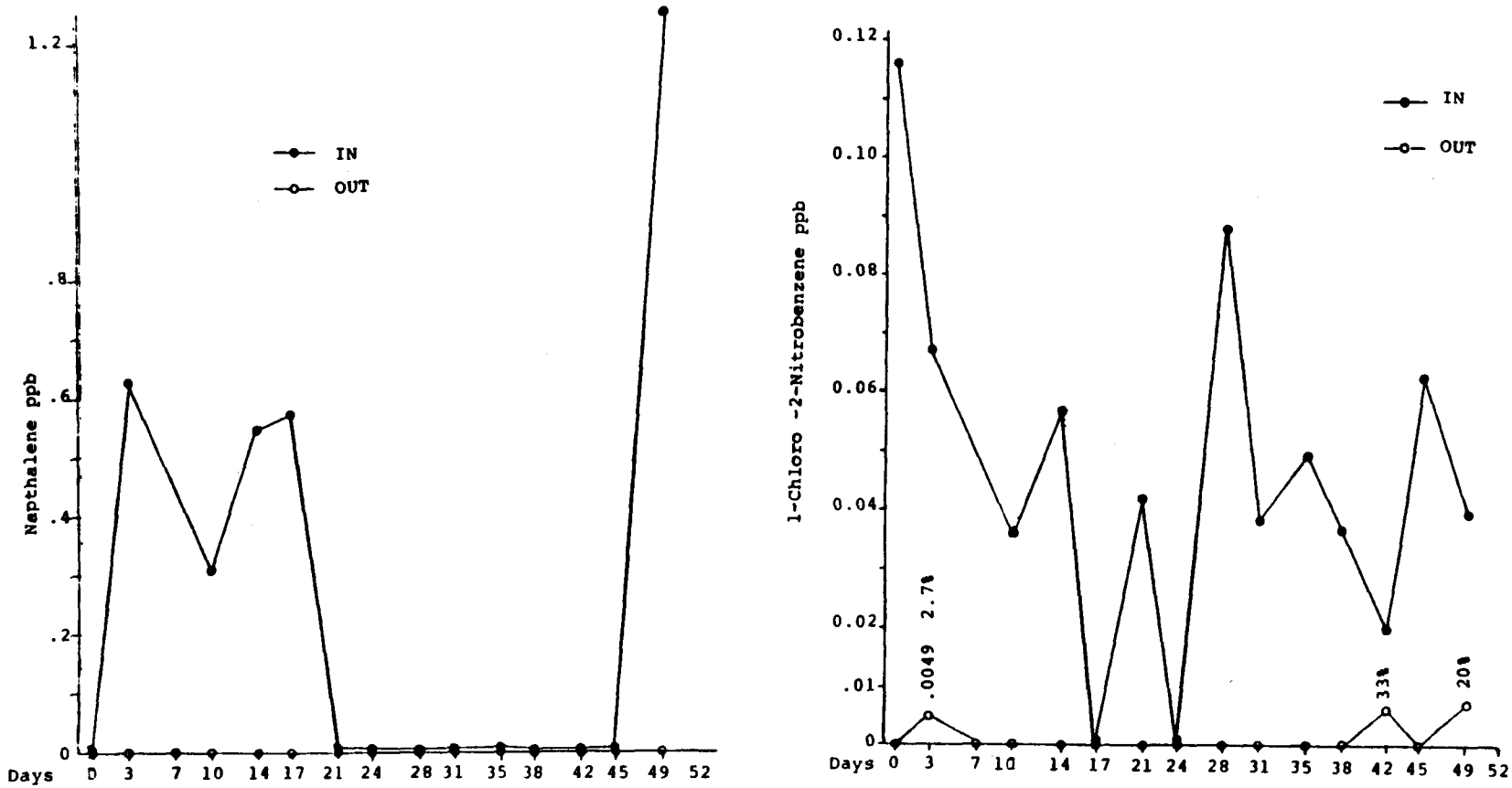
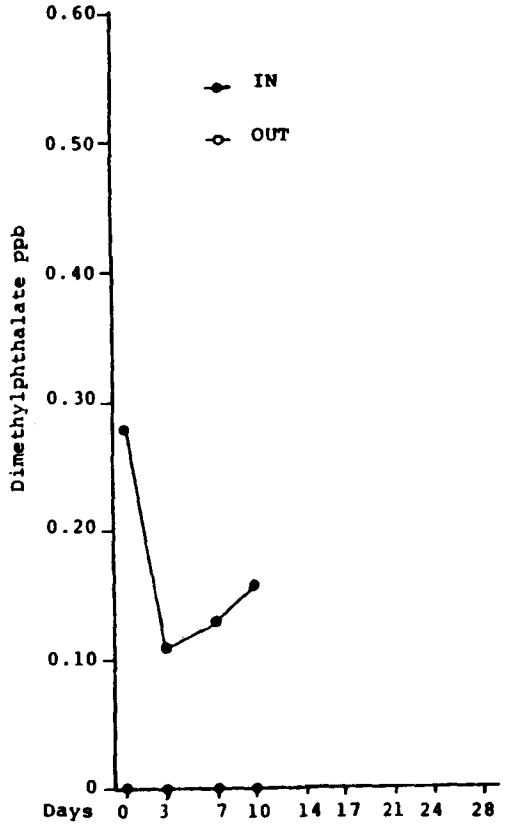


Figure 18. Concentration of Spiked Compounds In and Out of 3.75 Feet of GAC



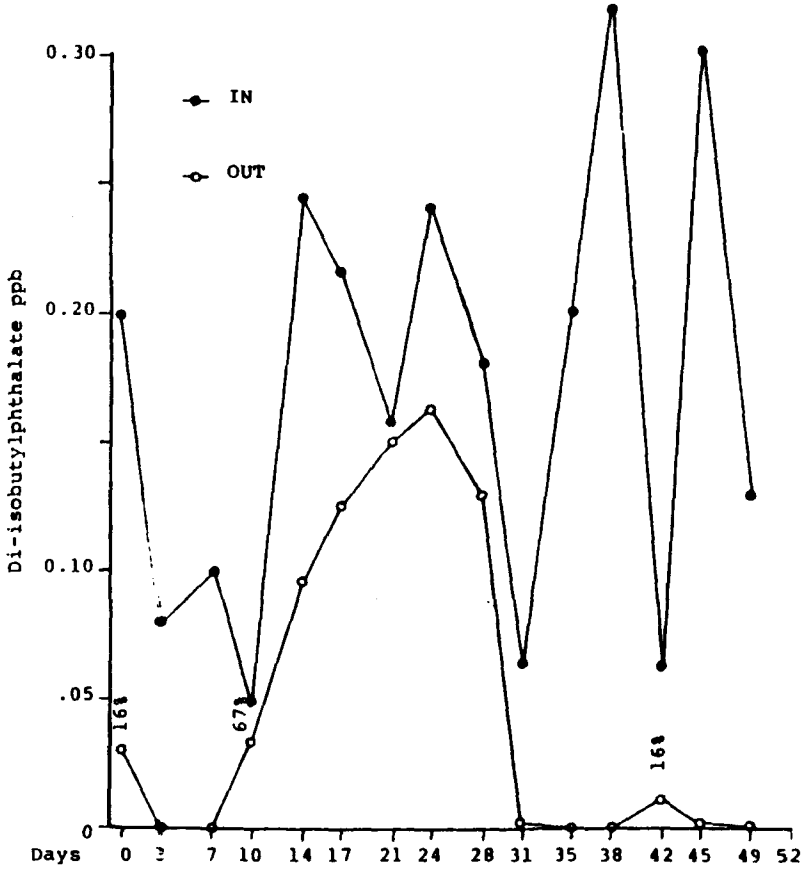


Figure 19. Concentration of Spiked Compounds In and Out of 3.75 Feet of GAC

preliminary stage. Other compounds will be studied for longer periods of time and desorption rates will be studied after deliberate spikes in influent levels are created.

CONCLUSIONS

A study of chloroform removal from finished water showed that equal volumes of four types of GAC removed 78 (W950), 53 (F400), 48 (ICI), and 40 (WVG) percent of the chloroform entering the water during a 59-day test period. On an equal weight basis, W950, ICI, F400, and WVG removed 78, 57, 56, and 36 percent, respectively. The removal data for 18 other purgeable halogenated organic compounds rated the carbons in a similar order.

Removal of THMFP substances from finished water showed that, during a 59-day test period, an equal volume of four types of GAC removed 27 (WVG), 26 (F400), 16 (ICI), and 8 (W950) percent of the total THMFP entering the water. On an equal weight basis, carbons F400, WVG, ICI, and W950 removed 26, 23, 18, and 8 percent, respectively.

In the Hialeah, Fla., water system, a sample of water from a GAC column rechlorinated to 3 mg/l of free chlorine and bottle-aged 2 days simulates the level of total trihalomethanes that will reach a consumer's tap. If a maximum level of trihalomethanes of 100 µg/l is chosen, the bed life of 0.75, 2.25, and 3 m (2.5, 7.5, and 10 ft) of carbon 1 is approximately 10, 65, and 81 days. The carbon use rate based on 3 m (10 ft) of F400 is 10 kg/ml (80 lb/mil gal).

The four types of GAC were evaluated at equal bed depths of 0.75 m (2.5 ft). Since bed life for this bed depth (based on the above criterion) is only 10 days, when the THMFP breakthrough curves were integrated at this time period, at an equal volume, carbons F400, WVG, ICI, and W950 removed 54, 35, 14, and 9 percent of the entering THMFP substances. At an equal weight, F400, WVG, ICI, and W950 removed 54, 29, 16, and 8 percent, respectively. The removal data for total organic carbon rated the carbons in a similar order.

A method of spiking water with high molecular weight industrial and agricultural chemicals was devloped and preliminary adsorption data are presented. Chlorinated pesticides exhibited early low level breakthrough. Overall, more than 80 percent of the spiked high molecular weight compounds were removed and more than 90 percent removal usually was obtained. Removal of 2-nitrobenzene, ethyl benzoate, naphthalene, 1-chloro-2-nitrobenzene, dimethylphthalate, and di-isobutylphthalate ranged from complete to poor. A wide range of chemicals will be tested for longer periods and desorption rates after periods of higher influent levels will be examined.

ACKNOWLEDGEMENT

This research was the joint effort of the U.S. Environmental Protection Agency, Cincinnati, Ohio, and of the Dade County Health Department, Miami-Dade Water and Sewer Authority, and the Drinking Water Research Center of Florida International University, all of which are located in Miami, Florida.

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1. Wood, P.R., et al. Removing Potential Organic Carcinogens and Precursors from Drinking Water. U.S. EPA, Cincinnati, Ohio (in press).

TREATMENT OF OHIO RIVER WATER

Richard Miller

The problems of trihalomethane formation during the treatment process and trace synthetic organic chemical concentrations in the source waters are of concern to many water utility managers. The Cincinnati Water Works has initiated both unilateral and multi-agency research to determine some of the causes, the scope, and possible solutions to these problems.

CINCINNATI WATER WORKS LOCATION AND WATER TREATMENT SYSTEM

Our primary source of water is the Ohio River at a point 463 miles (745 kilometers) downstream from its headwaters at the confluence of the Allegheny and Monongahela Rivers. Six tributaries enter the Ohio River in this 463 mile (745 kilometer) reach, but perhaps the most important is the Kanawha River. The Kanawha River valley accomodates most of the giant chemical corporations in this country and is the location of many points of possible toxic discharge. Also located along this reach of the Ohio's main stem are approximately 270 point sources of discharge from both municipal and industrial facilities (Figure 1). However, we are indeed fortunate that the 110 mile (177 kilometer) stretch immediately upstream of Cincinnati has very few major discharge points. This is the situation regarding our primary source of water.

Our raw water is obtained via intake structures on the Kentucky side of the river and flows through tunnels which terminate at our raw water pumping stations. Two stations with a combined capacity of 340 mgd (1.3 million cubic meters per day) lift the water to twin pre-settling basins having a combined capacity of 372 million gallons (mg) (1.4 million cubic meters). To my knowledge such basins are unique to only the Cincinnati and Louisville water systems in our area of the country. They are a definite asset to a system located on an industrial stream as they provide several days supply if intakes are closed due to a chemical spill.

From the pre-settling basins the water flows by gravity through coagulation and clarifier basins, then into our filter gallery. The filter gallery contains 47 rapid sand filters.

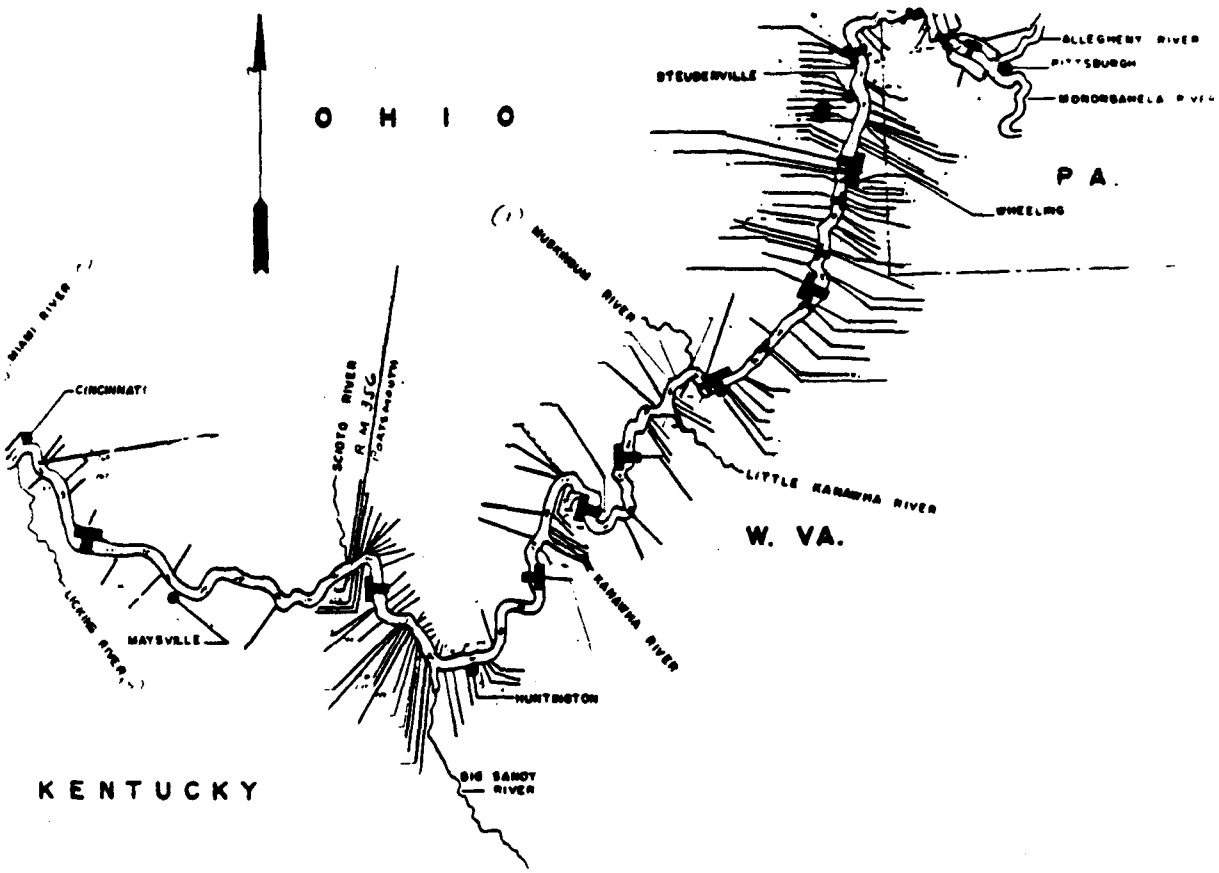

Figure 1. Known Industrial and Municipal Wastewater Discharges to the Ohio River. Lines Indicate Industrial Discharges. Solid "T's" Indicate Municipal Wastewater Discharges.

Each filter has a rated capacity of 5 mgd (19,000 cubic meters per day) at a loading rate of 2-1/2 gallons per minute per square foot (6 m/h). After filtration, the water collects in two clearwells with a combined capacity of 28 mg (106,000 cubic meters). A schematic of the treatment facilities is illustrated in Figure 2.

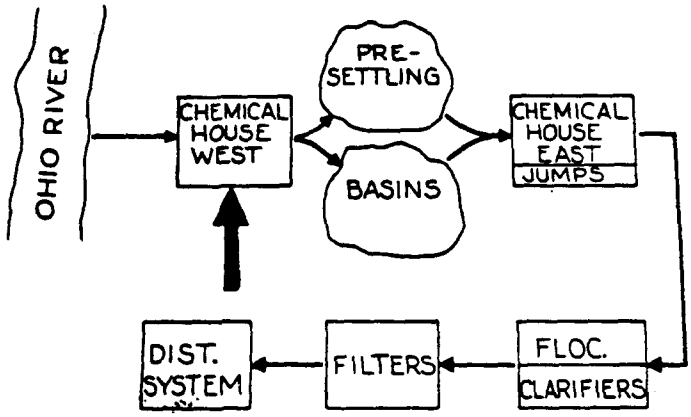

Figure 2. Schematic of Treatment Facilities

Facilities are available to apply chlorine, aluminum sulfate, and powdered activated carbon in the raw water lines upstream of the pre-settling basins. An additional facility provides for the capability of adding chlorine, ferric sulfate, lime, soda ash, and powdered activated carbon between the pre-settling basins and the coagulation basins. Recent improvements provided the capability of chlorinating downstream of the clarifier basins immediately ahead of the filters and increased the capacity of our post chlorinating facilities. Currently, all disinfection is by chlorination at these two points.

The relocation of the chlorine feed resulted from a unilateral research project conducted in 1975 and 1976. As a result of this relocation, we have reduced the formation of trihalomethanes approximately 80 percent. As an associated benefit of this change, we have been able to reduce our chlorine feed rates from 12 milligrams per liter (mg/l) to approximately 3.6 mg/l.

U.S. EPA CARBON ADSORPTION AND REGENERATION GRANT

Early in 1977, we applied to the United States Environmental Protection Agency (USEPA) for a research grant for a project entitled "Feasibility Study of Granular Activated Carbon Adsorption (GAC) and On-Site Regeneration." A grant award was made in August of 1977. This project will investigate both the cost and effectiveness of converting sand filters to GAC-filter-adsorbers in comparison to deep bed, post-filter carbon contactors.

A second phase, currently in progress, involves two pilot column studies. One study is investigating the effect of regeneration on the carbon's adsorptive capabilities (Figure 3). The other study is comparing bituminous and lignite based carbon in deep bed pilot columns (Figure 4). This latter study may also be used to investigate the reliability of deep bed, pilot carbon columns to predict performance of the plant-scale post filter carbon contactors. The final phase of this project will evaluate both the effectiveness and feasibility of on-site GAC regeneration.

Much of the analytical work for this project is being conducted in-house. A former lecture room has been converted into an acceptable temporary organics laboratory. It currently houses two gas chromatographs and all of the necessary ancillary equipment. A low-level module was added to our Total Organic Carbon (TOC) analyzer and a gas chromatograph mass spectrometer will soon be added to our equipment inventory.

In the first phase of our project we converted three sand filters, each rated at 5 mgd (19,000 cubic meters per day) to GAC filter adsorbers. In one filter, identified as 19A, 18 inches (0.46 meters) of sand was replaced with 18 inches (0.46 meters) of 12 x 40 mesh size GAC. This gives an empty bed contact time of 4-1/2 minutes. A second filter, identified as 21A, had all 30 inches (0.76 meters) of sand replaced with 30 inches (0.76 meters) of 12 x 40 mesh size GAC. A third filter, identified as 23A, had all 30 inches (0.762 meters) of sand replaced with 30 inches (0.76 meters) of 20 x 50 mesh size GAC.

Filters 21A and 23A both have an empty bed contact time of 7-1/2 minutes. All carbon is bituminous base and is from a single manufacturer. In all, 266,700 pounds (121,200 kilograms) of carbon were purchased at a cost of $101,500.

An effluent sample point and several intermediate depth sample points were installed in all filters. The intermediate depth samples were not reliable indicators of water from their respective depths due to the rapid development of air pockets around the sample intakes. It was found that the water quality improved at increasing depths.

The objectives of this phase of the study were:

- To determine if current water quality standards can be met and maintained without adhering to the Ten State Standard requirement of 12 inches (0.305 meters) of sand under the carbon media.

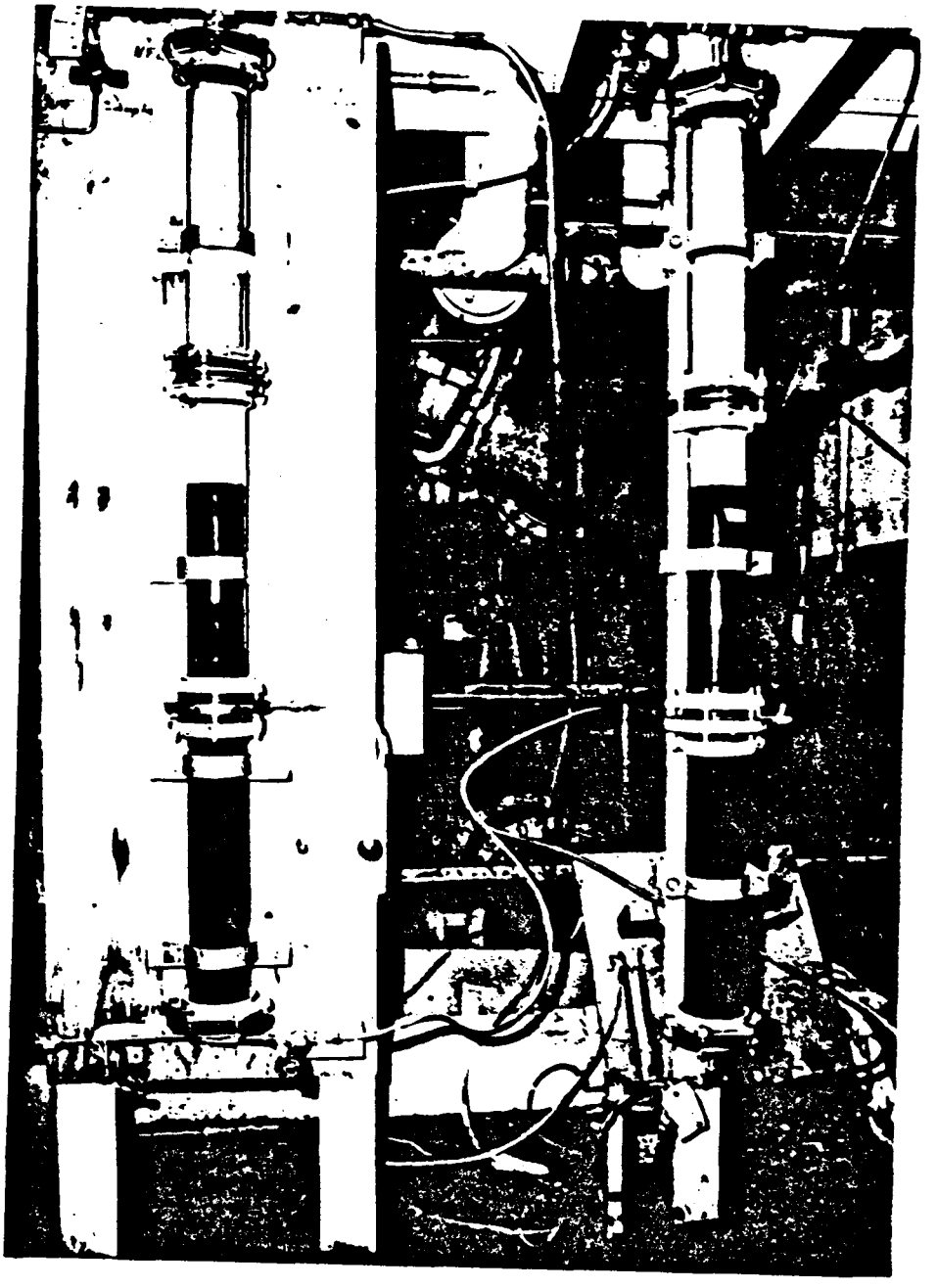

Figure 3. Pilot Column Study - Effect of Regeneration on Adsorption Capacity of Carbon

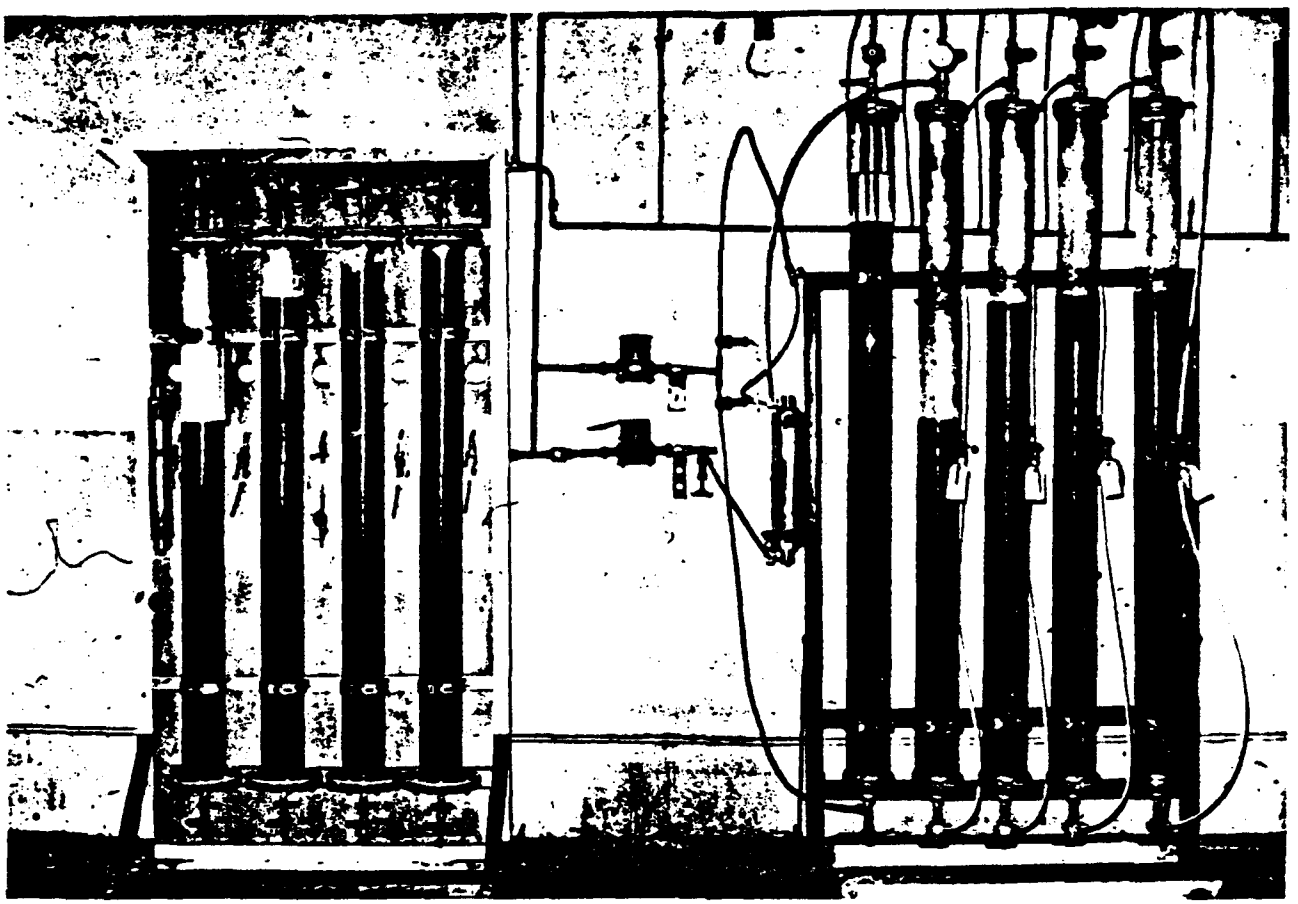

Figure 4. Bituminous and Lignite Based Carbon Pilot Columns

- To compare the carbon filters to the rapid sand filters with regard to physical, chemical, and bacterial data and to compare effectiveness in removing specific organics.

- To determine the life expectancy of the GAC filter based on TOC and trihalomethane (THM) data.

Analytical Results

Following the start-up (February 14, 1978), data were collected at least weekly from the three filters for six months, at which time the filters were well exhausted.

The physical-chemical data collected to compare the GAC filter to the sand filters were similar. The effluent from the carbon filters was, for the most part, equal in clarity to that of the sand filters. Three brief episodes of moderate turbidity occurred with filter 19A which were of little or no significance. Apparently the 12-inches (0.305 meters) of fine sand in filter 19A does not improve effluent clarity.

As expected, the carbon filters produced an effluent that was either odorless or had a barely discernible odor. The filter also removed all but marginal traces of free chlorine and moderate levels of chloramines.

Figure 5 shows a plot of the concentration of TOC in the influent and the effluents of the three GAC filters. It is apparent that, initially, the GAC filters are very effective in the removal of TOC. The proposed EPA regulations on organic contaminants were used to determine when the carbon filters would have needed to be replaced or regenerated. The criterion states that, when the effluent TOC rises by 0.5 mg/l above the baseline concentration in three successive weekly effluent samples, the carbon must be regenerated or replaced. From the figure it can be seen that filters 19A and 23A would have required regeneration 28 days after startup while filter 21A would not have required regeneration until 42 days after start-up. It is interesting to note that after six months the carbon filters are still removing TOC.

All three GAC filters were found to have high total bacteria plate counts (Table 1) and total coliform counts (Table 2). These findings have been reported in the literature and were, therefore, expected. The counts varied so much that it is difficult to draw any firm conclusion from the results; but it does appear that the counts in the effluent are higher than in the influent.

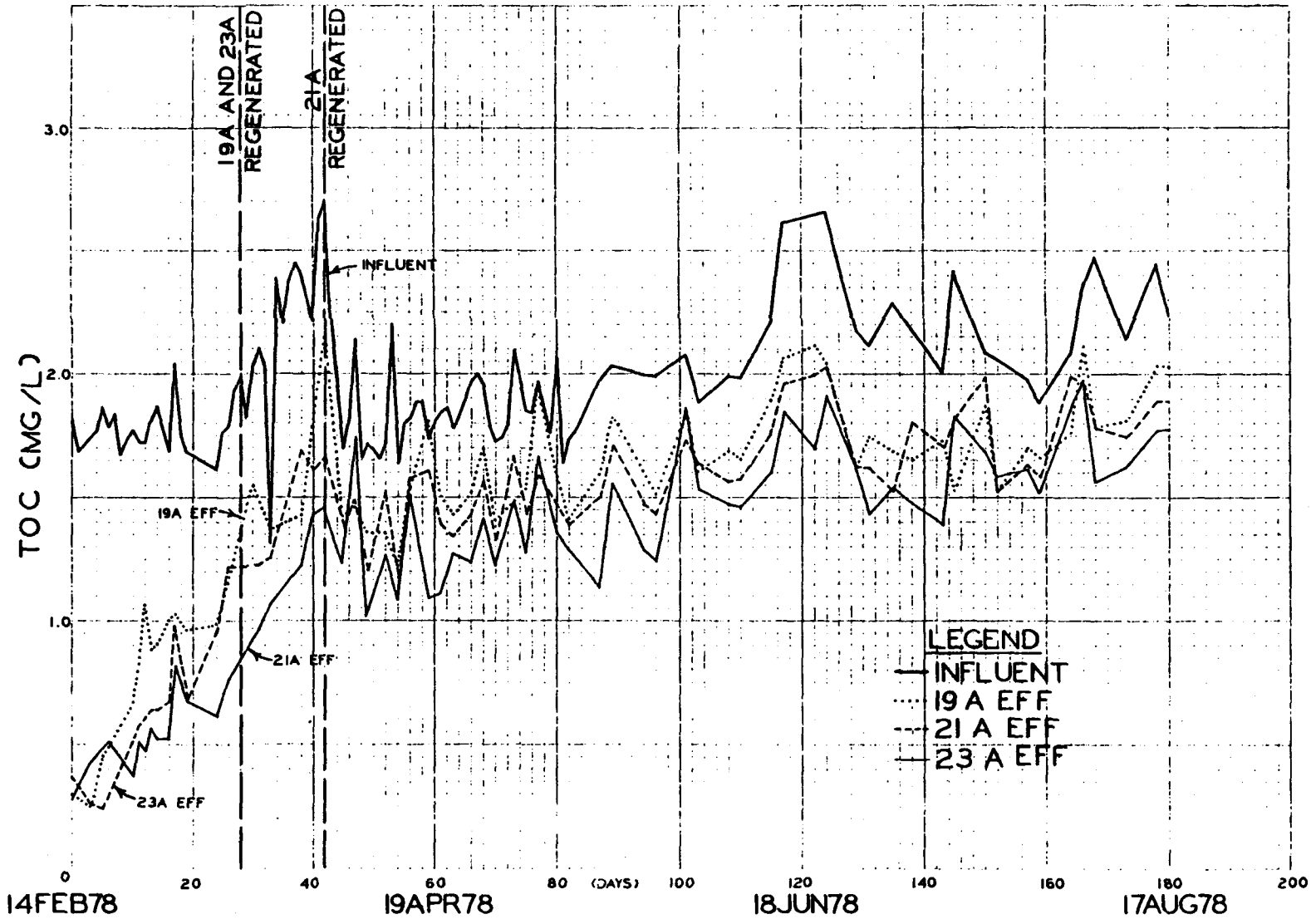

Figure 5. Total Organic Carbon Concentrations

Table 1. Total Bacteria Plate Counts

	Plate Count Per ml			
Day	Project Day	Raw	Influent	21A-EFF
18APR78	59	6,100	21	200
20JUN78	122	7,200	3	1,100
11JUL78	143	19,000	7	6,800

Table 2. Total Coliform Counts

	Total Coliform Per 100 ml			
Day	Project Day	Raw	Influent	21A-EFF
18APR78	59	2,700	1	1
20JUN78	122	32,000	1	28
11JUL78	143	27,000	1	300

Before discussing the effectiveness of the GAC filters in removing the trihalomethanes (THM), some terminology must first be explained:

- Trihalomethane, as referred to in this presentation is the summation of chloroform, bromoform, dibromochloromethane, and bromodichloromethane.

- Instantaneous Trihalomethanes are the THM already formed at the time of sampling.

- Trihalomethane Formation Potential (THMFP) is an indirect analysis of precursors available for chlorination under the test conditions and thus, a measure of removal of the same precursors by the GAC. In our case, the test conditions were set beyond those ever likely to exist in our water treatment system; they were as follows: to a 325 ml sample bottle, add 15 ml of buffer to obtain a pH of 9.5; then add chlorine solution to obtain 15 mg/l free chlorine residual, fill with sample, and incubate at 85° for 7 days.

- Seven-Day Simulated Distribution THM was intended to predict the effect of various water treatment measures on the quality of finished water at remote points in the distribution system. Tests were conducted as follows: to a 325 ml sample bottle, add 15 ml of buffer to obtain pH of 8.2, add sufficient chlorine solution to result in 2.5 mg/l free chlorine above what was in water at that time, and incubate for 7 days at finished water temperature using flow through water bath. The analysis is performed by analyzing for total THM after a water sample has been exposed to the same pH and chlorine dose used in the treatment plant at the prevailing temperature of the distribution system, for a length of time originally estimated to equal transit time to the more remote points of the distribution system. We recently found that these results are not truly indicative of our system; a very recent test, utilizing fluoride as an indicator, shows approximately three days travel time to the most remote points of our distribution system. Therefore, the values obtained in our research project would be greater than expected in the actual system.

The effectiveness of the GAC filters in removing Instantaneous THM can be seen in Figure 6. The section of dotted line on the influent data represents the THM data from a sampling point in the distribution system, which is water mainly composed of sand filter effluent since only a small fraction of the filters were converted to GAC. These somewhat higher THM values were used because of spurious influent samples caused by improper quenching of the chlorine.

From the figure, it is apparent that filters 21A and 23A were very similar in the amount of Instantaneous THM they removed. This result was expected as both filters have the same bed depth of carbon. Filter 19A was not as effective due to the fact that it contains less carbon.

If the criterion for filter exhaustion is defined as the point at which the filter effluent concentration passes 50 percent of the Instantaneous THM influent concentration, then filter 19A was exhausted on day 31, filter 21A on day 80, and filter 23A on day 87. This time span is longer than that expected for true values because of the sampling problem.

The effectiveness of the GAC filters in removing THMFP can be seen in Figure 7. The dotted section of the influent data corresponds to THMFP's determined from the same sampling point in the distribution system as mentioned above in regard to Figure 6. These approximations cause a decrease in apparent THMFP in the influent, while the effluent values are correct. The net result is that the adsorption effectiveness shown is inferior to actual performance.

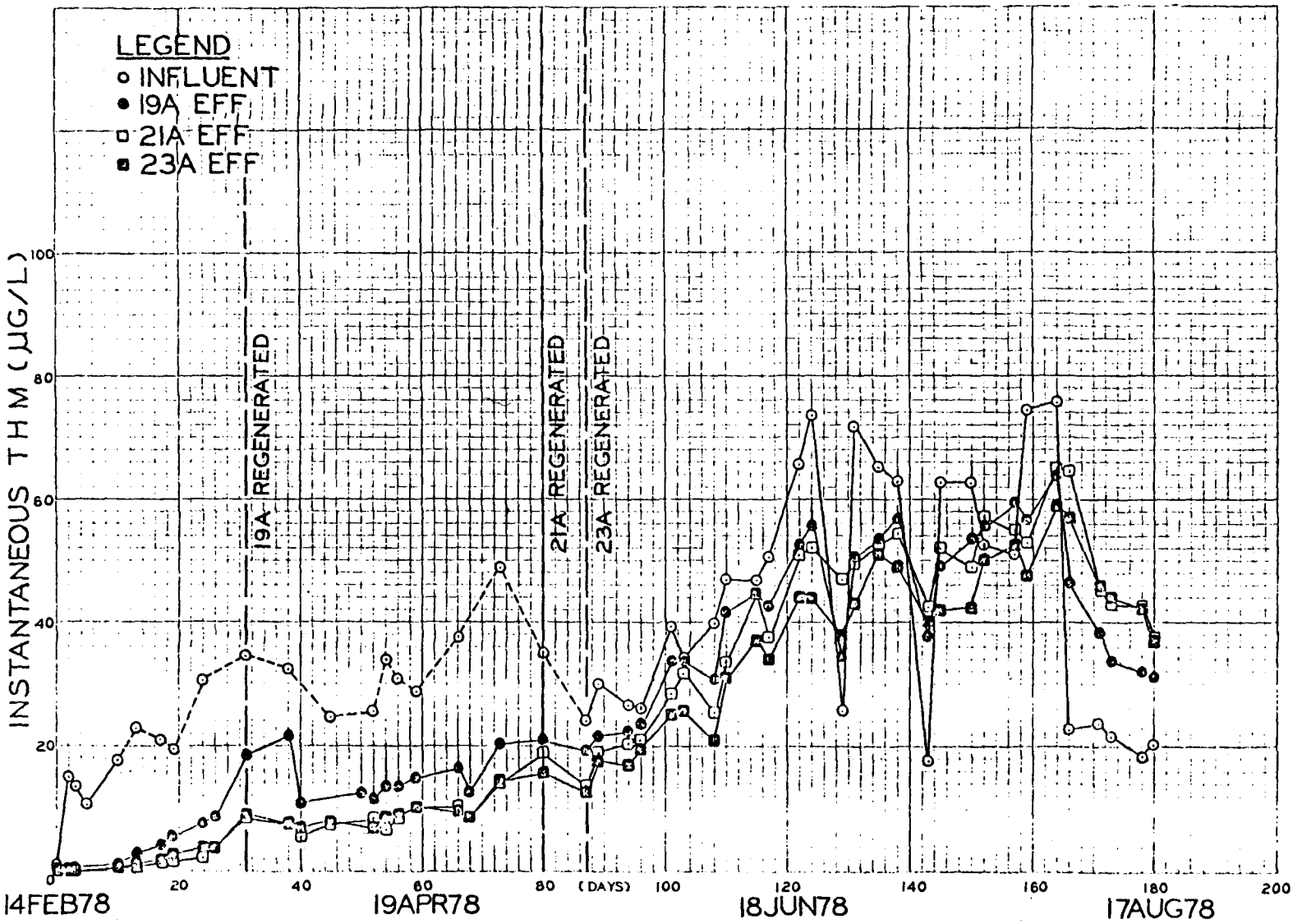

Figure 6. Removal of Trihalomethanes in GAC Filters

Note: The dashed vertical lines labeled "XXX Regenerated" denote the point at which the removal efficiency has declined to 50%.

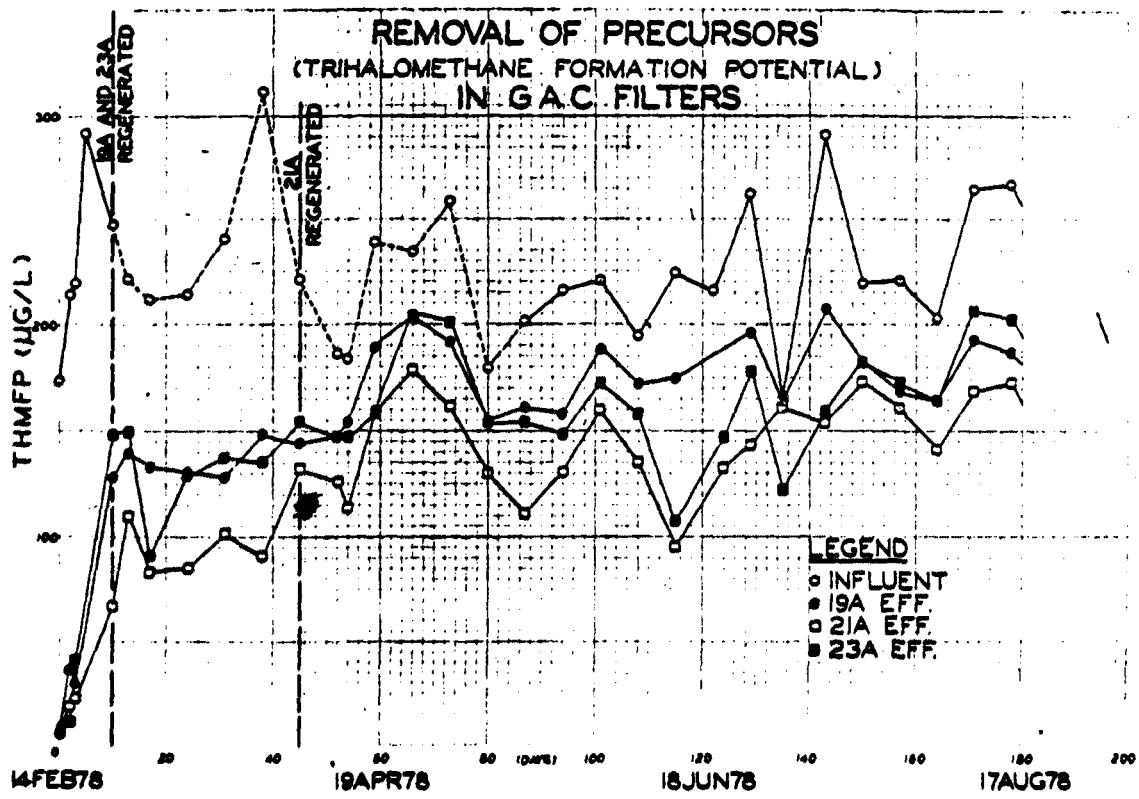

Figure 7. Removal of Precursors
(Trihalomethane Formation Potential)
in GAC Filters

Note: The dashed vertical lines labeled "XXX Regenerated" denote the point at which the removal in the respective column has declined to 50%.

The gradual loss in the effectiveness of the filters in removing THMFP can be seen by the gradual rise of the effluent concentrations to levels approaching those of the influent.

If the criterion for filter exhaustion is defined as the point at which the filter exceeds 50 percent of the influent THMFP concentrations, then filters 19A and 23A were exhausted on day 10 and filter 21A on day 45.

The effectiveness of the GAC filters in removing the Seven Day Simulated Distribution THM can be seen in Figure 8. Again, it is apparent that filter 21A is outperforming both filters 19A and 23A.

If the criterion for filter exhaustion is defined as the point at which the filter passes 50 percent of the Simulated Distribution THM, then filter 19A was exhausted on day 17, filter 21A on day 38 and filter 23A on day 24. However, if exhaustion is defined as the point at which the Simulated Distribution THM of the filter passes 0.1 mg/l (100 ppb), then filter 19A is not exhausted until day 102, filter 21A on day 116 and filter 23A on day 110. It should be noted that the influent exceeded the Maximum Contaminant Level (MCL) of 0.1 mg/l (100 ppb) on day 8.

Contract laboratories have been analyzing samples for purgeable nonhalogenated organics and base neutral extractables. The purgeable nonhalogenated organics of main concern are benzene, hexane, toluene, ethylbenzene, o-xylene, and tetralin. Base neutral extractables, specifically noted in the contract, are identified in Table 3. So far, nothing of significance has been found in either fraction.

Table 3

Base Neutral Extractables

Isophorone	Bis (2-Ethyl Hexyl Phthalate)	2-Picoline
Naphthalene	2,4-Dinitrotoluene	Aniline
Benzidine	2,6-Dinitrotoluene	Pyridine
Dimethyl Phthalate	2,4-Dimethyl Pyridine	O-Naphthylamine
Nitrobenzene	1,3-Dichlorobenzene	Di-n-Butyl Phthalate
Diethyl Phthalate	Butyl Benzyl Phthalate	Butyl Isobutyl Phthalate
Di-N-Octyl Phthalate	Diethylphthalate	Di-Isobutyl Phthalate

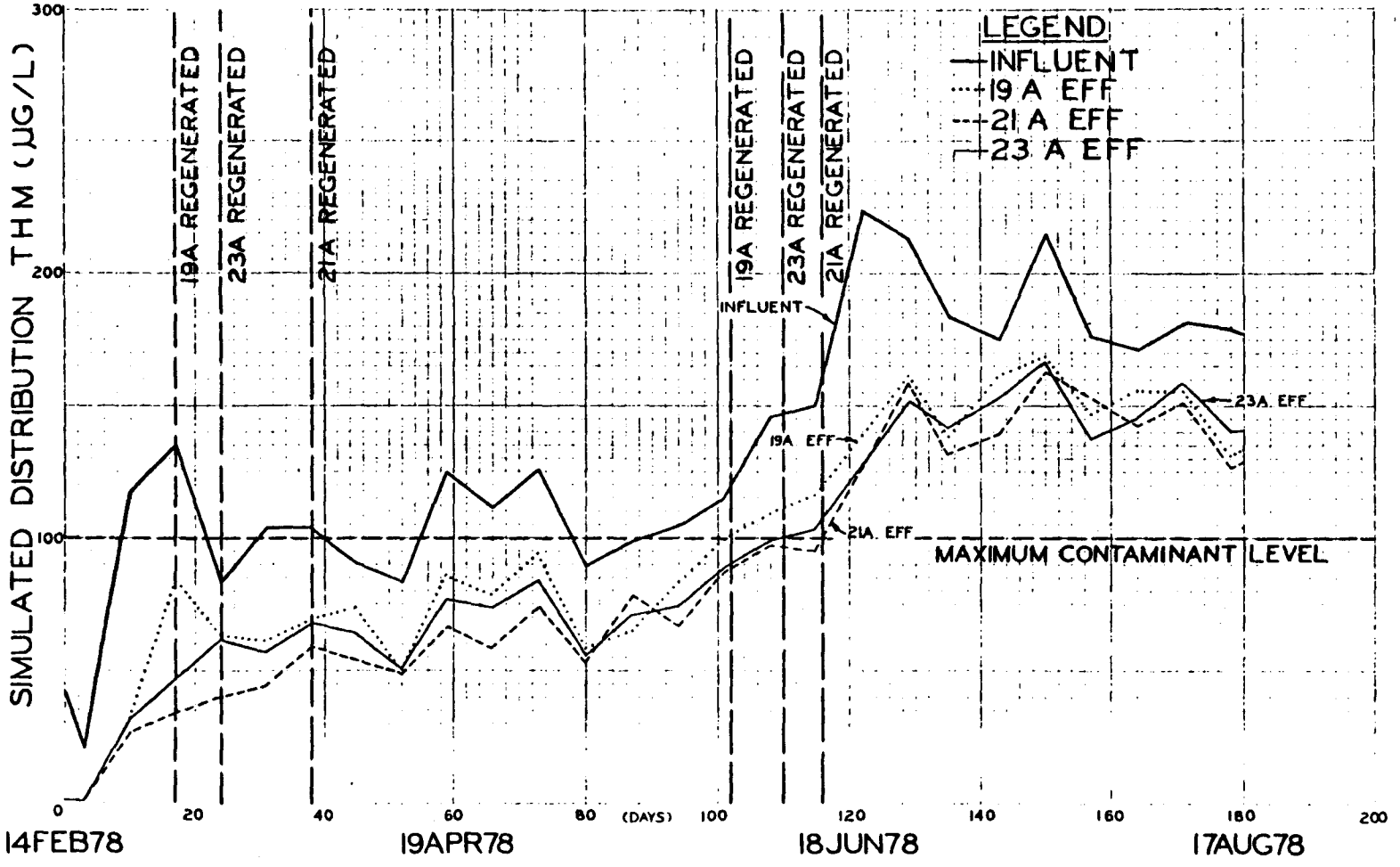

Figure 8. Removal of 7-Day Simulated Distribution System THM in GAC Filters

The dashed lines labeled "XXX Regenerated" denote the point at which the given column would have to be regenerated to meet a given standard: 50% removal (left), or MCL = 100 µg/l (right).

As mentioned earlier, we are currently performing pilot column studies to determine the effects of carbon regeneration. Virgin carbon was in service for six months and was then regenerated. The regenerated carbon was compared to virgin carbon. Figure 9 shows that regeneration had no apparent effect on the carbon's adsorption capability.

We are also currently conducting pilot column studies to compare the adsorption capabilities between bituminous- (Figure 10) and lignite-based GAC (Figure 11). As of May 1979, the data are still being evaluated.

Contracts have been awarded and construction is currently underway that will enable us to begin the third phase of our research. An initial contract for site preparation, sewer laterals, and floor slab to accommodate the post filter carbon contactors has been completed. The site is adjacent to our filter building. A connecting multi-purpose employee passageway-utility tunnel was also constructed as a part of this initial contract.

A second contract, currently very active, calls for furnishing and installing 4 deep bed carbon contactors (Figure 12) with allied controls, pumps, utilities and a protective building. Completion is scheduled for early 1979. The bid price for the contactors was $989,000.

Upon completion of the contactors, we will install carbon in at least one additional filter and begin parallel runs of both the filters and contactors. Please remember that these are full plant size units, not pilot scale or test tube models. Data so garnered will be difficult to refute.

Evaluation of the data generated by these parallel runs will enable us to make an intelligent decision as to the cost effectiveness of both methods with respect to the proposed U.S. EPA regulations. Naturally, both capital and operating costs will be considered in this decision.

Carbon Regeneration

The last phase of our project calls for construction of an on-site regeneration or reactivation furnace of limited capacity (Figure 13). The contract for this furnace has been awarded to the Westvaco Company; on a 500 pound per hour (227 kilograms per hour) fluidized bed model, at a cost of $604,130. Our project is the only one, to my knowledge, that invited competitive bids for furnaces with differing operating principles. Both fluidized bed and infrared models were evaluated with respect to initial capital costs, operating costs, and life expectancy.

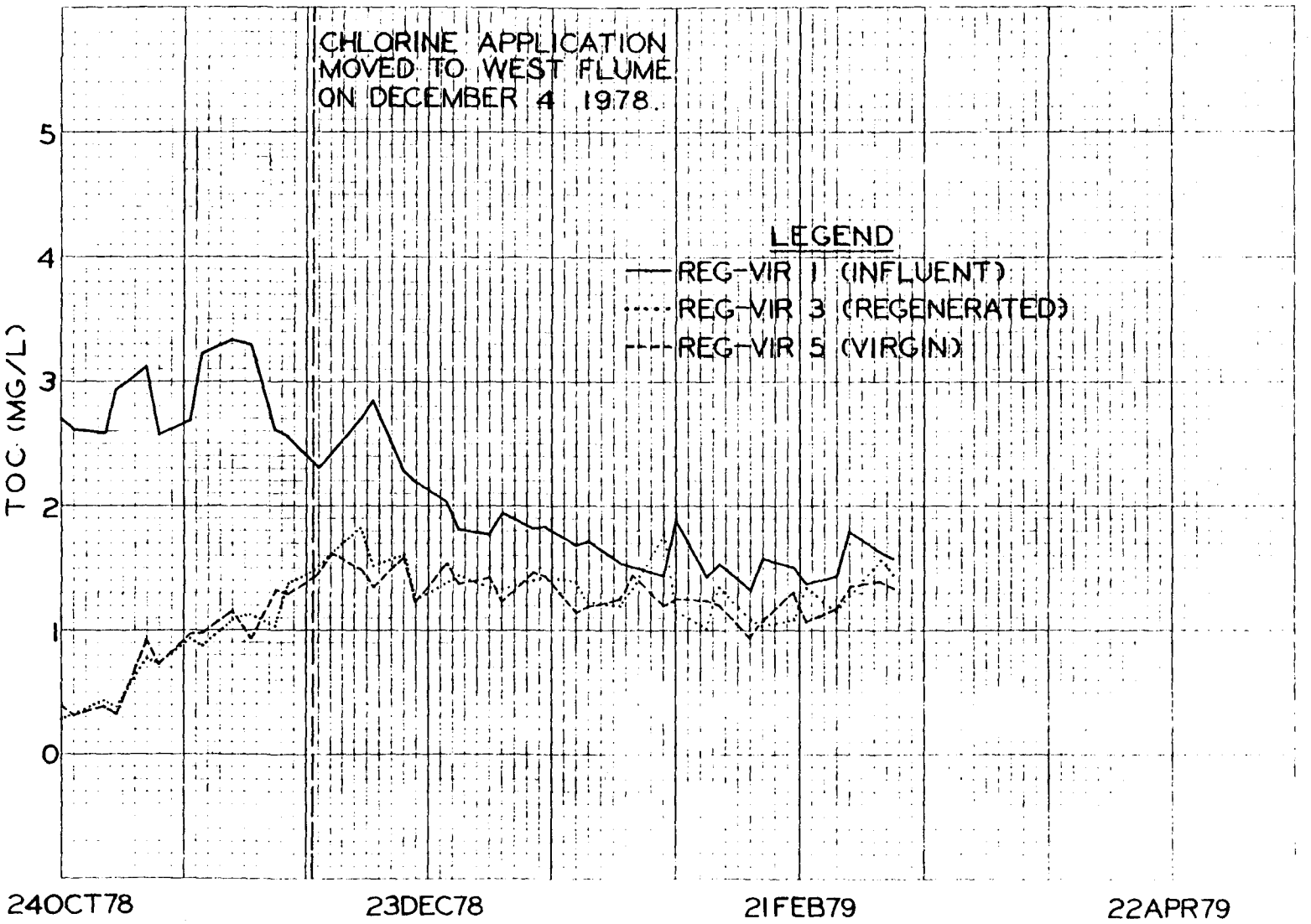

Figure 9. Total Organic Carbon (TOC) Concentrations in Westvaco WV-G Filter/Adsorber columns

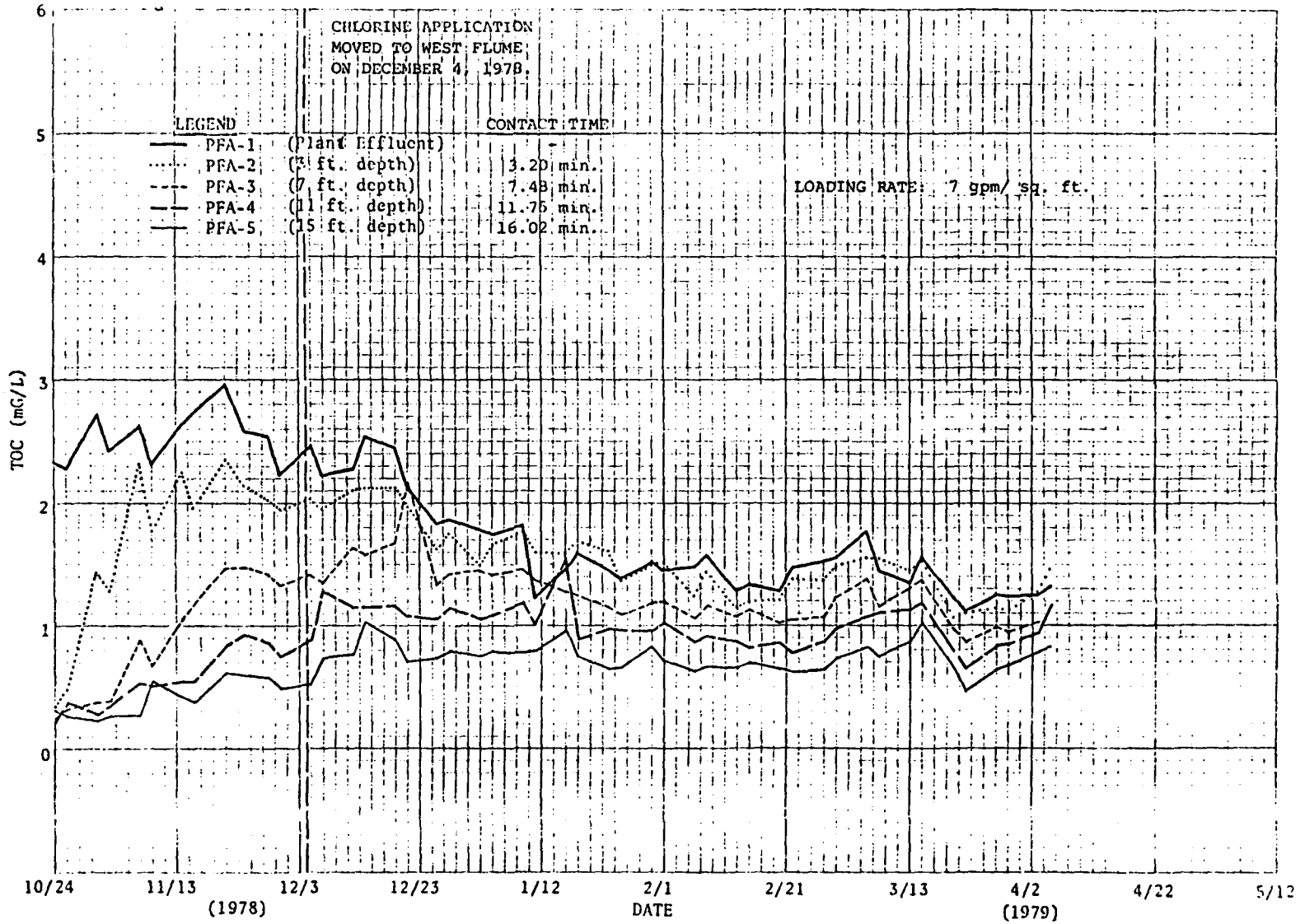

Figure 10. Total Organic Carbon (TOC) Concentrations in "Bituminous" Contactor Columns

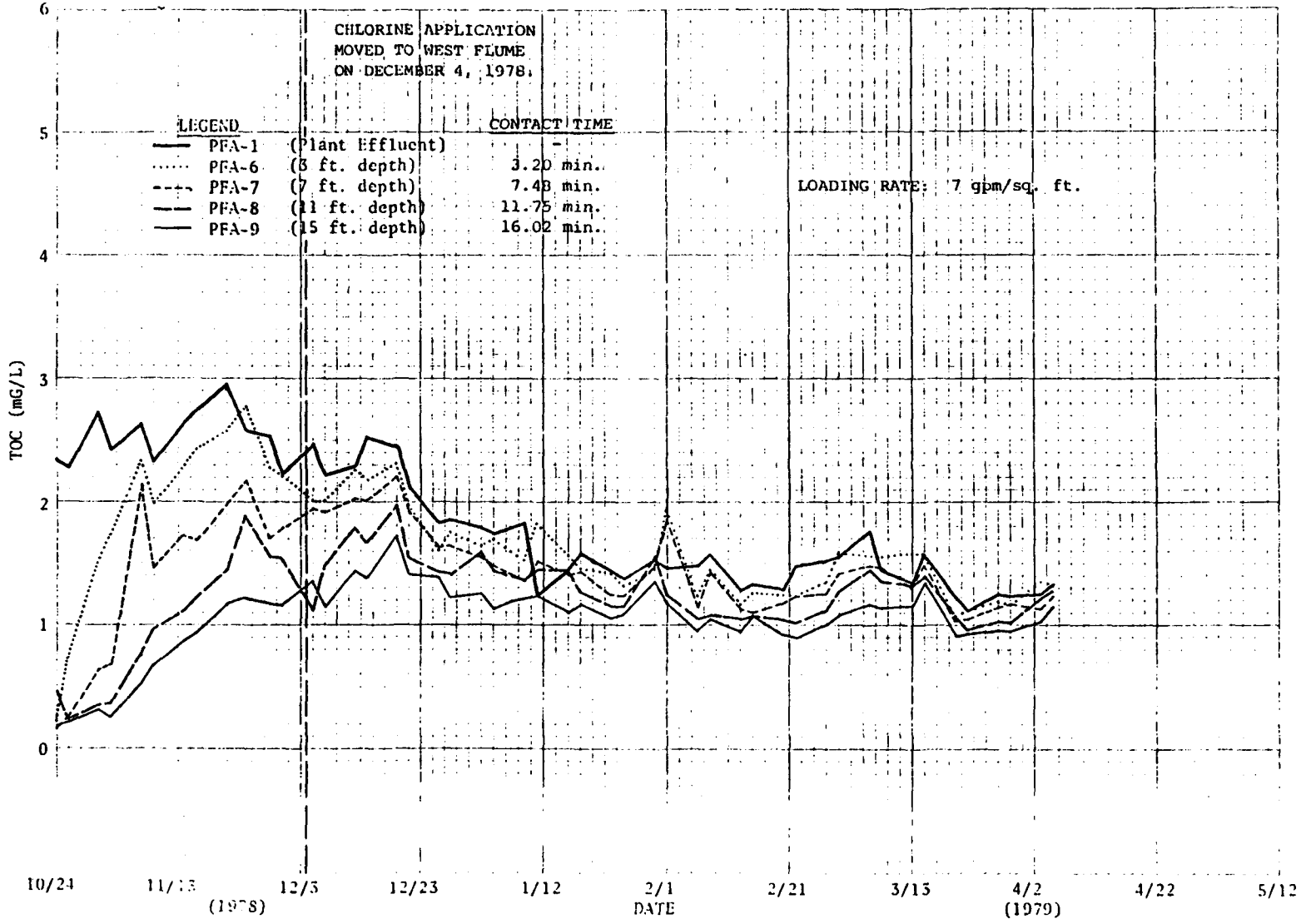

Figure 11. Total Organic Carbon (TOC) Concentrations in "Lignite" Contactor Columns

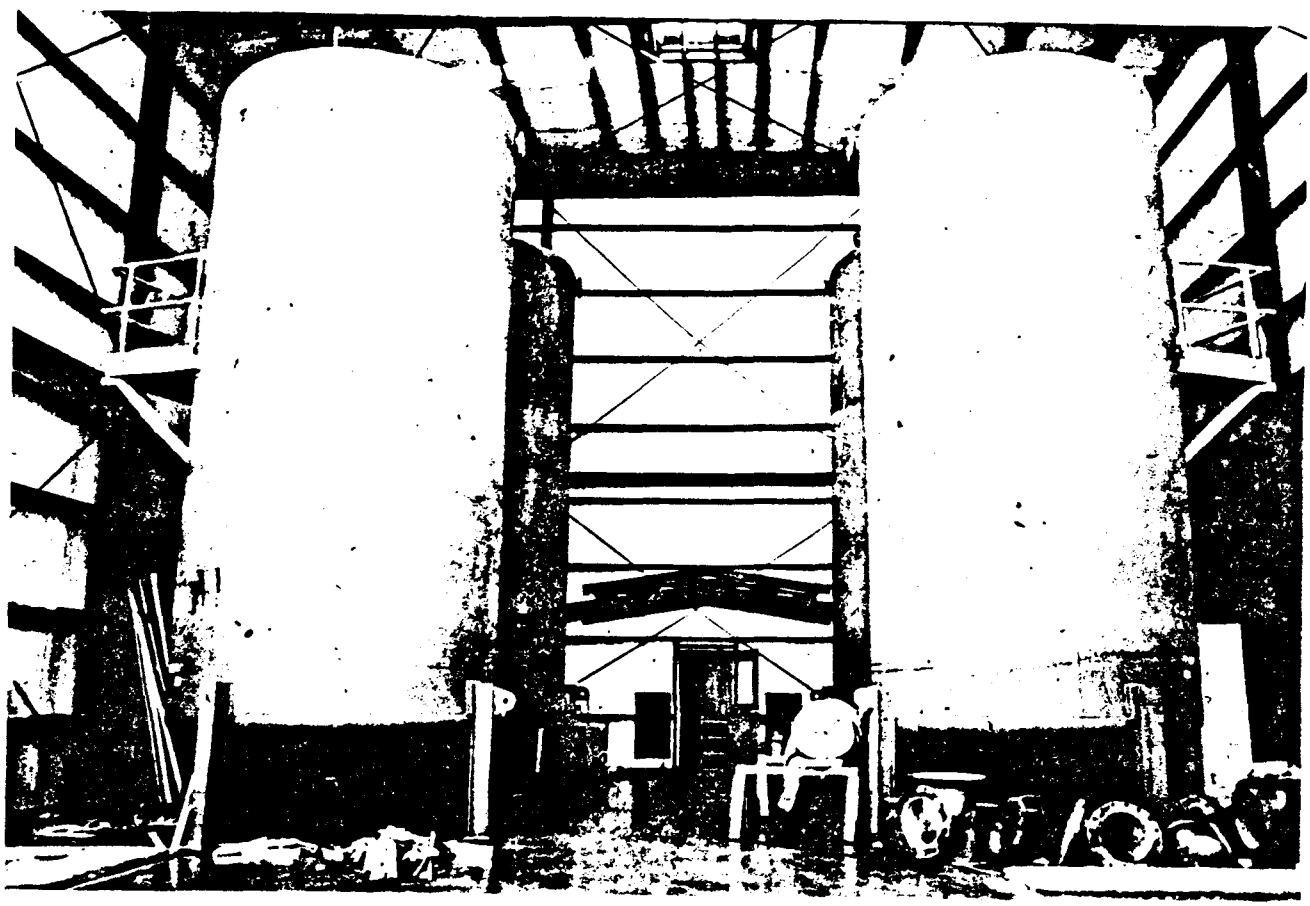

Figure 12. Deep Bed Carbon Contactors

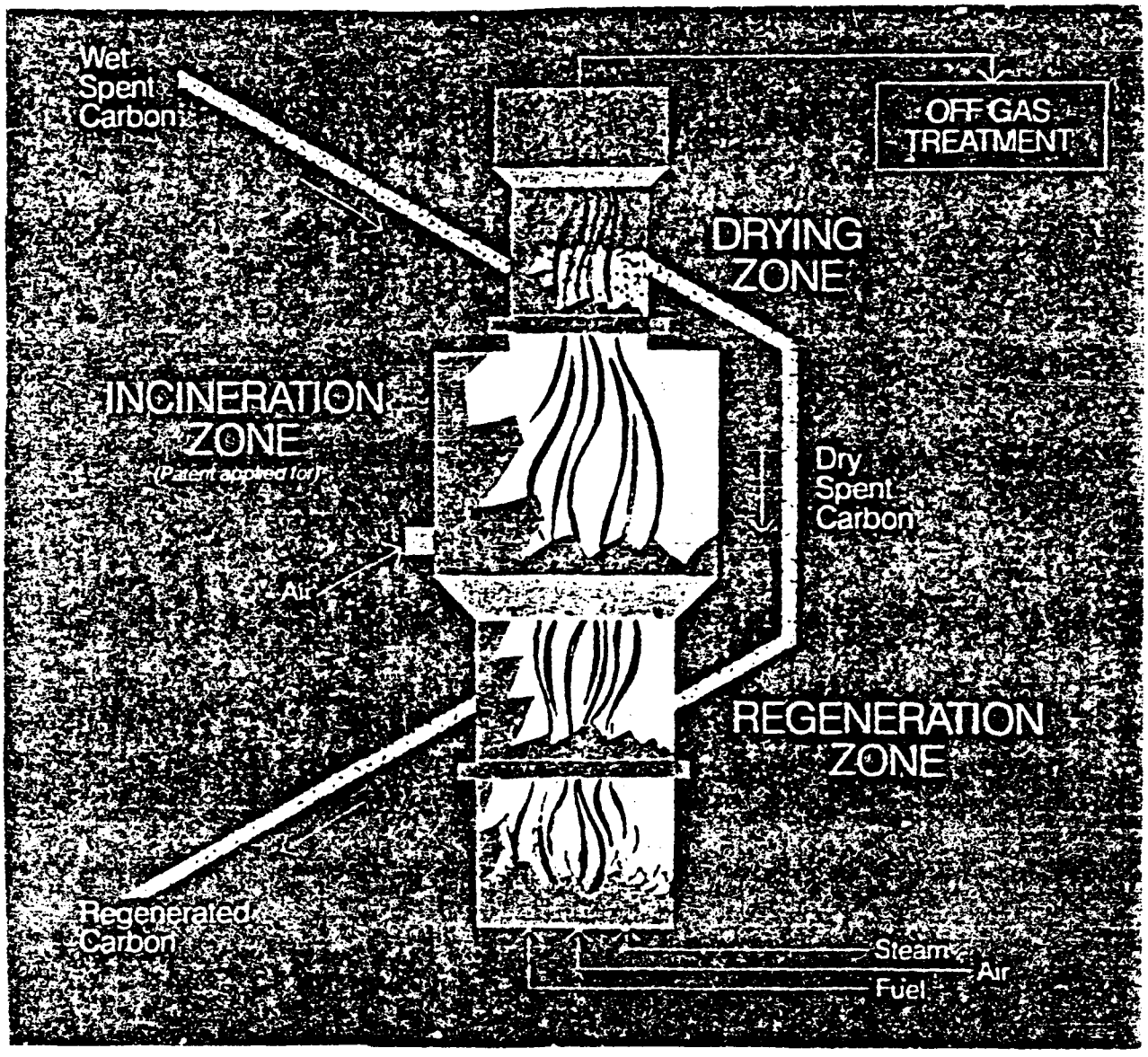

Figure 13. Regeneration Furnace - How it Operates

Completion of the furnace is scheduled for the fall of 1979. At that time we will reactivate the spent carbon from the original carbon filters. Spent carbon from the second carbon filters and the carbon contactors will be reactivated as needed.

Reactivation efficiencies and carbon attrition rates will be evaluated. Figure 14 is a schematic of the regeneration cycle. Information obtained from this project will be valuable in determining design criteria for in-plant carbon transportation systems. This information will also be necessary for the economic evaluation of the conversion of existing sand filters versus construction of new post filter carbon contactors.

CONCLUSION

Upon completion of the project and evaluation of all data, an engineering review will determine the most cost effective mode of operation for the entire treatment plant. A recommendation will then be made to our City Council who will probably make a final decision. Naturally, there will be citizen input.

In conclusion, I think that Cincinnati has taken a reasonable approach to develop possible solutions to problems of concern. It is hoped that the lessons we learn may be applicable to other water systems, particularly those on the Ohio River. However, we should all remember that rectifying a problem at the ultimate end, which is the water treatment plant, is far less desirable than preventing the problem at the original point of pollution discharge.

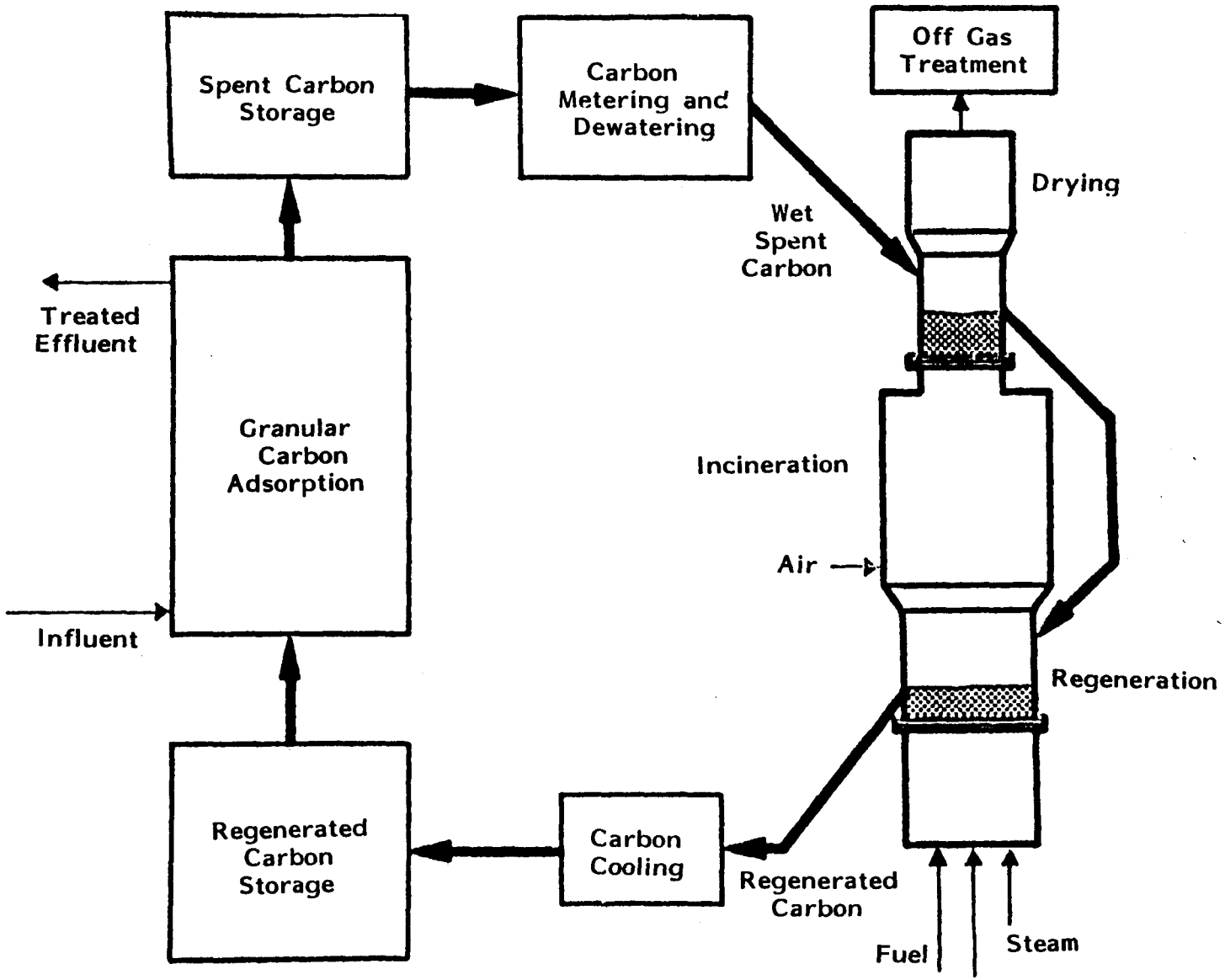

Figure 14. Westvaco Fluid Bed Regenerator in a Typical Adsorption System

RESULTS FROM OHIO RIVER VALLEY WATER SANITATION COMMISSION STUDIES

Richard J. Miltner

INTRODUCTION

In November 1976, the Ohio River Valley Water Sanitation Commission initiated a project, funded by 11 water utilities in the Ohio River Valley and by a United States Environmental Protection Agency research grant, to investigate trihalomethane formation and control at those utilities and to investigate the levels of other organic compounds in raw and treated waters. Three of the utilities employed granular activated carbon (GAC). They were the Huntington Water Corporation, West Virginia, the Beaver Falls Authority, Pennsylvania, and the Western Pennsylvania Water Company, Pennsylvania. Treatment at these utilities is described and major results of project studies examining GAC adsorption/filtration are discussed.

METHODS

Instantaneous and terminal level samples for analyses were collected and handled as suggested by Stevens and Symons (1). Terminal level samples were buffered to clear well pH, chlorinated sufficiently to satisfy a 7-day demand, and stored 7 days at clear well temperature. Samples were analyzed by a contract laboratory for trihalomethanes and carbon tetrachloride by purge, trap and desorption followed by gas chromatography and halogen-specific detection (2). Analyses for all other parameters were conducted by the utilities in accordance with Standard Methods (3). Discussion of organic analytical procedures and quality control is detailed elsewhere (2).

GAC OPERATION

GAC use at these three utilities was similar. At each, GAC was employed in the filtration/adsorption mode in beds originally designed for rapid sand filtration. The filter/adsorbers received chlorinated, settled water and preceded post-chlorination at the clear well.

Huntington Water Corporation

Westvaco WVW 14 x 40 GAC was evaluated at Huntington. The selection of GAC was based on its history of taste and odor control at the utility. The virgin GAC replaced taste-and-odor-exhausted GAC. No previous pilot scale studies had been conducted to determine optimum selection of GAC or bed depth for organics control. The bed was placed with 76 cm (30 inches) of GAC on top of 30 cm (12 inches) of sand and gravel. Hydraulic data demonstrated a mean loading rate of 6.1 m/hr (2.6 gpm/ft^2) and a mean empty bed contact time (EBCT) of 7.2 minutes. Treatment is illustrated in Figure 1. Water quality data for the utility during the time of the study are given in Table 1. The virgin GAC bed represented only 8 percent of the utility's total flow. Periodically, influent and effluent waters for older WVW 14 x 40 GAC beds were sampled in order to evaluate performance after long periods of time in operation.

Beaver Falls Authority

Three virgin GAC beds were evaluated. The utility had previously conducted pilot column studies with several GACs for taste and odor control. Those studies did not determine optimum selection of GAC or bed depth for organics control. The three beds were geometrically identical. One bed was placed with 61 cm (24 inches) of Calgon Filtrasorb 400 on top of 30 cm of sand and gravel. A second bed was placed with 61 cm of Calgon Filtrasorb C on top of 30 cm of sand and gravel. A third bed was placed with 61 cm of ICI Hydrodarco 8 x 16 on top of 30 cm of sand. Treatment is illustrated in Figure 2. All three beds were placed in service simultaneously. Hydraulic data collected during the study indicated mean loading rates of 3.1 - 3.5 m/hr (1.3 - 1.5 gpm/ft^2) and mean empty bed contact times of 10 to 11 minutes. Water quality data for the utility are presented in Tables 2, 3, and 4.

Western Pennsylvania Water Company

Treatment at this utility included filtration/adsorption with 2-1/2 year old Calgon Filtrasorb 400 GAC. Placement and operation of these beds were discussed by Ross (4). Treatment is illustrated in Figure 3.

FINDINGS FROM GAC STUDIES

Adsorption of Trihalomethanes

The GACs studied were exhausted for the removal of total trihalomethane (TTHM) and the trihalomethane precursors [as measured by trihalomethane formation potential, or THMFP (1)]

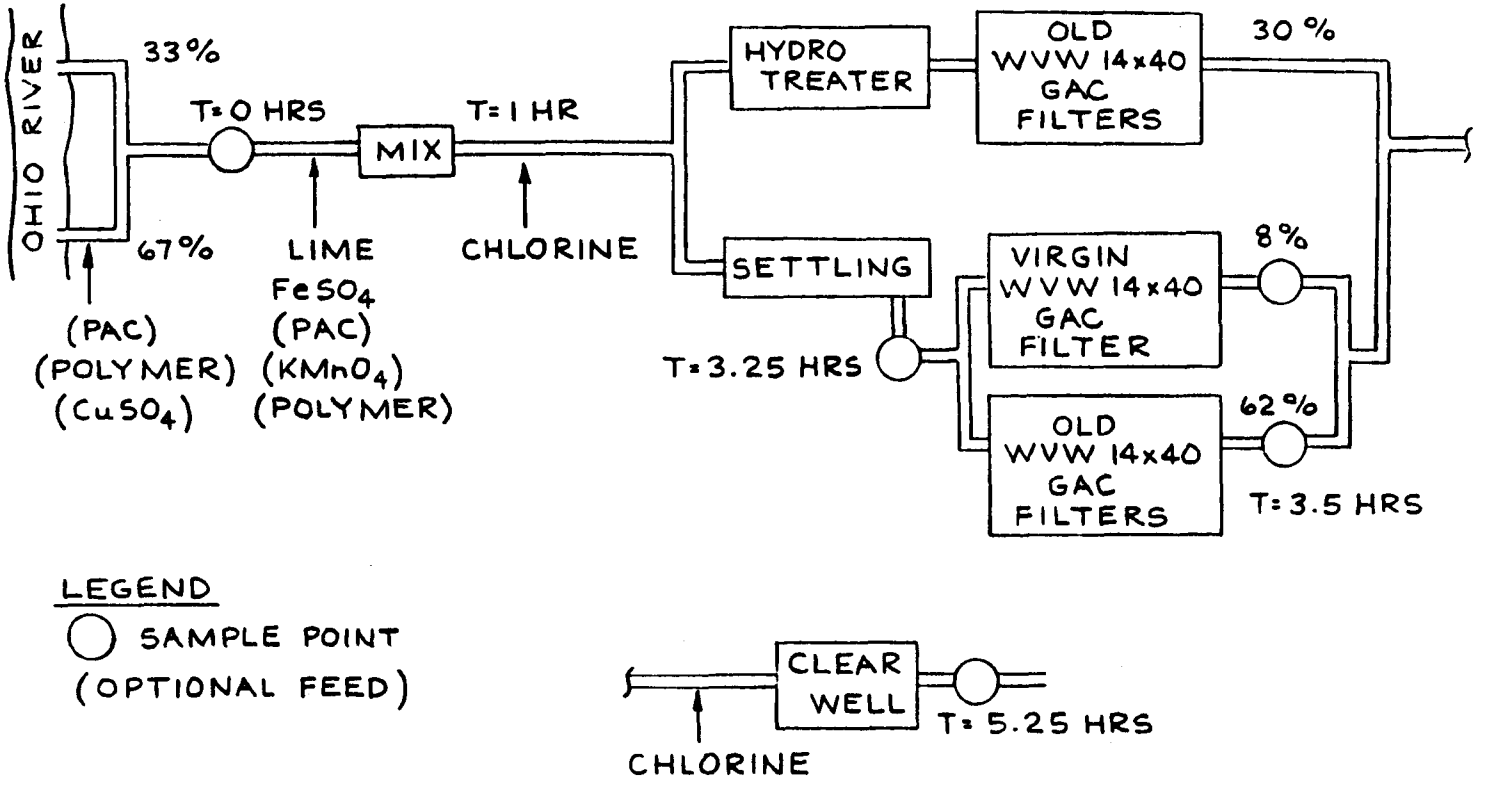

Figure 1. Treatment of Huntington Water Corporation
64,000 m^3/Day (17 MGD)
July 1977 - March 1978

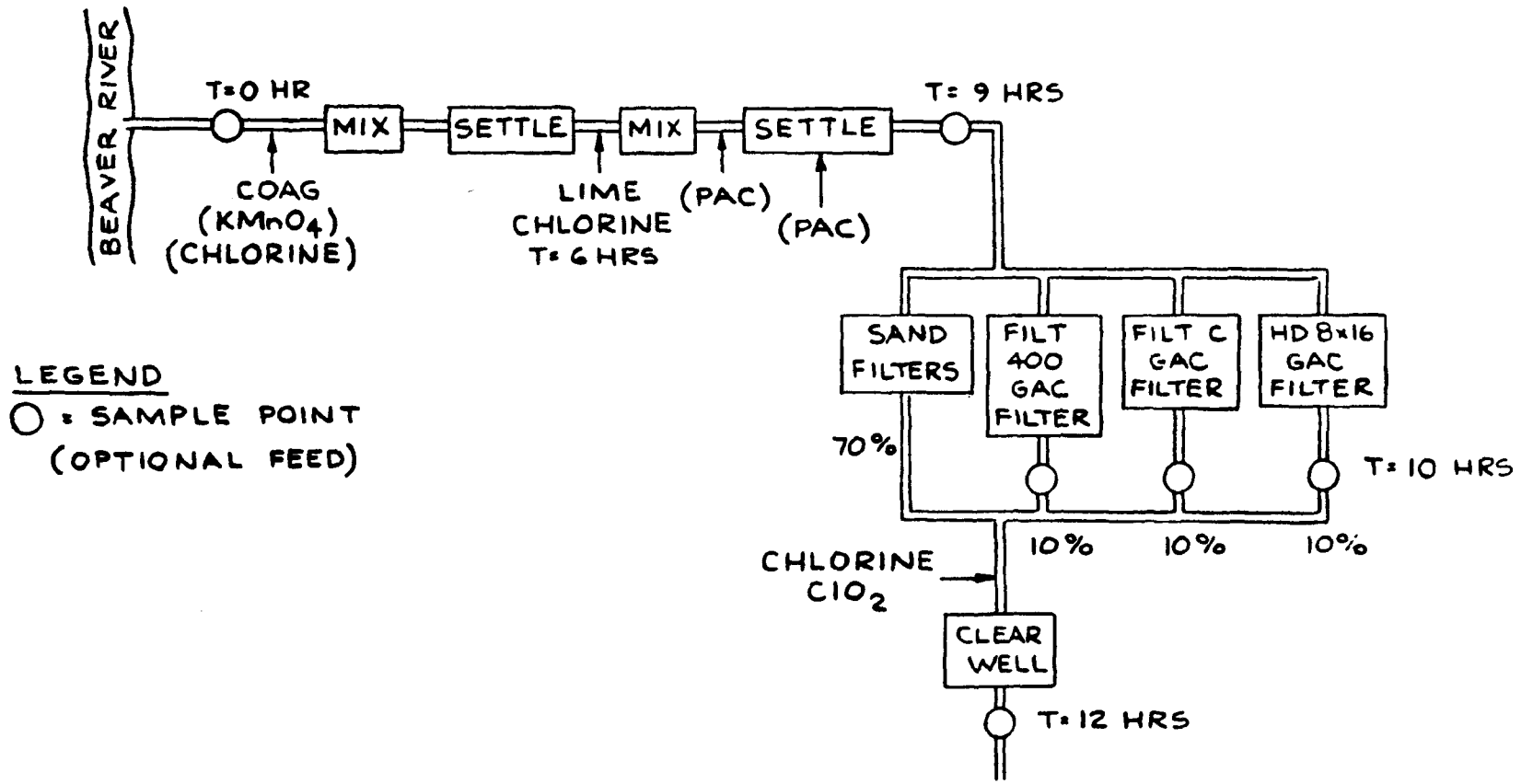

Figure 2. Water Treatment Scheme
Beaver Falls Authority
Eastvale Plant
17,000 m^3/Day (4.5 MGD)

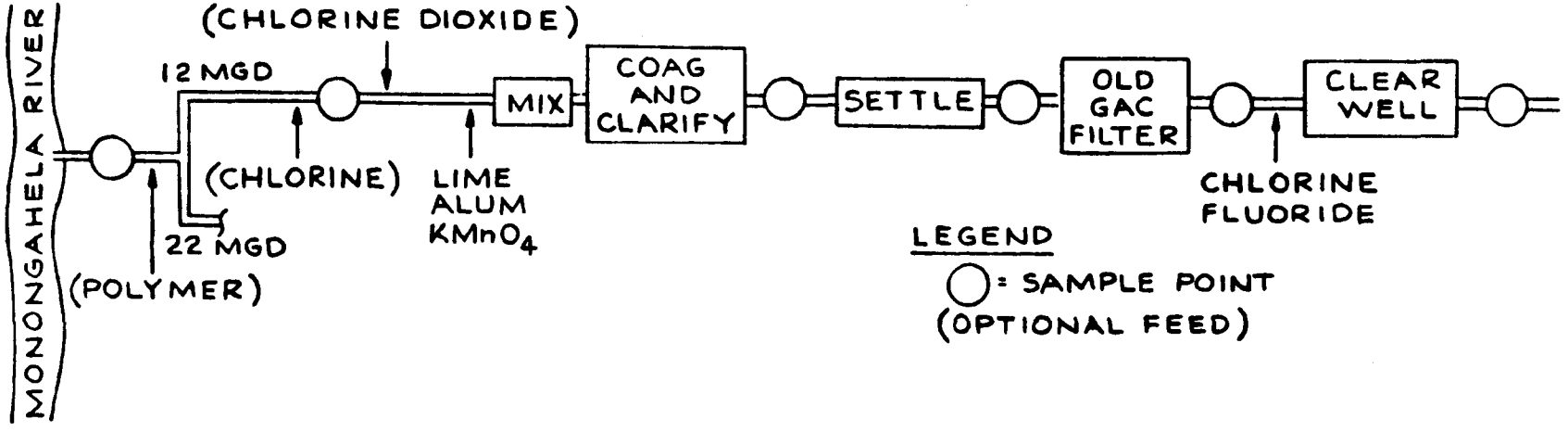

Figure 3. Treatment at Western Pennsylvania Water Company 129,000 m^3/Day (34 MGD)

Table 1

Water Quality Data (Mean Values)
Huntington Water Corporation
July 1977 - March 1978

Week of Virgin GAC Operation	Raw Water Mean pH = 7.5			GAC Influent (Settled) Mean pH = 8.9					Virgin GAC Effluent Mean pH = 8.7				
					Chlorine[a]					Chlorine[a]			
	Temp, °C	Turb[b]	TC[c]	Turb[b]	Free	Total	TC[c]	SPC[d]	Turb[b]	Free	Total	TC[c]	SPC[d]
1	27	14	1,600	2.0	0.8	1.4	<1	4	0.2	ND	ND	<1	100
2	28	21	1,200	4.6	0.3	0.4	<1	52	1.5	ND	TR	<1	53
3	28	26	910	4.9	1.8	3.7	<1	42	1.4	0.1	0.3	6	12
4	28	13	870	4.4	0.5	0.7	<1	7	1.7	TR	0.3	8	41
5	28	15	1,500	6.5	0.6	0.9	<1	18	1.8	0.4	0.6	5	18
6	27	80	3,000	5.8	0.5	0.8	<1	28	1.1	0.1	0.2	<1	13
7	27	37	5,300	3.8	0.4	0.7	<1	17	0.5	TR	0.1	<1	3
8	27	34	2,300	5.9	0.3	0.6	<1	22	1.5	0.2	0.4	2	25
9	27	17	1,400	3.3	0.5	0.7	<1	24	0.3	TR	0.2	2	46
10	27	18	970	4.6	0.5	0.7	<1	26	3.2	TR	0.2	<1	140
11	26	25	1,100	7.9	0.4	0.6	<1	28	1.7	TR	0.2	<1	23
12	24	24	1,700	4.4	0.5	0.7	<1	28	0.4	TR	TR	1	12
13	19	47	3,100	8.7	0.5	0.8	<1	31	0.4	TR	0.2	<1	30
14	19	98	4,300	4.3	0.5	0.9	<1	--	0.4	0.1	0.4	<1	--
15	14	34	3,900	16	0.5	0.7	<1	34	0.4	--	--	<1	2
16	15	22	2,600	9.1	0.5	0.9	<1	39	1.0	TR	0.5	<1	10
17	15	18	2,800	10	0.4	0.9	<1	18	0.5	TR	0.6	<1	2
20	11	42	3,900	5.5	0.6	0.8	<1	200	0.7	0.3	0.4	<1	4
22	8	240	1,400	9.8	0.2	0.3	<1	55	12	0.2	0.4	<1	11
23	5	160	26,000	8.0	0.5	0.6	<1	36	0.8	0.2	0.3	<1	3
25	3	24	2,800	7.0	ND	0.7	<1	30	0.5	ND	0.5	<1	<1
27	2	30	5,900	9.0	0.9	1.1	<1	--	0.2	0.3	0.5	<1	--
31	2	34	610	14	0.3	0.9	<1	--	0.3	0.4	0.8	<1	--

[a] [b] Chlorine, mg/l
[c] Turbidity, NTU
[d] Total coliform/100 ml
Standard plate count/ml

Table 2

Influent Water Quality Data (Mean Values)
Beaver Falls Authority
September 1977 - April 1978

Week of Operation	Raw Mean pH = 7.2			GAC Influent (Settled) Mean pH = 7.4				
				Chlorine[a]				
	Temp, °C	Turbidity[b]	TC[c] x 10^3	Free	Total	Turbidity[b]	TC[c]	SPC[d]
1	21	44	98	2.0	--	5.6	<1	--
2	21	28	71	1.7	1.7	4.8	<1	--
3	15	22	140	1.3	1.4	2.3	<1	--
4	11	9.5	150	1.1	1.3	2.9	<1	100
5	16	7.5	39	1.2	1.4	2.5	<1	800
6	16	9	190	1.4	1.6	3.3	<1	350
7	16	10	80	1.1	1.2	3.6	<1	10
8	10	9	98	1.0	1.0	3.2	<1	42
9	10	16	220	1.3	1.6	4.6	2	110
10	8	10	120	1.0	1.3	4.5	<1	33
11	6	14	120	1.4	1.6	3.7	<1	95
12	3	10	69	1.0	1.1	5.9	1	360
13	4	22	89	1.2	1.7	4.6	<1	660
14	2	10	75	1.3	1.5	6.6	1	200
15	1	10	65	1.0	1.2	4.8	<1	120
17	1	12	48	1.4	1.7	5.9	<1	150
18	1	8	27	1.0	1.1	5.5	<1	33
21	1	14	6	0.4	1.6	6.4	<1	30
23	4	10	23	0.3	1.6	5.8	<1	24
25	4	150	84	TR	1.4	6.6	<1	38
27	7	12	13	--	1.4	6.3	<1	58
29	10	8	24	0.2	1.1	1.7	<1	33
32	11	6	8.4	0.2	1.6	1.9	<1	17

[a] Chlorine, mg/l
[b] Turbidity, NTU
[c] Total coliform/100 ml
[d] Standard plate count/ml
TR = trace

Table 3

Effluent Water Quality Data (Mean Values)
Beaver Falls Authority
September 1977 - April 1978

Week of Operation	Raw Water Temp, °C	GAC Effluent: Filtrasorb 400 Mean pH = 7.3					GAC Effluent: Filtrasorb C Mean pH = 7.3					GAC Effluent: HD 8x16 Mean pH = 7.3				
		Chlorine[a]					Chlorine[a]					Chlorine[a]				
		Free	Total	Turb[b]	TC[c]	SPC[d]	Free	Total	Turb[b]	TC[c]	SPC[d]	Free	Total	Turb[b]	TC[c]	SPC[d]
1	21	ND	ND	0.4	64	--	ND	ND	0.5	85	--	ND	ND	0.6	46	--
2	21	ND	ND	0.4	75	--	ND	ND	0.3	95	--	ND	ND	0.4	25	--
3	15	ND	ND	0.3	98	1,000	ND	ND	0.4	130	740	ND	ND	0.3	33	1,700
4	11	ND	ND	0.3	45	1,400	ND	ND	0.3	50	60,000	ND	ND	0.3	23	1,100
5	16	ND	ND	0.4	34	25,000	ND	ND	0.4	28	42,000	ND	ND	0.3	12	3,800
6	16	TR	<0.1	0.6	42	2,000	TR	<0.1	0.5	12	40,000	<0.1	0.2	0.6	13	3,000
7	16	TR	<0.1	0.3	28	20,000	TR	<0.1	0.4	12	52,000	TR	<0.1	0.3	2	45,000
8	10	TR	<0.1	0.4	22	29,000	TR	<0.1	0.4	21	32,000	TR	<0.1	0.4	8	92,000
9	10	TR	TR	0.5	13	6,500	TR	<0.1	0.6	7	6,500	TR	<0.1	0.4	2	21,000
10	8	TR	<0.1	0.3	12	1,600	TR	<0.1	0.4	18	1,800	TR	<0.1	0.3	5	1,800
11	6	TR	<0.1	0.6	2	960	TR	<0.1	0.5	1	820	TR	<0.1	0.5	1	900
12	3	TR	<0.1	0.6	1	270	TR	<0.1	0.6	2	380	TR	<0.1	0.7	<1	320
13	4	TR	<0.1	0.4	<1	480	TR	<0.1	0.4	<1	540	TR	<0.1	0.4	<1	380
14	2	TR	TR	0.1	1	440	TR	<0.1	0.3	<1	110	TR	<0.1	0.1	<1	200
15	1	TR	<0.1	0.4	<1	44	TR	<0.1	0.3	<1	50	TR	<0.1	0.4	<1	74
17	1	TR	<0.1	0.4	<1	50	TR	<0.1	0.5	<1	16	TR	0.1	0.5	<1	26
18	1	TR	<0.1	0.5	<1	21	TR	<0.1	0.5	<1	20	TR	<0.1	0.6	<1	9
21	1	TR	0.3	0.6	<1	30	TR	0.4	0.6	<1	23	<0.1	0.4	0.7	<1	47
23	4	TR	0.4	0.6	<1	13	TR	0.2	0.5	<1	10	TR	0.4	0.4	<1	15
25	4	TR	0.2	0.6	<1	21	TR	0.2	0.6	<1	35	TR	0.2	0.6	<1	24
27	7	--	0.1	0.3	<1	41	--	0.1	0.3	<1	27	--	0.2	0.4	<1	10
29	10	--	0.1	0.3	<1	31	--	0.1	0.3	<1	28	--	0.1	0.3	<1	17
32	11	--	0.3	0.3	<1	69	--	0.2	0.3	<1	82	--	0.3	0.3	<1	19

[a] Chlorine, mg/l
[b] Turbidity, NTU
[c] Total coliform/100 ml
[d] Standard plate count/ml

TR = trace
ND = not detected

Table 4

Water Quality Data (Mean Values)
Beaver Falls Authority
September 1978 - December 1978

Week of Operation	Raw		GAC Influent (Settled)		GAC Effluent					
					Filtrasorb 400		Filtrasorb C		HD 8x16	
	Temp, °C	TC[a]	Free Chlorine[b]	TC[a]	Free Chlorine[b]	TC[a]	Free Chlorine[b]	TC[a]	Free Chlorine[b]	TC[a]
53	26	18,000	1.4	<1	TR	100	TR	64	TR	130
54	23	10,000	1.2	<1	TR	120	TR	25	TR	240
55	22	22,000	1.6	<1	TR	230	TR	21	TR	730
56	19	9,200	1.6	<1	TR	470	TR	5	TR	330
57	14	31,000	1.4	<1	TR	62	TR	9	TR	82
58	12	10,000	1.1	<1	TR	44	TR	10	TR	55
59	14	8,700	1.4	<1	TR	30	TR	3	TR	31
60	13	19,000	1.3	<1	TR	8	TR	<1	TR	9
61	11	5,000	1.5	<1	TR	--	TR	2	TR	<1
62	9	12,000	0.8	<1	TR	1	TR	<1	TR	<1
63	8	82,000	1.2	<1	TR	<1	TR	<1	TR	<1
64	6	8,000	1.0	<1	TR	<1	TR	<1	TR	<1

[a]Total coliform/100 ml
[b]Chlorine, mg/l
TR = trace

after 7 to 15 weeks of operation. Figure 4 illustrates trihalomethane control at Huntington. WVW 14 x 40 was exhausted for the removal of TTHM after 7 to 8 weeks of operation. Prior to that time, influent concentrations exceeded effluent concentrations. Following that time, effluent concentrations exceeded influent concentrations, or effluent and influent concentrations could not be differentiated as determined by the precision of project trihalomethane data (2). WVW 14 x 40 was exhausted for the removal of THMFP after 7 to 10 weeks of operation as illustrated by Figure 4.

Figure 5 illustrates trihalomethane control by one of the GACs at Beaver Falls. Filtrasorb 400 was exhausted for the removal of TTHM after 9 to 10 weeks and for the removal of THMFP after approximately 11 weeks of operation.

GACs studied were exhausted for the removal of chloroform after 7 to 15 weeks of operation. Chloroform control by Filtrasorb C at Beaver Falls is illustrated in Figure 6. After 12 to 15 weeks of operation, effluent and influent chloroform concentrations could not be differentiated as determined by the precision of project chloroform data (2), indicating that exhaustion had occurred. WVW 14 x 40 was exhausted for the removal of chloroform after 7 to 8 weeks of operation as illustrated by Figure 7.

GACs studied were exhausted for the removal of bromodichloromethane and dibromochloromethane after 8 to 15 weeks of operation. Figures 6 and 7 illustrate exhaustion for the removal of dibromochloromethane after 13 to 15 weeks of operation by Filtrasorb C at Beaver Falls and exhaustion for the removal of bromodichloromethane after 11 to 14 weeks of operation by WVW 14 x 40 at Huntington, respectively.

Evaluation of the GACs for the control of bromoform and dichloroiodomethane was complicated by the fact that at the concentrations typically present (i.e., below 0.5 µg/liter), the precision of the data may be ±100 percent (2). This was generally found to be the case for other volatile halocarbons. GACs at Beaver Falls could not be evaluated because, when detected, concentrations of these trihalomethanes were below 0.5 µg/liter. However, bromoform and dichloroiodomethane concentrations at Huntington are given in Table 5. These data indicate that adsorption of bromoform occurred during week 12, but that influent and effluent bromoform concentrations could not be differentiated beyond this week.

Thus, the virgin GACs at these two utilities were an effective trihalomethane control for 2 to 3 months when operating in the filtration/adsorption mode, in beds designed

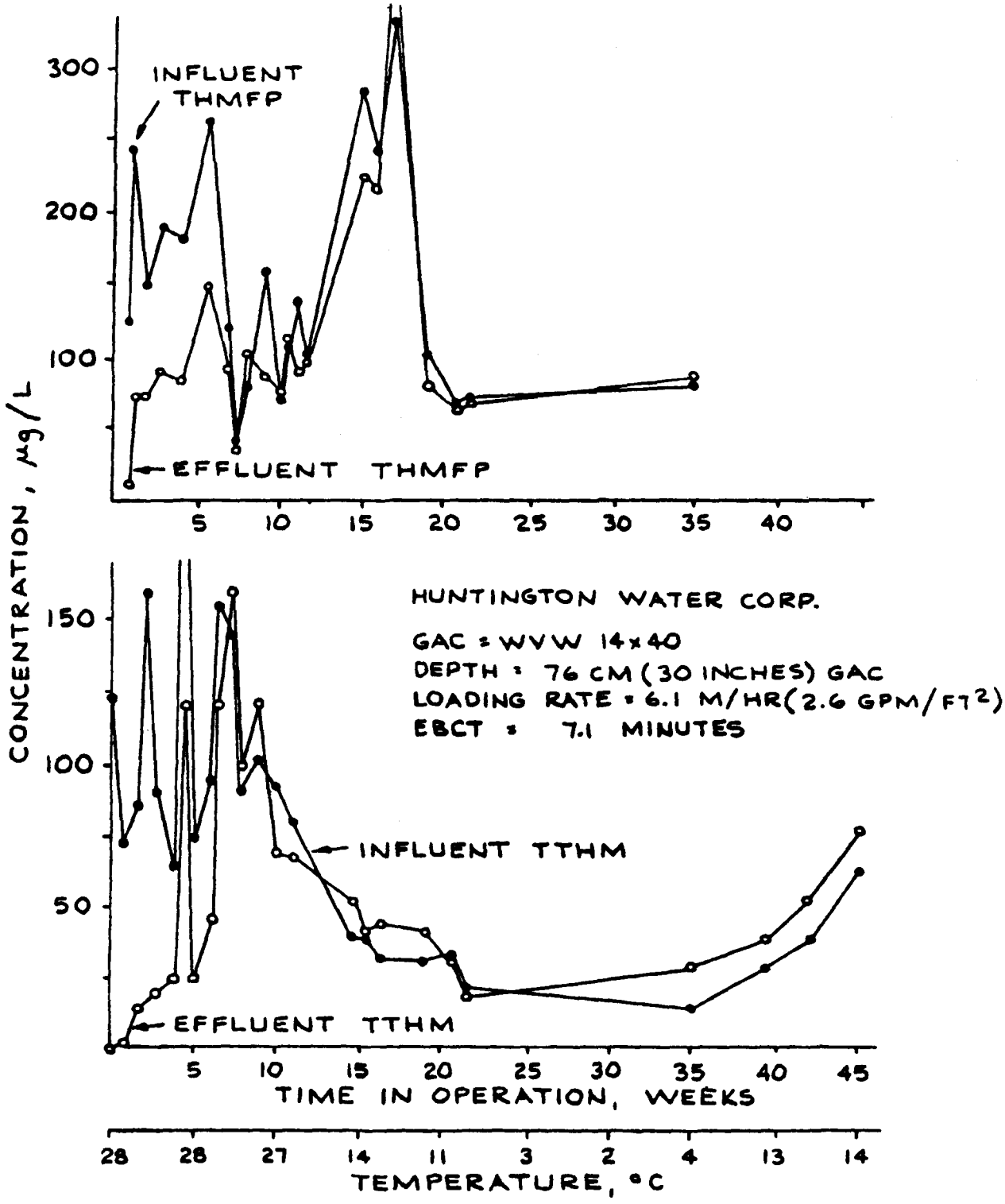

Figure 4. Trihalomethane Removal by Granular Activated Carbon

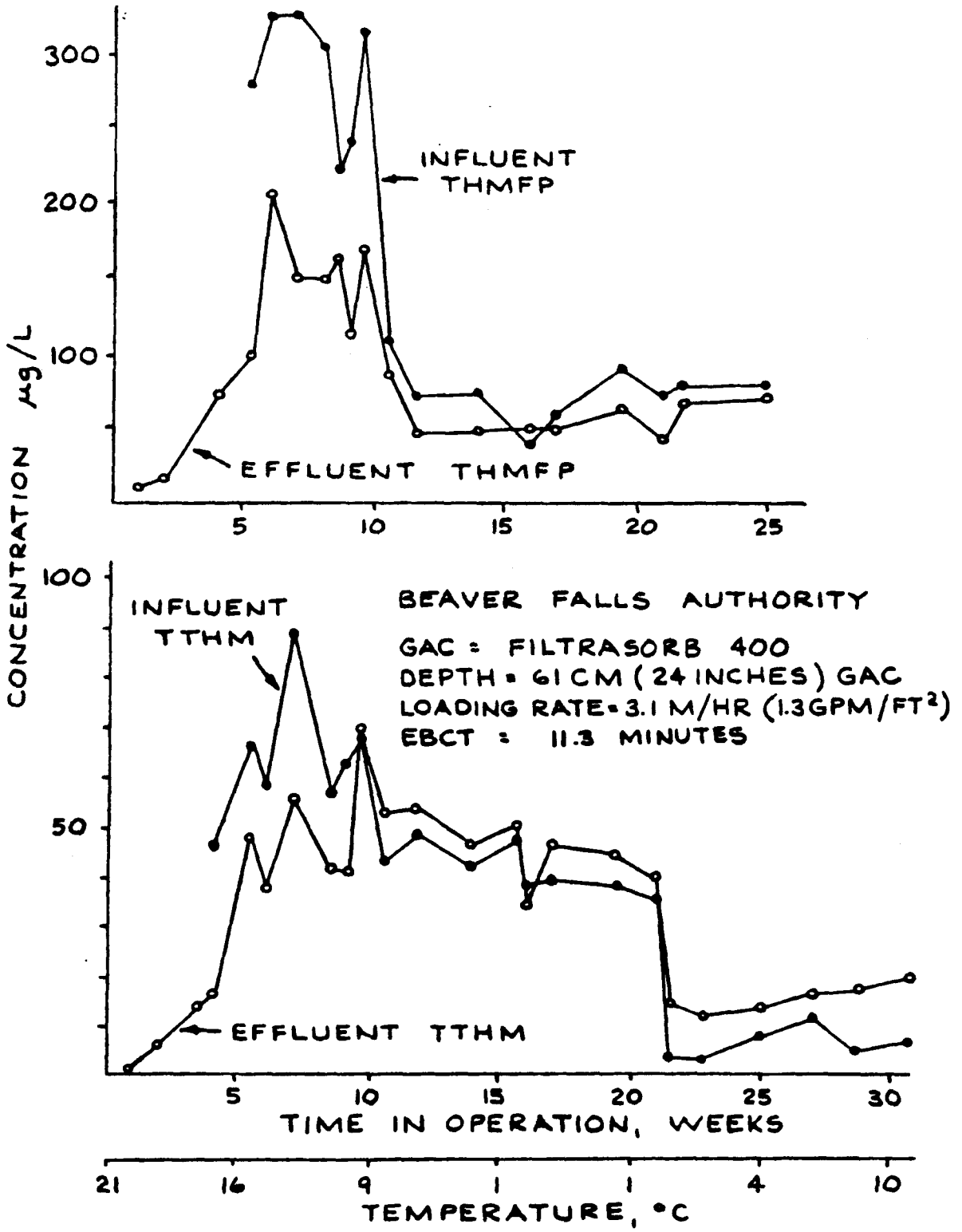

Figure 5. Trihalomethane Removal by Granular Activated Carbon

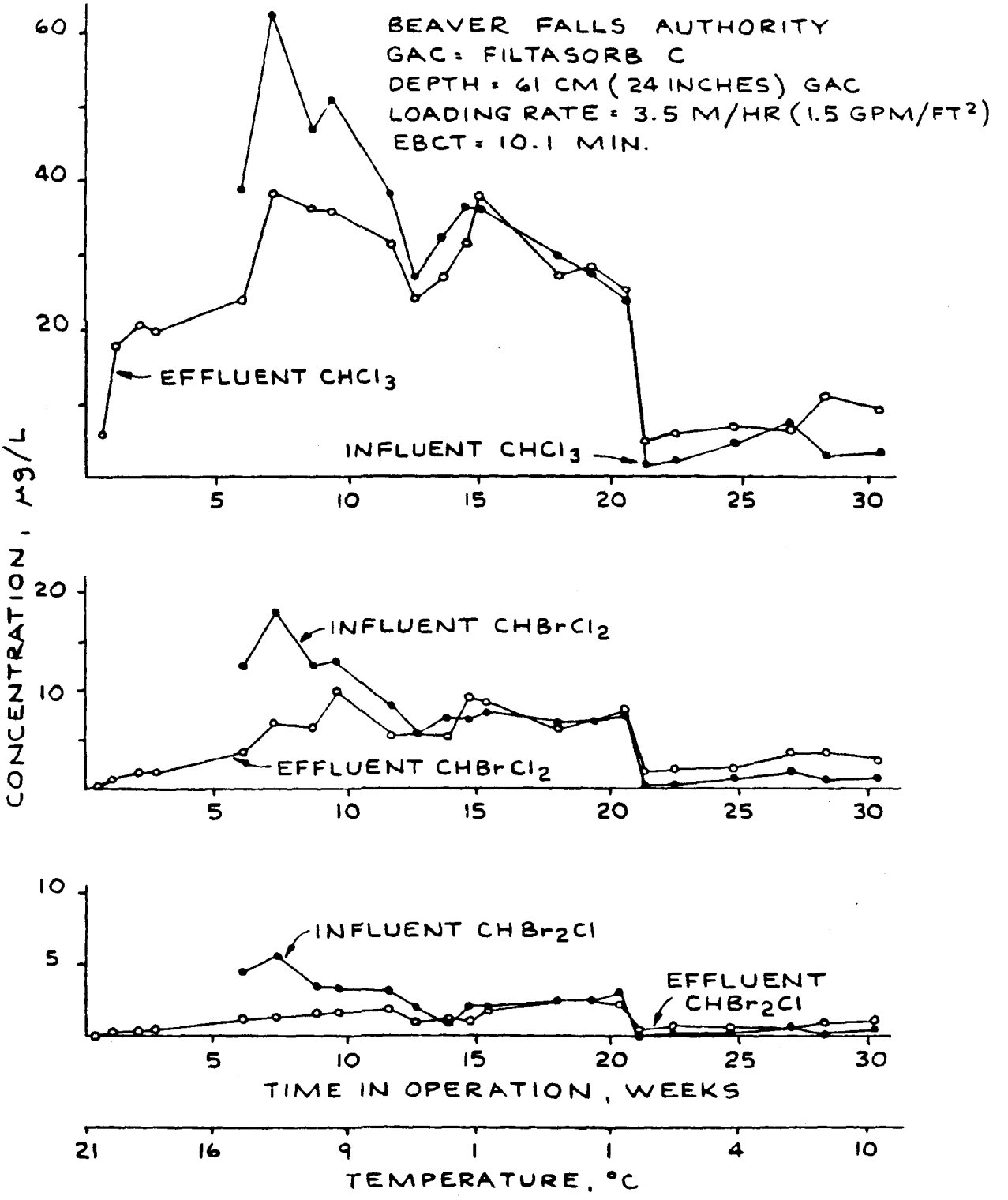

Figure 6. Trihalomethane Removal by Granular Activated Carbon

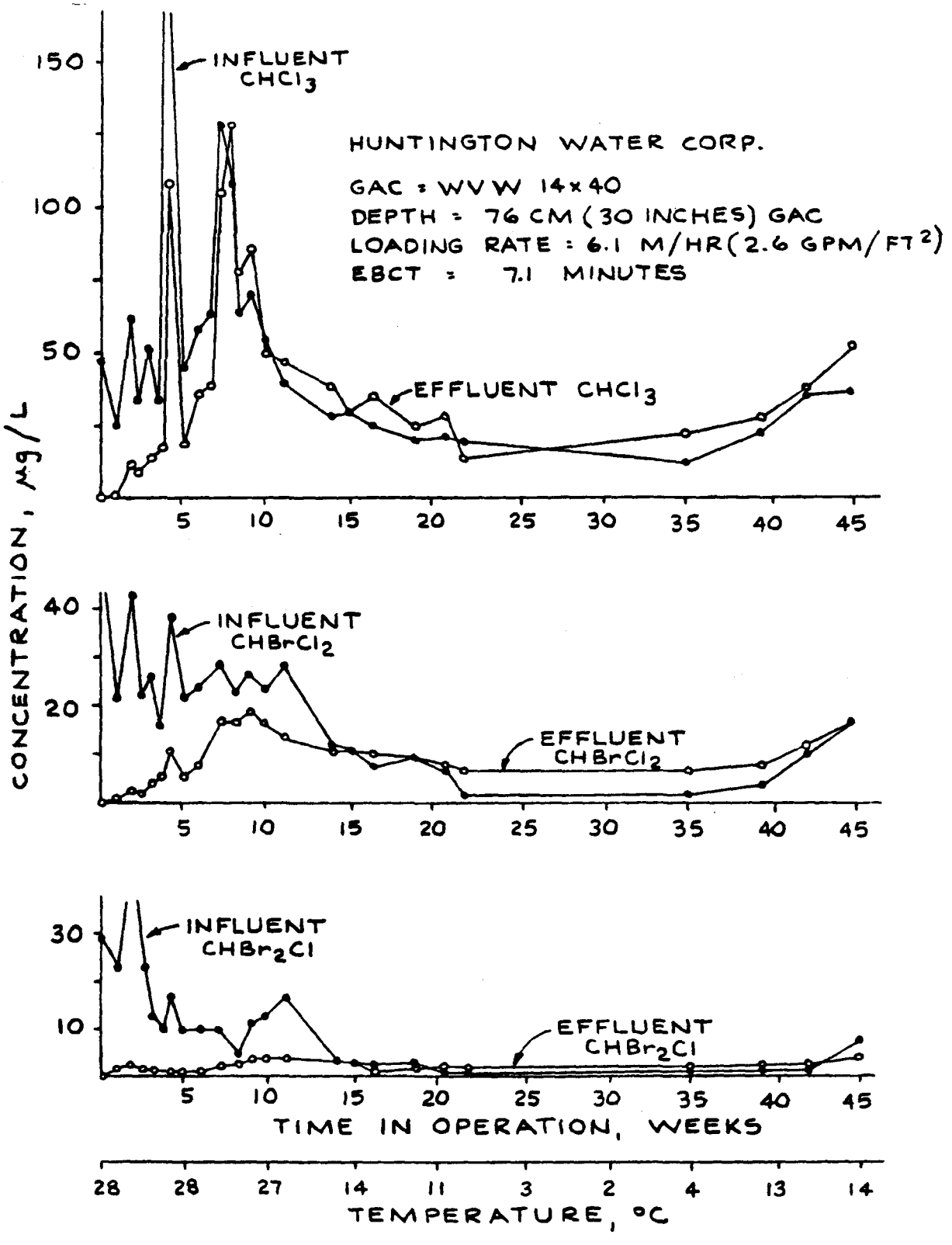

Figure 7. Trihalomethane Removal by Granular Activated Carbon

Table 5

Removal of Trihalomethanes By Granular Activated Carbon[a]
Huntington Water Corporation
July 1977 - May 1978

Week of Operation	Concentration,[b] µg/l			
	Bromoform		Dichloroiodomethane	
	Influent	Effluent	Influent	Effluent
1	1.6	ND	<0.1	ND
2	4.4	<0.1	0.1	ND
3	1.2	<0.1	0.3	ND
4	0.3	ND	0.2	<0.1
5	0.2	<0.1	0.2	<0.1
6	0.2	ND	0.4	<0.1
7	0.1	ND	0.7	<0.1
8	0.5	<0.1	0.6	<0.1
9	0.6	0.1	0.4	ND
10	1.5	0.2	0.2	<0.1
11	1.6	0.2	0.2	<0.1
12	1.9	0.2	0.1	0.1
15	<0.1	0.1	<0.1	<0.1
16	0.1	<0.1	<0.1	<0.1
17	0.1	0.1	0.1	<0.1
19	0.2	<0.1	<0.1	ND
21	ND	ND	ND	<0.1
22	ND	<0.1	ND	<0.1
35	ND	ND	ND	<0.1
39	ND	<0.1	0.1	<0.1
42	ND	ND	<0.1	<0.1
45	0.5	0.2	0.2	<0.1

[a]GAC = WVW 14x40
Bed depth = 76 cm (30 inches) GAC
Loading rate = 6.1 m/hr (2.6 gpm/ft^2)
EBCT = 7.2 minutes
[b]GC/Hall detector, approximate lower detection level = 0.1 µg/l
ND = not detected

for sand filtration, receiving chlorinated water, and when placed in operation during summer months when temperatures were high. Figures 4 and 7 illustrate higher influent trihalomethane concentrations when temperatures were high and lower influent trihalomethane concentrations when temperatures were low, suggesting that time to exhaustion might have exceeded 2 to 3 months had the beds been placed in operation during colder months.

Adsorption of Carbon Tetrachloride

Organic compounds other than trihalomethanes were not frequently found at detection levels of 0.1 µg/liter, and when detected, were generally at concentrations below 0.5 µg/liter where influent and effluent concentrations often could not be differentiated because the precision of the data below 0.5 µg/liter may be ±100 percent (2). Thus, it was difficult to evaluate the adsorption capacity of the GACs for other compounds.

Carbon tetrachloride was frequently found at Huntington, however. These data are presented in Table 6. Breakthrough was not observed until the 9th week of operation. GAC was an effective barrier for relatively high carbon tetrachloride loading, as demonstrated during the 10th week of operation when 13 µg/liter influent and 0.4 µg/liter effluent concentrations were observed. After 11 weeks of operation, however, the compound was always detected in GAC effluent waters. Although influent and effluent concentrations were low after 11 weeks of operation and oftentimes could not be differentiated, these data suggest that GAC was not an effective barrier for routine, low level carbon tetrachloride loading after 3 months of operation.

Desorption from GAC

Desorption from GAC was observed whenever GAC influent loading was significantly lowered. This was observed at each of the three utilities.

At the Western Pennsylvania Water Company, chlorine dioxide was substituted for chlorine as the raw water disinfectant, see Figure 8. When chlorinating raw water, no difference was observed in TTHM concentration influent to (35 µg/liter) and effluent from (35 µg/liter) the 2-1/2 year old Filtrasorb 400. With chlorine dioxide applied and little or no free chlorine present, the GAC influent concentration was significantly lowered (to 2.4 µg/liter) and the difference between TTHM influent (2.4 µg/liter) and effluent concentration (12 µg/liter) was attributed to desorption of trihalomethane from GAC.

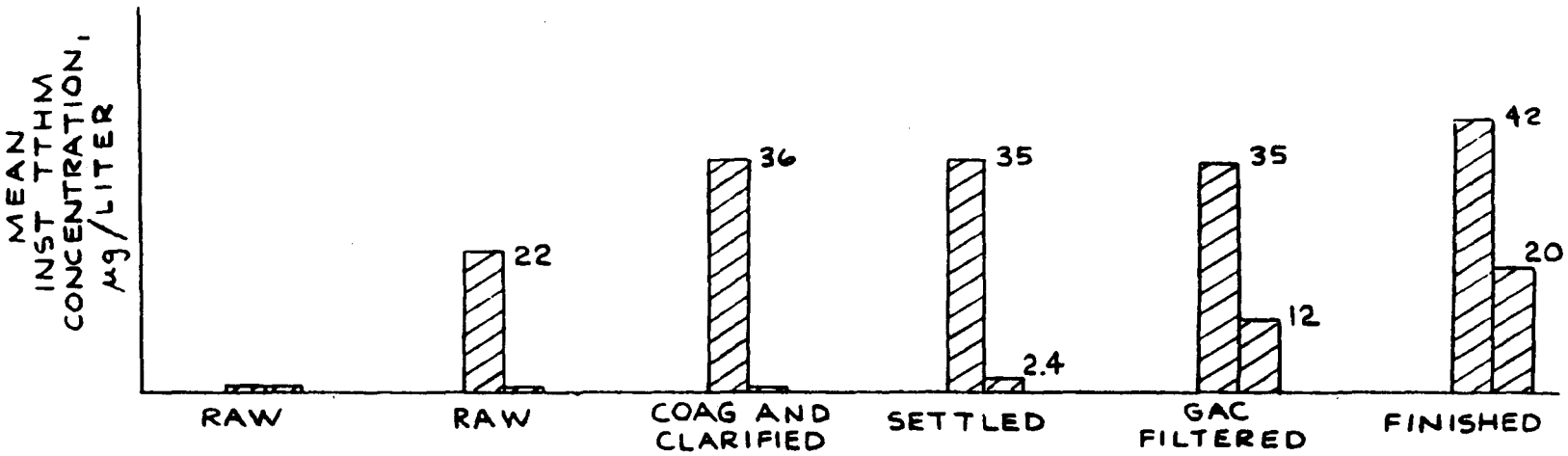

Figure 8. Trihalomethane Formation (Mean Values)
Western Pennsylvania Water Company

Table 6

Removal of Carbon Tetrachloride By
Virgin Granular Activated Carbon[a]
Huntington Water Corporation
July 1977 - May 1978

Week of Operation	Concentration,[b] µg/l Influent	Effluent	Week of Operation	Concentration,[b] µg/l Influent	Effluent
1	<0.1[c]	ND	12	0.5	0.1
2	ND	ND	14	0.2	<0.1
3	NFB	NFB	15	0.2	0.1
4	0.4[c]	ND	16	0.3	0.3
5	0.6[c]	ND	18	0.2	<0.1
6	0.1[c]	NFB	22	<0.1	<0.1
7	0.1	NFB	35	<0.1	0.1
8	0.1[c]	NFB	39	<0.1	0.1
9	0.3	<0.1	42	0.1	0.2
10	13[+]	0.4[+]	46	0.3	0.2
11	0.4	0.1			

Table 7

Removal of Carbon Tetrachloride By
Older Granular Activated Carbon[a]
Huntington Water Corporation

GAC placed October 1976			GAC placed April 1975		
Month of Operation	Concentration,[b] µg/l Influent	Effluent	Month of Operation	Concentration,[b] µg/l Influent	Effluent
9	ND	2.2[c]	27	ND	1.5[c]
9½	ND	2.3[c]	27½	ND	0.7[c,+]
11	0.5	1.0	28	0.1	0.6
13	0.2	0.4	29	0.2	0.7
14	0.1	0.3	31	0.2	0.3
			32	0.1	0.2

[a] GAC = WVW 14x40
Bed depth = 76 cm (30 inches) GAC
Loading rate = approximately 6.1 m/hr (2.6 gpm/ft^2)
EBCT = approximately 7.2 minutes
[b] GC/Hall detector, approximate lower detection level = 0.1 µg/l
[c] Co-elution with 1,1,1-trichloroethane
+ = GC/MS confirmed as carbon tetrachloride.
ND = Not detected
NFB = Not found after blank correction.

Beaver Falls halted the practice of breakpoint chlorination after 21 weeks of operation, see Figures 5 and 6. With little or no free chlorine present, GAC influent trihalomethane concentrations were significantly lowered and desorption of trihalomethanes resulted. For example, in Figure 5 at week 21, influent and effluent TTHM concentrations of 37 µg/liter and 41 µg/liter, respectively, could not be differentiated. After breakpoint chlorination was halted, however, the effluent TTHM concentration of 15 µg/liter was differentiable from the influent TTHM concentration of 3 µg/liter and was attributed to desorption of trihalomethane from GAC.

Desorption of carbon tetrachloride was observed from older GAC beds at Huntington. These older beds were in operation in February 1977 when GAC influent concentrations of carbon tetrachloride exceeded 100 µg/liter during a spill condition. When sampled from July 1977 to December 1977, carbon tetrachloride influent concentrations were below 0.5 µg/liter (i.e., significantly lower than 100 µg/liter), but effluent concentrations reach 2.3 µg/ liter indicating desorption of carbon tetrachloride occurring several months after the spill, see Table 7.

GAC Bacterial Densities

GAC effluent bacterial densities oftentimes exceeded GAC influent bacterial densities at each of the three utilities during warmer months.

Table 1 presents bacterial densities in the influent to and effluent from the virgin GAC bed at Huntington. Throughout the study, influent total coliform (TC) counts were less than one per 100 milliliter. At lower temperatures effluent TC counts were less than one per 100 milliliter, but at higher temperatures effluent TC counts reached eight per 100 milliliter.

Tables 2 and 3 present bacterial counts in the influent to and effluent from the three virgin GAC beds at Beaver Falls. These data demonstrate significantly higher GAC effluent TC and standard plate counts (SPC) than the corresponding influent values, when temperatures exceed 10°C. Note that effluent TC counts reached 130 per 100 milliliter and SPC values reached 92,000 per milliliter. Influent and effluent values generally could not be differentiated when temperatures dropped below 10°C. This phenomenon was observed again one year later and is seen in data presented in Table 4. Again, at higher temperatures effluent TC counts were significantly higher than influent values, but as the temperature dropped, influent and effluent TC counts could not be differentiated.

Similar phenomena were observed in a 2-1/2 year old GAC bed at the Western Pennsylvania Water Company when disinfectant studies were conducted during a period when temperatures exceeded 20°C. However, at each of these three utilities, post-chlorination at the clear well assured the bacterial integrity of the finished water.

These data indicate that pre-chlorination does not stop bacterial growth on GAC during warmer months of operation and that utilities employing GAC as filter/adsorbers must take care to monitor the bacterial quality of their water.

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DESIGN AND OPERATIONAL EXPERIENCES WITH ACTIVATED CARBON ADSORBERS: TREATMENT OF DELAWARE RIVER WATER, U.S.A.

Patrick R. Cairo
and
Irwin H. Suffet

Removal of trace organics at a drinking water treatment plant is one of the most difficult problems facing U.S. water utilities today. The Environmental Protecton Agency is considering regulatory alternatives either to specify treatment technologies to reduce organic levels or to impose specific limitations (MCLs) on certain organic compounds that are shown to be significant human health risks (1). Regardless of the initial approach taken, it is expected that drinking water standards will be imposed for specific organics on the basis of health effects studies currently underway. It is also very likely that both the drinking water limits and the types of compounds regulated will be more stringently controlled while new treatment processes are being constructed and placed in operation. The expected evolutionary nature of the regulations presents a unique challenge both to scientists and engineers performing the studies that will determine design and operating characteristics for organic removal processes. Research protocols in analytical chemistry, aquatic microbiology, and process engineering must be employed to ensure proper consideration of all factors.

This paper discusses design and operational experiences with pilot plant testing of carbon adsorption systems used in the treatment of Delaware River water at Philadelphia. This experience is presented in the context of the chemical and biological considerations that must be merged in an engineering evaluation to design and operate a GAC facility. Because specific process design objectives are expected to evolve during the operating lifetime of the facility, a framework for in-process evaluation of the chemical and biological data also is developed.

The significant elements that must be integrated in the design and subsequent operation of the granular activated carbon facility are shown in Figure 1. These begin with biological and chemical considerations measured by specific and nonspecific analytical tests as well as screening protocols utilizing isolation methods such as macroreticular resin (MRR), continuous liquid-liquid extraction (CLLE), purge-and-trap (P&T), and

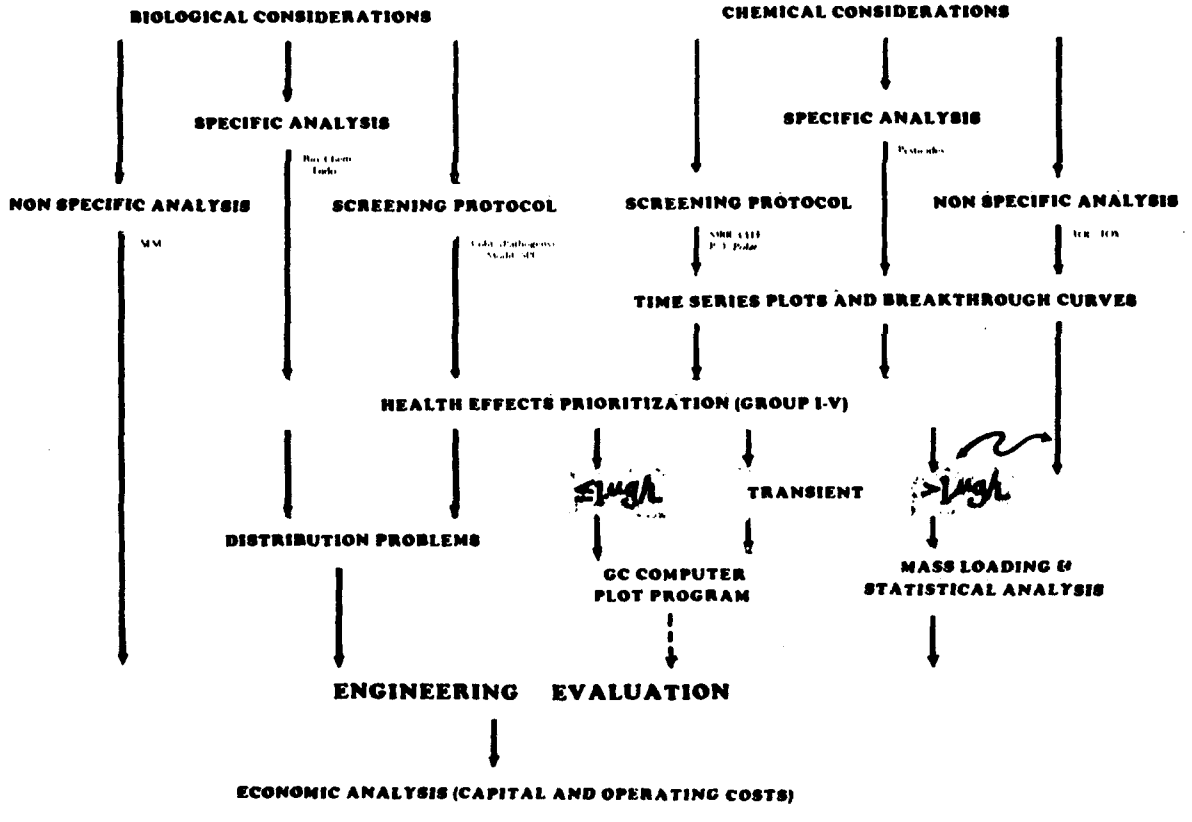


Figure 1. Design Elements for Adsorption Process

bacterial analysis by coliform and standard plate count (SPC) tests. The data generated must next be evaluated in the context of potential health effect prioritization. This would include both direct impacts to human health and indirect impacts affecting the operating performance of the GAC process or esthetic problems arising in the treated water during its transmission in the distribution system.

Through chemical and microbiological testing the engineering aspects of alternative GAC configurations are evaluated. This work can be performed using bench, pilot, and full scale systems. Each scale presents certain advantages and disadvantages that must be evaluated carefully. Bench scale experiments permit maximum flexibility and can be performed quickly and economically. However, the direct application of these results to full scale installations is not recommended since the experiments usually do not represent µg/l concentration levels or the types of hydraulic and water quality problems encountered when large volumes of river water are being treated. Pilot scale testing seems to be the optimal level since it still retains considerable flexibility and allows for continuous treatment of significant quantities of river water. It is recommended that after the screening of several alternative GAC configurations by pilot testing, a 3.8 to 38 ML/day (1 to 10 mgd) system of the selected design be tested to determine if scaleup effects must be incorporated in the design of the full scale facility. The final element that needs to be evaluated is the economic implication of the carbon system. Here, both initial capital investment and long-term operating and maintenance expenses must be weighed (2).

The engineering evaluation using chemical and biological considerations requires detailed discussion. Its implications are demonstrated through the research findings that evolved during the testing of Delaware River water.

CASE STUDY: DELAWARE RIVER

The Delaware River which flows past Philadelphia shares the common plight of most developed surface water systems in the U.S. In a 61-km (38-mi) stretch between the start of the Delaware's estuarial portion at Trenton and the point of confluence with the Schuylkill River, more than 11 municipalities and 360 industries discharge treated wastewater. A massive effort is currently underway to upgrade the level of wastewater treatment, and the best available technology economically achievable for treatment of toxic wastes will be imposed on 21 industrial categories by 1983 (3). However, trace levels of organic compounds will continue to be present in the Delaware River as a result of their discharge from advanced treatment plants as well as from accidental spills and nonpoint sources.

For more than 7 years the Philadelphia Water Department, with the assistance of Drexel University, has been engaged in a major organics research program to assess the nature of the organics problem and to evaluate treatment processes that could be installed at each of its three water treatment plants. Most of the work to date has been performed at the Torresdale Plant [1,070 ML/day (282 mgd)], since it is the city's largest and draws its water from the Delaware estuary. The initial years were spent developing analytical techniques that could be used to concentrate, extract, and identify specific organic compounds and led to the creation of a special laboratory with personnel and equipment devoted to this task. Treatment research first was performed on laboratory scale studies and in 1976, was expanded to a pilot scale level with the construction of 7.5 to 30-cm (3- to 12- in.) glass columns and a 114-m^3/day (30,000-gpd) advanced water treatment pilot plant made of stainless steel, glass, and PTFE parts. The activities of the past 7 years are summarized in figure 2. The work has entailed evaluation of oxidation, coagulation, and adsorption by granular activated carbon and synthetic resins. In 1978, a 3-year laboratory and pilot scale study of ozonation and carbon adsorption in the so-called biologically activated carbon (BAC) mode was begun under a research grant from EPA (4).

HEALTH EFFECT PRIORITIZATION

The first step in designing the carbon adsorption process is to develop a prioritization scheme to guide the evaluation of data. The chemical and biological analytical procedures outlined in Figure 1 and detailed below must be evaluated by a priority rank based on health effects and GAC operating characteristics.

Chemical Considerations

The chemical compounds entering an adsorption water treatment process consist of high molecular weight and lower molecular weight organic compounds covering a wide range in polarity. The National Academy of Science estimated that 90 percent of the total organic matter is of high molecular weight (5). This would correspond to the natural organic compounds of little direct toxicological importance [class 5 as defined by the EPA (6)], but these compounds may affect the process by competitive adsorption or support of microbial growth. A fraction of these high molecular weight organic compounds are precursors that react with disinfectants to produce disinfectant byproducts [class 3 (6)]. The remaining 10 percent of the total organic matter includes, but is not limited to, synthetic organic chemicals that are present in source water and organic chemicals that are disinfection byproducts [classes 2 and 4 (6)]. A subgroup of chemicals in the last 10 percent group are the presently known chemicals of

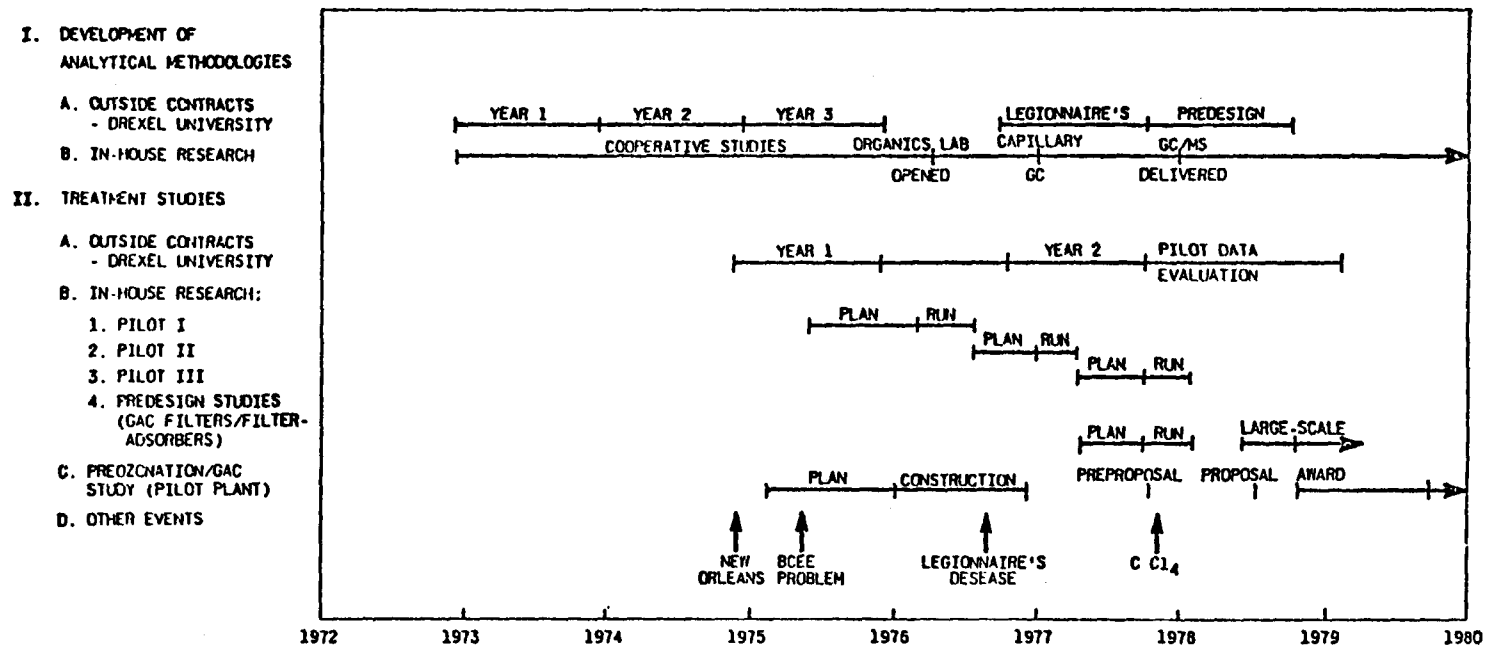


Figure 2. Philadelphia Case History: Time Schedule
Figure From M. McGuire (15)

health concern, listed by certain organizations as suspected animal or human health problems (5, 7-9) and by the EPA as priority pollutants (3).

Table 1 shows the chemical groups being considered for design of GAC systems in priority order. The primary aim for design considerations would be to assure removal of chemicals of known health concern - group I. Maximum contaminant levels (MCLs) have already been proposed or established for certain group I compounds, such as chloroform and pesticides (1, 10). A well-designed adsorption process must be flexible enough to accommodate the removal of other group I compounds to protect the public health. It would be expected that when other MCLs are developed, group I compounds would be primary targets. In consideration of design, group IA, II, and III compounds should be evaluated to see if, indeed, they would be removed by carbon. Trace organic screening protocols are available for this task. Group IV compounds fall into a different category of concern as disinfectant type, dose, and concentration are primarily utilized for their control. The trihalomethane formation potential (THMFP) and total organic halide tests can monitor this category.

Group V compounds are of concern because of their effect on Group I-III compounds. This group can be monitored by trace organic screening protocols. The effects of group V compounds would include those of competition and reequilibration. Competitive effects occur when a strongly adsorbed compound enters the carbon bed and displaces a weakly adsorbed compound. In this case the concentration of the displaced compound may be higher in the effluent than in the influent until a new equilibrium is reached. A reequilibrium effect occurs when the concentration of a compound in the influent decreases. Desorption of this compound from the carbon then occurs and, again, the concentration in the effluent could be higher than in the influent until a new equilibrium is established. Finally, a compound might appear in the effluent that was never in the influent, due to chemical or microbial reactions on the column involving compounds previously adsorbed from the influent. These new compounds would also be influenced by the breakthrough, exhaustion, and competition processes.

Table 2 lists the prioritized compounds identified in Torresdale (Philadelphia, Pa.) drinking water during eight sampling surveys conducted between Feb. 6, 1975, and Jan. 3, 1977 (11). One hundred sixteen different compounds were found including 40 isomers (e.g., xylene isomers). Compounds consistently identified in concentrations greater than 1 µg/l are chloroform and dichlorobromomethane. Compounds periodically identified at this level include dibromochloromethane, 1,2-dichloroethane, 1,2-dichloropropane, trichloroethylene, toluene, and diacetone-L-sorbose. Many of the 116 compounds

TABLE 1

Health Effect Prioritization of Chemical Parameters

Group I - CARCINOGENS AND SUSPECTED CARCINOGENS listed by

(1) National Academy of Science (1977)

(2) National Cancer Institute (1978)

Group IA - MUTAGENS, TERATOGENS AND PROMOTORS listed by

National Cancer Institute (1978)

Group II - *PRIORITY POLLUTANTS listed in NRDC v Train (1976)*

Group III - OTHER COMPOUNDS OF POTENTIAL HEALTH EFFECT listed by

National Academy of Science (1979)

Group IV - PRECURSORS - Organic Compounds that react with a Disinfectant to produce a by-product which falls into Groups I - III.

Group V - HUMIC SUBSTANCES AND NON-HEALTH EFFECT COMPOUNDS IN HIGH CONCENTRATION which can compete with compounds of Groups I - III and cause earlier breakthrough of these compounds.

TABLE 2

Categories of Organic Compounds Identified at Torresdale

	TOTAL NUMBER	I CARCINOGENS & SUSP. CARC.	Ia MUTAGENS TERATOGENS & PROMOTERS	II PRIORITY POLLUTANTS
HALOGENATED a.) ALIPHATIC	24	CHLOROFORM CARBON TETRACHLORIDE BIS (2-CHLOROETHYL) ETHER TRICHLOROETHYLENE	BROMOCHLOROMETHANE BROMOFORM DIBROMOCHLOROMETHANE DICHLOROACETONITRILE DICHLOROETHANE DICHLOROBROMOMETHANE 1,2 DICHLOROPROPANE 1,1,1 TRICHLOROETHANE	4
b.) AROMATIC	10	0	0	6
AROMATIC	50	BENZENE	0	7
ALIPHATIC	7	0	DECANE	0
PHTHALATE ESTERS	7	0	0	7
MISCELLANEOUS	18	0	0	ISOPHORONE
TOTAL	116	5	9	25

were found to be highly variable during weekly composite analyses (11, 12). Prioritizing these compounds according to the categories listed in Table 1 yields 39 compounds in groups I and II. Of these, 32 were usually in the 1-µg/l or lower range.

Biological Considerations

The granular activated carbon used in treatment of drinking water has been found to be an ideal habitat for bacterial growth because of the large surface area and pore structure of GAC and its affinity for organic compounds. Total coliforms were not found to proliferate in GAC adsorbers and were not recovered in their effluents. However, total bacterial levels in GAC contactors and their effluents are significantly higher than those found in sand filter effluents (13). This established microbial flora in the GAC adsorber represents a potential for an unknown health risk which should be carefully examined. A priority scheme for this evaluation is proposed in Table 3.

TABLE 3

HEALTH EFFECT PRIORITIZATION OF BIOLOGICAL PARAMETERS

Group I	PATHOGENS AND OPPORTUNISTIC PATHOGENS
Group IA	TOTAL COLIFORM SUPPRESSORS
Group II	ENDOTOXINS
Group III	CHLORINE-RESISTANT BACTERIA
Group IV	HARMLESS INDICATORS OF UNSTERILE CONDITIONS
Group V	BENEFICIAL ORGANISMS TO THE BREAKDOWN OF ORGANIC COMPOUNDS

Group I includes pathogenic organisms and opportunistic pathogens capable of infesting an altered or already debilitated host. Group IA are those organisms that can inhibit or suppress the growth of existing coliform bacteria and therefore mask the survival of waterborne pathogens. Group II are endotoxins which are lipopolysaccharide-protein complexes produced in the cell walls of gram-negative aerobic bacteria. Group III bacteria are of concern because these could develop into a flora of chlorine resistant microbes that would present possible regrowth, taste and odor, or chlorine demand problems in the distribution system. Group IV includes harmless microbial indicators of the treatment process, and group V includes organisms that could be beneficial to the breakdown of organic compounds.

The bacterial flora in the GAC adsorption system therefore may have either a beneficial or a detrimental effect. The role of these organisms in the GAC column and subsequent distribution system must be thoroughly investigated before full scale carbon systems are implemented in the water treatment process. Table 4 lists the biological parameters that should be considered in the design of a GAC system. These include specific analyses to determine the taxonomy of predominant bacterial groups, non-specific analyses using scanning electron microscopy to investigate the morphology of bacteria and their location on the carbon structure, and surrogate procedures (e.g., MF total coliform test, SPC test) to measure general classes of organisms. The primary aim of the microbiological design considerations would be to assure the removal of all organisms falling in Group I. It is expected that a properly designed postdisinfection system also would remove groups II and III.

TABLE 4

MICROBIAL PARAMETERS

PARAMETER		OBJECTIVE
TOTAL COLIFORM	-	INDICATOR OF POLLUTION
MODIF. STANDARD PLATE COUNT	-	DEGREE OF DISINFECTION
BIOCHEMICAL	-	BACTERIAL SPECIATION
ENDOTOXINS	-	POTENTIAL HEALTH EFFECT
SCANNING ELECTRON MICROSCOPY	-	PHYSICAL CHARACTERISTICS OF MICROBIAL GROWTH

At the present time no conclusive information is available on endotoxins (group II). Before this parameter can be regarded as a serious design consideration, additional research is necessary. This experimentation must evaluate the levels of endotoxin in GAC effluents, the effect of postdisinfection on the endotoxin complex, and the human health risk of ingested endotoxins.

ENGINEERING EVALUATION

The framework of chemical and biological considerations presented in Figure 1 must be optimized during the field testing of activated carbon adsorbers. An engineering evaluation encompasses the choice of design and operational characteristics of the GAC system. The planned carbon process must economically meet acceptable treatment goals at startup and be restored to its full efficiency after the carbon has been exhausted. Field

testing in Philadelphia has included a number of hydraulic and vessel configurations using both virgin and regenerated carbon. These experiments are summarized in Table 5. As shown in Figure 1, both numerical and qualitative evaluations of GAC process efficiency have been employed to ensure maximum flexibility in meeting future water treatment objectives.

Chemical Considerations

Figure 1 shows that three groups of chemicals can be defined after the health prioritization step - > 1 µg/l, transients, and ≤ 1 µg/l.

Two different pilot plant monitoring approaches can be used to determine specific organic compounds. The first approach includes single compounds selected because of their effect on human health. The second is a general screening procedure for any prioritized organic compounds.

Table 2 lists the specific pollutants of primary health concern that have been identified in Torresdale drinking water. Specific quantitative analytical methods for each compound found in concentrations greater than 1 µg/l were completed during pilot plant studies by purge-and-trap analysis (23).

The transient compounds and those compounds present in the influent with concentrations of ≤ 1 µg/l were monitored by another analytical approach, a screening procedure utilizing a GC computer plot program (24). A screening procedure consists of a qualitative analysis with subsequent quantitative evaluation of the constituents found. A general sequence which is followed for screening of trace organics is shown in Figure 3. The flow diagram is a general, flexible scheme describing the successive laboratory operations necessary. The isolation method is a critical choice of the analyses, as it defines the type of compounds studied and the maximum recovery of a compound (25).

The screening methods have been employed to develop chromatographic profiles. Each chromatographic profile contains the complex group of trace organics present in the extracted water and is a fingerprint of the sample. This constitutes an information pattern. When many profiles are plotted in the same manner, all the chromatographic profiles can be compared. GC-MS identifications help evaluate the consistencies and differences observed among profiles.

In the Philadelphia work the set of screening protocols has included analyzing the most volatile organics by the purge-and-trap method (23) and analyzing the less volatile higher molecular

Table 5

Philadelphia Water Department: Organic Treatment Studies

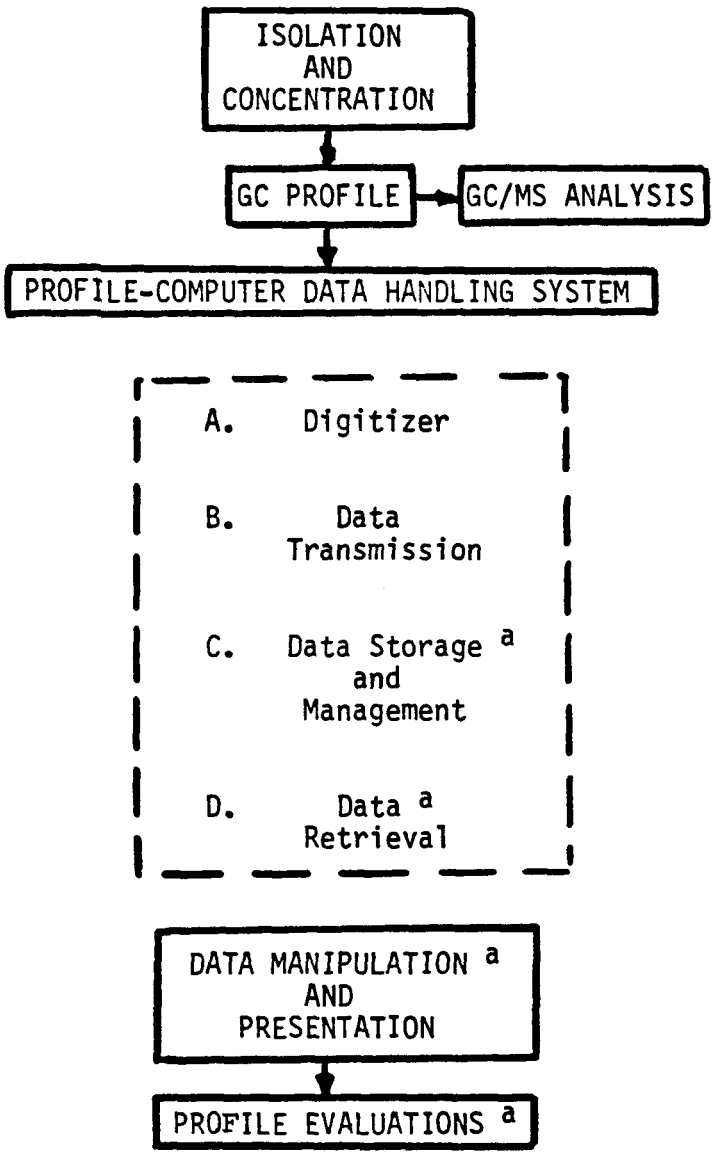
STUDY	OBJECTIVE	ADSORBENTS	COLUMN[a] HYDRAULICS	CHLORINE	ANALYTICAL[b] METHODS	START & DURATION	REFERENCES
Bench 1	GAC Theoretical Mechanisms	Filtrasorb-400 carbon	Isotherms; Column Studies	Chlorination and non-chlorination	4 Polarity Probes - Nitromethane; Methyl Ethyl Ketone; n-Butanol; 1,4-Dioxane	1976 to 1977	McGuire, 1977
Bench 2	Oxidizing Agents	--	Batch and Continuous Reactors	Chlorine, Permanganate, Ozone	16 Organic Compounds	1977	McGuire, et al., 1978
Pilot I	Adsorbent Types	Filtrasorb 400 carbon and XAD-2 resin	Carbon and resin columns operated in series and parallel, EBCT= 3.0-9.7 min.; CD=4 @ 3in. and 3 @ 6 in.; BD= 1.75-5.71 ft.	Free Cl_2 residual, 1.5-2.0 mg/l	TTHM, VOA, TOC, selected Organic Profiles (MRR), GC/MS	3/76 (18 weeks)	Suffet, et al., 1978
Pilot II	Adsorbent Types	Calgon BPL & Filtrasorb 400 carbons; XAD-2, XAD-4, & XE-340 resins; Westvaco WV-G 1240 & ICI Hydrodarco 1030 carbons	EBCT=7.3-7.5 min.; CD=3 @ 3 in., & 4 @ 6 in.; BD= 3.0-3.2 ft.	Combined Cl_2 residual, 2.0 mg/l	TTHM, RFM, TOC selected Organic Profiles (MRR), GC/MS	12/76 (15 weeks)	Suffet, et al., 1978 Boettger, et al., 1977
Pilot III	GAC Hydraulics (Contact time & surface loading)	Filtrasorb 400 carbons	EBCT-7.5 to 60.0 min.; SL=0.4-4.0 gpm/ft.^{2}; CD= 4 @ 6 in. & 1 @ 3 in.; BD=3.0 & 4.0 ft.	Free Cl_2 residual, 1.0-2.0 mg/l	TTHM, VOA, TOC, Organic Profiles (MRR & CLLE) GC/MS, SPC, Micro.	9/77 (18 weeks to 1.5 yrs.)	Cairo, et al., 1979 McElhaney, et al., 1978
Pilot IIIa	GAC Pretreatment (Chlorination vs. Dechlorination)	Filtrasorb 400 carbons	EBCT=7.5 min.; SL=3.0 gpm/ft.^{2} CD=2@ 3 in.; BD=3 ft.	Free Cl_2 residual 1.0-2.0 mg/l; Dechlorination with sodium sulfite	TTHM, VOA, TOC Organic Profiles (CLLE) GC/MS, SPC, Micro.	9/77 (18 weeks)	Yorne, et al., 1979 McElhaney, et al., 1978

Table 5

Philadelphia Water Department:Organic Treatment Studies (Continued)

STUDY	OBJECTIVE	ADSORBENTS	COLUMN[a] HYDRAULICS	CHLORINE	ANALYTICAL[b] METHODS	START & DURATION	REFERENCES
Pilot IV	GAC Modes (Filter/Ads vs. Contactor)	Filtrasorb 400 & 300 carbons	EBCT=15.0 min; SL=2.0 gpm/ft^2 CD=2 @ 12 in. & 2 @ 2'x2.5'; BD=4.0 ft.	Free Cl_2 residual 1.0-2.0 mg/l	TTHM,VOA,TOC Organic Profiles (MRR) GC/MS,SPC, Micro.	10/77 (20 weeks)	Cairo, et al., 1978
Plant Scale	THM reduction	--	Belmont Plant 78 MGD	Chlorine addition point and amount altered	THM, THMFP, SPC	6/77 (12 mos.)	Aptowicz, et al., 1978
Pilot V	GAC Regeneration	Filtrasorb 400 & 300 carbons. Regenerated at 1000°F & 1750°F	EBCT=15.0 min; SL=1.5-1.75 gpm/ft^2; CD= 5 @ 6 in & 3 @ 12 in. BD=37-42 in.	Free Cl_2 residual 1.0-2.0 mg/l	THM, VOA Organic Profiles (MRR) GC/MS, SPC	11/78 (5 mos.)	--
Bench 2	GAC Regeneration (Theoretical Capacity)	Filtrasorb 400 & 300 carbons. Regenerated at 1000°F & 1750°F	Isotherms & Column Studies	None	4 Polarity Probes	1978	--
Pilot VI	GAC Scale-Up (Full Scale vs. Pilot Scale Filt/Ads)	Filtrasorb 400 carbon	EBCT=9 min; SL=2 gpm/ft^2 CD=1044 ft^2 & 5 ft^2; BD= 28 in.	Free Residual 1.0-2.0 mg/l	TTHM, VOA Organic Profiles (MRR), GC/MS, SPC	3/78 (6 mos.)	--
Pilot VII	GAC Scale-Up (Full Scale vs. Pilot Scale Filt/Ads-Regenerated)	Filtrasorb 400 carbon	EBCT=9 min; SL=2 gpm/ft^2; CD=1044 ft^2 & 5 ft^2; BD= 28 in.	Free Residual 1.0-2.0 mg/l	TTHM, VOA Organic Profiles (MRR), GC/MS, SPC	11/78 (6 mos.)	--
BAC I	Ozone & Carbon	Filtrasorb 400 carbon	BAC; carbon alone; sand	Chlorinated & non-chlorinated columns	TTHM, VOA Organic Profiles (MRR, CLLE), GC/MS, SPC, Micro.	1979 (in progress)	EPA Grant

a EBCT-Empty bed contact time; SL-Surface loading, CD-Column diameter, BD-Bed depth
b TTHM-Total trihalomethanes; TOC-Total organic carbon; SPC-Standard plate count; MRR-Macroreticular resin; CLLE-Continuous liquid-liquid extraction; GC/MS-Gas chromatography/mass spectrometry; VOA-Volatile organic analysis; Bacte.-Bacterial speciation; RFM-Rapid fluorometric method.



[a] Chromatographer controls these steps

Figure 3. Screening Procedure for Trace Organics

weight volatile organics by a resin* accumulator and a continuous liquid-liquid extraction method (25).

Engineering Evaluation for Compounds > 1 µg/l--

For compounds in concentrations greater than 1 µg/l, either formed through the chlorination process (such as trihalomethanes) or consistently present in the Delaware River, the adsorption mechanism can be evaluated using breakthrough and loading curves based upon quantification of trace organic compounds in the influent and effluent to the GAC columns. Thus, in comparing the performance of GAC in a filter-adsorber mode and in a contactor mode for pilot test 4 (21), the breakthrough curve for chloroform shown in Figure 4 was first developed. Leakage of chloroform in the filter-adsorber effluent is evident in the initial week of operations. This is in sharp contrast to the contactor effluent which does not exhibit any significant leakage until the sixth week. The difference in the concentration of chloroform between the two modes of operation is approximately 15 µg/l from week 2 until week 9, when 80 percent breakthrough for chloroform takes place. Complete saturation of chloroform occurs in all GAC systems by week 12.

The second step in analyzing the performance of the carbon was to make the comparison on a mass loading basis. Figure 5 was developed by plotting the cumulative loading of chloroform adsorbed on the carbon against the total mass of chloroform applied to the carbon. One hundred percent removal is a straight line whose tangent is 45 deg, and increased divergence from the straight line indicates progressively poorer removal characteristics. It is evident from the plot that the carbon used in the contactor mode performed better, removing more chloroform than the carbon used in the filter-adsorber mode. At the point of saturation, carbon used in the contactor mode adsorbed more than 20 percent more chloroform than the GAC used in the filter-adsorber mode. If these data are analyzed in a different fashion--namely, at the instantaneous 50 percent removal point as determined from the breakthrough curve (indicated in Figure 5 by asterisks)--a difference of approximately 30 percent in performance between the two modes is found. Also shown in Figure 5 is the fact that carbon 1** (12 by 40 mesh size) was more effective at removing the mass loading of chloroform than carbon 5*** (8 by 30 mesh size).

A statistical modeling approach was next applied to these data to test the significance of the difference in performance found between the two modes of operation. When percent breakthrough is plotted as a function of time, the S-shaped curve

*XAD-2, Rohm and Haas, Philadelphia, Pa.
**Filtrasorb F400, Calgon Corp., Philadelphia, Pa.
***Filtrasorb F300, Calgon Corp., Philadelphia, Pa.

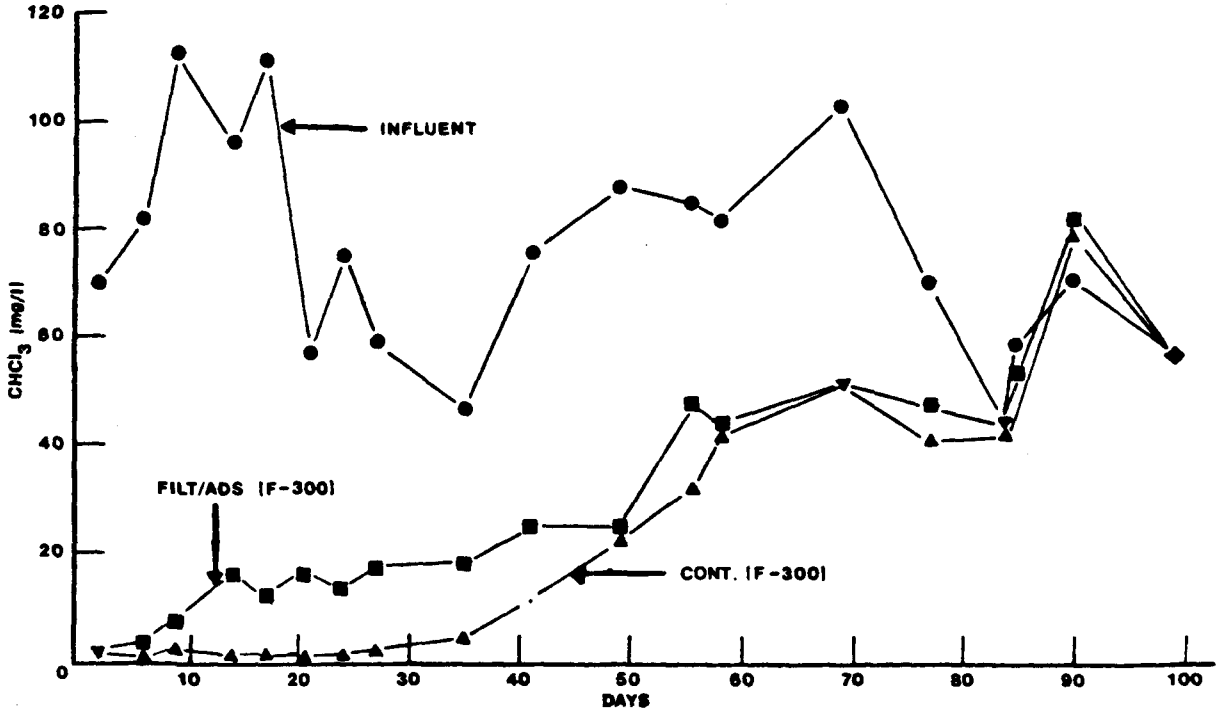


Figure 4. $CHCl_3$ Removal by FILT/ADS versus Contactor

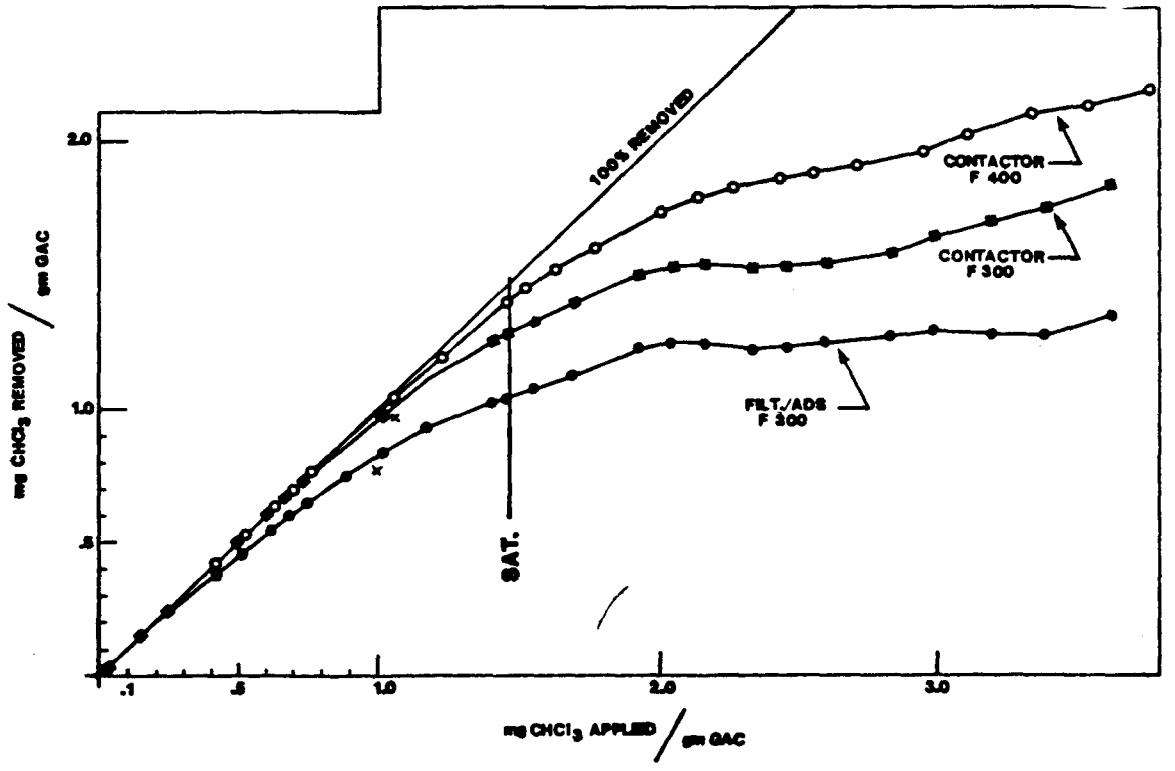


Figure 5. Cumulative Mass Loading of $CHCl_3$

shown in Figure 6 is obtained. The relationship between percent breakthrough and time can be given by

$$P = \frac{e^{a+bt}}{1 + e^{a+bt}} \quad (1)$$

where P is percent breakthrough; t is time at which the sample was taken expressed as sequential day number; and a and b are the parameters that define the curve whose values are estimated from the data.

Equation (1) is nonlinear; however, a transformation can be used to linearize the relationship. Defining a new variable P' by

$$P' = \log_e \frac{P}{1 - P} \quad (2)$$

reduces Eq (1) to

$$P' = a + bt \quad (3)$$

The correlation coefficient r^2 ranged from 0.85 to 0.93 for the chloroform data. The curve parameters, a and b, for each carbon vessel were then statistically analyzed using a Student's t test. The results indicated that the filter-adsorber and the contactor performed statistically differently in adsorbing chloroform. It is important to note that a direct application of the t test to the field data would not have been appropriate, since the character of the process is changing throughout time. Therefore, the entire set of collected data represent a set of single observations from many different populations, rather than many observations from a single population. This analysis has demonstrated that monitoring and designing a GAC plant for compounds of > 1 µg/l can be accomplished by mass loading and statistical analysis.

Engineering Evaluation of Transient Compounds and Compounds $\leq$ 1 µg/l--

An engineering evaluation is much more difficult for trace organics in concentrations less than or approximately equal to 1 µg/l, or for those transient organics present in the influent to the carbon columns (Figure 1). For this category of organics, competitive adsorption among specific compounds may produce displacement and reequilibrium effects. Adjunct to this category of organics are those that may be the product of chemical and microbial reaction in the carbon column. These characteristics create a seemingly nonconservative reaction on the carbon column and its performance cannot be effectively analyzed using mass loading curves. For these classes of compounds, a qualitative screening approach using a time-series representation with a GC

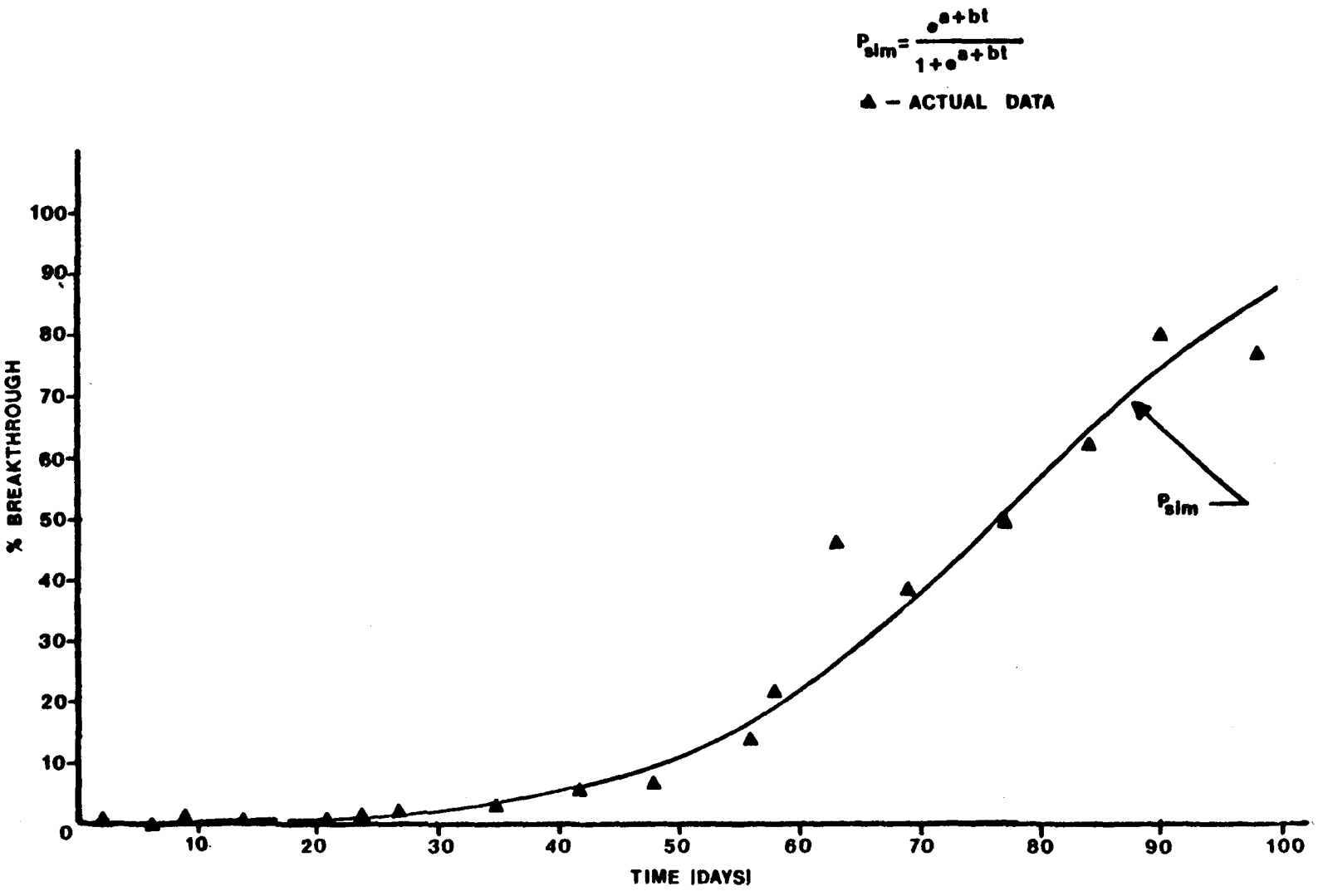


Figure 6. Simulated versus Actual $CHCl_3$ Breakthrough Curve for Contactor [F-400]

computer plot has been employed (12, 19), as well as analysis of organics on the carbon particle itself (20).

The organic profile screening procedures employed on each sample of the Delaware River typically identify 40 different compounds of concentrations $\leq$ 1 µg/l using a packed GC column and more than 100 different compounds using a capillary column. Because of this large number of compounds, a computer program was developed to present a GC profile in a comparative mode (24). In this program each peak of the GC profile can be plotted as a spike proportional to concentration on a relative retention time scale. Figures 7 and 8 show typical computer-reconstructed GC profiles of the influent and the GAC column effluent for weeks 1 to 18. These data are from pilot test 1 (12). The data are semiquantitative and represented on the GC profile plot by the relative scale shown in Table 6.

TABLE 6

Relative Scale for Pilot Plant 1 Data*

Integrator Area Response Units	GC Profile Peak Height	Estimated Concentration Range ug/l
10,000 or higher	1.0	>1
5,000-10,000	0.5	1
0-5,000	0.25	<1
Interpolated response	0.1	0.1-<1

*Internal standard: 2-ethyl-1-hexanol = RRT 1.00

As indicated in Figures 7 to 9, it is possible to categorize these compounds on the basis of their appearance or disappearance from week to week both on the influent and on the effluent from the carbon column. Another approach would be to categorize these compounds on the basis of the health effects priority classification (Table 1). For compounds with enforceable MCLs or recommended MCLs (nonenforceable health-based goals), a consistent level beyond the acceptable concentration would indicate exhaustion of the carbon for those compounds. Compounds in lower priority classifications do not present long-term health effect problems at an approximately 1-µg/l concentration, but need to be considered as well since these may displace the high toxicity or carcinogenic compounds.

A serious problem with this qualitative approach occurs for compounds that are present intermittently in the Delaware River. In this case pilot studies for the design of activated carbon

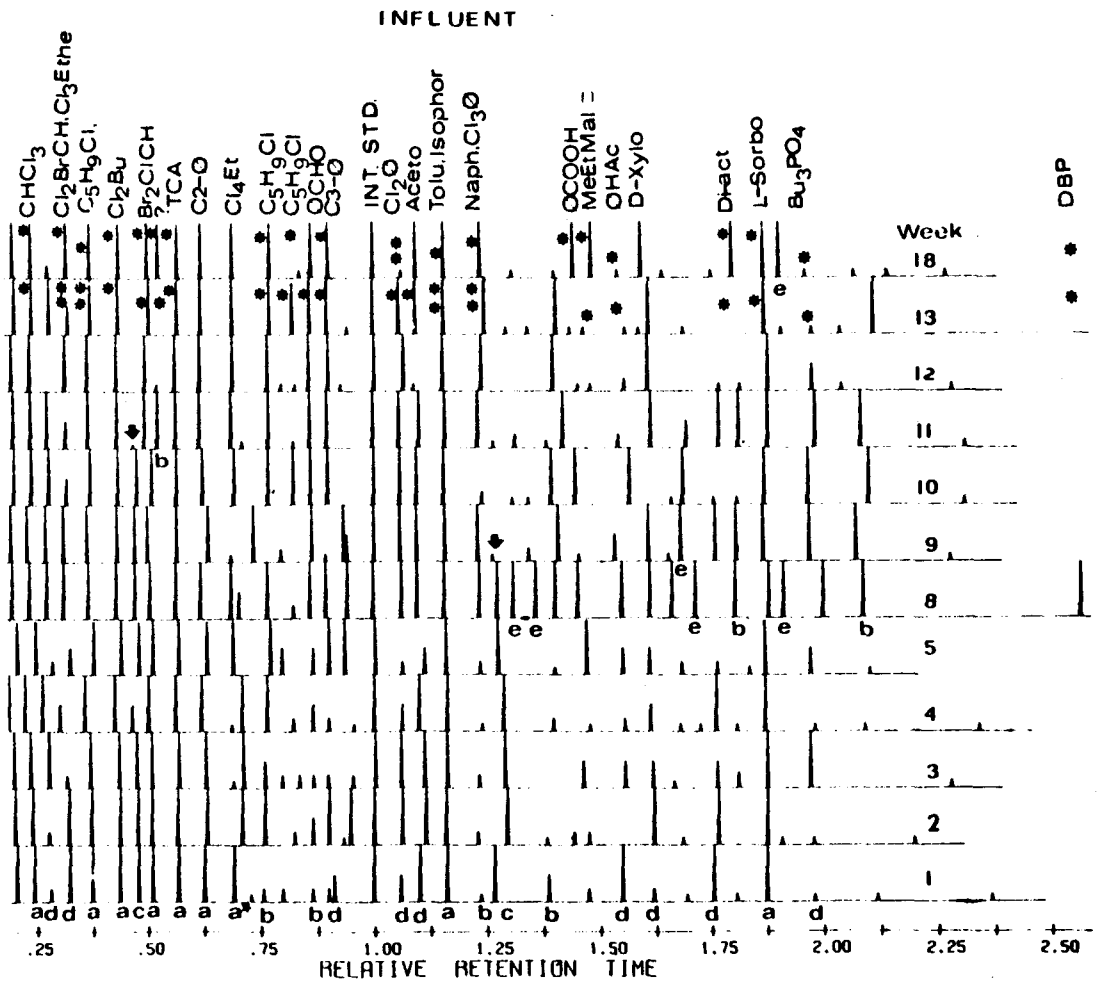


Figure 7. Computer Reconstructed GC Profile of Influent

☐ Tentatively identified compounds (Cl_2Bu-dichlorobutane, MeEtMal-methyl maldemide). *Compounds confirmed by GC/MS. Compounds noted as specific retention times based upon GC/MS analysis. a) Major peaks present in all samples; b) peaks which appear as a major peak after not being present or were previously very small peaks; c) peaks which disappear or are very small after being major peaks; d) peaks which change from major to minor; e) peaks present for only a few weeks.

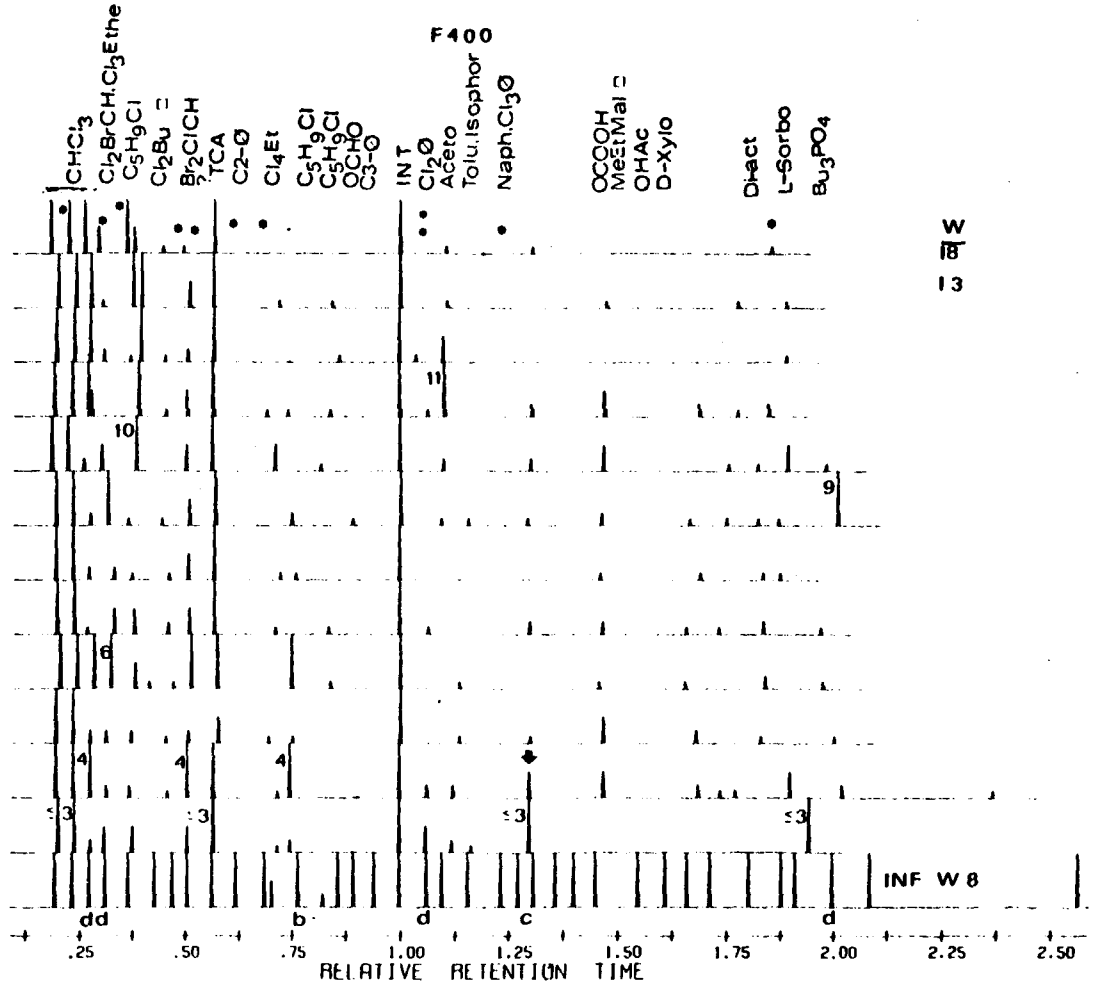


Figure 8. Computer Reconstructed GC Profile of Effluent from Carbon Column (F400)

Letters b-e and ☐ same as for legend of Figure 7. Letter a compounds not marked. Compounds noted at specific retention times based upon GC/MS analysis.

A. Halogenated

- 1. Chloroform [$CHCl_3$]
- 2. dibromochloromethane [Br_2ClCH]
- 3. dichlorobromomethane [Cl_2BrCH]
- 4. dichlorobenzene isomer [Cl_2-0]
- 5. 1,1,1-trichloroacetone [TCA]
- 6. trichloroethylene [Cl_3ethe]
- 7. 1,1,2,2-tetrachloroethane [Cl_4Et]
- 8. trichlorobenzene isomer [Cl_3O]
- 9. chloromethylbutene isomer [C_5HgCl]

B. Aromatic

- 1. acetophenone [Aceto]
- 2. benzaldehyde [CCHO]
- 3. C3-benzene isomer [C_3-0]
- 4. ethylbenzene or xylene isomer [C_2-0]
- 5. phenylacetic acid [OHA_c]
- 6. m/p-tolunitrile [Tolu]
- 7. toluene [OCH_3]
- 8. benzoic acid [OCOOH]
- 9. naphthalene [Naph]

C. Miscellaneous

- 1. 2,3:4,6-di-O-isopropylidene-L-sorbofuranose* [L-Sorbo]
- 2. di-n-butyl phthalate [DBP]
- 3. tributyl phosphate [Bu_3FO_4]
- 4. dihydroactinidiolide [Di-act]
- 5. ethyl acetate [EA]
- 6. 1,2,3,5-di-O-isopropylidene-D-xylofuranose† [D-Xylo]
- 7. isophorone [Isophor]
- 8. On EPA list of priority compounds

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*Alternate name: diacetone-L-sorbose
†Alternate name: diacetone-D-xylose

Figure 9. Compounds Found by GC-MS

systems are entirely dependent on the particular river conditions present during the test. Since many organic compounds are in this category, several research approaches are being considered at this time. One such approach would involve the use of theoretical adsorption models such as the net adsorption energy concept (26), to classify health effect compounds and select polarity probes representative of distinct phases. A mixture of these probes, each in a concentration range of approximately 1 µg/l, then could be spiked to the influent river water to the carbon column. Although this would represent much more severe conditions than would normally be expected in the Delaware River, the resulting breakthrough curves would enable a conservative estimation to be made of the carbon vessel's bed life.

Biological Considerations

Historically the microbial quality of water has meant the assessment of the water in terms of possible transmission of waterborne infectious disease. The common approach to the detection of pathogens in water has been to use an indicator organism in place of the pathogen; that is, an organism whose presence suggests that pathogens may be present. The total coliform group was chosen for this purpose because it is part of the normal fecal flora; the presence of a member of the total coliform group in a water sample indicates possible fecal contamination and therefore possible pathogens.

In GAC adsorber effluents the presence of total coliforms has been notably lacking. However, recent research indicates that while no coliforms have been found in the GAC effluents, large numbers of bacteria have been recovered using a revised standard plate count test (13, 27, 28). Thus, reliance on the total coliform test alone as an effective indicator of microbial disinfection is inadequate for the GAC system. The standard plate count test which measures the total bacterial population, may be the best indicator available today for measuring the GAC effluent for microbial contamination and also the disinfection process prior to the release of GAC-treated drinking water into the distribution system. The SPC test does not, however, differentiate between harmless and potentially dangerous bacteria and cannot be used as an indicator of fecal pollution. It is therefore suggested that the SPC test be used in conjunction with a total coliform test for a more complete bacterial analysis of GAC effluents. Moreover, the identification of the predominant bacteria in the GAC effluents also should be examined for each GAC system to determine the nature of the organism in terms of human pathogenicity and chlorine tolerance.

Although no significant coliform population has been observed in the GAC adsorbers or their effluents, other gram-negative bacteria are present in significant numbers. Therefore, the possible existence of endotoxins in GAC effluents must also

be examined. A recent review of the research completed on this topic by Love and Symons (29) indicates that no increase in endotoxin concentrations occurs in GAC effluents. The National Academy of Sciences (7) has concluded that the potential health risk of ingested endotoxins is low. Nevertheless, until further research has been done to determine the health risk involved with ingested endotoxins, their levels in GAC effluents should be analyzed on a periodic basis as a precaution.

Microbial Findings--

A significant aspect of research work during the GAC treatment studies of the Delaware River involved the investigation of microbiological effects. Four parameters were used to determine the microbiological quality of the GAC system. These included the membrane filter total coliform test, standard plate count test, biochemical identification of bacteria, and scanning electron microscopy.

Six primary areas of microbial concern were examined: the physical characteristics of biological growth on granular activated carbon; total coliform levels in GAC effluents; total bacterial levels in GAC effluents; total bacteria on carbon particles in GAC adsorber; biochemical identification of bacteria isolated from GAC effluents; and physical parameters affecting bacterial levels in GAC effluents, including empty bed contact time and chlorine vs. dechlorinated influents.

The physical surface of a GAC particle (e.g., carbon 1) from an operating GAC column (60-min. EBCT) and accompanying biological growth first were examined using the scanning electron mirroscope. The activated carbon particle surface (Figure 10) was found to have a rough, porous texture capable of providing a favorable and protected enviornmental surface for bacterial growth. Figure 11 shows a typical bacterial population on a GAC particle. Bacteria, on the GAC particles examined, were found to be scattered over the carbon surface with heavier concentrations in the macropore areas. Bacteria were not observed to form a uniform biofilm over the entire surface area of the carbon particle as has been hypothesized. Few higher forms of life, such as protozoa, were observed on the carbon particle surface. Although such an advanced ecosystem was observed in wastewater GAC systems by Weber (30), lower concentrations of nutrients in the potable water GAC system may be responsible for the limited biological colonization on the GAC particles.

The major purpose of the microbiological GAC study was to determine the levels of total coliform and total bacteria in the GAC adsorber effluents and changes in these levels over time. Evaluation of the virgin carbon using the SPC test indicated that no bacteria were present on the carbon prior to its use. No total coliforms were present in the influent waters and the total bacterial levels ranged from 0 to 300/ml. In the GAC adsorber

Figure 10. Electron Microscope Magnification of Carbon Particle (60X)

Figure 11. Electron Microscope Magnification of Carbon Particle (4000X) Showing Bacterial Growth

effluents no total coliforms were found throughout the test program; however, as shown in Figure 12, total bacterial levels rose sharply in the first month to maximum densities of 10^3 to 10^4 bacteria per milliliter, after which they decreased and remained at slightly lower levels for the rest of the study. In comparison, the effluent of a pilot plant sand filter, also shown in Figure 12, had a total bacterial density that ranged from 0 to 91/ml throughout the study. These levels are significantly lower than the bacterial levels found in the GAC column effluents. It must be pointed out that for both GAC and sand filter systems the influent water was prechlorinated to a free residual concentration of approximately 2 mg/l. While the sand filter maintained this residual throughout the bed, the carbon effectively removed chlorine in the top layer of the bed and thus did not inhibit bacterial growth on the GAC.

A study was also undertaken on the bacterial densities found on carbon particles in the GAC contactor. Figure 13 represents the change over time in the number of bacteria on the carbon particles in a GAC column and the corresponding number of bacteria in the GAC effluent. The upper curve represents the bacterial population on the carbon particles. This curve shows that the bacterial population on the carbon particles follows a sigmoidal growth curve; that is, the bacteria after an initial short lag phase will increase exponentially until the environment begins to limit their growth and a negative growth acceleration phase occurs. At this point the population will stabilize itself with respect to its environmental limits and population changes will occur only with shifts in the environment.

Bacterial densities in the effluent closely follow the bacterial population dynamics on the carbon particles. The lower curve indicates that bacterial levels in the GAC effluent are highest during the exponential phase of bacterial growth on the carbon particle when the dividing bacterial cells are most vulnerable. Bacterial levels decrease and level off in the effluent only after the bacterial population in the GAC adsorber has become established and has reached a pseudosteady-state situation.

One important aspect of this study was to identify the bacteria that were isolated from the GAC effluents. Unfortunately, many of the bacteria isolated were nonreactive to the standard biochemical tests and many were not identified. Table 7 lists the bacteria that were isolated and identified from the GAC columns or their effluents using the API system and other biochemical tests for enterobacteriaceae and other gram-negative bacteria. The most predominant bacteria that were isolated and identified belonged to the genus Pseudomonas. Members of the genus Bacillus also were found in large numbers. The bacteria that were identified in this study were predominantly soil or water saprophytic chemo-organotrophs and have no known pathogenic significance to man. However, some species of Flavobacterium,

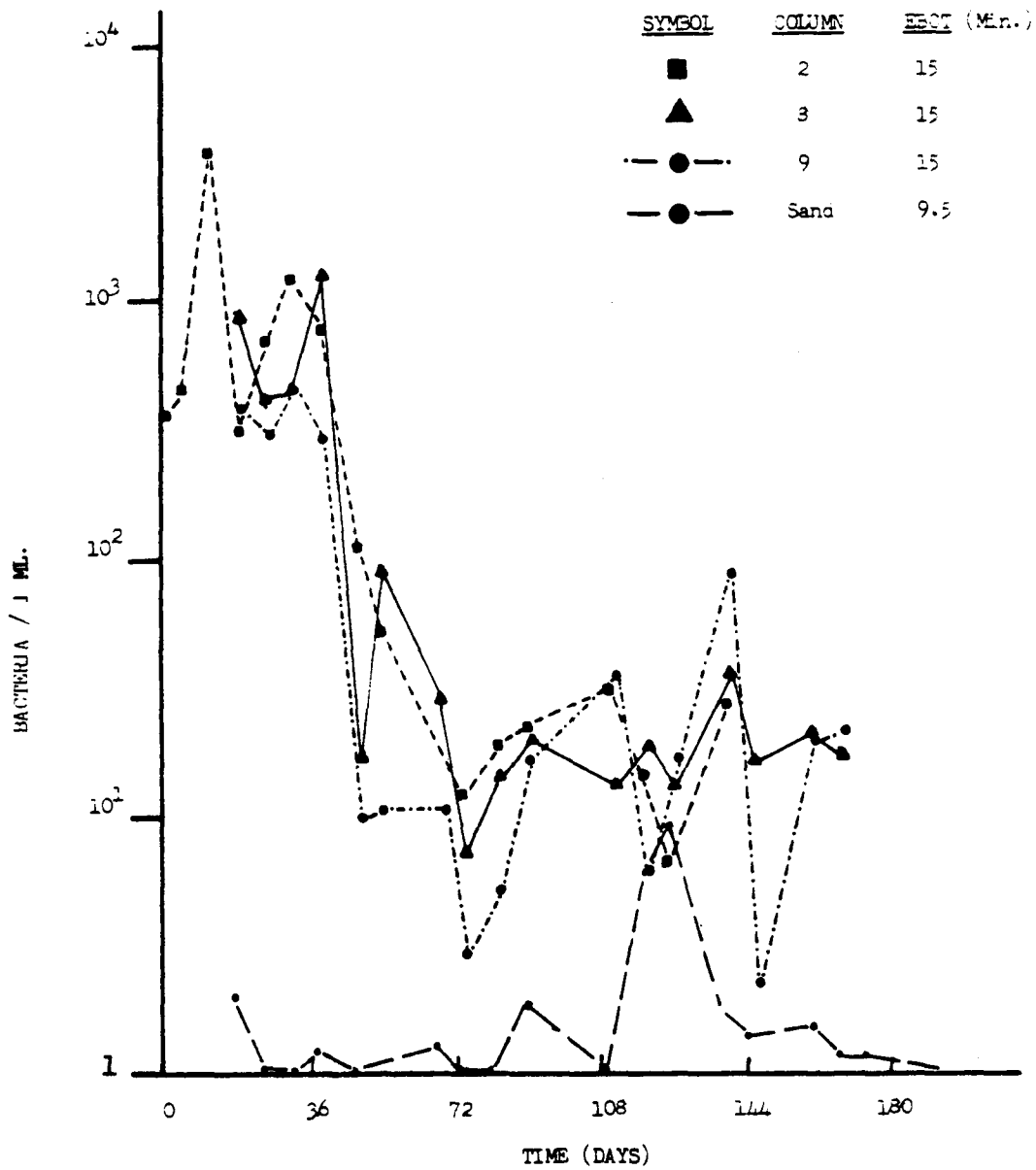

Figure 12. Bacteria in the Column Effluents

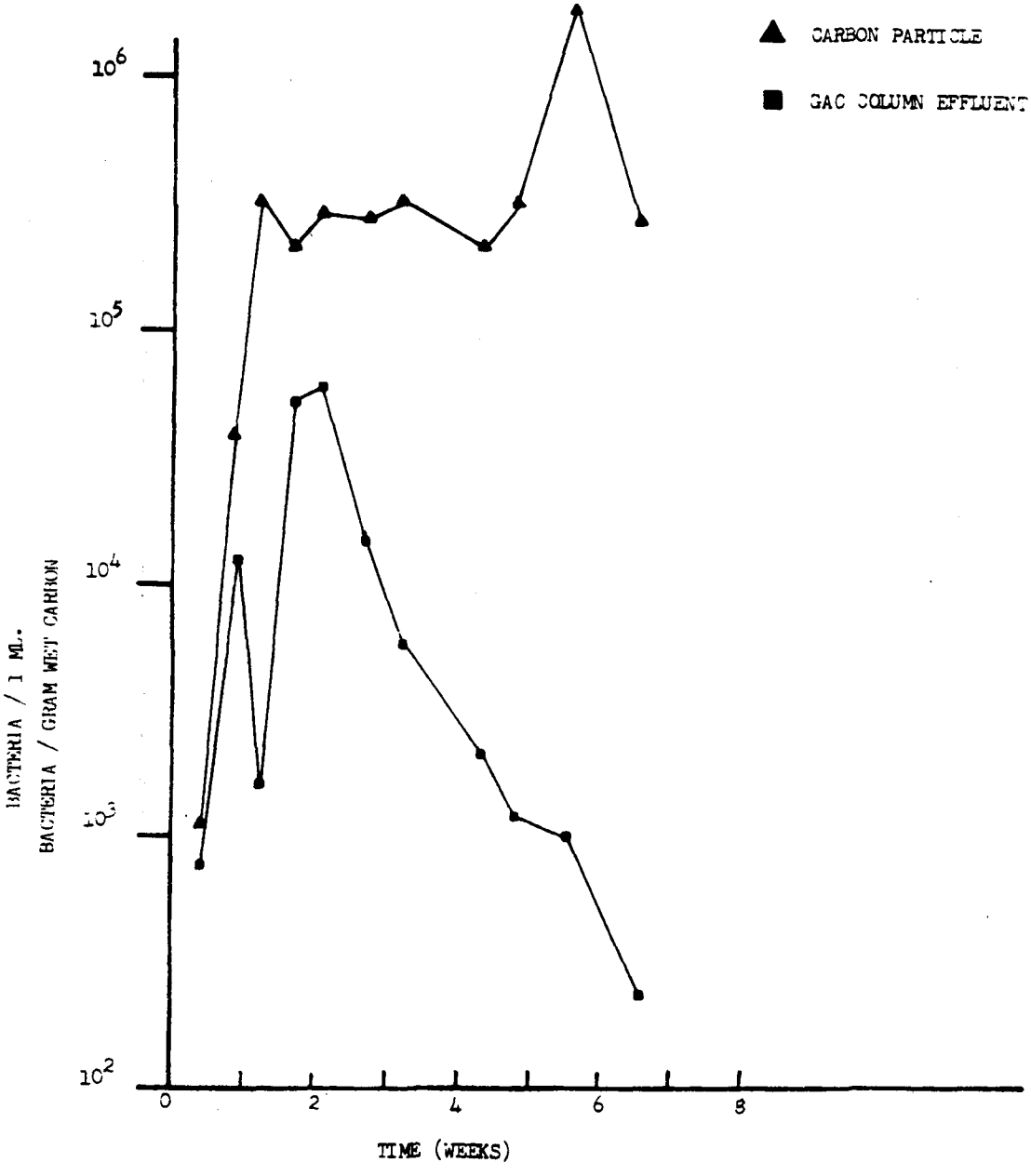

Figure 13. Bacteria On the Carbon and in the Effluents of a GAC Column

TABLE 7

BACTERIA ISOLATED FROM THE GAC SYSTEM,
THEIR API CODE AND COMMENTS

IDENTIFICATION	API CODE	COMMENT
Ps. putida	2 200 004 41	Acceptable
	2 201 004 41	Acceptable
Ps. fluorescens	2 005 006	Excellent
Ps. maltophilia	1 000 000 41	Acceptable
	1 202 000 51	Very Good
Ps. pseudoalcaligenes	0 000 004 50	Best Fit
Pseudomonas spp. Other	2 000 004 50	Good Liklihood but Low Selectivity
" " "	0 000 004 50	"
" " "	0 000 004 51	"
" " "	0 002 004 41	"
" " "	0 002 004 40	"
" " "	0 001 004 50	"
" " "	2 200 004 51	"
Achromobacter sp.	1 010 004 41	Best Fit
Alcaligenes odorans	0 001 004 50	Best Fit
Alcaligenes sp.	0 000 004 40	Best Fit
Flavobacterium odoratum	0 002 004 01	Best Fit
CDC IV F	0 010 004 01	Best Fit
CDC II F	0 202 004 00	Best Fit
	0 242 004 00	Excellent

Pseudomonas, and Alcaligenes are known to be opportunistic pathogens, chlorine resistant, or suppressors of total coliform.

Two engineering considerations were examined in relationship to bacterial levels on the GAC effluents: the effects of empty bed contact time and of pretreatment (chlorination) conditions.

Figure 14 graphs the bacteria in the effluents of three GAC contactors with EBCTs of 7.5, 15, and 30 min, respectively. Even after the volumetric flow rate effect was taken into consideration, it was found that the greater the EBCT, the higher the bacterial levels found in the adsorber effluents. However, experiments using an extremely long EBCT of 60 min did not indicate a similar pattern. Figures 15 and 16 demonstrate the effect of chlorinated influent water on the bacterial levels in the carbon particle and in the adsorber effluent. As can be seen from these figures, chlorinated influent water has a detrimental effect on the microbial ecosystem in the GAC column and also decreases the levels of bacteria in the GAC effluents.

Finally, it was found that the recommended standard plate count method for analysis of water and wastewater (2-day incubation at 35°C) (31) is not adequate for the enumeration of bacteria from GAC columns. In Table 8, a statistical analysis of the standard plate count test at 2-day and at 7-day incubation periods indicates that bacterial recovery rates were very poor at 2 days but increased dramatically at 7 days. Preliminary studies also have indicated that the standard 35°C temperature for incubation further limits the bacterial recovery rate compared to results at a 22°C or 28°C incubation temperature.

CONCLUSION

A framework has been developed for designing, and subsequently evaluating, the operating performance of a granular activated carbon process. It begins with the need to classify chemical and biological data in a health effect prioritization scheme. This scheme includes both direct impacts to human health and indirect impacts affecting the operating performance of the GAC. Esthetic problems arising in the treated water during its transmission in the distribution system should also be considered. These chemical and biological considerations then are used in performing an engineering evaluation and economic analysis of the alternative GAC process configurations.

Seven years of research studies by the Philadelphia Water Department have shown that a complex mixture of organic compounds exists in the Delaware River at Philadelphia. A total of 116 different compounds (including 40 isomers) were found, generally in a concentration range of 1 ug/l or less. Only chloroform and dichlorobromomethane were consistently found in concentrations greater than 1 ug/l. Dibromochloromethane, 1,2-dichloroethane,

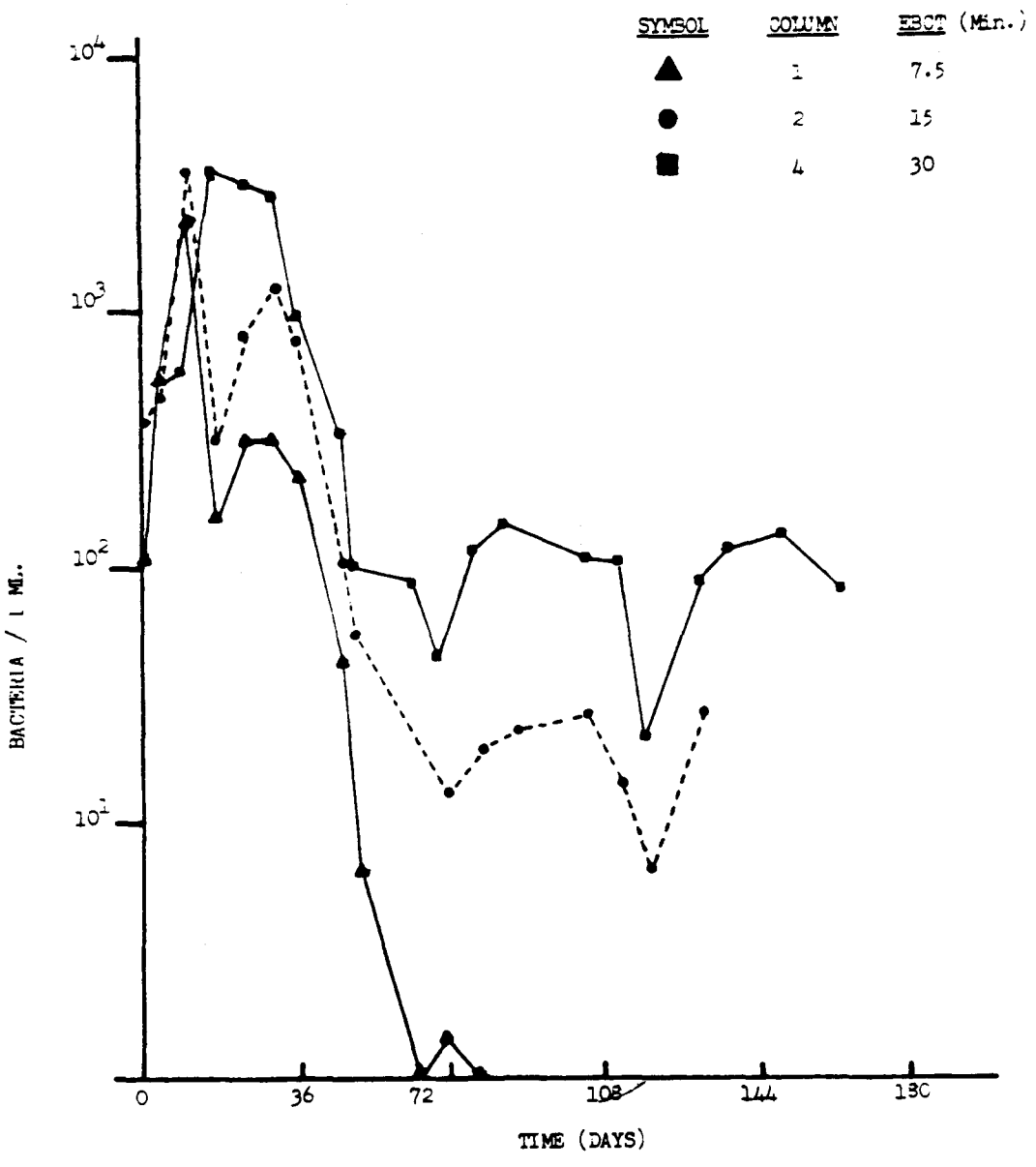

Figure 14. Effect of Contact Time on Bacteria Levels in GAC Effluent

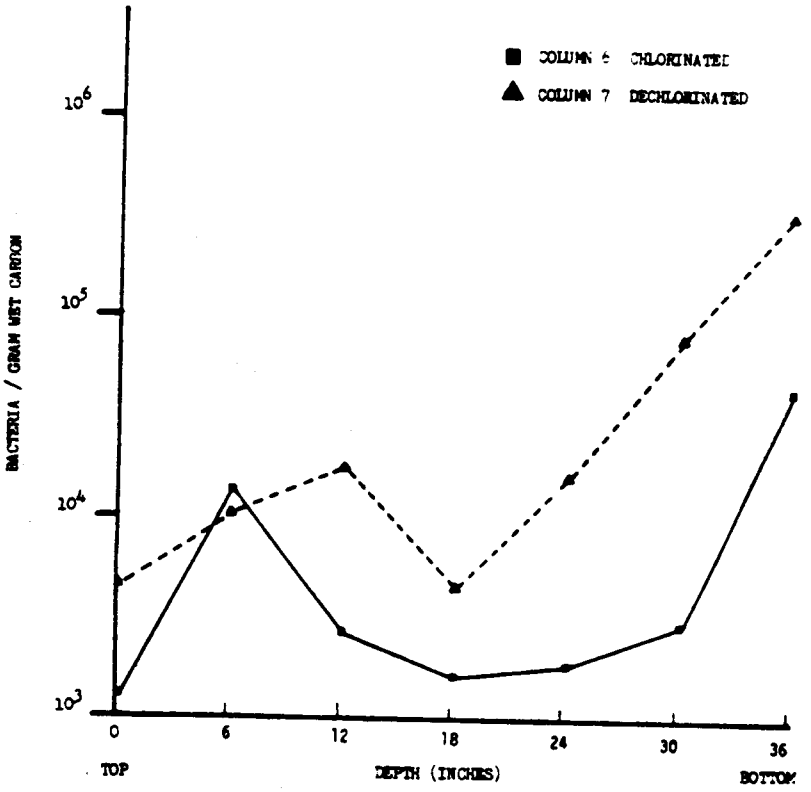

Figure 15. Bacteria on the Carbon Particles in a GAC Column (Chlorinated vs Dechlorinated Influent Waters)

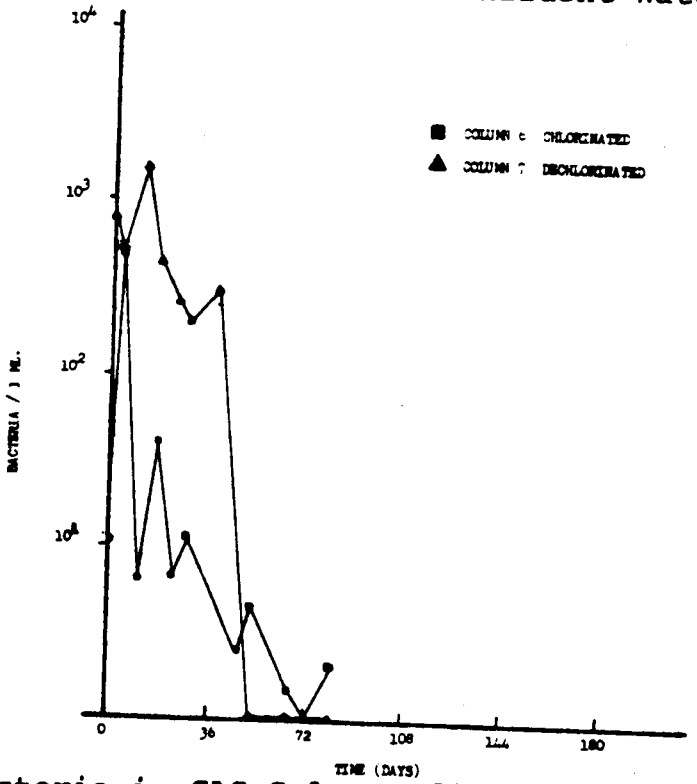

Figure 16. Bacteria in GAC Column Effluents (Chlorinated vs Dechlorinated Influent Waters)

TABLE 8

Statistical Analyses of the 2 Day vs 7 Day S.P.C. Study

	2 Day			7 Day				
Samples	No. Obs.	Mean	Variance	No. Obs.	Mean	Variance	Equal Means	Equal Variance
1	11	30.9	334.89	11	409.4	1640	No	No
2	15	74.8	141.61	11	459.4	4542	No	No
3	15	27.3	88.36	14	312.1	1900	No	No
4	50	184	40555	50	3248	1933983	No	No
5	50	236	64800	50	2628	685730	No	No

1,2-dichloropropane, trichloroethylene, toluene, and diacetone-L-sorbose were periodically found at this level. The presence and concentration of organic compounds in the river were highly variable depending upon the amount discharged, the point of origin, and the hydrodynamics of the Delaware estuary.

The engineering evaluation performed, thus far, has encompassed a number of hydraulic and vessel configurations using virgin and regenerated carbon. Because of the variable chemical nature of the Delaware River, both numerical and qualitative evaluations of GAC process efficiency have been utilized. For organics that are consistently found in concentrations greater than 1 µg/l, a rigorous quantitative analysis has been developed using breakthrough curves, mass loading curves, and statistical testing of the compounds found in the influent and in the effluent. For transient compounds and those in concentrations less than or equal to 1 µg/l, a qualitative screening approach using a time-series representation with a GC computer plot program has been applied. The transient compounds, depending upon their human health impact, may be the critical elements in the design of the GAC facility for Philadelphia. Presently, several research approaches are being considered to address this problem.

The biological considerations are based upon the ability to properly kill those organisms passed from the effluent of the GAC process to ensure that no subsequent problems are created in the distribution system. This does not preclude the existence of a biological population on the carbon to achieve the beneficial objective of assisting in the removal of organic compounds.

Research studies performed in Philadelphia have demonstrated that a relationship exists between the level of bacteria found on the carbon particle and the level of bacteria in the effluent from GAC adsorbers. Examining the physical characteristics of the biological growth on the carbon using scanning electron microscopy revealed that the bacteria were scattered over the carbon surface with heavier concentrations in the macropore areas. The most predominant bacteria that were isolated and identified belonged to the genus Pseudomonas. Members of the genus Bacillus also were found in large numbers. The bacteria that were identified in this study were predominantly soil or water saprophytic chemo-organotrophs and have no known pathogenic significance to man. However, some species of Flavobacterium, Pseudomonas, and Alcaligenes are known to be opportunistic pathogens, chlorine resistant, or suppressors of total coliform. Further microbiological studies are needed to establish the significance of these bacteria in relation to health effect and distribution system problems. The research also showed that a revised standard plate count test should be incorporated into routine bacterial analysis of GAC effluents to ensure bacterial removal.

The interaction of chemistry and biology in a GAC system with predisinfection must be more carefully investigated before any conclusive engineering evaluation and economic analysis can be made. Research studies must determine if microorganisms can decompose specific organic compounds of human health concern and high molecular weight organics that compete with these lower weight compounds for adsorption sites on the carbon. In addition, research is needed to establish if certain species of microorganisms are more efficient in this process than others. An understanding of these key issues then may lead to the development of optimal operating conditions that will enhance the growth of the most beneficial microbial population in the carbon vessel.

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OPERATIONAL EXPERIENCES WITH ACTIVATED CARBON ADSORBERS AT WATER FACTORY 21

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David Argo
Martin Reinhard

Water Factory 21 is a 0.66-m^3/s (15-mgd) advanced wastewater treatment plant operated by the Orange County (Calif.) Water District. It is designed to improve the quality of biologically treated municipal wastewater for injection into groundwater, thereby preventing sea-water intrusion. The processes and concerns of this facility are similar to those of facilities treating highly contaminated water supplies for potable purposes. The processes implemented at the water factory are lime treatment, air stripping, recarbonation, chlorination for algae control, filtration, granular activated carbon adsorption (GAC), reverse osmosis, and final chlorination for disinfection and ammonia removal.

This paper describes Water Factory 21's 2-1/2-year operational experience with GAC. While GAC is generally associated with organics removal, lime treatment, air stripping, and reverse osmosis also are important in increasing the overall reliability and efficiency of water treatment.

OPERATIONAL PERIODS AT WATER FACTORY 21

Figure 1 designates the sampling locations at the water factory by a number preceded by the letter Q.

The three operational periods at Water Factory 21 are described by Table 1. During the first period Water Factory 21 was started and the processes were tested. The influent was trickling filter effluent from treated municipal wastewaters with a high ammonia concentration. No water was injected into the ground, so breakpoint chlorination was not used. Analysis of organic removals by various treatment processes was begun during period 2, while the trickling filter effluent still was being treated. The effluent was blended with water from a deep aquifer to reduce electroconductivity to below 900 u/cm before injection. Air stripping and breakpoint chlorination were used to meet the ammonia limitation. During period 3, municipal wastewater began to be treated by an activated sludge process and flows were segregated. Thus, the concentration of trace organic

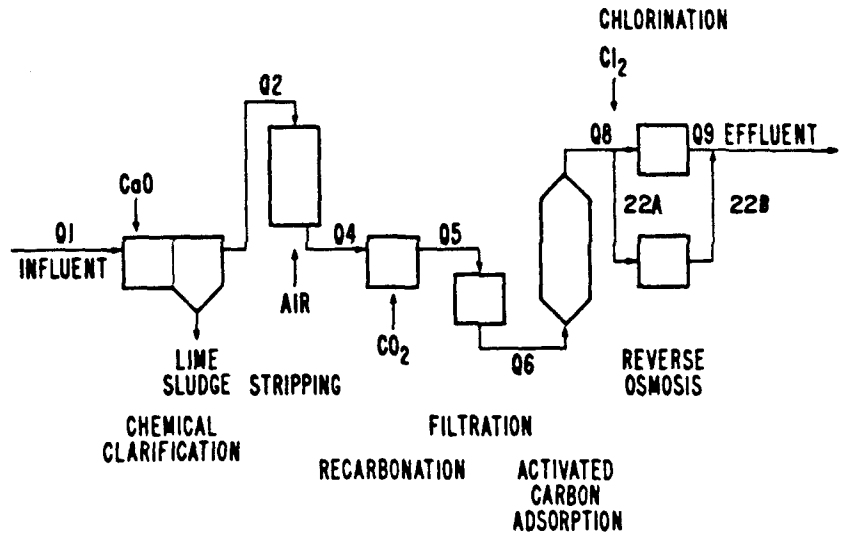

Figure 1. Schematic of the 0.66-m^3/s Advanced Water Reclamation Plant at Water Factory 21

TABLE 1

Different Operational Periods at Water Factory 21

Period	Dates	Operational Characteristics
1	Jan. 1976 to Oct. 1976	Trickling filter influent, no breakpoint chlorination, no reverse osmosis, no injection
2	Oct. 1976 to Mar. 1978	Trickling filter influent, breakpoint chlorination, no reverse osmosis, injection
3	Mar. 1978 to Jan. 1979	Activated sludge influent, no forced air circulation in stripping, partial ammonia removal by chlorination, reverse osmosis, injection

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Material and ammonia decreased significantly. However, water continued to be passed through the stripping towers because trace organics removal was found to be quite effective, even without forced air circulation. Also in period 3, a 0.22-m^3/s reverse osmosis (RO) system was added to reduce the mineral content of the blended water.

Figure 2 illustrates one of the 17 carbon adsorption columns in service at the Water Factory. Each is a coal tar, epoxy-lined steel pressure vessel with an overall height of 12.5 m, a side wall height of 7.3 m, and a diameter of 3.7 m. The column inlets and outlets use stainless steel well screens over a 0.38-mm slot opening to retain the carbon within the contactor. Each column contains approximately 35 metric tons of 8 by 30 mesh GAC* with a bulk density of 420 kg/m^3. The columns are designed to provide a 34-min empty bed contact time at design flow which is equivalent to a surface loading rate of 3.8 mm/s.

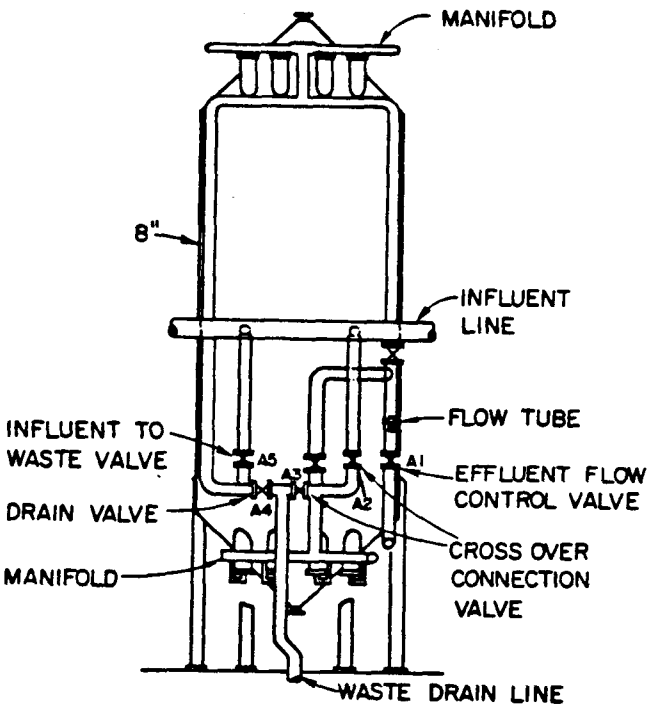

Figure 2. Granular Activated Carbon Contactor Vessels

*Filtrasorb 300, Calgon Corp., Pittsburgh, Pa.

Originally, the columns acted as upflow countercurrent packed bed contactors. Water was introduced through the bottom inlet screens and flowed upward through the carbon, exiting through the top screens. A space was left void at the top of each column to allow backwashing by expanding the normal flow rate in the upflow direction. The columns were piped so that water could be introduced at the top of the contactor to clean the stainless steel outlet screens of carbon fines and to reduce head loss when required.

In mid-1977, while pilot studies were being conducted to determine the feasibility of reverse osmosis demineralization of the GAC effluent, it was discovered that operating the carbon columns in the upflow configuration caused continual bleedoff of carbon fines, in the size range of 25 μm or less, to the RO system. Even at hydraulic loading rates of 3.2 mm/s there was sufficient fluidization of the GAC bed and interparticle collision to cause a slow attrition of the carbon and a carryover of the fines. Operation of the columns by downflow gravity tended to arrest this process. For confirmation, a series of samples from upflow and downflow operations were analyzed with a particle counter.* The results (Table 2) indicated that the total particle count for an upflow GAC column was approximately four times that of a downflow column. Most of the particles were 25 μm or less in size. In several further tests the accumulation of material on 1-μm cartridge filters during upflow and downflow operations was compared. The downflow mode produced an accumulation of a brown residue associated only with biological materials, while the filter receiving upflow water was rapidly blackened with GAC fines. Thus, all GAC columns were modified to receive the downflow water so that the RO membranes were protected from fouling by carbon fines.

TABLE 2

Comparison of Particle Counts Found in WF-21 Upflow and Downflow GAC Contractors

Sample	Number of Particles in 10 ml						Total Particles per ml
	2.5-5 μm	5-10 μm	0-25 μm	25-50 μm	50-100 μm	100-150 μm	
Upflow GAC Effl	9500	4085	1837	192	29	1	1560
Downflow GAC Effl	2796	1221	297	70	14	1	440

*Coulter Electronics, Inc., Hialeah, Fla.

The change from the upflow to the downflow mode made regeneration of GAC more difficult. In the upflow mode the bottom carbon becomes more contaminated and is easily removed for regeneration, after which it is replaced at the top of the column. In the downflow mode the upper carbon is the most contaminated, but it is difficult to remove from the system. The lower carbon first must be removed and stored; the top carbon then is removed, regenerated, and placed on the bottom. This is a workable scheme, but is more likely to result in additional carbon loss because of the increased handling. In spite of this problem the change to downflow was considered desirable because it improved the effluent quality.

When organic removal through a GAC column decreases significantly, the column is removed from service and the exhausted carbon is regenerated in the system, as shown schematically in Figure 3. Exhausted carbon is extracted in slurry form and transferred to a dewatering bin with screen drains. About 8 kg water/kg carbon is needed to form a slurry suitable for transfer through a flanged pipe with large-radius bends. The dewatering bins are coated with epoxy to protect the steel from corrosion. Draining the carbon takes about 10 min. After draining, the carbon retains 40 to 45 percent of its weight in moisture which is optimal for thermal regeneration.

Subsequently, the carbon is transferred by a stainless steel screw conveyor (40 to 200 kg/hr dry basis) for discharge into the top of the carbon regeneration furnace. This is a gasfired, six-hearth unit rated at 5.5 metric tons/day of dry carbon. Six burners are provided: two each on hearths 4, 5, and 6. The temperatures of the hearths are regulated independently by an automatic temperature control and the furnace operates at temperatures up to 930°C on hearths 5 and 6. Each burner is adjusted so that the atmosphere holds no excess oxygen that otherwise might burn the carbon. Steam is added to hearths 4 and 6 to give a more uniform temperature distribution throughout the furnace. The carbon is moved across each hearth by four rotating stainless steel rabble arms. The high temperature causes volatilization of the adsorbed organics which are combusted in an afterburner on top of the furnace. A venturi wet scrubber removes carbon fines from the furnace exhaust.

After regeneration the carbon is cooled in a quench tank and pumped by two carbon slurry pumps to a defining chamber. Once defined, the carbon is transferred in slurry form back to the GAC adsorbers for reuse.

The overall operation of the GAC system has been relatively trouble free. While in the upflow mode the columns were backwashed when head loss buildup caused a drop in flow. Usually this happened once a week. The need to backwash was associated with buildup of carbon fines on the top effluent screens and not

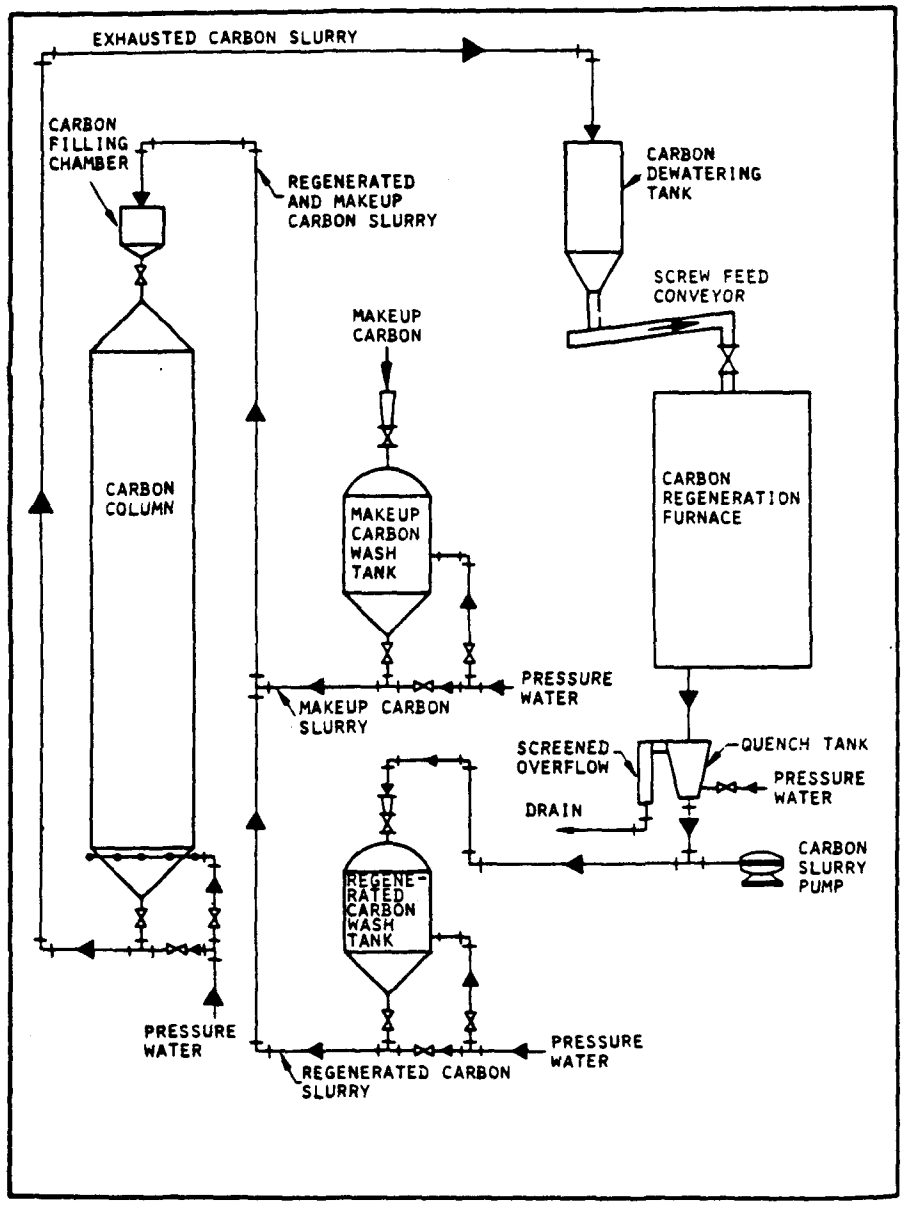

Figure 3. Carbon Regeneration System

with biological growth or accumulation of suspended solids in the GAC beds themselves. The change to downflow operation coupled with improved quality of applied water further reduced the need for backwashing; the GAC columns are backwashed about every two weeks. Apparently, little buildup of biological solids or other suspended material occurs in the carbon bed. The water applied to the GAC columns generally is free of suspended solids, and influent and effluent turbidities typically are lower than 0.5 NTU. At no time during the operation of the carbon adsorbers have anaerobic conditions been detected. The air stripping process prior to GAC adsorption supplies water high in dissolved oxygen.

GAC ROLE IN ORGANICS REMOVAL

GAC is just one of several unit processes used at Water Factory 21 for organics removal. Figure 4 illustrates the frequency distribution of chemical oxygen demand (COD) at various sampling locations during period 3. The distribution of COD and trace organics at various locations was found to follow a log normal distribution (1), characterized by the geometric mean concentration M located at the 50 percent point, and a spread factor S represented by the slope of the line. The spread factor is similar to a standard deviation; 68 percent of the time the concentration lies between M/S and MS, and 95 percent of the time between M/S^2 and MS^2.

Figure 4 indicates that lime treatment and reverse osmosis, as well as GAC, are effective in organics removal. Lime treatment not only removes suspended organics but also a portion of the dissolved organics, some of which are not removed effectively by GAC (2). Reverse osmosis is very efficient in removing the higher molecular weight organics which are very poorly characterized to date.

Figures 5, 6, and 7 illustrate removals of three representative trace organics by various processes during period 3. The first, 1,4-dichlorobenzene, is removed effectively by stripping (Q4) and GAC (Q9), but not by lime treatment (Q2) or filtration (Q6). The second, tetrachloroethylene, is removed efficiently by stripping (Q4), but not by GAC or any other process. The third diisobutylphthalate, is removed best by GAC (Q9). These results indicate the importance of the total system in organics removal. During period 3, forced air circulation was not used in the stripping towers.

PERFORMANCE OF GAC

Table 3 and 4 summarize the performance of GAC for the removal of COD, TOC, trace organic contaminants, and various heavy metals during periods 2 and 3. Included in these tables are the geometric mean concentrations, the number of samples

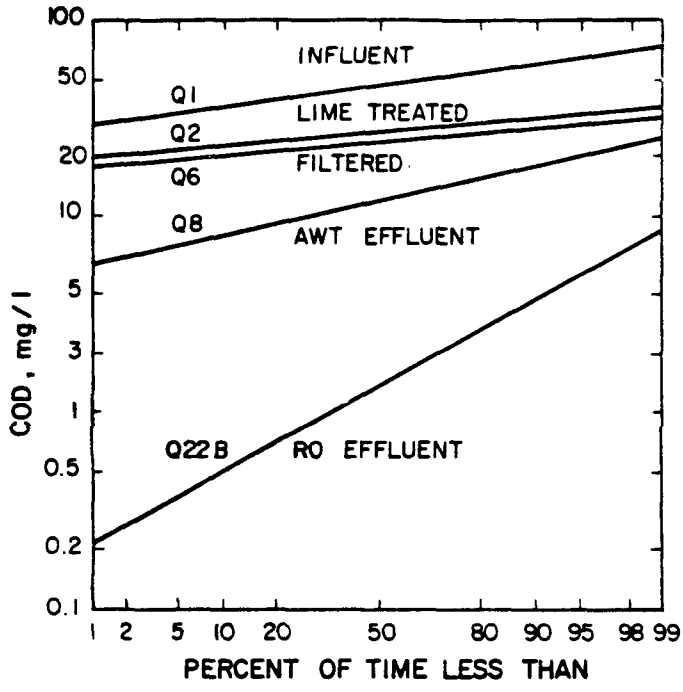

Figure 4. Frequency Distribution of COD Concentrations at Various Sampling Locations During Period 3

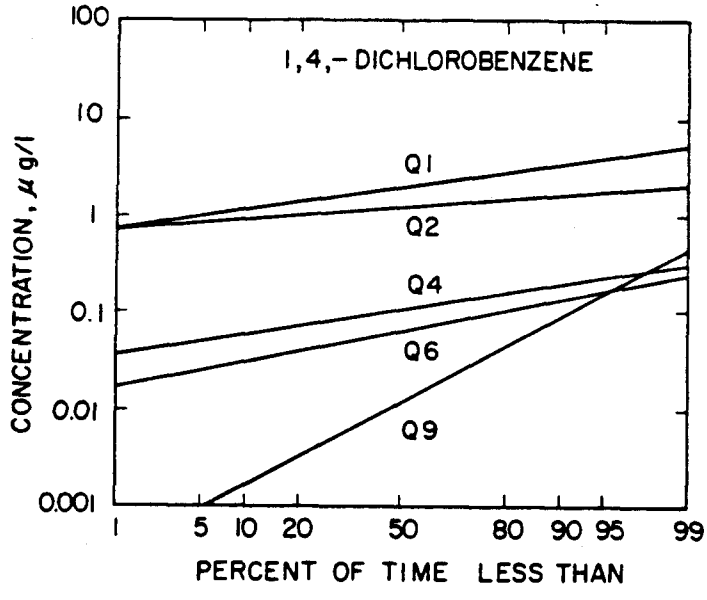

Figure 5. Frequency Distribution of 1,4-Dichlorobenzene at Various Sampling Locations During Period 3

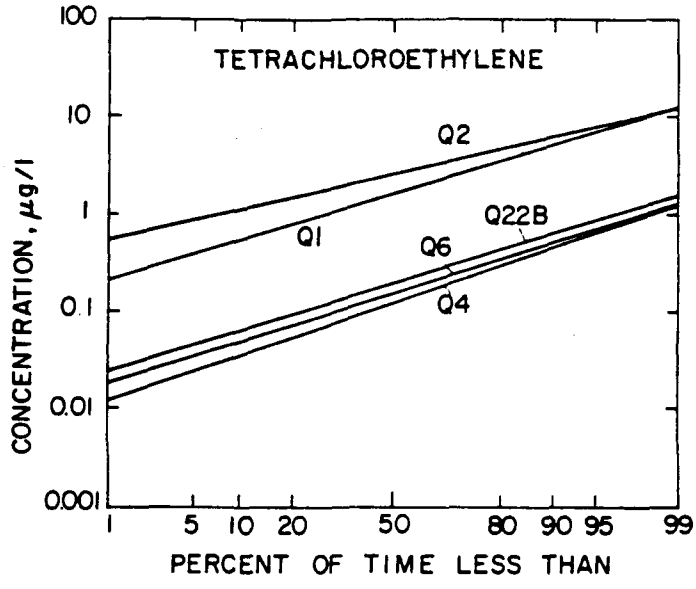

Figure 6. Frequency Distribution of Tetrachloroethylene at Various Sampling Locations During Period 3

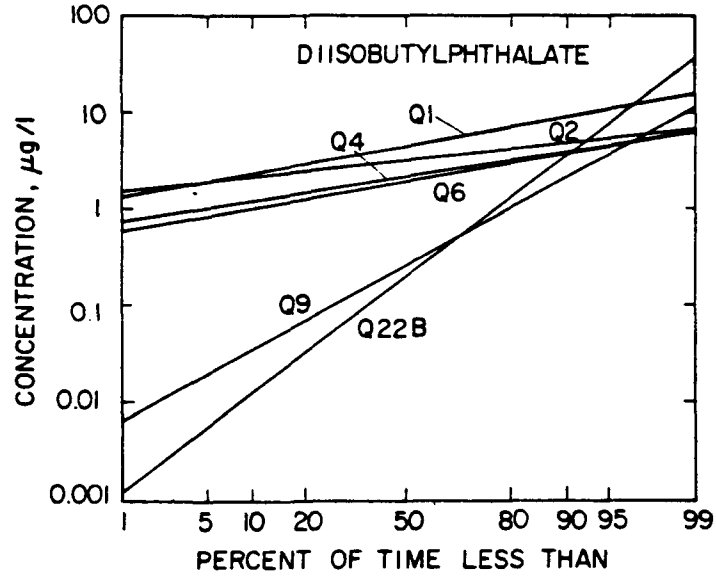

Figure 7. Frequency Distribution of Diisobutylphthalate at Various Sampling Locations During Period 3

Table 3. Removal of Organic Materials by GAC During Periods Two and Three

Contaminant	Period Two Inf. Conc.* (No. Samp.) Q6	Period Two % Removal (95% CI)	Period Three Inf. Conc.* (No. Samp.) Q6	Period Three % Removal (95% CI)
COD	42(272)	60(58 to 63)	24(155)	49(46 to 52)
TOC	14(156)	51(48 to 54)		
1,4-Dichlorobenzene	0.02(6)	17(-750 to 90)	0.07 (16)	98(43 to 100)
1,2-Dichlorobenzene	0.01(6)	82(0 to 97)	0.02 (16)	91(-150 to 100)
Diisobutylphthalate			2.0 (16)	87(61 to 95)
Tribromomethane			0.41 (17)	81(40 to 94)
Dimethylphthalate			1.3 (16)	64(24 to 83)
Chlorobenzene/o-xylene	0.09(7)	46(-5 to 72)	0.11 (16)	63(30 to 80)
Bromodichloromethane	4.8(33)	72(46 to 86)	1.8 (16)	54(5 to 77)
Dibromochloromethane	1.4(29)	84(58 to 94)	0.65 (17)	52(2 to 77)
M-xylene			0.05 (16)	50(7 to 73)
Naphthalene			0.05 (16)	50(-8 to 76)
Di-n-butylphthalate			0.59 (14)	44(-90 to 84)
Styrene			0.03 (16)	40(-190 to 88)
Carbon Tetrachloride			0.07 (17)	20(-110 to 70)
Ethylbenzene	0.06 (7)	45(3 to 69)	0.02 (16)	17(-77 to 61)
Bis-[2-ethylhexyl]-phthalate			3.4 (5)	9(-69 to 51)
1-Methylnaphthalene			0.02 (16)	0(-660 to 87)
Trichloroethylene			1.0 (16)	-6(-220 to 65)
Tetrachloroethylene	0.04(28)	72(-260 to 98)	0.16 (17)	-6(-190 to 61)
Methylene chloride	1.5 (38)	-7(-98 to 43)		
1,1,1-Trichloroethane			0.16 (17)	-12(-430 to 76)
2-Methylnaphthalene			0.02 (16)	-18(-150 to 45)
Chloroform	8.2 (32)	21(-70 to 63)	5.3 (17)	-41(-146 to 19)

*Geometric mean conc. in ug/L except COD and TOC which are in mg/l.

Table 4. Removal of Heavy Metals by GAC During Periods Two and Three

Contaminant	Period Two Inf. Conc.* (No. Samp.) Q6	Period Two % Removal (95% CI)	Period Three Inf. Conc.* (No. Samp.) Q6	Period Three % Removal (95% CI)
Ag	2.6 (27)	4(-27 to 27)	0.77 (6)	10(-250 to 77)
Ba	26 (26)	0(-37 to 27)	7.8 (6)	5(-150 to 64)
Cd	1.4 (32)	7(-32 to 35)	7.2 (6)	-32(-210 to 43)
Cr	29 (33)	38(9 to 58)	5.6 (6)	45(-3 to 70)
Cu	56 (27)	64(51 to 74)	36 (6)	56(-85 to 89)
Fe	105 (33)	66(41 to 80)	28 (6)	-50(-530 to 64)
Hg	1.9 (26)	11(-47 to 46)		
Mn	3.2 (33)	-16(-83 to 27)	1.3 (6)	-35(-270 to 51)
Pb	3.0 (26)	27(-56 to 66)	3.1 (6)	68(-780 to 99)

*Geometric mean conc. in ug/l

analyzed, the average percent removal, and the 95 percent confidence interval for the percent removal (1). During period 2 about 14 percent of the GAC in each column was regenerated every 40 to 70 days, while during period 3 about 50 percent was regenerated every 6 months. The trace organic contaminant data in Table 3 are arranged in order of removal efficiency by GAC (except for COD) during period 3. The analytical methods used are described elsewhere (1). In general, chlorinated benzenes, some of the phthalates and aromatic hydrocarbons, and the brominated trihalomethanes were removed at least as efficiently as COD. The one- and two-carbon chlorinated compounds, on the other hand, were not removed by GAC under the existing operating conditions. These compounds were removed by stripping. The confidence intervals on the percent removal are quite broad, so care must be taken in interpreting these data.

The heavy metal data in Table 4 show that chromium, copper, and lead are partially removed by GAC treatment. Iron was fairly efficiently removed during period 2, but during period 3, GAC treatment increased the effluent iron concentration. This change is probably caused by wear on the linings and increased corrosion of the GAC vessels. The number of samples collected for heavy metal analyses during period 3 is low, and the resulting confidence interval is broad. Thus, some caution is warranted in drawing conclusions from these data.

Instead of COD, TOC frequently has been proposed as a general monitoring tool for GAC performance. At the Water Factory, however, COD is more often used as a control parameter since the TOC instrument was not always operable and the accuracy of TOC analyses has been questionable. Table 5 compares COD with TOC results. The COD/TOC ratio normally lies between 2.0 and 3.0.

FRESH VS. OLD GAC

Figure 8 summarizes the effectiveness of a single GAC column in the removal of COD toward the end of period 2 and through period 3. During the upflow operation in period 2 the column influent concentration of COD generally was greater than 35 mg/l, and an average of about 30 mg/l COD was removed. Whenever effluent COD from a column reached 20 mg/l, about 5.5 metric tons were regenerated and about 0.8 kg COD were removed for each kilogram of regenerated carbon.

At the beginning of period 3 the influent COD decreased considerably; accordingly, the carbon needed to remove less organic matter from the water to maintain the COD limitation of 20 mg/l in the effluent and did not have to be regenerated as frequently. Assuming that 3800 m^3 (10^6 gal) of throughput is equivalent to one day of operation, almost 6 months of operation were possible before regeneration was necessary. During this time, COD removal by activated carbon treatment averaged about 7 mg/l, for a

Table 5. COD to TOC Ratios at Various Sampling Locations for Different Periods of Operation at WF-21

Period	Parameter	Chem. Eff. Q2	Filt. Eff. Q6	GAC Eff. Q8
Two	COD*, mg/l (no. samples)	52 (274)	42 (272)	16.6 (264)
	TOC*, mg/l (no. samples)	21.5 (19)	14.4 (156)	7.0 (163)
	COD/TOC ratio	2.41	2.92	2.37
	95% CI for ratio	2.3-2.6	2.8-3.0	2.2-2.5
Three	COD*, mg/l (no. samples)	27 (156)		12.3 (125)
	TOC*, mg/l (no. samples)	10 (44)		6.2 (91)
	COD/TOC ratio	2.70		1.98
	95% CI for ratio	2.6-2.8		1.8-2.2

*Geometric Mean Concentration

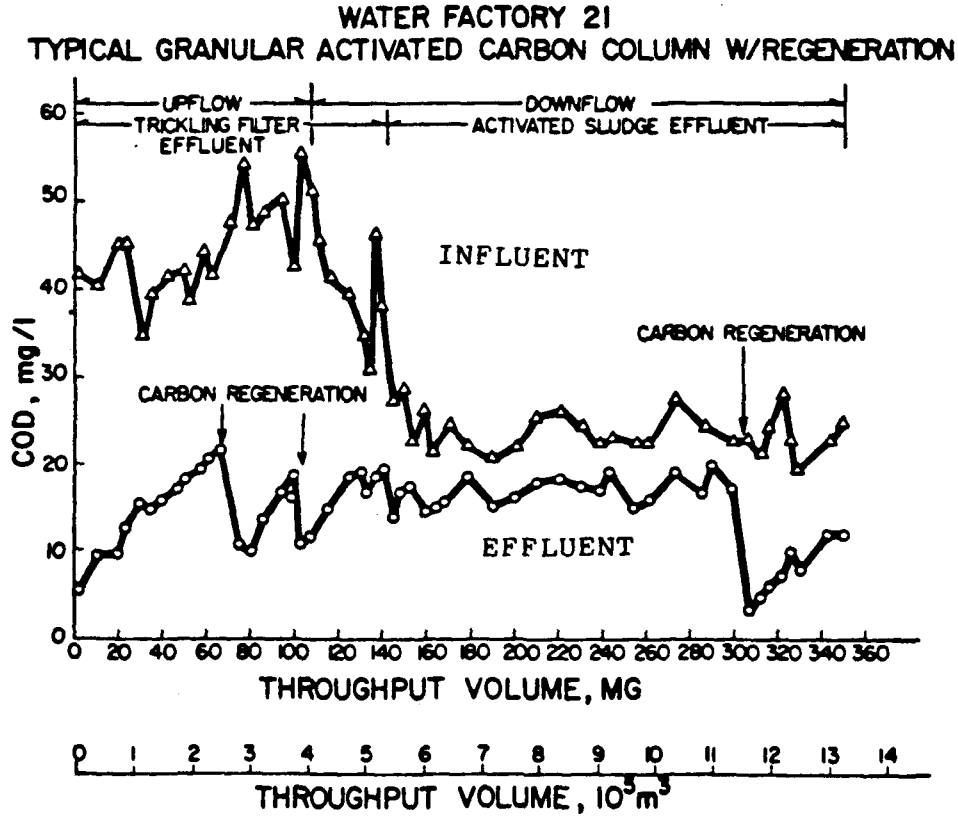

Figure 8. Influent and Effluent COD for a Typical GAC Column During the Latter Part of Period 2 and Into Period 3

cumulative total over the period of about 1.7 kg COD/kg regenerated carbon.

To evaluate the effect of biological processes within the activated carbon system, one GAC column, started during phase 2, was operated continuously with no regeneration. The COD removal by this system is shown in Figure 9. For the first 475,000 m^3 (125 mil gal) of throughput, COD removal gradually decreased. For the next 475,000 m^3 (125 mil gal), COD removal remained nearly constant at about 32 percent. This removal is believed to be the result of the activity of microorganisms growing on the GAC. The trickling filter effluent received by the Water Factory at that time was inefficiently treated and no doubt contained a significant amount of biodegradable organics.

With the change to the more efficiently treated activated sludge wastewater, the fractional removal of COD by this GAC column decreased after a short acclimation period to about 20 percent. The operation of this column indicates that biological processes are significant in GAC performance, which may explain the high organic removals per kilogram of GAC obtained.

TRACE ORGANICS REMOVAL BY FRESH AND OLD GAC

A comparative evaluation was made of trace organics removal during period 3 by a regenerated fresh GAC column and an old GAC column (Figure 10). The effluent from the fresh GAC is designated as Q7-12, and that from the old GAC as Q7-5. At the start of this evaluation (Jul. 5, 1978) about 75,000 m^3 water had been passed through the fresh GAC since the previous regeneration, and about 380,000 m^3 (100 mil gal) water had been passed through the old GAC since it was put in service. The GAC had just been transferred to a new vessel and about 10 percent new GAC was added. Thus, its initial performance was similar to that of freshly regenerated GAC. Water was passed through the column at the design flow rate until September 1, when 100 percent of the GAC was regenerated. The unit was put back into operation on October 1. Data on trace organics were gathered from July 5 through December 31.

Figure 10 shows the COD of daily composite samples for the fresh and old GAC after the complete regeneration on October 1. The effluent COD from the fresh column was initially about 5 mg/l which is typical for regenerated carbon, and rose at a rate of about 0.17 mg/l/day for the first 60 days. This corresponds to an increase in effluent TOC of about 0.08 mg/l/day.

The usual practice is to regenerate only one half of the GAC in a bed. Accordingly, the rate of effluent COD increase is twice that depicted in Figure 10. This figure also indicates an apparent variation in effluent COD which parallels the variation in influent COD. This variation is an important consideration

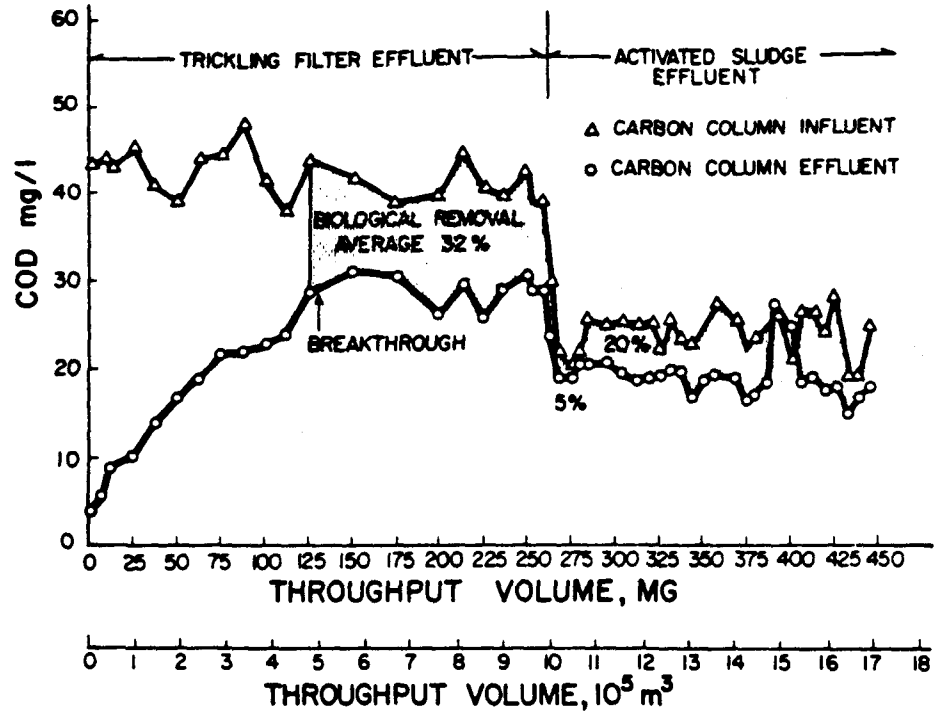

Figure 9. Influent and Effluent COD for a GAC Column Over an Extended Time Period Without Regeneration

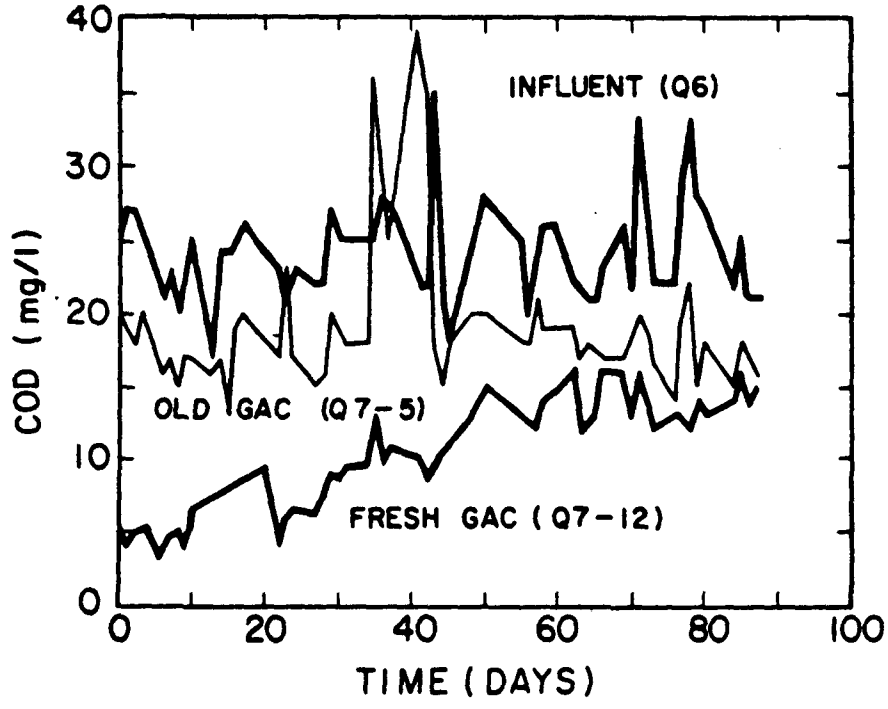

Figure 10. Comparison of Influent and Effluent COD Concentration Over Time for Fresh and Old GAC

when criteria for GAC performance and regeneration are being developed.

The geometric mean concentrations and spread factors for the trace contaminants in the influent and effluents from the two GAC columns are summarized in Table 6.

Table 7 presents the geometric mean influent concentration and the percentage removal of each trace constituent based upon the differences between the influent and effluent geometric means, together with the 95 percent confidence interval for the percent removal (1). The constituents are arranged in order from that with the highest calculated removal (by fresh GAC) to that with the lowest. Many of the constituents were present in low concentrations, very near the detection limit. Nevertheless, the data show a sufficient indication that many but not all trace constituents are removed very efficiently by GAC. Chloroform and the two-carbon chlorinated solvents are not removed efficiently.

A surprising result of this analysis is that the efficiency of trace constituents removal by old GAC is comparable to that by freshly regenerated GAC. To evaluate this result further a test was conducted to determine whether a statistically significant difference existed between the GAC effluent concentrations for any of the constituents. The data from this analysis are given in the last column of Table 7. Numbers lower than 0.1 indicate that the differences are statistically significant. Only for the two THMs, dibromochloromethane and bromodichloromethane, and for dimethylphthalate did the data show significant differences in performance between fresh and old GAC.

An analysis was attempted of the data obtained following regeneration of the GAC for the Q7-12 samples. Because of the general day-to-day variability of influent trace organic concentrations and the effect this has on effluent variability, no significant trend in most constituent concentrations could be detected. The significant problem in detecting differences or trends with such input variability should be recognized when performance standards are set for GAC and for the frequency of regeneration. Treatment objectives that are both desirable and feasible also must be established. The current requirements of the Orange County Water District for the combined effluent from all GAC columns is a COD not to exceed 30 mg/l. The requirement was met about 90 percent of the time during period 2 and has not been exceeded during period 3. This level is practical for day-to-day operation but probably is too high for potable supplies used directly.

EFFECTIVENESS OF GAC FOR TRIHALOMETHANE REMOVAL

The difficulty of removing THMs and other halogenated one- and two-carbon compounds is well recognized (Tables 3 and 7).

Table 6. Summary of Trace Contaminant Geometric Mean Concentration, M, Spread Factor, S, Number of Samples analyzed, N, and Number of Analyses Above Detection Limit (Nu).

	Influent GAC (Q6)			Effluent Fresh GAC (Q7-12)			Effluent Old GAC (Q5)		
Contaminant	M µg/l	S	N and Nu	M µg/l	S	N and Nu	M µg/l	S	N and Nu
Heptaldehyde	0.28	1.56	15(11)	0.009	5.12	11(2)	0.034	5.93	14(5)
Naphthalene	0.046	1.67	16(9)	0.002	7.77	11(2)	0.004	4.87	15(3)
Tribromomethane	0.41	2.19	17(9)	0.02	30	11(3)	0.17	3.69	14(5)
1,4-Dichlorobenzene	0.066	1.78	16(3)	0.006	3.6	11(3)	<0.02	-	15(1)
Dibromochloromethane	0.65	3.4	17(16)	0.09	6.66	11(6)	0.62	1.98	14(14)
Diisobutylphthalate	2.0	1.66	16(16)	0.35	2.49	13(2)	0.26	2.32	15(6)
Styrene	0.030	2.61	14(7)	0.006	3.53	10(2)	0.014	1.93	13(5)
Bromodichloromethane	1.76	3.4	16(15)	0.55	3.35	11(10)	1.88	1.98	13(13)
Diethylphthalate	0.62	2.56	16(10)	0.21	2.85	13(2)	0.27	2.62	15(5)
Dimethylphthalate	1.32	2.13	16(16)	0.47	2.43	13(8)	1.72	1.83	12(9)
1,1,1-Trichloroethane	0.16	11.3	17(12)	0.23	2.90	11(6)	0.26	9.06	14(13)
Chlorobenzene/o-xylene	0.11	1.93	16(15)	0.043	3.39	11(9)	0.07	1.85	15(14)
m-Xylene	0.046	2.24	16(15)	0.037	3.63	10(8)	0.018	2.16	14(8)
p-xylene	0.012	2.63	16(6)	0.01	4.10	10(4)	<0.02	-	14(3)
Di-n-butylphthalate	0.59	3.04	14(6)	0.50	3.29	13(5)	0.35	2.49	13(2)
Bis-[2-ethylhexyl]-phthalate	3.4	1.72	16(5)	3.3	2.40	13(6)	4.8	1.21	15(5)
Chloroform	5.3	3.0	17(17)	5.3	2.50	10(10)	7.06	2.21	13(13)
Trichloroethylene	0.98	2.75	16(7)	1.0	2.30	11(5)	1.1	2.32	13(6)
Ethylbenzene	0.023	2.42	16(10)	0.024	2.84	10(7)	0.015	1.85	14(5)
Tetrachloroethylene	0.16	2.47	17(13)	0.23	7.81	11(9)	0.19	4.32	14(9)
Pentachloroanisole	0.078	2.00	13(8)	0.004	2.79	13(4)	<0.01	--	--

Table 7. Average Percentage Removal of Trace Contaminants by GAC and 95% Confidence Interval for Average Percentage Removal

	Fresh GAC (Q7-12)		Old GAC (Q7-5)		Level of Significance for Difference Between Effluent Means*
Contaminant	Removal %	95% CI	Removal %	95% CI	
Heptaldehyde	97	59 to 100	88	32 to 98	0.5
Naphthalene	96	-13 to 100	91	33 to 99	>0.5
Pentachloroanisole	95	82 to 99	>87	-	-
Tribromomethane	95	-280 to 100	59	-65 to 90	0.5
1,4-Dichlorobenzene	91	54 to 98	>70	-	-
Dibromochloromethane	86	22 to 98	5	-97 to 54	0.05
Diisobutylphthalate	83	30 to 96	87	72 to 94	>0.5
Styrene	80	-85 to 98	53	-30 to 50	0.5
Bromodichloromethane	69	13 to 89	-7	-130 to 50	0.01
Diethylphthalate	66	-96 to 66	56	-33 to 86	>0.5
Dimethylphthalate	64	24 to 83	-30	-130 to 26	0.01
1,1,1-Trichloroethane	63	-110 to 93	69	-87 to 95	>0.5
Chlorobenzene/o-xylene	61	3 to 84	36	-3 to 61	0.5
m-Xylene	20	130 to 71	61	20 to 81	0.5
p-Xylene	17	-400 to 87	-	-	-
Di-n-butylphthalate	15	-300 to 82	17	-200 to 77	>0.5
Bis-[2-ethylhexyl]-phthalate	3	-150 to 63	-41	-150 to 21	0.5
Chloroform	0	-130 to 55	-33	-170 to 34	0.5
Trichloroethylene	-3	-230 to 68	-9	-230 to 64	>0.5
Ethylbenzene	-4	-190 to 63	35	-51 to 72	0.5
Tetrachloroethylene	-44	-560 to 68	-19	-270 to 62	>0.5

* Values below 0.1 indicate differences are statistically significant

Generally, THM's are removed much better by fresh GAC than by old GAC. The more highly brominated THM's are removed more efficiently than chloroform. Further comparisons between the fresh and old GAC are shown in figures 11 to 13. The water applied to GAC had been chlorinated in the recarbonation basin for control of algae. The higher effluent compared with influent concentrations of chloroform frequently found perhaps resulted from additional formation when the chlorinated water passed through the GAC column.

After 100 days the concentration of THM in the influent to the GAC increased as a result of a decrease in the influent ammonia concentration and a resulting free chlorine residual in the recarbonation basin. However, after 180 days, when the influent concentrations of THMs decreased, the effluent concentrations remained high for a short period during which they exceeded the influent concentrations. These results are similar for the fresh and old GAC, although the fresh GAC was more efficient in THM removal.

A comparison of the relative effectiveness of new versus old GAC is given in Figure 14. With chloroform, freshly regenerated GAC performs a little better than old GAC. Over time the difference is diminished and after 180 days the chloroform concentration in the fresh GAC effluent was higher than that in the old GAC effluent. The removal of brominated trihalomethanes by freshly regenerated GAC was much better, but the ability of fresh GAC to remove these materials decreased rapidly; 50 days after regeneration little difference in removal between fresh and old GAC was evident.

CHARACTERISTICS OF TRACE ORGANICS REMOVAL

Even though the calculated removals of the specifically measured trace organics demonstrate wide confidence intervals and no definite relationship between the chemical structure of the contaminant and its removal can be deduced, some trends in Tables 3 and 7 appear to be consistent. Within the group of the THMs the removal increases with an increasing number of bromines. Dichlorobenzene is better removed than chlorobenzene and within the group of aromatic hydrocarbons, naphthalene is more efficiently removed than the xylenes and ethylbenzene. These increases in removal may be ascribed to an increase in the hydrophobicity of these compounds as measured by the n-octanol water partition coefficient, P_{oct}(3). P_{oct} increases in the sequence

$$CHCl_3 < CHBrCl_2Cl < CHBr_3$$

and also

chlorobenzene < dichlorobenzene

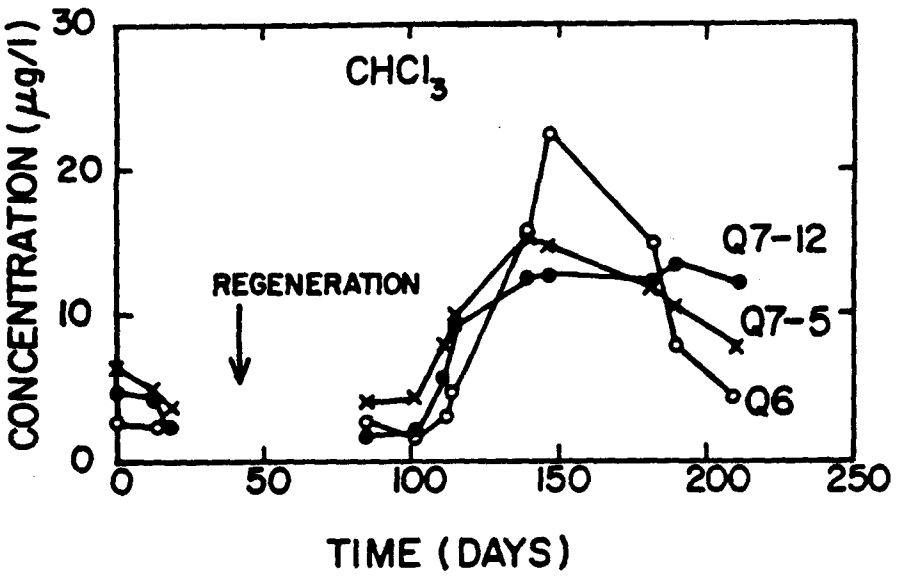

Figure 11. Comparison of Chloroform Removal by Fresh (Q7-12) and Old (Q7-5) GAC

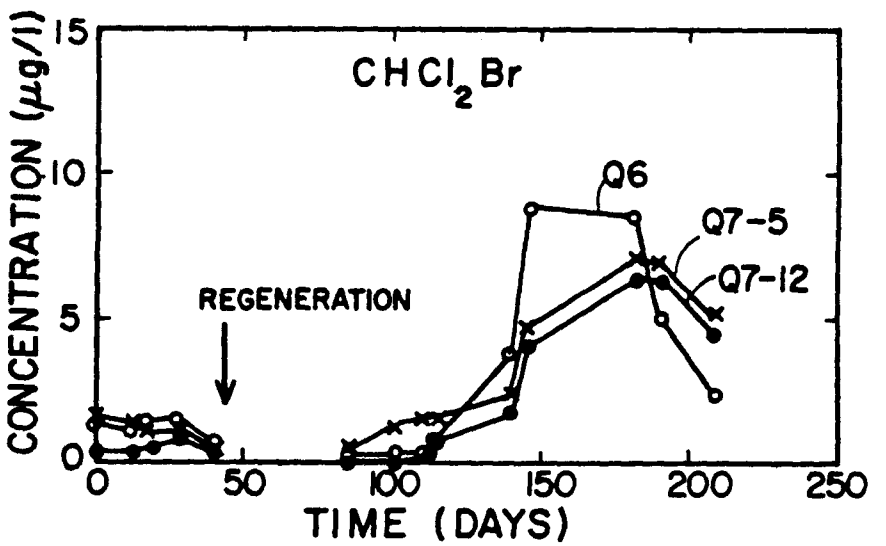

Figure 12. Comparison of Bromodichloromethane Removal by Fresh (Q7-12) and Old (Q7-5) GAC

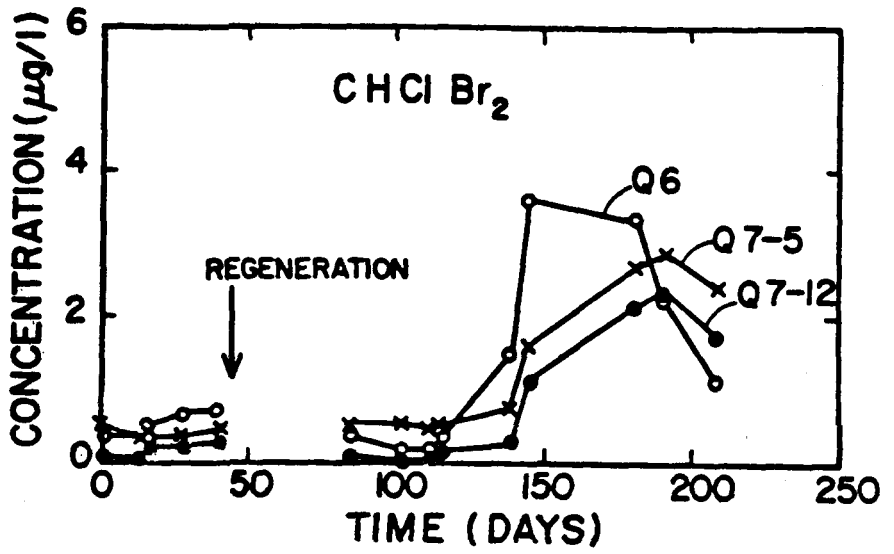

Figure 13. Comparison of Dibromochloromethane Removal by Fresh (Q7-12) and Old (Q7-5) GAC

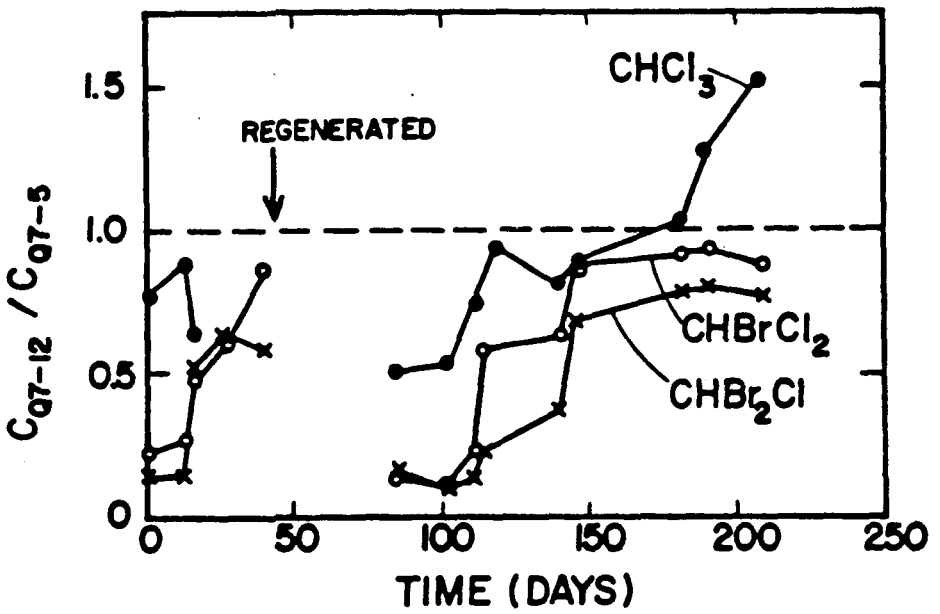

Figure 14. Ratio of Effluent Trihalomethane Concentrations for Fresh (Q7-12) and Old (Q7-5) GAC

and

xylenes, ethylbenzene < naphthalene

This finding indicates that the hydrophobic properties of the trace organics are directly related to their removal by GAC, although other factors may play important roles.

The phthalate esters show an erratic behavior in such a scheme with bis-[2-ethylhexyl]-phthalate being the least removed compound of this group, possibly because of a lack of specificity in the analytical methods and as yet undetected interferences. The low removal or increase in tetrachloroethylene and alkylated benzene concentrations is difficult to explain. Elevated concentrations may result from leaching from the tank coating which is known to contain tetrachloroethylene. Alkylated benzenes may originate from GAC which contains aromatic hydrocarbons in its structure.

If individual THM removals by the old GAC column are ranked from most efficient to least efficient, the order is the same as for the fresh GAC, even though the absolute percent removals are different (i.e., tribromomethane is still removed to the greatest extent and chloroform to the least in both columns). The same comparison holds for the chlorobenzenes and the aromatic hydrocarbons, an indication that biological processes also may be important in the removal of many trace organics.

Using old GAC, the phthalate esters again show an inconsistent behavior, which differs when fresh GAC is used in that dimethylphthalate appears to be removed. The effluent concentrations of alkylated benzenes seem to be lower when old GAC is used, suggesting that leakage was reduced during prolonged use or that biological factors are important in the removal of trihalomethanes.

SUMMARY AND DISCUSSION

For the removal of organic materials in the Water Factory 21 treatment system, GAC is one of the important processes. It is not the only effective process for this purpose, however, and lime treatment, stripping, and reverse osmosis also are relied upon. The efficiency and reliability of GAC treatment must be assessed with respect to its effectiveness as part of an overall treatment system. It constitutes the main process for removal of some organics, a collaborative process for others, and an ineffective process for still others. For many of the materials not effectively removed by GAC, stripping has proved to be an efficient and relatively inexpensive complementary process.

Full-scale GAC systems can be operated continuously with a minimum of operational problems. Higher efficiencies of organic

carbon removal can be obtained by more frequent regeneration than is generally practiced at the Water Factory 21. The requirements of the Orange County Water District system necessitated regeneration of about 14 percent of the carbon at 40- to 70-day intervals during period 2, when an inefficiently treated trickling filter effluent was received. After a well-treated activated sludge effluent was received, carbon regeneration once every 6 months proved sufficient.

Biological activity in GAC has proved quite effective for the removal of a significant portion of the influent organic materials measured as COD; it was responsible for removal of roughly 30 percent of the influent organics during phase 2 and 20 percent during phase 3. Biological activity also may be associated with the removal of a significant fraction of many trace organic materials. Whether these are decomposed biologically or simply sorbed by the microorganisms attached on GAC itself was not investigated. This phenomenon deserves further study.

The present study also has indicated the great difficulty of detecting analytically significant differences in the removal of trace organic materials. This is attributed to the great variability of influent concentrations in the full-scale system and the general lack of sufficient analytical precision when concentrations are near the analytical detection limit. For this reason caution should be exercised when regulations based upon removal efficiencies of such materials are established. COD removal is a good indicator of GAC performance and of the need for carbon regeneration, and it can be readily evaluated by the Water Factory personnel. However, difficulties could be expected at water treatment plants where COD concentrations are near the detection limit of 1-2 mg/l. Suitable GAC performance indicators need to be evaluated further.

ACKNOWLEDGEMENTS

This study was supported by the Wastewater Research Division, U.S. EPA, through grant EPA-S-803873; the Office of Water Research and Technology, U.S. Department of the Interior through grant 14-34-0001-7503; and the California Department of Water Resources through grant B52353. Appreciation is extended to James Graydon, Joan Schreiner, Kenneth Sutherland, Lewis Yee, and Huong Nguyen for their assistance in sample analyses.

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EFFECT OF PRECHLORINATION ON ACTIVATED CARBON ADSORPTION

Richard Sander

INTRODUCTION

Recently there has been an increasing interest in the problem of organic contaminants in water, especially with the chlorinated organic compounds which may be carcinogenic (1). We know now that the concentration of chlorinated organic compounds in drinking water should, in general, be minimized.

One of the methods recommended for the improvement of drinking water is the removal of organic compounds by granular activated carbon (GAC) filters. This is because GAC has excellent removal efficiency for many undesirable substances and is a simple and convenient unit operation.

First Column Test

In a research program sponsored by the Ministry of Research and Technology of the Federal Republic of Germany, a continuous-flow water-treatment pilot plant was installed at Stuttgart.

Efforts were made to find a process scheme for combined removal of haloforms, other chlorinated organics, and ammonia, using controlled chlorine dosage in combination with activated carbon filters. A simplified flow diagram of the pilot plant is shown in Figure 1.

After dosing sodium hypochlorite solution and alum directly into the raw-water pipe, 3 m^3 per hour of Neckar River water were pumped into the sludge-blanket clarifier, which was operated with an average retention time of 2.5 hours. The clarifier effluent was then passed through a dual-media gravity filter filled with sand and anthracite coal, followed by two GAC filters which were operated in parallel. Each adsorber consisted of acrylic tubes, 10 cm in diameter, with a total depth of 2.4 m of granular activated carbon. Two carbon types F300 and LSS were used for the tests. The filtration rate was 7.5 m/h and the total empty bed contact time was 20 minutes. Samples were taken about once a week from raw water, clarifier effluent, filter effluent, and carbon adsorber effluents.

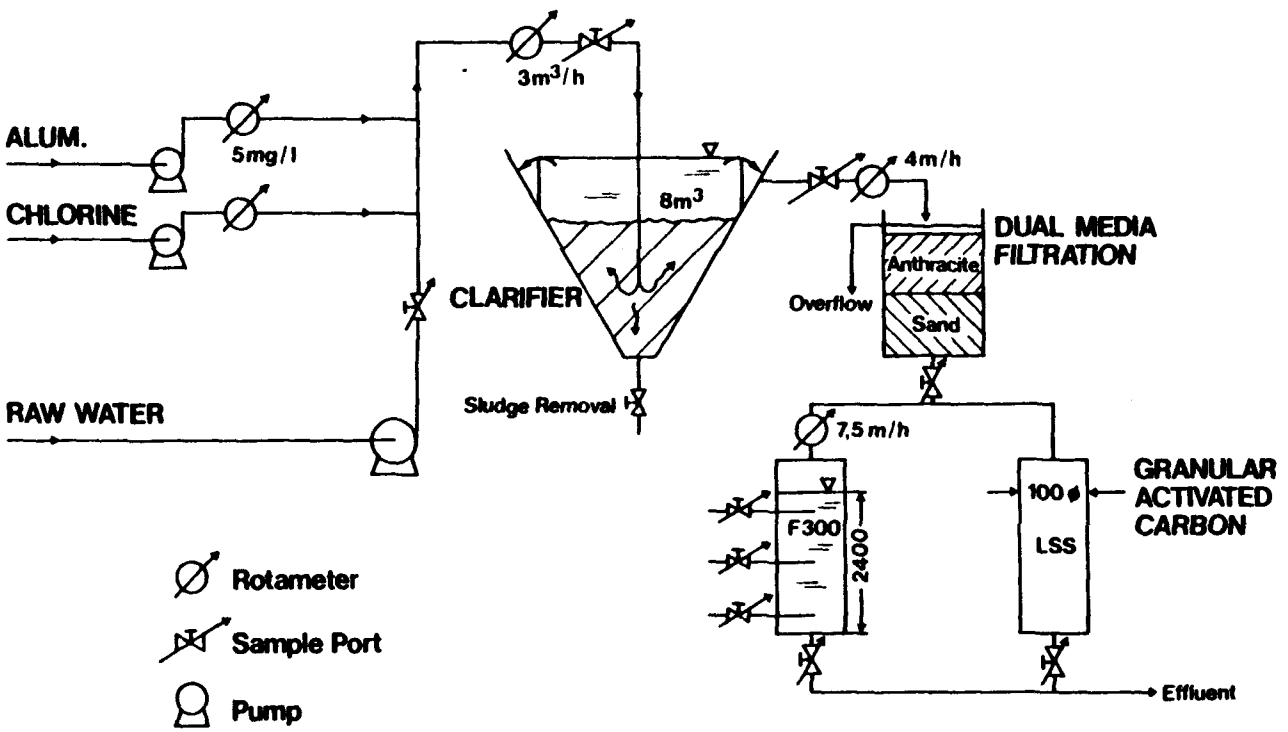

Figure 1. Schematic of Stuttgart Pilot Plant for the Treatment of Neckar River Water

In the first run, from the beginning of August 1977 to October 1977, conventional treatment with breakpoint chlorination, using chlorine dosages of 20 mg/l was applied.

In Table 1 the most important analytical data for raw water and clarifier effluent are summarized, covering the first period of the test.

Table 1

Average values of DOC, UV Absorbance, Ammonia, Haloforms and TOCl during the First Test Period (Breakpoint Chlorination)

Parameter	Raw Water	Clarifier Effluent
DOC [mg/l]	4.9	4.4
$UV_{254\ nm}$ [m^{-1}]	11.8	8.8
NH_4^+ -N [mg/l]	1.2	0
$\Sigma CHCl_3$+$CHBrCl_2$ [µg/l]	0.5	48
TOCl [µg/l]	100	660

Breakingpoint chlorination and subsequent clarification result in a 10 percent removal of DOC and in 25 percent reduction of UV absorbance. As expected, ammonia is completely removed by breakpoint chlorination, but the concentrations of haloforms and Total Organic Chlorine (TOCl) increase significantly from an average of 0.5 to 48 ug/l and from 100 to 660 ug/l, respectively.

The relative performance of the two different carbon filters in terms of DOC and UV absorbance removal as a function of throughput, are shown in Figure 2.

It can be clearly seen that there are considerable differences in the performance of the two carbon systems. While GAC type F300 still removes about 50 percent of DOC at the end of the run, the DOC reduction of LSS only amounts to 30 percent, which corresponds to a breakthrough of 70 percent. Based on the measurement of UV absorbance, the removal of organic matter was quite similar to that of DOC reduction, as shown in the lower part of Figure 2.

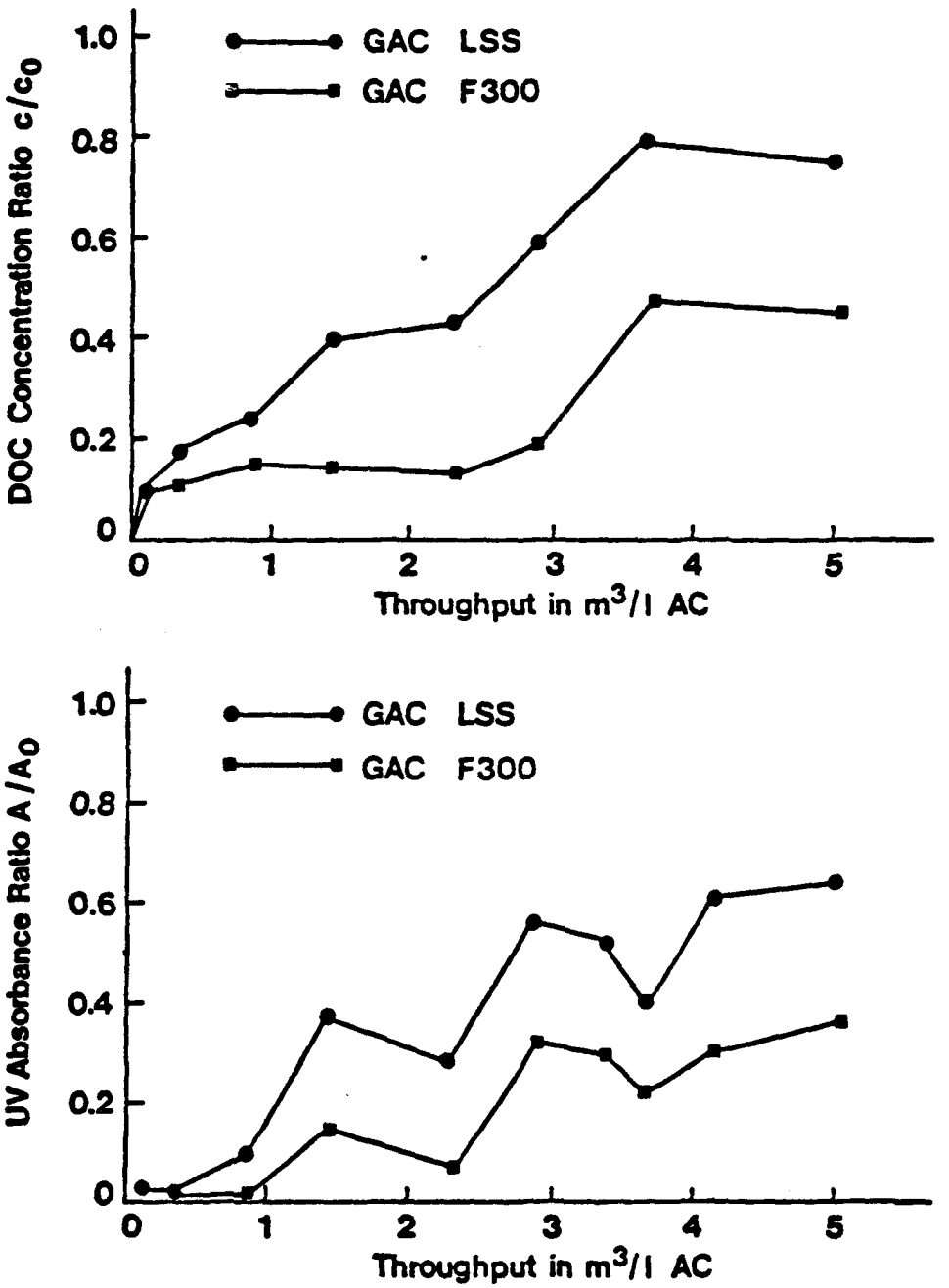

Figure 2. DOC and UV Absorbance Breakthrough Curves for Carbon After Breakpoint Chlorination and Clarification of Neckar Water

Table 2 contains the data for the concentration of the total organic chlorine compounds after breakpoint chlorination, determined by the pyrohydrolysis technique (2). It can be seen that the fairly high initial concentrations are reduced to the same extent as the DOC, and we can observe the same differences between the two carbons; i.e., a better efficiency for the F300 carbon.

Table 2

Reduction of TOCl Concentration in Breakpoint Chlorinated and Clarified Neckar River Water using Granular Activated Carbon

Throughput Ratio* m^3/m^3	Clarifier Effl. [µg/l]	GAC LSS		GAC F300	
		[µg/l]	% of Reduction	[µg/l]	% of Reduction
140	890	-	-	-	-
360	740	-	-	-	-
860	600	-	-	-	-
1440	660	-	-	-	-
2660	1140	-	-	-	-
3670	400	330	82	200	50
4180	330	290	88	240	73
5040	510	270	53	190	37

*m^3 water treated per m^3 GAC bed volume

Figure 3 illustrates a striking contrast to these findings; carbon F300 is less effective in removing haloforms.

One can see that the chloroform concentration in the effluent of F300 reaches that of the influent at the end of the run, while at the same time the effluent concentration of LSS increases only to about 70 percent of that of the influent. Apparently the bromine-containing bromodichloromethane is more effectively reduced by both carbon types than is chloroform.

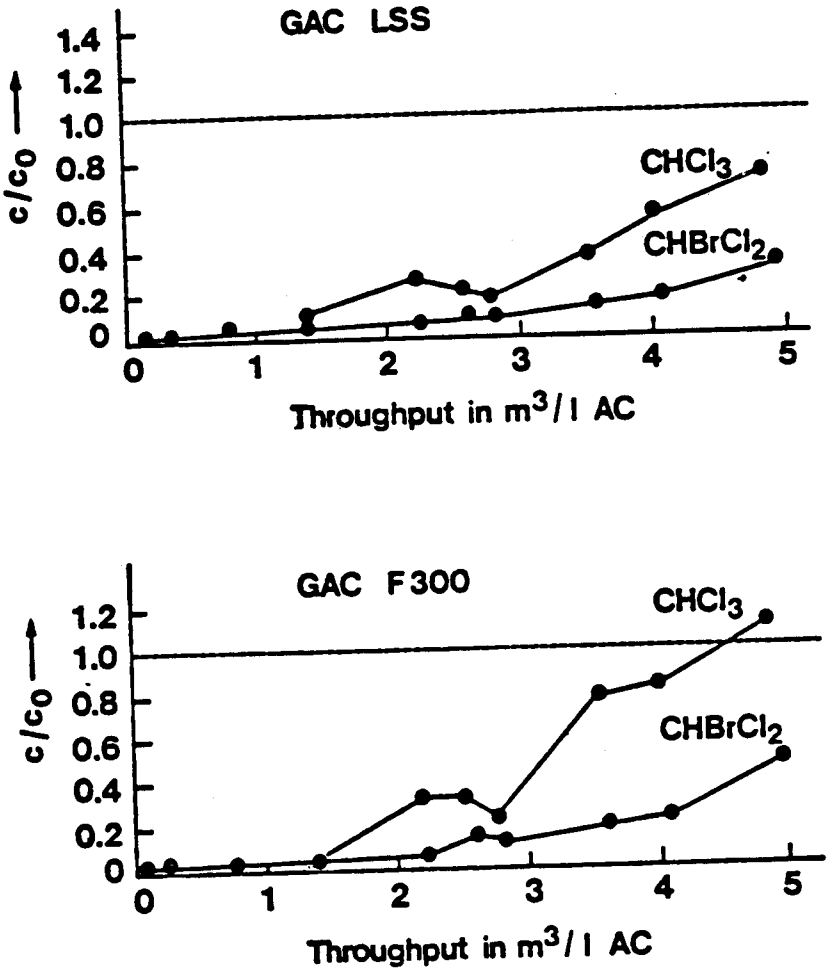

Figure 3. Chloroform and Bromodichloromethane Breakthrough Curves for Carbon, after Breakpoint Chlorination and Clarification of Neckar Water

Batch Tests

To confirm the results obtained with the column studies and to get further information on the influence of chlorine concentration on the removal of organics by activated carbon, a series of laboratory batch tests were conducted using simulated natural waters. Different dosages of sodium hypochlorite were added to a solution of humic acid extract from the Neckar River in Karlsruhe tap water, spiked with 2 mg/l ammonia. After 24 hours reaction time the solutions were dechlorinated with sodium sulfite and analyzed for DOC, UV absorbance, TOCl, and haloforms.

The humic acid used was extracted from Neckar River water by a method developed by Rudek and Jekel (3). All experiments were conducted at room temperature and at a pH of 7.5.

The effect of increasing initial chlorine concentration on DOC, UV absorbance, and organic chlorine compounds is shown in Figure 4. As expected, chloroform and TOCl increase markedly with chlorine addition while the DOC of the humic acid solutions remains almost constant and the UV absorbance decreases 50 percent.

Batch adsorption tests were performed by adding different doses of ground carbon F300 or LSS to a series of 2-liter bottles containing the same solution. The sealed bottles were placed on a magnetic stirrer for 48 hours, after which time equilibrium concentrations of DOC, TOCl, UV absorbance, and haloforms were determined. The pH of the chlorinated humic acid solutions was not affected significantly by the adsorption process.

Adsorption Isotherms

In Figure 5, logarithmic plots of the isotherm for the removal of DOC from the reaction mixtures by F300 and LSS are compared.

Obviously, the data show very little influence of the initial chlorine concentration since all points can be described by the same curve. This might be due to the fact that, in chlorine treatment of humic acid solutions, neither the splitting of high-molecular-weight molecules nor the production of more soluble matter by oxidation processes takes place. Consistent with the results of the first column test, carbon type F300 exhibits a greater capacity for the humic acid than type LSS. The slopes of the isotherms indicate multi-component adsorption, with a small fraction of fairly well adsorbable substances producing the steep slopes at high equilibrium concentrations. These problems are discussed in more detail in these proceedings by Frick (4), using the same experimental data.

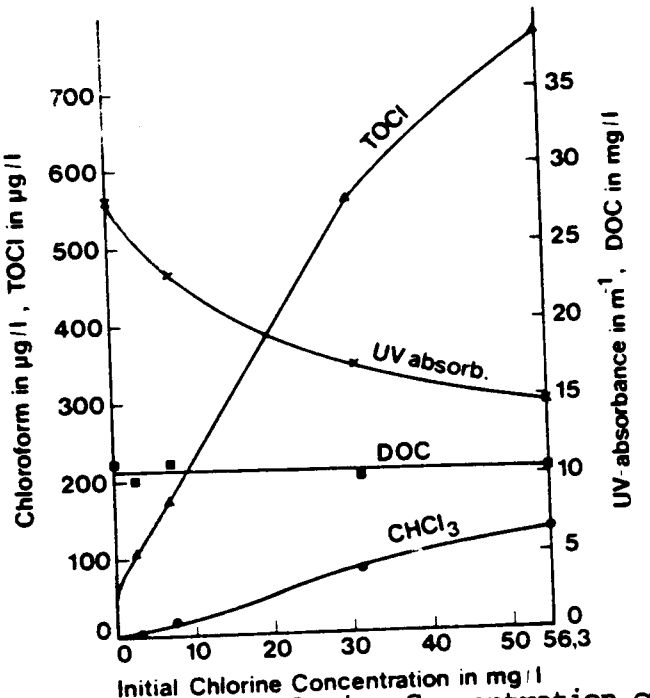

Figure 4. Effect of Initial Chlorine Concentration on Chloroform Production, TOCl Formation, DOC Value, and UV Absorbance (26mg/l Humic Acid, 2mg/l Ammonia, pH 7.5, 20°C)

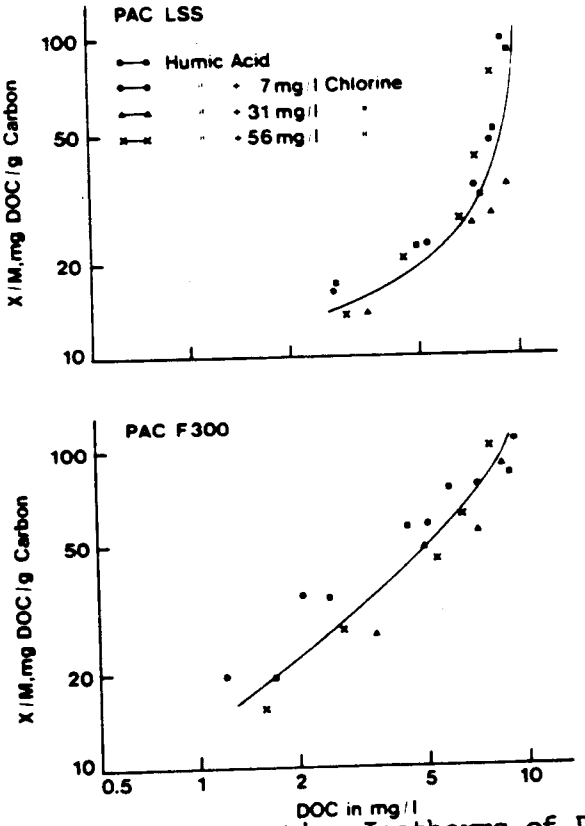

Figure 5. Batch Adsorption Isotherms of DOC from a Chlorinated Solution of Humic Acid

Isotherms for the adsorption of chlorinated organic compounds based on the measurement of TOCl are plotted in Figure 6.

Again, carbon F300, which has proved more effective for the removal of DOC, showed a higher capacity for chlorinated humics than LSS. The isotherms show increasing slopes at high final concentrations, i.e., low carbon dosages, thus indicating also a strongly adsorbable fraction. At low equilibrium concentrations the curves for different chlorine dosages converge. Apparently, chlorination of humic acid solutions only results in the formation of chlorinated humics yet does not change the adsorptive properties of these compounds significantly.

In Figure 7, UV absorbance has been used as an indicator of organic matter in the solutions. As a result of prechlorination, the isotherms show steeper slopes at higher initial chlorine dosages indicating less adsorption of UV-absorbing organics onto carbon. Because there had been almost no influence of the chlorine concentration on the DOC isotherms, this effect might be due to the fact that chlorine will react preferably with a small fraction of humics which are highly effective in UV absorbance and strongly adsorbable. Apparently the increasing slopes at high equilibrium concentrations are attributable to less reactive but well adsorbable matter.

The isotherms for the adsorption of chloroform are shown in Figure 8. As expected from the first column test, carbon LSS exhibited higher loadings than F300. These somewhat surprising results can be explained by assuming that competitive adsorption takes place at the carbon. While strongly adsorbable compounds in the humic acid solution account for the very effective DOC removal by carbon F300, this fact inversely lowers the extent of adsorption of less adsorbable substances such as chloroform.

Second Column Test

Isotherms obtained under identical conditions using the same test solutions for the two carbons can be quickly and conveniently compared with each other to reveal their relative advantages. However, granular carbon columns are dynamic systems, thus, not only are the equilibrium adsorption properties of the carbon important but also the adsorption rates. Furthermore, it is not possible to use batch tests for measuring the potential effect of biological activity which may occur in a column. Therefore, in most cases carbon performance has to be determined by pilot tests.

In a second run, the pilot plant was operated from January to October 1978 under almost the same conditions as in the first run. The chlorine to ammonia ratio was in this case held constant at 5:1 by weight, thus producing chloramine only. This

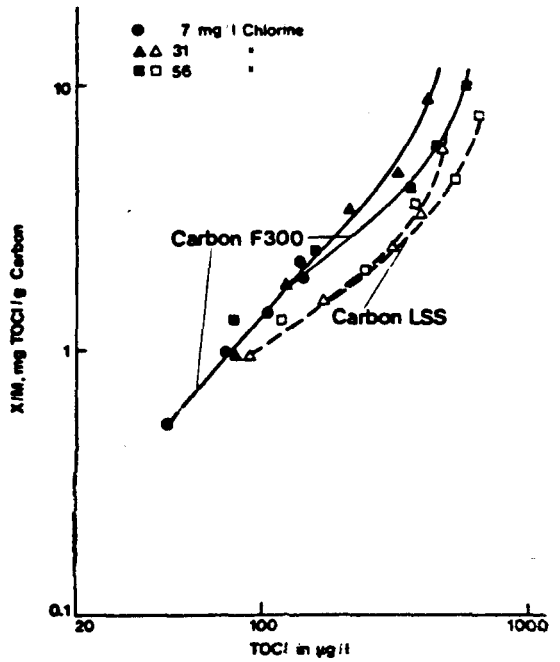

Figure 6. Batch Adsorption Isotherms of TOCl from a Chlorinated Solution of Humic Acid

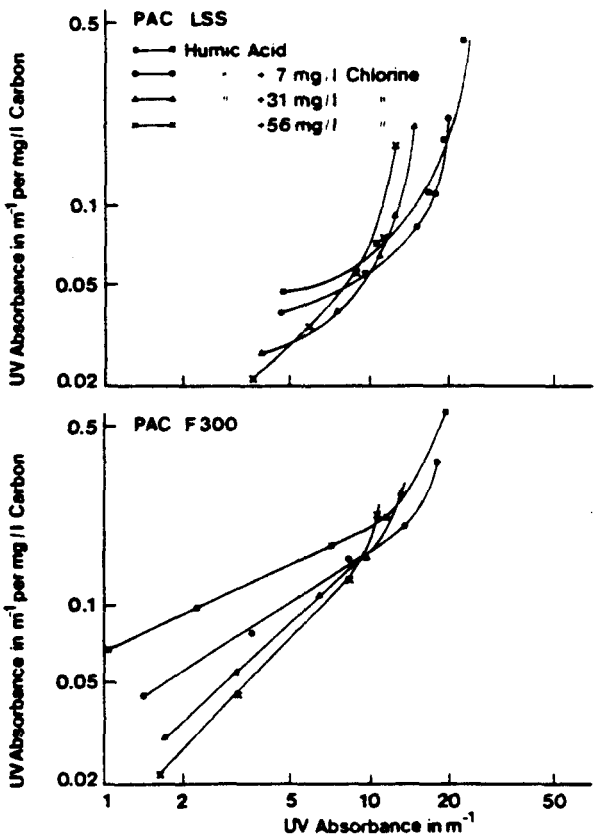

Figure 7. Batch Adsorption Isotherms of UV Absorbance from a Chlorinated Solution of Humic Acid

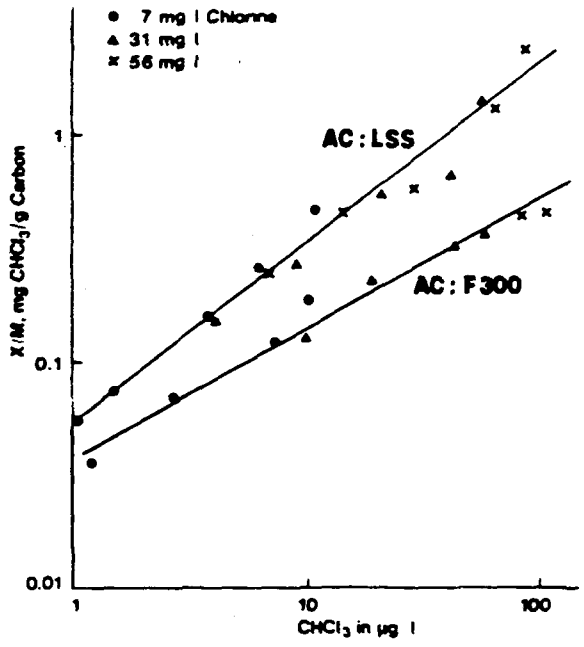

Figure 8. Batch Adsorption Isotherms of Chloroform from a Chlorinated Solution of Humic Acid

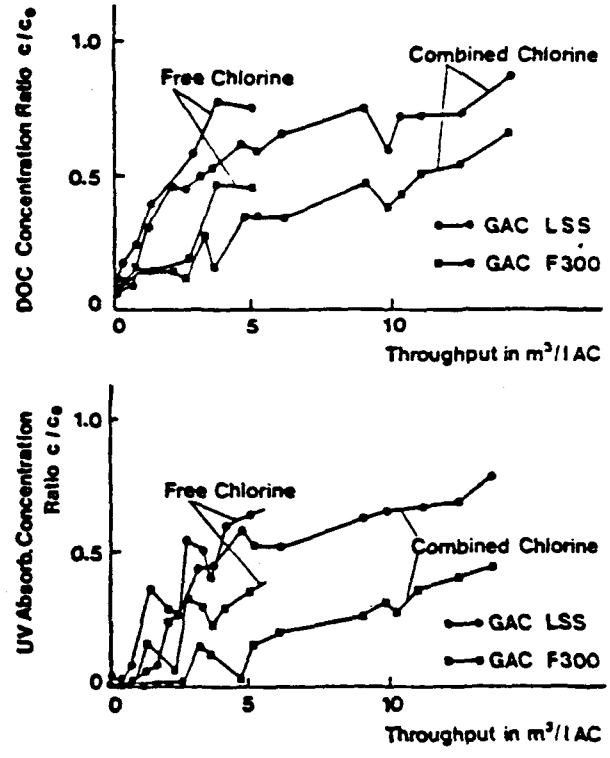

Figure 9. DOC and UV Absorbance Breakthrough Curves for Carbon after Breakpoint Chlorination Compared with Breakthrough after Chlorination below the Breakpoint

was in contrast to the first pilot test run where breakpoint chlorination had been used.

Average values of plant operation data are shown in Table 3. While DOC and UV absorbance removal by chlorination and clarification vary only slightly from the results of breakpoint chlorination (shown in Figure 1), ammonia concentration only decreases from 1.4 to 0.9 mg/l in the clarifier effluent. As expected from the batch tests, the concentration of chlorinated organic compounds is markedly lower than the corresponding values for the first test period.

Table 3

Average values of DOC, UV Absorbance, Ammonia, Haloforms and TOCl during the First Test Period (Chlorination below the Breakpoint)

Parameter	Raw Water	Clarifier Effluent
DOC [mg/l]	3.9	3.2
$UV_{254\ nm}$ [m^{-1}]	7.8	5.2
NH_4^+ [mg/l]	1.4	0.9
$\Sigma CHCl_3+CHBrCl_2$ [µg/l]	0.3	5.6
TOCl [µg/l]	30	80

In Figure 9, the relative performances of the two carbon filters are illustrated for both runs in terms of DOC and UV absorbance removal as a function of throughput. One can see that there are apparent differences in performance of the two carbons. Consistent with the isotherm data, F300 exhibits greater capacities for organic matter than LSS. It is also apparent that, compared to the first run, the life-time of the carbon beds is prolonged by about 150 percent. This effect is attributable to biological activity in the carbon beds. Although free chlorine reacts very rapidly with carbon, and residual chlorine is not likely to penetrate the bed very far, bacterial growth cannot be expected because high concentrations of chlorinated matter are formed by breakpoint chlorination which are almost non-biodegradable. Further evidence of microbial action

during the second test was indicated by the complete disappearance of ammonia and oxygen from the effluent within a few weeks.

The corresponding TOCl values are presented in Figure 10. Obviously more reduction of chlorinated organic compounds is achieved by GAC F300 than by GAC LSS. Depending on factors like concentration of combined chlorine and concentration of organics in the raw water, the TOCl of the clarifier effluent exhibits considerable variations throughout the period of study. This is also reflected in the effluent of the carbon columns.

In Figure 11, chloroform concentrations and relative performances of the applied carbons are plotted against the throughput. In contrast to the findings mentioned above, but in accordance with the results of the first run and with the isotherm tests, the efficiency of GAC F300 is lower than of LSS. A somewhat surprising observation is the existence of periods where the effluent concentration of the carbon beds exceeds the influent concentration. These phenomena are attributable to competitive adsorption processes between chloroform and organic matter in the water. This effect is especially strong in the case of carbon type F300 which exhibits such effects at low influent concentrations of chloroform. Presumably chloroform is displaced by humic substances; carbon type F300 was shown to be very effective for the removal of total organic matter.

CONCLUSIONS

The conclusions which can be drawn from these results are as follows:

- The formation of chlorinated organic compounds can be minimized by chlorine dosages below the breakpoint, resulting in chloramines only.

- Based on the measurement of DOC and TOCl isotherms, the effect of initial chlorine concentration on the adsorption of humic material onto activated carbon is almost non-existent. The better efficiency observed in the second pilot test using chlorine concentrations in small amounts below the breakpoint is due to biological activity within the carbon filters.

- The relative efficiencies of the carbons, as indicated by column tests, correspond to the results of the isotherm test. The data show that it is very important to know the objective for which the carbon is to be used in order to choose the best quality carbon.

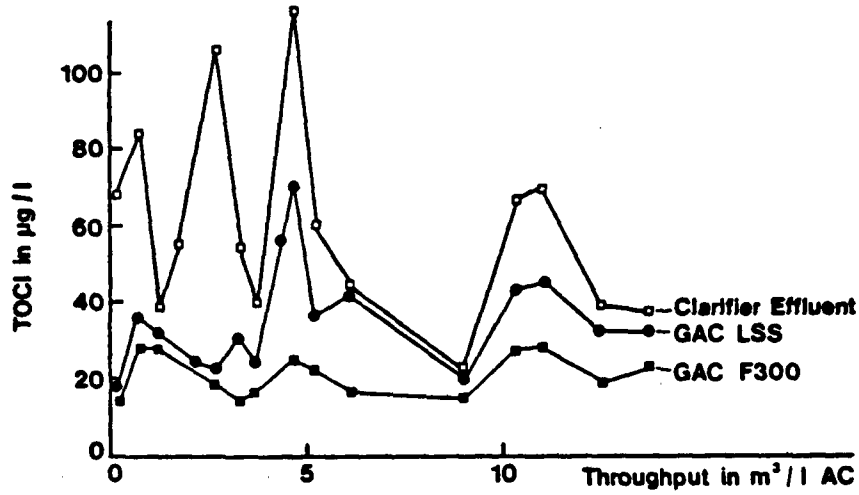

Figure 10. TOCl Values at Various Treatment Stages after Chlorination of River Neckar Water below the Breakpoint

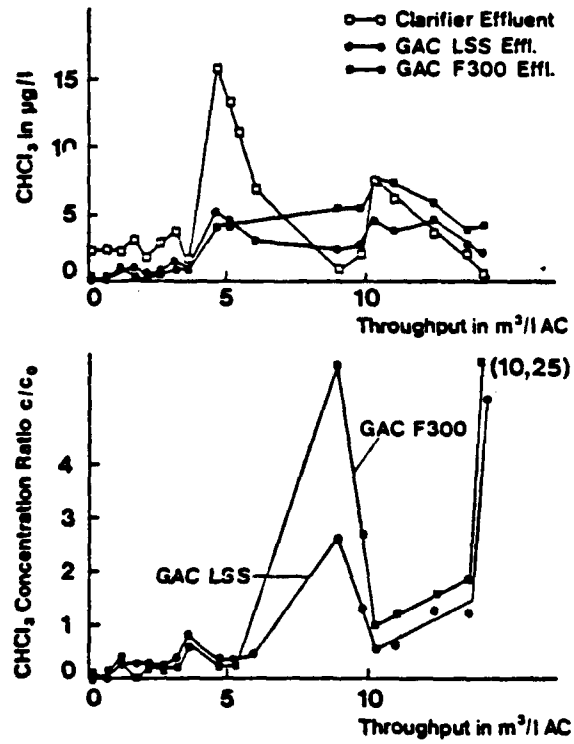

Figure 11. Chloroform Concentrations at Various Treatment Stages and Chloroform Breakthrough Curves for Carbon after Chlorination below the Breakpoint

- The results clearly indicate that a combination of low dosage chlorination and biological action within granular activated carbon filters will induce the removal of ammonia and organics and will lead to a much better quality of the water than when using breakpoint chlorination.

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Removal of Purgeable Organic Chlorine Compounds by Activated Carbon Adsorption

B. Fokken
and
R. Kurz

The increasing demand for drinking water in the city of Cologne could no longer be met solely by ground water resources. A group of wells was placed in a meander of the Rhine River south of Cologne in order to draw bank-infiltrated ground water from the river. Geohydrological conditions at that location assure that the pumped raw water is mainly bank-infiltrated water from the Rhine River. The relatively long underground passage, of about 600 m, provides significant pretreatment of the river water.

Biological Growth

After commissioning the wells, it was noticed in 1969, that the number of microorganisms which form a gelatinous substance, strongly increased in both wells and pipes.

In order to design treatment facilities, tests were performed with a pilot filter. The experimental results showed that there was a substantial increase in filter head loss after a short time of filter run due to the slimy biological growth. Further investigations became necessary to identify and safely control the problem-causing bacteria.

The bacteria were identified to be of the following species: Sphaerotilus natans or Sphaerotilus discophorus, as well as a variation of Pseudomonas fluorscens. The first two organisms appear to grow rapidly in activated carbon filters under typical water treatment conditions. They cause a typical slimy coating of strands as shown in Figure 1.

In the experimental stage, chlorine was applied to kill the bacteria. While a concentration of 3 g/m^3 chlorine could not stop the growth, complete kill was achieved with concentrations above 5 to 6 g/m^3 chlorine.

The existing fibre structure was almost completely destroyed so that the remaining tiny particles which entered the filter did not cause any measurable increase in filter head loss. After

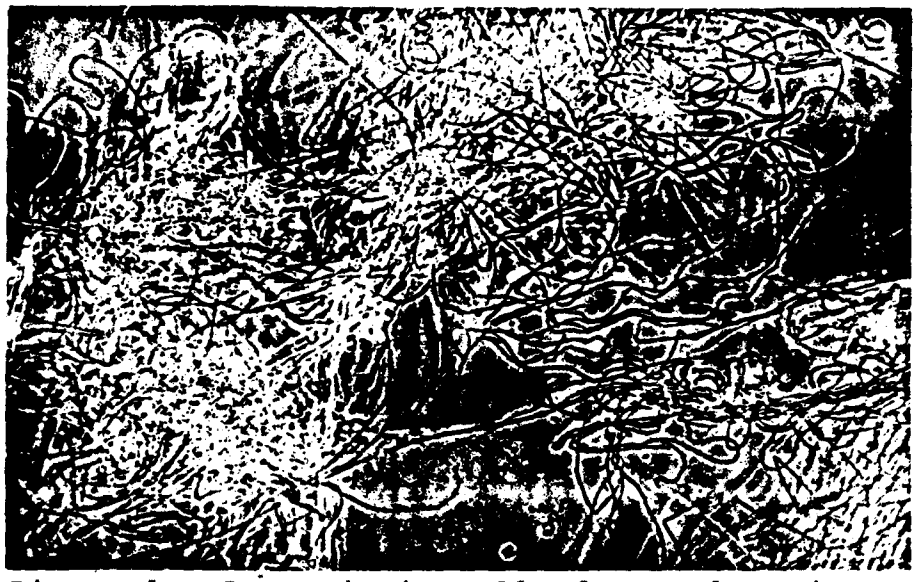

Figure 1. Bacteria in Wells for Reclamation of Bank-infiltrated Ground Water

	River Rhine	Bankinfiltrated Ground Water before Chlorination	Bankinfiltrated Ground Water after Chlorination
UV-Extinction 254 nm in m^{-1}	8,5 ± 1,0	1,4 ± 0,2	1,3 ± 0,1
DOC (g/m^3)	4,4 ± 0,6	1,1 ± 0,2	1,1 ± 0,2
$CHCl_3$	6,5 ± 3,4	0,50 ± 0,1	0,64 ± 0,1
$CHCl_2Br$	–	–	1,6 ± 0,3
$CHClBr_2$	–	–	2,8 ± 0,6
$CHBr_3$	–	–	2,9 ± 0,8
CCl_4	0,47 ± 0,6	0,16 ± 0,1	0,16 ± 0,1
C_2-Cl_3H	0,30 ± 0,2	0,60 ± 0,1	0,61 ± 0,1
C_2-Cl_4	0,31 ± 0,3	1,60 ± 0,1	1,6 ± 0,1
	Halocarbon Concentrations in mg/m^3		

Table 1. Influence of Bank Infiltration and Chlorination on Concentrations of Different Substances

treatment facilities with activated carbon filters had been installed in the water works of Hockirchen, the system was chlorinated with the same high concentrations that were administered during the experimental tests. When operating the plant it turned out that the growth could also be prevented by smaller chlorine concentrations in the raw water.

Under today's delivery and treatment conditions, it is sufficient to have a chlorine concentration of 1 g/m^3 at the beginning of the supply system. This chlorinate reacts with the precursor organic substances and causes an increased formation of chlorinated organic compounds. The organic carbon concentration is about 1.1 g/m^3. Tests showed that bank infiltration removes part of the chlorinated organic compounds that occur in the river water. Chlorination, however, produces these compounds again in even much higher concentrations.

Bank Filtration

Data characterizing the Rhine River water and the bank filtrate before and after chlorination are shown in Table 1. One can clearly see the removal capacity of the filtration path with regard to the UV-extinction and dissolved organic carbon (DOC). Furthermore it can be stated that chloroform and carbon tetrachloride are extensively retained by the subsoil, while tri- and tetrachlorethylene increase. It is remarkable that due to chlorination the brominated organics monobromodichloromethane, dibromochloromethane, and bromoform are formed. This can be explained by the bromide concentration of about 0.2 g/m^3 in the bank filtrate: the added chlorine reacts with bromide ions to form bromine, which then reacts rapidly with the existing organic compounds.

In a series of bench tests, 2 g/m^3 of chlorine were added to bank infiltrated ground water; a second series of tests were conducted under identical conditions, except that bromide was dosed to a concentration of 1 g/m^3. Figure 2 shows the corresponding curves of the haloform development. The curves with solid symbols represent the haloform development provided by a natural bromide content of 0.2 g/m^3. The addition of bromide promotes the formation of bromoform, but retards the development of bromochloromethane compounds. Bromochloromethane compounds develop better in water with a low concentration of bromide, but the chloroform concentration (not shown in Fig. 2) varies little in both series of tests. After a 24 hour reaction period, the haloform concentration is 11 mg/m^3 with natural bromide content and 20.5 mg/m^3 if bromide is added. This result indicates that an intensified formation of haloform is to be expected if bank infiltrated ground water has an increased concentration of bromide.

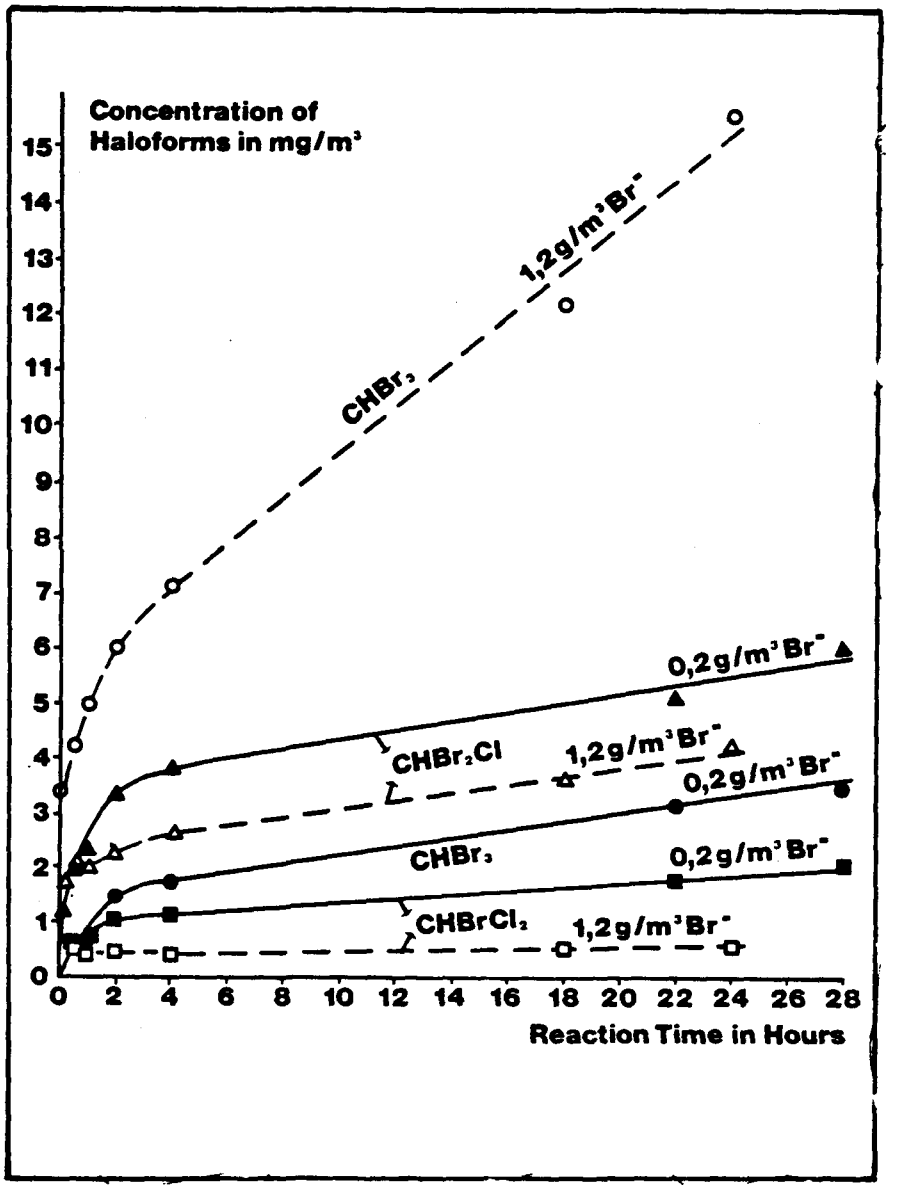

Figure 2. Influence of Different Bromide Concentrations on the Formation of Haloforms

Adsorption of Organic Substance and Chlorinated Organic Compounds

Because of the high chlorine loading and the content of odour- and taste-intensive substances, treatment of the bank-infiltrated ground water with activated carbon is required. In a research program sponsored by the Ministry for Research and Technology of the Federal Republic of Germany, the adsorption of haloforms by activated carbon in the presence of other organic substances was studied. Three kinds of activated carbons used in filtration plants were tested: ROW-08-S, LSS, and LEV 693. As the isotherms of the UV-absorbing organic sustances in Fig. 3 show, the activated carbon ROW-08-S is best qualified to remove these substances. A maximum load of 0.3 g organic substances in water (OSW) per g activated carbon may be achieved for ROW-08-S with extrapolation of the isotherms to an inlet concentration of 1.3 g/m^3. In LSS the maximum load is 0,16 g OSW per g activated carbon, under the assumption that an extinction unit of one m^{-1} at 254 nm is equated with a concentration of 1 g organic substances per m^3.

The breakthrough curves of the filters in Fig. 4 demonstrate a behaviour which is similar to that of the isotherms. That means it should be possible to describe the breakthrough curves of the filter for UV-active organic substances by the adsorption isotherms. Martin (2) provided a method based on the assumption that the filter is a totally mixed vessel in equilibrium. However, the breakthrough curves for a filter in equilibrium which were achieved by this approach have to be adjusted to the actual observations by a system calibration factor, since kinetics also play a part in an ordinary carbon filter. Preliminary experiments with a pilot filter showed that the breakthrough curves at several layer depths could indeed be calculated by an adjustment at only one point. As had been expected, the factor was the smallest with the thinnest filter layer.

Fig. 4 also shows that the equilibrium data allow an approximate calculation of the breakthrough curves. So far, however, it is still unknown which parameters could theoretically define the appointed factor; i.e., to what extent does kinetic data of both the carbon and the substances enter this factor. This adjustment is valid only for collective parameters like DOC, UV, and dissolved Organic Chlorine (DOCl) with a sudden abrupt breakthrough.

Haloforms differ widely in their solubility in water. The more bromine they contain, the less soluble these compounds will be in water. This characteristic is also reflected in the equilibrium isotherms of the activated carbon ROW-08-S, shown in Fig. 5. At the same equilibrium concentration, the load of this activated carbon is up to 8 times higher with bromoform than with chloroform. If the adsorption in the filter is mainly determined by the position of the isotherms, it has to be expected that

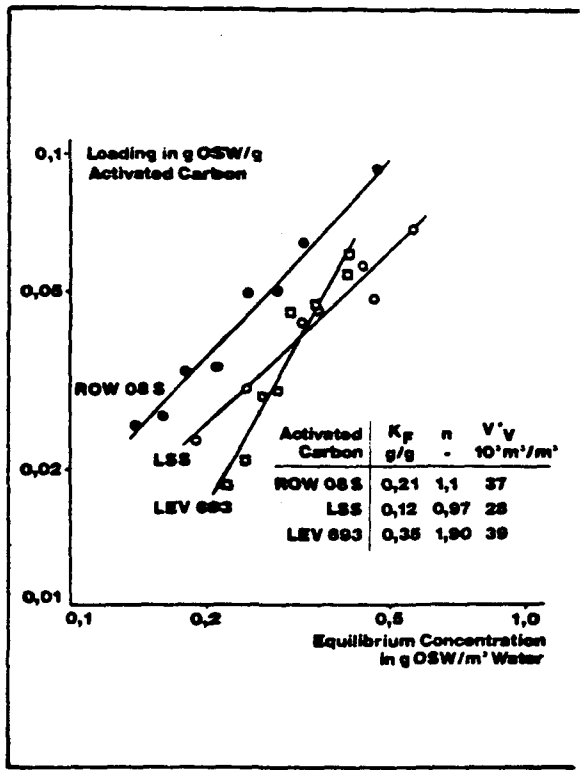

Figure 3. UV-equilibrium Isotherms of Organic Substances in Water for Different Activated Carbons

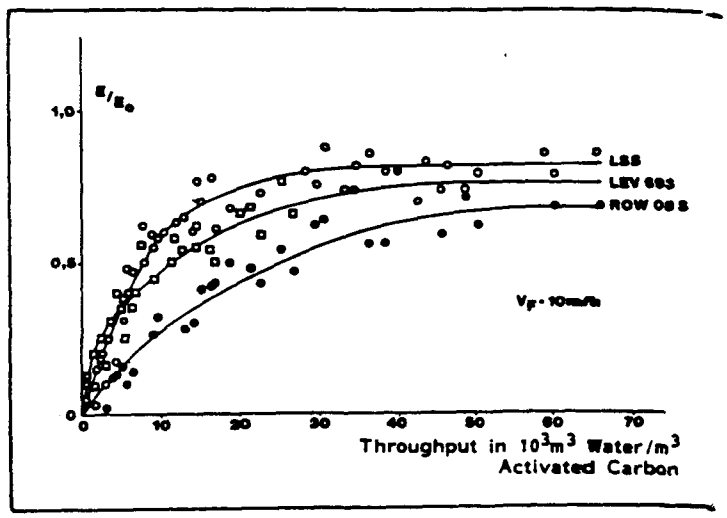

Figure 4. UV-breakthrough Curves for Different Activated Carbons

chloroform breaks through prior to bromochloromethanes. This is confirmed by the measured filter breakthrough curves, shown in Fig. 6. Note the areas (lobes) of the breakthrough curve above $C/C_o = 1$. The chloroform lobe can be accounted for with the explanation that chloroform is displaced by more strongly adsorbed substances, so that higher concentrations appear in the filter effluent than in the filter influent. These lobes are of much smaller magnitude with monobromodichloromethane and dibromochloromethane and might also be traced back to the reaction of excess bromine and chlorine with the activated carbon. With tetrachlorethylene, the filter still removes 75% of the applied concentration after a load of 60,000 m^3 water per m^3 activated carbon. This is mainly due to the low aqueous solubility and the nonpolar nature of this compound. It also turns out that the slope of the filter breakthrough curves can be determined by the position of the isotherms.

The lobe of the chloroform concentration is believed to be caused mainly by displacement. Fig. 7 shows breakthrough curves of chloroform for various filter layers. It can be seen that, as the filter depth is increased, the breakthrough of chloroform indeed occurs later, but the lobes are much more distinct. Based on these results it can be concluded that relatively high chloroform concentrations (i.e., almost twice as much as observed in the filter inlet), may be encountered in the filter discharge. To avoid this problem, the filter run length of those filters with large bed depths, as typically used in major filtration plants, should be controlled by the breakthrough of chloroforms. Merk (3) has proposed that the maximum lobe can be calculated for binary mixtures by simulations based on the isotherms of both the displaced and the displacing substances, since kinetic effects are negligible. However, the displacing substances are generally unknown in filter breakthrough curves for a natural raw water, so that at best an approximate calculation might be possible under certain assumptions. In binary mixtures the displacing substance is characterized by a better adsorption behavior so that higher loads compared to the displaced substance can be reached at a given equilibrium concentration.

Different qualities of activated carbon show different breakthrough characteristics of chloroform, as can be seen in Fig. 8. Type LSS, for example, which provides far better removal rate of organic chlorine compounds, shows only a small lobe, whereas higher outlet than inlet concentrations occurred with types LEV 693 and ROW-08-S. If reactivation is required when 50 percent of the chloroform breaks through, the maximum allowable throughput ratio is 7,000 m^3 water per m^3 activated carbon for LEV 693, 14,600 m^3/m^3 for ROW-08-S, and 20,000 m^3/m^3 for LSS. These relative capacities reverse with simultaneous removal of UV-active substances; i.e., LSS has a much smaller capacity for UV-active organic substances than ROW-08-S.

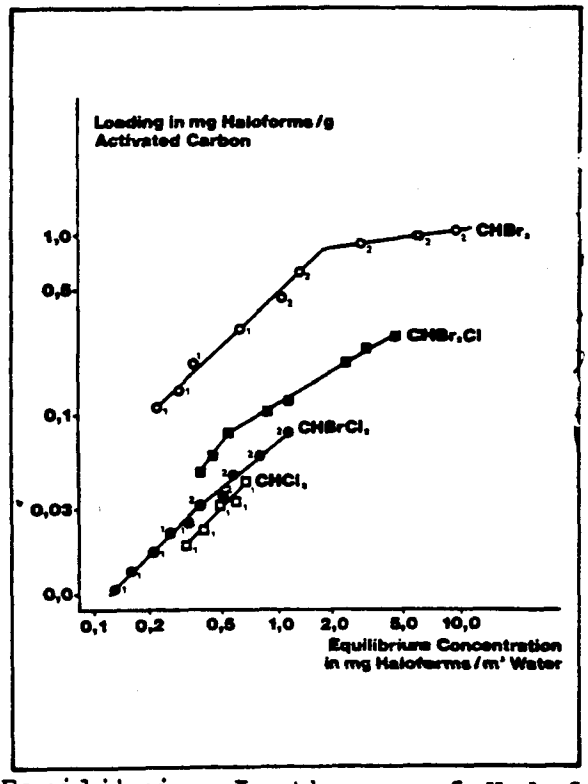

Figure 5. Equilibrium Isotherms of Haloforms for the Activated Carbon, Norit ROW-08-S

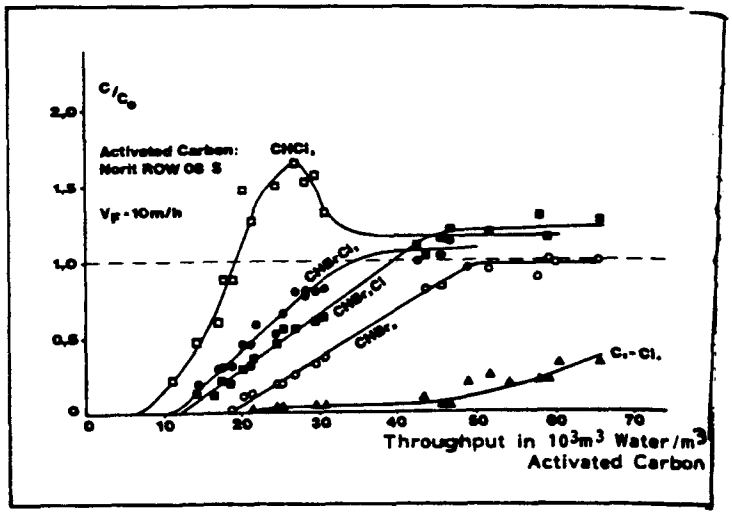

Figure 6. Breakthrough Curves of Different Haloforms and Tetrachlorethylene for the Activated Carbon Norit ROW-08-S

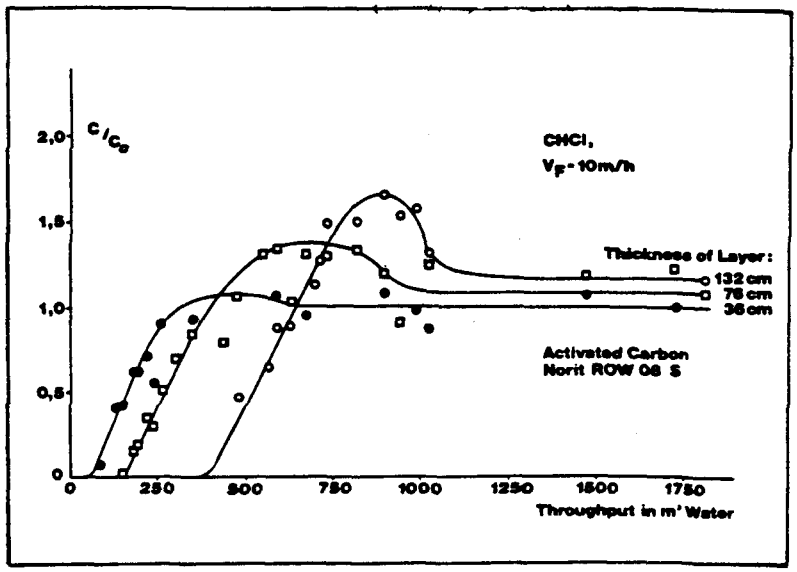

Figure 7. Breakthrough Curves of Chloroform in Different Layers of an Activated Carbon Filter Filled with NORIT ROW-08-S

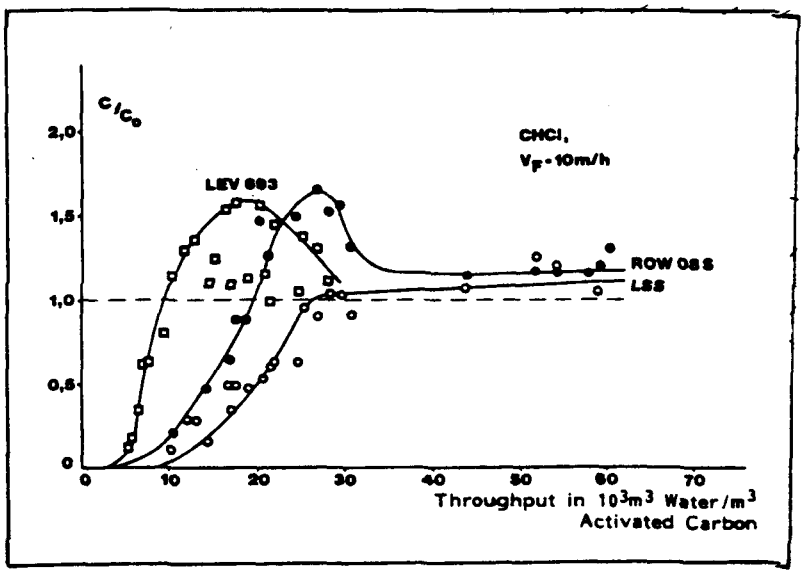

Figure 8. Breakthrough Curves of Chloroform for Several Types of Activated Carbon

Presently we do not know of a carbon which effectively removes haloforms as well as total organic substance (TOC).

Judging by the position of the isotherms for dibromochloromethane, shown in Fig. 9, it can be said that LSS adsorbs this compound much better than the activated carbons ROW-8-S and LEV-693. Furthermore, it can be inferred from the isotherms that certain maximum loads can be reached with a filter in equilibrium. Under the existing conditions an effect of displacement occurs in ROW-08-S, indicated by the negative slope of the isotherm. The corresponding breakthrough curves in Fig. 1 demonstrate that a lobe also occurs in the filter effluent of ROW-08-S, which is not observed with type LSS. Using previously made kinetic measurements, filter breakthrough curves of haloforms probably can be described by film diffusion if the position of the equilibrium isotherms is taken into consideration. This assumption is strengthened by the fact that the available surface area (4) of the individual activated carbon correlates with the existent isotherms.

An investigation of the maximum possible filter load, which can be calculated from the breakthrough curves presented, revealed that ROW-08-S and LEV-693 nearly attained the equilibrium load; in the case of LSS, the equilibrium load deviated extremely from the actual load of LSS. If, on the other hand one compares the load of dibromochloromethane calculated from the filter data with the equilibrium loading determined in laboratory tests, then it appears that the smaller the final load, as calculated from the equilibrium data, the earlier this final load is reached. For example, the load in LEV 693 filter is 0.18 g/kg activated carbon; the equilibrium load, however, could reach 0.36 g/kg. In an LSS filter, the possible equilibrium load is 1.42 mg/kg, but the load reached in the filter is only 0.37 mg/kg.

The only explanation for these results is that there is a mixed-solute system in equilibrium as far as the isotherms are concerned, whereas fronts of loaded and unloaded zones prevail in the filter. Hence, an intensified adsorption of various compounds can partially take place due to their better kinetics, so that in the various filter layers a higher loading can be achieved than could have been expected based on equilibrium assumptions.

As is shown in Fig. 11 for UV-absorbance, the processes in the filter have to be described by both the equilibrium and the kinetics. Hence, it appears that at a high filtration rate of 20 m/h, the breakthrough occurs earlier than at 10 m/h. The worse breakthrough behaviour at 5 m/h may be explained by kinetic effects; i.e., substances that are slowly but strongly adsorbed may have displaced UV-active substances.

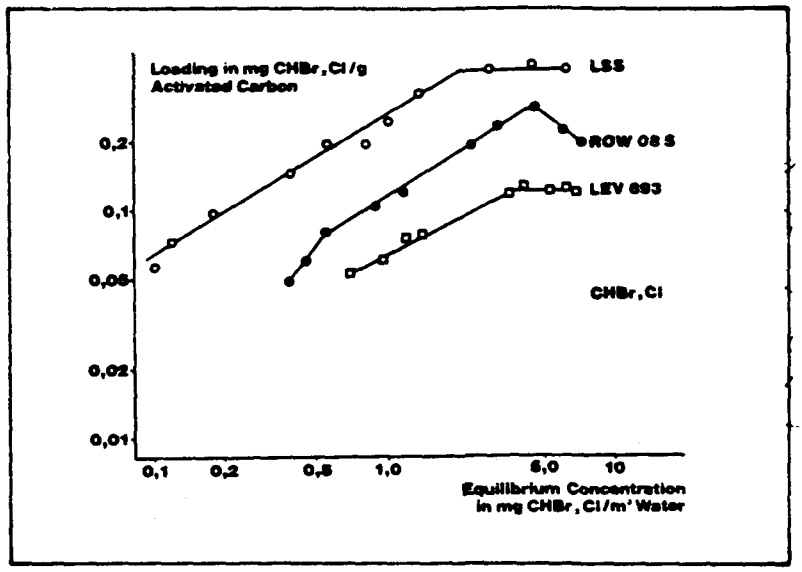

Figure 9. Equilibrium Isotherms of Dibromochloromethane for Different Activated Carbons

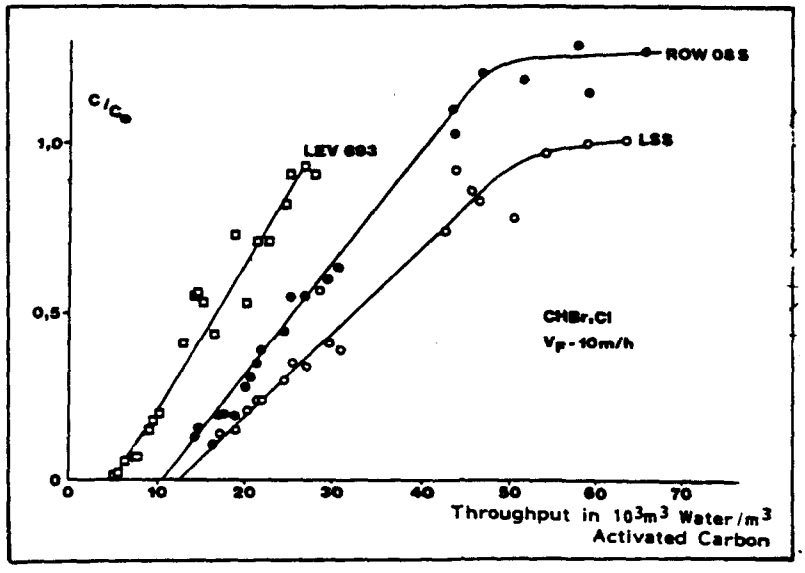

Figure 10. Breakthrough Curves of Dibromochloromethane for Different Activated Carbons

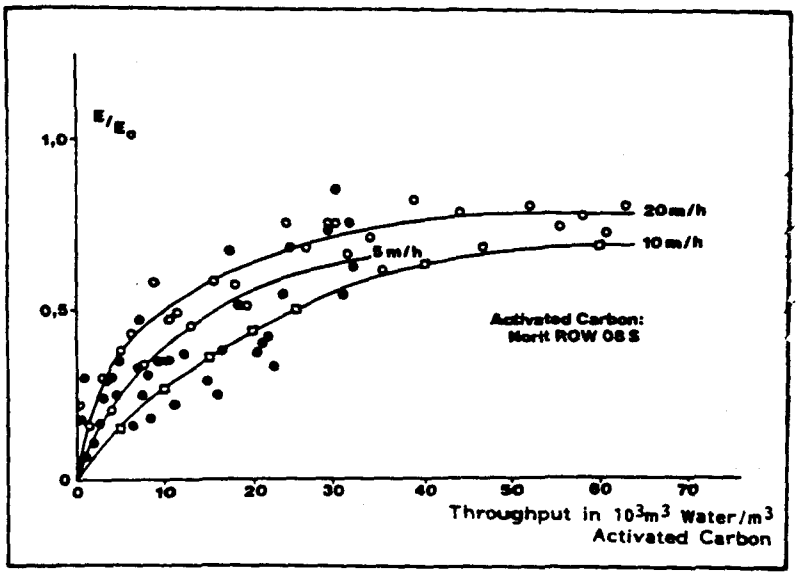

Figure 11. UV-breakthrough Curves for Different Filtration Rates

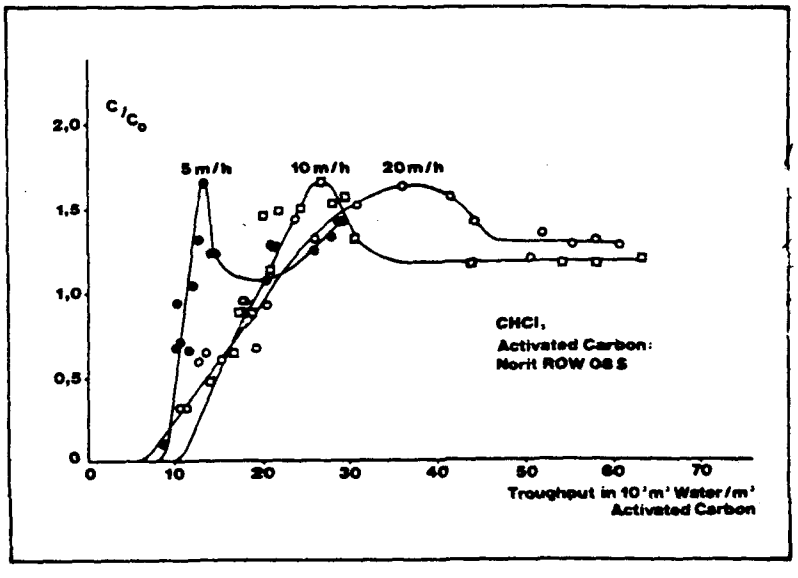

Figure 12. Breakthrough Curves of Chloroform for Different Filtration Rates

This theoretical assumption is confirmed by the breakthrough curves of chloroforms in Fig. 12. Here, the chloroform is also the first which breaks through at a filtration rate of 5 m/h, whereas the various slopes of the breakthrough curves at 10 and 20 m/h can be related to the increased filtration rates. The lobe of the discharge concentration of chloroform which is reached by an increased throughput can again only be explained by kinetics. The results with the various filtration rates are still to be analysed in detail, as existing explanations of their behavior are not completely satisfying.

Summary

Tests were performed on the adsorption of organic substances in activated carbon filters. It was found that the removal of purgeable organic compounds is possible by using ordinary activated carbons as used in major filtration plants. However, due to displacement effects, higher concentrations of haloforms than had been found in the raw water, especially chloroform, may show up in the drinking water. It was also observed that activated carbons, which guarantee an optimum removal of the UV-absorbing organic substances, are not necessarily most effective in removing haloforms. Due to the short filter run because of chloroform breakthrough, it is necessary to change the treatment scheme so that the formation of chlororganic substances (notably haloforms) can be diminished or avoided before the water enters the activated carbon filters. To solve these problems further research will be required.

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REMOVAL OF HIGHER MOLECULAR WEIGHT ORGANIC COMPOUNDS BY THE GRANULAR ACTIVATED CARBON ADSORPTION UNIT PROCESS

A. A. Stevens, D. R. Seeger
J. DeMarco and L. Moore

ABSTRACT

The granular activated carbon adsorption unit process in drinking water treatment typically removes purgeable organic compounds for time periods on the order of a few weeks. Experimental evidence indicates that less volatile compounds of generally higher molecular weight than the purgeable fraction, but still detectable by gas chromatography, are efficiently removed for longer periods. Field data substantiate this. Explanatory mechanisms may include stronger adsorption affinities or biodegradation. Non-gas chromatographable, higher molecular weight materials such as humic acids, as measured by Total Organic Carbon (TOC) or trihalomethane formation potential revert to lower removal efficiencies. Biodegradation may be responsible for a continued long term removal of a fraction of these materials.

INTRODUCTION

A summary of the available literature regarding the usefulness of the granular activated carbon (GAC) unit process for removing specific organic compounds from drinking water supplies has been compiled by Symons (1). Although some acknowledged analytical weaknesses existed in the overall data base at that time, the conclusion was confidently drawn that GAC is correctly described as a broad spectrum adsorbent for removal of organic compounds from water. Symons' review acknowledged a spectrum of removal efficiencies for the compounds, as measured by gas chromatography, in the studies. Further, and as a general rule, in the studies described, compounds that eluted late during the gas chromatographic analysis were generally better removed than the more volatile, early eluters.

The elution order of compounds in a gas chromatograph is closely related to volatility, and that factor is related inversely to molecular weight in that, within a homologous series,

as molecular weight increases, volatility decreases. Thus, from the gas chromatographic evidence available from broad spectrum adsorption studies, a favorable relationship between adsorbability and increasing molecular weight seems to exist. Of course, other factors are much more important in influencing adsorption, such as solubility and polarity of the compound, than volatility or molecular weight, per se. Increasing molecular weight within a homologous series simply influences these parameters in a favorable way as to improve adsorption, thus explaining in a general way the apparent relationship between gas chromatographic retention times, molecular weight, and adsorbability. Of course, very high molecular weight substances that will not pass through a gas chromatograph do not fall into this category and, therefore, this generalization cannot be made about that class.

On-going work by the U.S. EPA Laboratories, their grantees, contractors, and many others worldwide has been focusing on further investigation of the effectivenes of GAC for removal of organic contaminants, both disinfection by-products and synthetic organic contaminants from drinking water supplies. Early results from some of these studies plus information available from the literature (1), have given the U.S. EPA cause to propose the required use of the GAC unit process as the best broad spectrum approach to control synthetic organic contaminants in certain vulnerable supplies (2). Recent data from pilot and full-scale adsorbers has indicated, however, that certain volatile halogenated organic compounds, generally common solvents conveniently measured at the same time as trihalomethanes, are often present in relatively high individual concentrations and are somewhat poorly removed by GAC or are efficiently removed for only short perids of time.

Because of the analytical convenience of measuring these volatile organohalides, they are monitored with greater frequency and quantitative accuracy than the multitude of other synthetic organic contaminants that can be found in certain drinking waters (approximately 460 compounds in one tap water sample alone) (3). Because of this, the noted early breakthrough of these few individual compounds tends to cause underestimates of the capacity of the GAC unit process to protect the consumer from synthetic organic contaminants in general.

Much can be determined on a laboratory scale, about the equilibrium capacities of GAC for certain individual compounds with or without the influence of competing species. Equilibrium and kinetic studies, both static and dynamic, can be used to model the adsorption behavior of compounds in continuous flow dynamic systems. Beyond the subjects of adsorption capacities,

kinetics, and solubility parameters, however, interpretations of field results are always severely complicated by variations of loadings with time, relative loads of different compounds (also varying with time), relative concentrations of substances differing in concentration by several orders of magnitude, and finally, biological activity within the adsorber. Thus, theoretical aspects of adsorption will not be addressed and this discussion will be limited to in-practice observations interpreted under the described inherent limitations.

IN-PLANT EXPERIENCES

Experiences with the removal of specific "higher molecular weight: compounds at a number of U.S. water treatment plants were discussed elsewhere in these Proceedings. Two utilities will be discussed in this paper; both operate full-scale GAC adsorbers that demonstrate particularly well, the usefulness of GAC as a barrier against source water contaminants of "higher molecular weight" contrasted to the GAC's performance for the removal of organohalide solvent co-contaminants.

Additionally, examples of biologically derived removals of trihalomethane precursors and two synthetic organic compounds are presented as examples of protection provided by the GAC unit process beyond that which might be predicted by results of studies of the adsorption phenomenon itself.

MT. CLEMENS, MICHIGAN

The water treatment plant at Mt. Clemens, Michigan is an 8 million gallon/day plant (32,000 m^3/day) employing conventional alum coagulation, settling in a parallel pair of basins, followed by GAC, with a 6.2 min empty bed contact time, installed in a sand replacement mode for taste and odor control. Historically, the GAC has been replaced every 3 years, corresponding to taste and odor breakthrough. During the period of the most recent GAC replacement (beginning April 1978), this Laboratory agreed, on a technical assistance basis, to evaluate the performance of the new GAC for trihalomethane and precursor removal. At the same time, the opportunity was presented to do a more extensive organic analysis to further evaluate the GAC performance.

The analyses employed in the study were: (1) the conventional purge and trap GC with electrolytic conductivity detection in the specific halogen mode for the trihalomethanes and other volatile halogenated compounds; and (2) solvent extraction with methylene chloride of acidified, 1 gallon (3.7 liter) samples, followed by capillary column gas chromatography with flame ionization detection (GC/FID) or gas chromatography with mass spectrometric detection (GC/MS) analysis of the solvent concentrates for measurement or detection of less volatile organic species.

Methyl chloroform (1,1,1-trichloroethane) is a chlorinated solvent frequently found in this utility's source water and is an example of the group of compounds that is poorly removed by GAC. Figure 1 is a plot of the settling basin effluent (GAC influent) and GAC effluent from a single 1 mgd (4,000 m^3/d) filter unit at the Mt. Clemens plant. Note the range of concentrations of 1,1,1-trichloroethane found within the basin all on the same day. This is not an analytical artifact, but reflects the highly variable load of this compound challenging the GAC at this plant, severely complicating any attempt at a concise quantitative assessment of the adsorber's performance. Even given this difficulty, the data in Figure 1 show that the adsorber was ineffective for removal of this compound on the first day of sampling, only 8 days into the run. In fact, the adsorber effluent exceeded the influent on three of the six sampling occasions during the first 120 days of the run, without doubt, reflecting high variations in loadings not detected because of infrequent sampling.

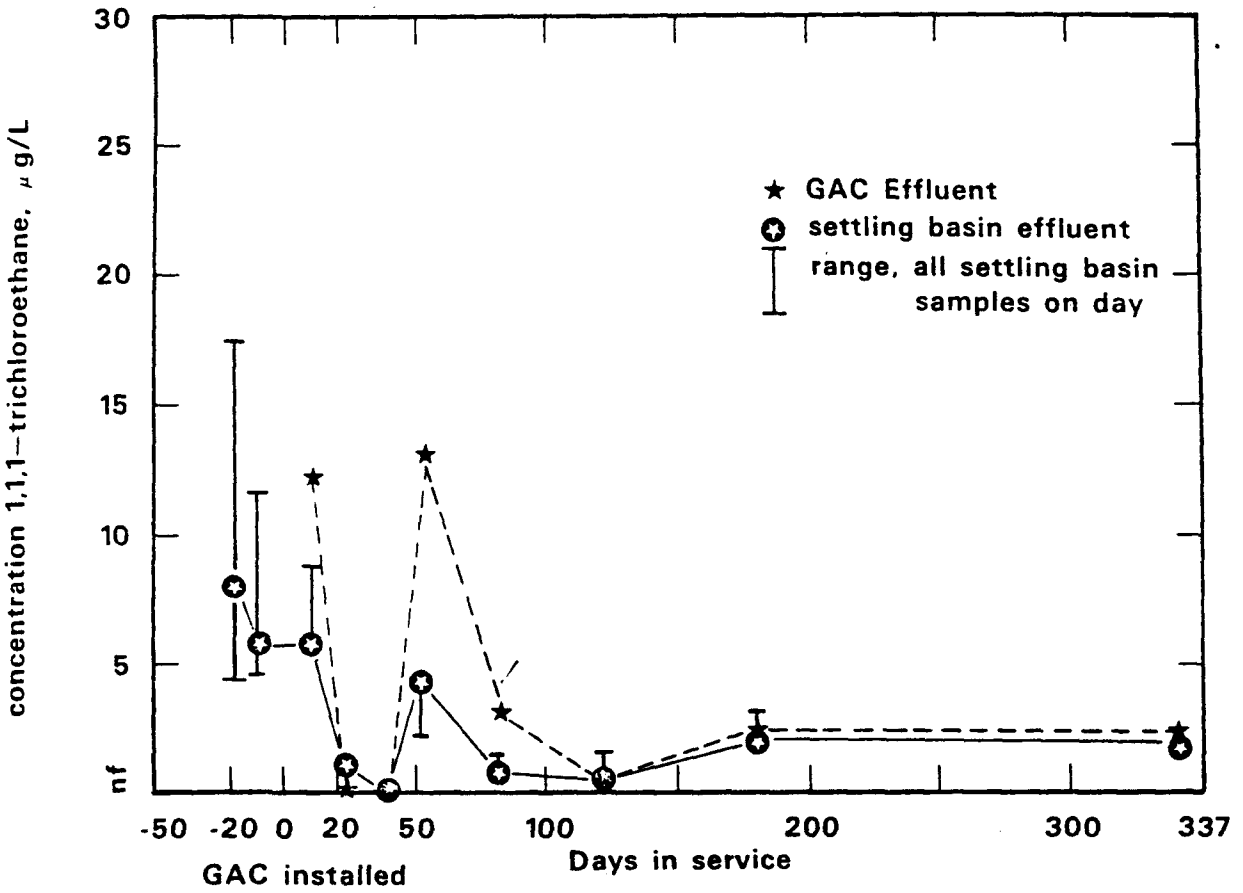

Figure 1. 1,1,1-Trichloroethane Removal at Mt. Clemens, 4/78-2/79

The more extensive analysis performed using capillary column GC/FID, however, demonstrated a contrasting good performance for a group of less volatile compounds. Investigations by capillary GC/MS provide some information as to the nature of these compounds. Some of the compounds that were identified in this analysis have their corresponding peaks labelled in Figure 2. Those with an asterisk are in the solvent or are identified as an artifact of the analytical method and should be ignored. Most important to this discussion is the large unresolved group of compounds whose peaks are simply labelled as hydrocarbons; the retention time of n-$C_{18}H_{38}$ is marked to show that the molecular weight range of these hydrocarbons is mostly above that of $C_{18}H_{38}$ (234). Figure 3 shows a reproduction of the same chromatogram above a corresponding chromatogram generated in an identical manner from a sample of 7 week old GAC modular filter/adsorber unit effluent. The data have been normalized on the internal standard, so, within limits, the chromatograms can be compared with one another quantitatively. For quantitative reference, the internal standard theoretically corresponds to 0.25 µg/l of anthracene. Clearly, the GAC was effectively removing this group of high molecular weight hydrocarbons. At this time, total organic carbon (TOC) reduction through the filter was 43 percent.

After the May 1978 episode, the hydrocarbon contamination did not reappear until February 1979. Recently acquired GC/FID results indicate that at this time, the GAC was still as effective as earlier in acting as a barrier to penetration of the filters by the hydrocarbon materials, even though the GAC was nearly one year old and TOC reductions were found to be down to 16 percent. The recurrence of the contamination has provided an opportunity to follow up and determine the source of contamination. This investigation is now underway.

JEFFERSON PARISH, LOUISIANA

Gas Chromatographable Compounds

The second site is at the Jefferson Parish Water Department, Jefferson Parish, La.; this site was selected as being a particularly good example of a full-scale operating GAC filter module demonstrating contrasting performance for removal of a light halogenated solvent as compared to higher molecular weight compounds. At this location, the U.S. EPA has an ongoing research project to assess the effectiveness of GAC to remove synthetic organic contaminants from the lower Mississippi River water source.

The treatment scheme employs a cationic polymer as a primary coagulant, followed by potassium permanganate addition for taste and odor control, then lime and ferrous sulfate

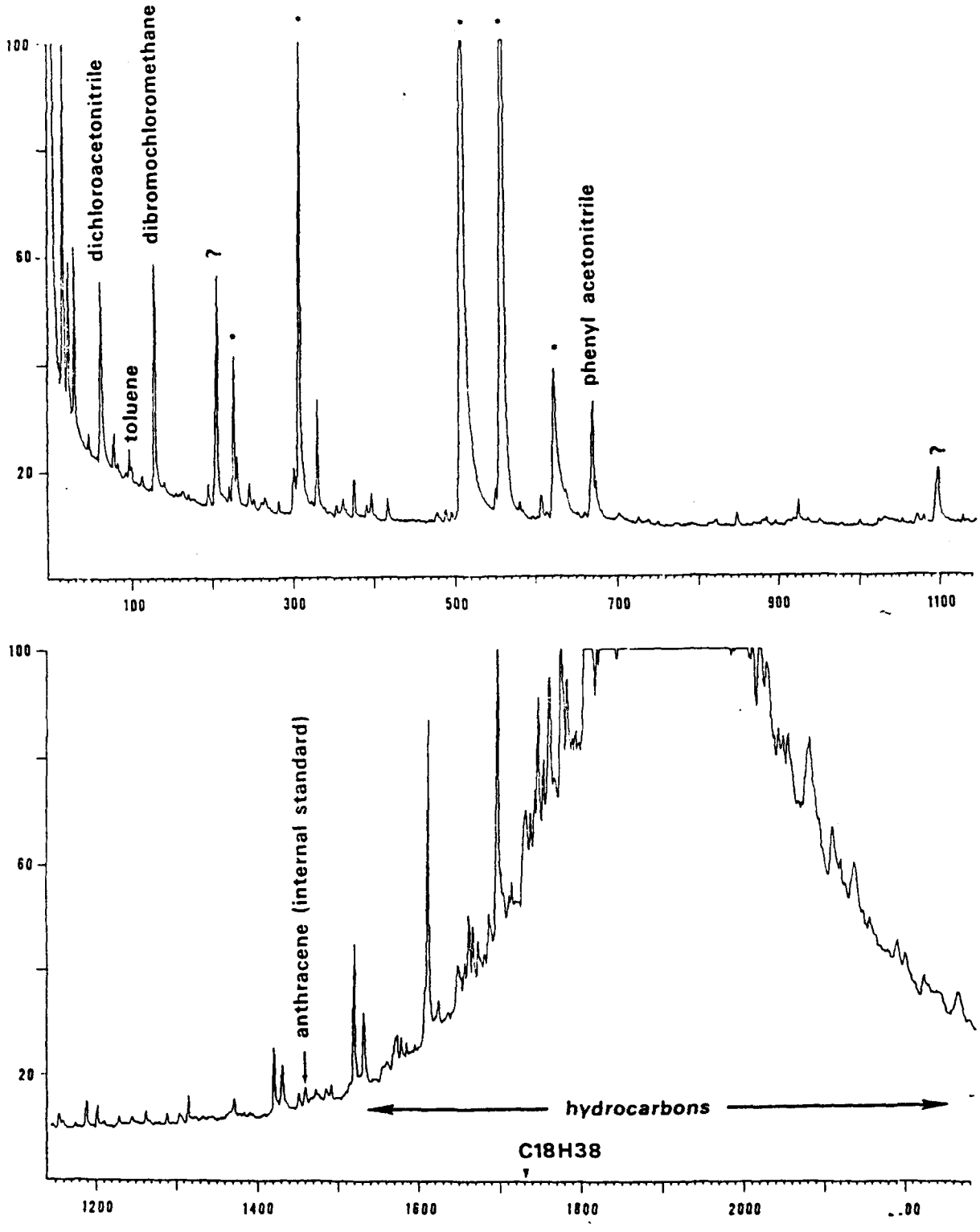

Figure 2. Reconstructed Gas Chromatogram, Setting Basin (Effluent) Mt. Clemens, 5/16/78

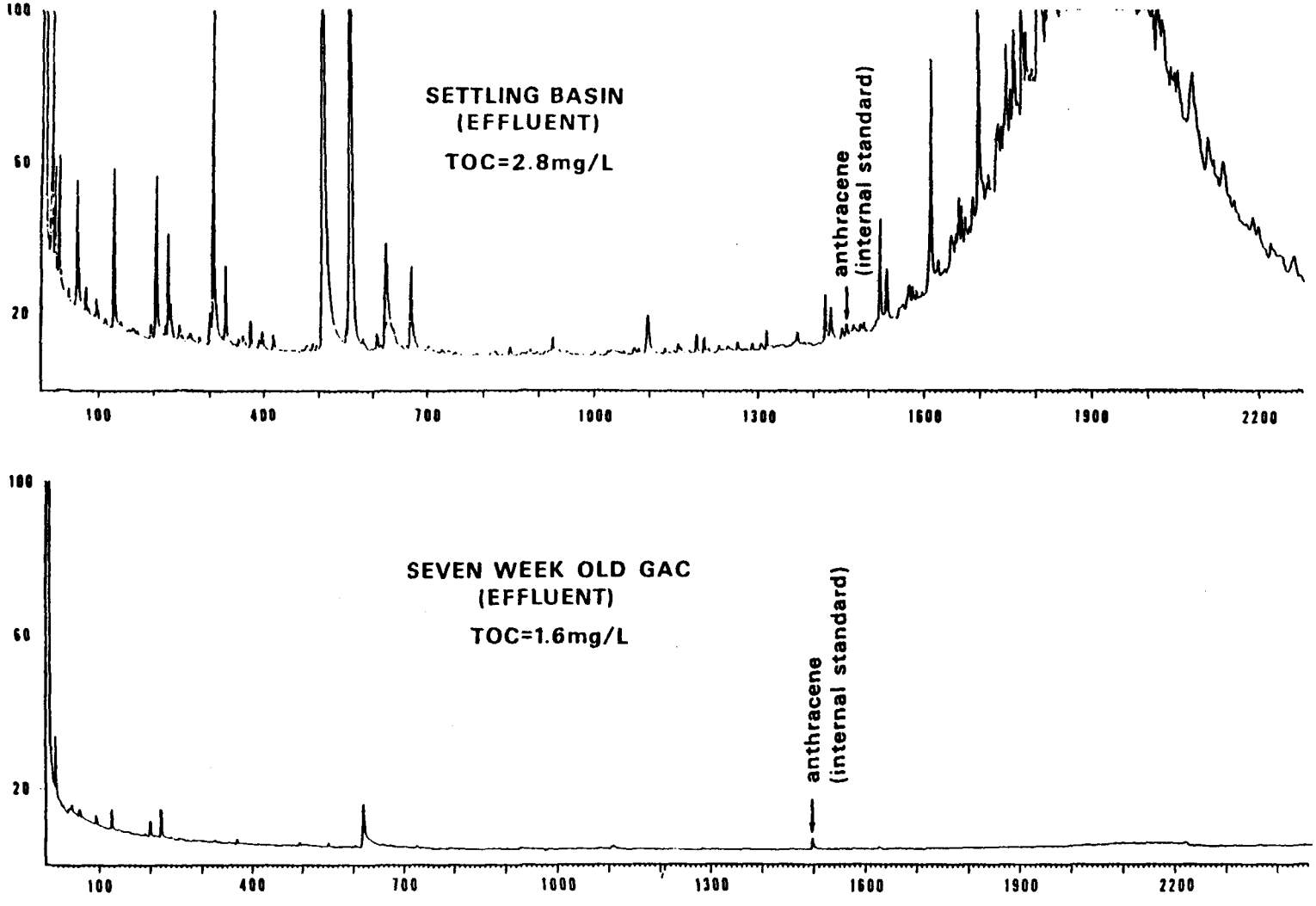

Figure 3. GAC Performance, Mt. Clemens, 5/16/78

addition, upflow clarification, disinfection with combined chlorine, and rapid sand filtration. The experimental scheme at Jefferson Parish included the testing of a single 1 mgd (4,000 m^3/d) sand replacement filter-adsorber and a second, identical module as a post filter adsorber where the adsorber unit was plumbed in series with a remaining operating rapid sand filter. The performance of the post filter adsorber (20 min EBCT) is the subject of this discussion.

Table 1 lists compounds that were of particular interest for treatment studies at Jefferson Parish at the start of the project. For this discussion, the performance of the adsorber for removal of 1,2-dichloroethane will be contrasted with the removal of a group of pesticides, essentially those compounds numbered 14 to 23 in Table 1.

Table 1
Compounds of Interest, Jefferson Parish GAC Study

1.	trichloroethylene	18.	chlordane
2.	p-dichlorobenzene	19.	dieldrin
3.	carbon tetrachloride	20.	endrin
4.	chloroform	21.	DDT isomers
5.	bromoform	22.	DDD isomers
6.	bromodichloromethane	23.	DDE isomers
7.	dibromochloromethane	24.	atrazine
8.	1,2-dichloroethane	25.	diethylatrazine
9.	vinyl chloride	26.	hexachlorobutadiene
10.	tetrachloroethylene	27.	HCB
11.	benzene	28.	toxaphene
12.	toluene	29.	methoxychlor
13.	xylenes	30.	strobane
14.	BHC isomers	31.	PCB's
15.	lindane	32.	phthalates
16.	heptachlor	33.	PAH's
17.	heptachlor epoxide	34.	bis (2-chloroethyl) ether

1,2-dichloroethane is measured during the routine purge-and-trap trihalomethane analysis. The chlorinated hydrocarbon insecticides (CHI) are isolated from 6-liter water samples by use of a solvent extraction procedure followed by glass capillary column chromatography with electron capture detection. Because the concentrations of individual CHI are very low, and occurrences are quite variable, GAC treatment effectiveness was most conveniently evaluated using a total CHI parameter (reported in picomoles/L as the units of concentration)

Figure 4 shows the performance of a GAC post-filter adsorber for the removal of 1,2-dichloroethane (DCE). Although the influent concentration of DCE was quite variable, 1 to 24 µg/l, a fairly smooth breakthrough curve was observed for this compound during the 180 day run. Ten percent breakthrough was observed at approximately 44 days, 50 percent at approximately 90 days, and equilibrium ($C_{eff} = C_{inf}$) at about 110 days. By contrast, however, Figure 5 shows the effluent and influent curves for total CHI during the same run. The curves show that only when the influent concentration of CHI decreased to near the detection limits did GAC effluent concentrations reach those of the influent. This occurred during the period 45 to 64 days into the run, again between 56 and 62 days, and once again at 100 to 106 days. Following 106 days, when influent CHI returned to relatively high concentrations, the GAC was quite effective through the 180th day. For the duration of the run, a removal efficiency for total CHI of 83 $\pm$ 5 percent was calculated, again demonstrating the effectiveness of GAC as a barrier to this group of synthetic organic contaminants. This long term removal of CHI confirms the conclusions of Robeck, et al. (4), that GAC beds are efficient for the removal of certain pesticides even after exhaustion by other criteria.

Non-Gas-Chromatographable Compounds

The parameter "Term TTHM" is a measure of non-gas-chromatographable trihalomethane precursor materials obtained by chlorination and storage of a sample under controlled conditions and is defined as the concentration of trihalomethanes at the end of the storage period, simulating the effects of disinfectant contact time. Precursors are generally considered to be aquatic fulvic and humic acids of a molecular weight range of 500 to 50,000 or more (5).

Continuing the discussion of the same Jefferson Parish experimental filter run described above, Figure 6 is a plot of the influent and effluent terminal concentrations of total trihalomethanes (term TTHM). From this pair of curves, two important observations can be made. Firstly, 10 percent breakthrough is reached quite early (18 days) in the run in contrast again to CHI. Although, with humic acid or fulvic acid from the same source, lower molecular weight fractions generally are more

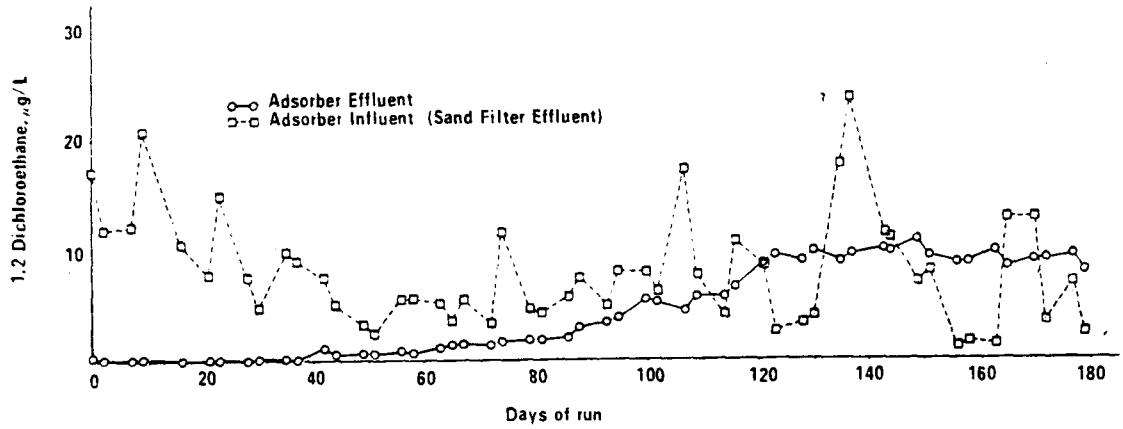

Figure 4. Performance of Post Filter Adsorber for Removal of 1,2DCE (Feb.-Oct. 1977) - Jefferson Parish, La.

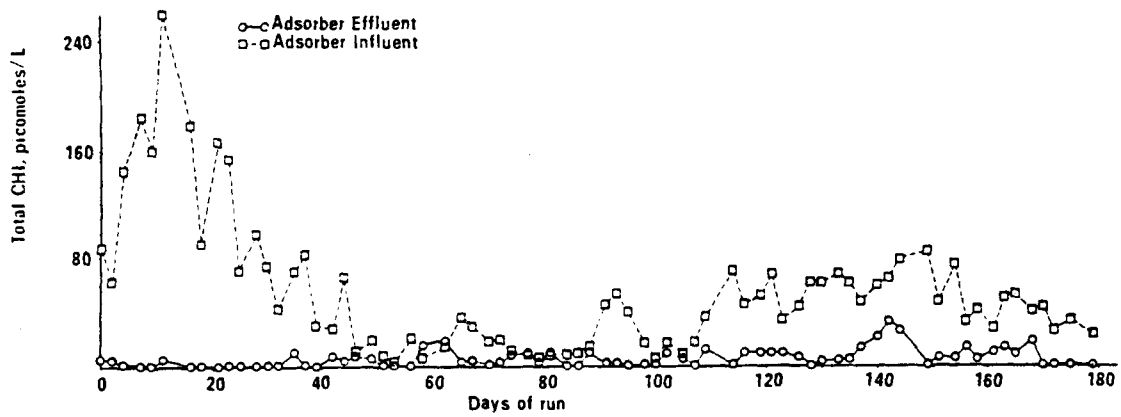

Figure 5. Performance of Post Filter Adsorber for Removal of Total CHI (Feb.-Oct. 1977) - Jefferson Parish, La.

adsorbable than higher molecular weight fractions (500, 10K, 50K) (6). This 10 percent fraction of material could consist of either very low molecular weight, soluble biodegradation products or very high molecular weight material. Highly soluble molecules may not be adsorbed strongly even though they are small enough to penetrate into the carbon grains; substances of extremely high molecular weight may be excluded by size effects from diffusing through the internal pores of the carbon grains to reach vacant adsorption sites.

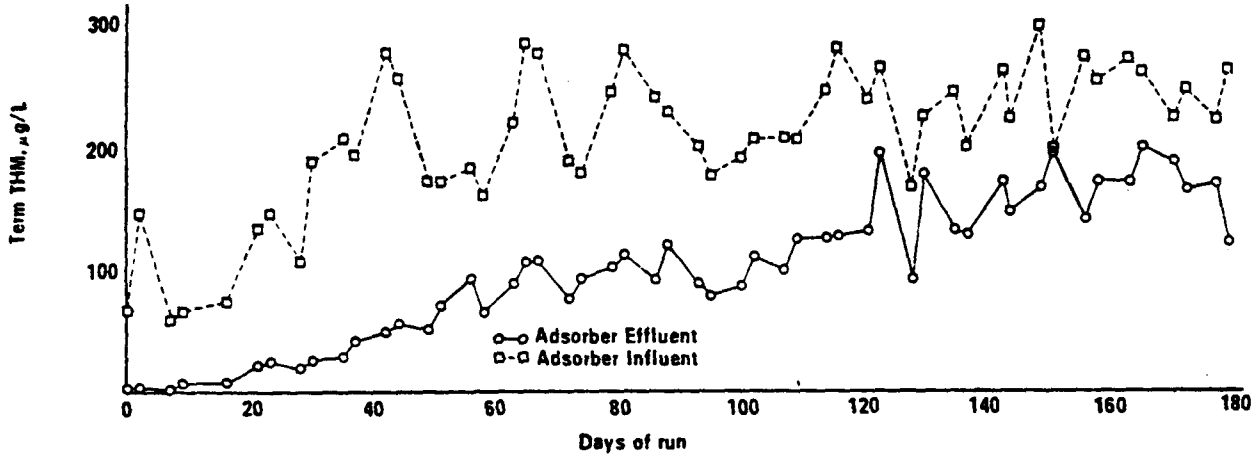

Figure 6. Performance of Post Filter Adsorber for Removal of Term THM (Feb.-Oct. 1977) - Jefferson Parish, La.

Secondly, 50 percent breakthrough is not reached until 102 days. Further, equilibrium ($C_{inf} = C_{eff}$) is not reached during the 180 day run, but a steady state around 70 to 75 percent remaining in the effluent seems to be achieved. This kind of result is also observed when TOC is used as a measurement parameter and has been observed at numerous other locations to varying degrees. This means that either a 25 to 30 percent fraction of the humic material is very strongly adsorbed, or that some other mechanism of removal is acting. Current thinking is that biological activity is an important mechanism for this continuing removal of natural organic materials. Evidence is available that indicates a preoxidation step, which will render the compounds more polar, and therefore less adsorbable, actually enhances this long-term removal phenomenon, presumably because the oxidation products are more biodegradable (see other papers in these Proceedings).

Recent experiments at the EPA Laboratory investigating the treatability of certain chlorinated volatile compounds, have indicated that the apparent biological removal process is not

restricted to natural humic materials, that is, to trihalomethane precursors. The synthetic organic contaminants chlorobenzene and o-dichlorobenzene were found to exhibit distinct signs of biodegradation during the treatment, presumably enhancing the effectiveness of the overall unit process.

CONCLUSIONS

For the removal of synthetic organic contaminants, GAC is a good, broad-spectrum adsorbent. Although the effectiveness of GAC is marginal for some easily measured low molecular weight synthetic organic contaminants, excellent protection is still provided for other co-contaminants, especially in a higher molecular weight range.

Biological activity has a likely role in the continuing long-term removal of a 25 to 30 percent fraction of natural, very high molecular weight humic acids, and a less well recognized role in removal of some synthetic organic contaminants as well.

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MONITORING TECHNIQUES FOR THE CONTROL OF THE ADSORPTION PROCESS

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A REVIEW OF ANALYSIS TECHNIQUES FOR ORGANIC CARBON AND ORGANIC HALIDE IN DRINKING WATER

Y. Takahashi

INTRODUCTION

Most drinking water, especially that which comes from surface sources, is contaminated with a modest amount of organics. Typically these organics come from natural sources and are reasonably innocuous. In recent years, however, it has been discovered that many drinking waters contain organics which are potentially hazardous to human health. These can come from industrial sources as well as from the chlorination process itself. Accordingly, extensive work is now underway in many countries throughout the world to develop treatment processes that will effectively remove these contaminants.

To support this work and to better understand the health effects of trace organics in drinking water, sophisticated and expensive analytical techniques have been developed to detect and identify these contaminants. To date, more than 700 trace organics have been identified in various raw and treated drinking waters. Despite this, a large portion of the organics present are still unidentified.

Thus, while the complete identification and quantification of trace organics in drinking water is desirable, it appears that such comprehensive information is neither technically nor economically feasible as a routine process evaluation and control tool. Accordingly, several group parameters have been studied as surrogates for undesirable contaminants in water. Two of these which are particularly useful are total organic carbon (TOC) and total organic halides (TOX).

ORGANIC CARBON DETERMINATION

Total organic carbon (TOC) in water exists in a number of forms and phases. These can be classified as purgeable organic carbon (POC), dissolved nonpurgeable organic carbon (NPOC), and suspended organic carbon (SOC). The NPOC is defined as the organic carbon fraction which passes through a 0.45 micron filter and is then nonpurgeable.

The determination of TOC in water containing SOC is always a problem. The reproducibility of the analysis is poor even if the SOC is broken down to smaller particles or homogenized prior to the TOC determination. Some TOC techniques may not quantitatively respond to the SOC (1).

When the measurement of TOC is used to evaluate the efficiency of organic removal in drinking water treatment systems, the NPOC determination throughout the treatment process should provide the most useful information since most of the SOC is rather easily removed by simple coagulation and/or filtration. The remaining carbon (NPOC) can be a measure of the amount of the additional treatment required.

On the other hand, if trihalomethane formation is compared with the TOC in raw water where prechlorination is performed, the SOC should be taken into account. Some trihalomethane precursors exist as SOC or as adsorbed on the SOC (2).

The instrumental method for determining TOC was first reported by Van Hall, et al., in 1963 (3). Since then, numerous TOC techniques have been developed and many different TOC analyzers are commercially available. It is beyond the purpose of this article to review all available techniques and minor variations used by these analyzers. However, TOC methods which represent the fundamental trends in this analysis field are summarized in Table 1.

Initially the TOC parameter was introduced to correlate with biochemical oxygen demand (BOD) and chemical oxygen demand (COD) for industrial and domestic waste waters. The TOC of these waste samples is typically 5 mg/l and higher. Van Hall's method is well suited for this purpose and has been widely used.

The method is based upon the high temperature oxidation of carbonaceous matter in water to carbon dioxide (CO_2) followed by CO_2 detection with a nondispersive infrared (NDIR) analyzer. A small amount of water sample is injected into a combustion chamber maintained at 900°C. All carbonaceous matter is oxidized to CO_2 in the presence of oxygen and a catalyst. Oxygen carries the gaseous products through the NDIR which measures the CO_2 content of the gas stream. The detector output is graphically displayed on a strip chart recorder; the peak height is proportional to the carbon content of the sample.

Since all carbonaceous materials in the sample, including inorganic carbon (IC), liberate CO_2, IC has to be either removed prior to the analysis or determined separately.

Another common high temperature method is based on the reductive pyrolysis of organics to methane- and flame-ionization-detection (FID) (4). In this method an acidified sample is

Table 1

TOC Method Comparison

HIGH TEMPERATURE METHODS (~800°C)

METHOD	DETECTOR	DETECTION LIMITS(mg/l) NPOC	POC	REFERENCES
Catalytic Oxidation	NDIR	2	Lost	Van Hall, et al., (3)
Catalytic Reduction	FID	1	0.5	Takahashi, et al., (4)
Oxidation then Reduction	FID	0.1	Lost	Croll (5)

LOW TEMPERATURE METHOD (~60°C)

METHOD	DETECTOR	DETECTION LIMITS(mg/l) NPOC	POC	REFERENCES
Persulfate Oxidation	NDIR	0.2	Lost	Menzel and Vaccaro (6)
Silver-catalyzed Persulfate	NDIR	0.05	Lost	Baldwin and McAtee (7)
Ultraviolet Oxidation	NDIR	0.001	Lost	Wolfel and Sontheimer (8)
UV-Persulfate Oxidation	NDIR	0.01	0.05	Goulden and Brooksbank (9)
UV-Persulfate Oxidation	Conductivity	0.1	Lost	Ehrhardt (10)
UV-Persulfate Oxidation then Reduction	FID	0.01	0.001	Takahashi (11)

injected into a sample boat containing an oxidizer and is heated at 115°C. CO_2 (from IC) and volatile organics (VOC) are transferred into the gas phase; the gases are passed through a column packed with porous polymer resin. VOC is retained on the column, but CO_2 is eluted and discarded. Then, the column is backflushed and the VOC is carried into the high-temperature reduction zone where the VOC is converted to methane in the presence of hydrogen and a catalyst. Methane is detected by the FID. The residual organic carbon (ROC) remaining in the boat is then heated to 800°C, pyrolyzed, and oxidized. The pyrolysis products are reduced in the reduction zone mentioned above and the resulting methane is detected by the FID.

Both of the methods described above have been selected as standard methods by the American Society for Testing and Materials (ASTM) (12).

The majority of high temperature TOC analyzers lack precision and accuracy below 2 mg/l. Certainly the FID is sensitive enough to detect less than 0.1 mg C/l with a 50 µl water sample. The principal problems are that there are organic contaminants in the carrier and reactant gases and trace carbon contaminants in the catalyst. When a discrete water sample is injected, steam at high temperature reacts with carbonaceous contaminants in the pyrolysis chamber to cause an apparent carbon reading. This is generally defined as the method blank or the system zero bias which often varies between 1 and 5 mg/l.

In the method reported by Croll (5), the erratic system blank problem is minimized when a sample is continuously introduced at a constant rate. An acidified and sparged sample is introduced at the rate of 0.6 ml/min into a metal chamber (800°C) packed with solid oxydizer (CuO). The CO_2 produced is carried with nitrogen into a high temperature reduction chamber containing nickel catalyst. The methane produced is detected with an FID. The reading is taken when a signal has reached a plateau. The relative standard deviation of $\pm$ 38, $\pm$ 7, $\pm$ 1.5 and $\pm$ 1.7 percent were reported at the organic carbon levels of 0.15, 0.65, 5.15 and 50.15 mg/l, respectively (5).

An advantage of the high-temperature TOC methods is the short analysis time, 2 to 5 minutes per analysis. Also, because of exhaustive oxidation and reduction conditions at above 800°C, complete destruction of organics in water is expected.

A disadvantage of the high temperature methods is that the TOC values in river water, well water, and treated drinking water, including granular activated carbon (GAC) filter effluent, are below its detection limit.

To achieve low-level TOC analysis for such applications, the following criteria must be satisfied:

1. Efficient inorganic carbon removal.

2. High sensitivity, from 10 to 50 µg/l.

3. Repeatable and low system blank.

In order to satisfy these requirements, low temperature oxidation techniques are much more attractive. Selected low temperature TOC methods are also listed in Table 1.

In all the low temperature techniques mentioned, the oxidation reactions are carried out in the aqueous phase under severe oxidizing conditions. Such conditions are created by addition of strong chemical oxidizing agents such as peroxides or persulfates, or by irradiating the water with high energy sources, such as ultraviolet light.

Initially trace level TOC was of concern only to oceanographers for sea water studies. Their main interest in seawater TOC was not primarily for pollution-oriented reasons but rather to understand the interactions of dissolved organic matter and the living and nonliving organic matter of the ocean environment.

The range of TOC in uncontaminated seawater is 0.3 to 3.0 mg/l. The low level of TOC and high salt contents in seawater make TOC analysis by high temperature techniques almost infeasible on a routine basis.

In 1964, Menzell and Vaccarro (6) reported the wet chemical oxidation with potassium persulfate ($K_2S_2O_8$); this subsequently became the standard method in limnology and oceanography.

In this method, 1 to 5 ml of seawater is acidified and sparged in a glass ampule. Persulfate is then added to the ampule. The solution is then autoclaved at 130°C for 30 minutes to oxidize organics to CO_2. The CO_2 is purged with an inert gas and the concentration is detected with an NDIR.

Recently, the kinetics of persulfate oxidation of organic materials in fresh water was thoroughly studied by Goulden and Anthony (13). This work showed that organics in fresh water can be oxidized at 90 to 100°C in a few minutes.

The differences in the oxidation of organics in fresh water and seawater seemed to be twofold. The first difference is their slow oxidation reaction in the presence of approximately 3 percent salt. Skopintsev, et al. (14), reported that the organic matter in fresh water, including humic substances,

is completely oxidized to CO_2 by persulfate. However, sodium chloride addition to the same sample interfered with the oxidation so much that complete oxidation was not achieved within 15 minutes at 100°C.

The second difference is the nature of organics in seawater. These can be highly refractory against persulfate oxidation. Takahashi and Mar (22) compared the oxidation rates of organics in seawater and in fresh water spiked with salt. This work confirmed the presence of very refractory organics in natural seawater.

The efficiency of persulfate oxidation of organics in natural water samples is still in question. Some TOC values obtained by various oxidation techniques are summarized and compared in Table 2. It indicates that the average TOC obtained by persulfate oxidation is 80 to 90 percent of the values obtained with high temperature or photochemical oxidation.

It has long been known that when water is exposed to high intensity ionizing radiation, such as X-ray or fast proton recoils formed by the passage of fast neutrons, hydroxyl radicals (OH) are produced in high concentration. The hydroxyl radical is also produced by ultraviolet (UV) irradiation. Such radiation can be easily and conveniently produced with a mercury discharge lamp. The benefit of the hydroxyl radical is that it is an extremely strong oxidizing agent. Accordingly, many organics are oxidized to CO_2 when exposed to UV radiation. The oxidation is probably aided by a number of mechanisms in addition to that caused by the hydroxyl radical. Some may undergo photodecomposition directly. Organics that absorb UV energy are raised to an excited electronic state that leaves them more susceptible to OH oxidation.

Even though photolytic oxidation of trace organics to CO_2 in fresh water was investigated by Beattie, et al. (15), much literature about this technique has been investigated and reported for the oxidation of organics in seawater. [Armstrong, et al. (16), and Armstrong and Tibbits (17)].

Recently, Woelfel and Sontheimer (8) obtained 0.001 mg/l sensitivity using this photooxidative technique for fresh water. A low pressure mercury lamp was immersed into a sealed reaction vessel with a sparge gas inlet and outlet.

In this technique the sample is first acidified and sparged, then the mercury lamp is energized. Organic matter is oxidized to CO_2 which is then detected by an NDIR. The reaction time may vary depending upon the type of organics in the sample being analyzed; the typical reaction time is less than 5 minutes. The apparatus for the oxidation of organics and the typical CO_2 generation is illustrated in Figure 1.

Table 2

TOC Data Comparison

Number of Determinations	TOC Range (mg/l)	RELATIVE MEAN VALUES				REFERENCES
		High Temp.	Persulfate	UV	UV-Persulfate	
24	0.35-1.22		90	(100)		Willaime (20)
68	0.57-1.74	(100)	78			Sharp (21)
--	1.49-3.08	(100)	97		101	Goulden and Brooksbank (9)
38	0.13-1.63	(100)	86	95		Gershey, et al. (1)
7	0.65-1.42	(100)			107	Takahashi and Mar (22)

(100) Data normalized to this value.

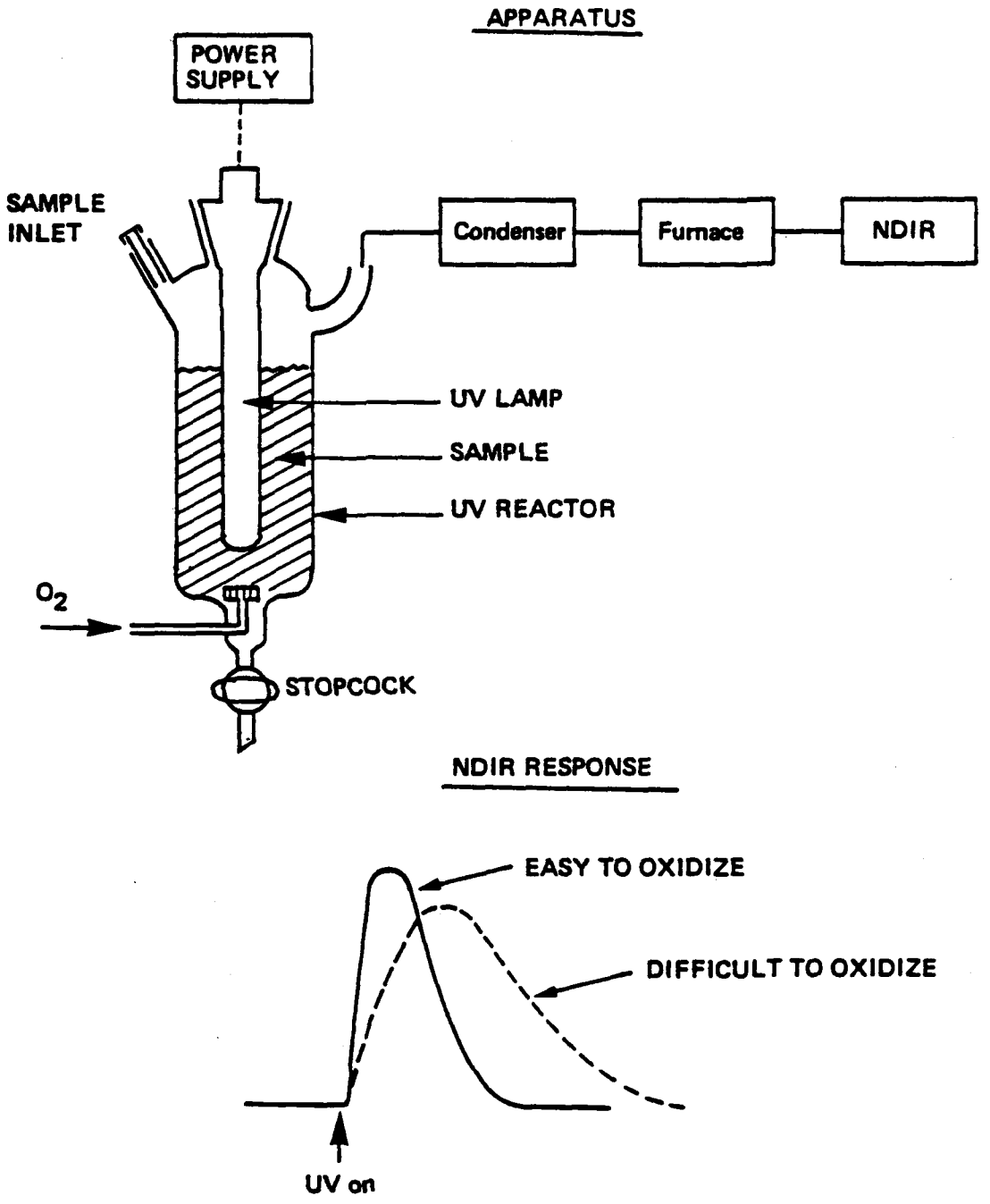


Figure 1. TOC By UV Oxidation

The addition of persulfate to the photooxidation process increases the oxidation rates of many organics. This is due to the excitation of organics with UV radiation and formation of the active species SO_4 as well as OH at higher concentration. Ehrhardt (10), and Goulden and Brooksbank (9) used this technique for seawater, and fresh water, respectively.

During the last 5 years or so, the formation of trihalomethanes during disinfection, mainly chlorination of drinking water, has been intensively studied.

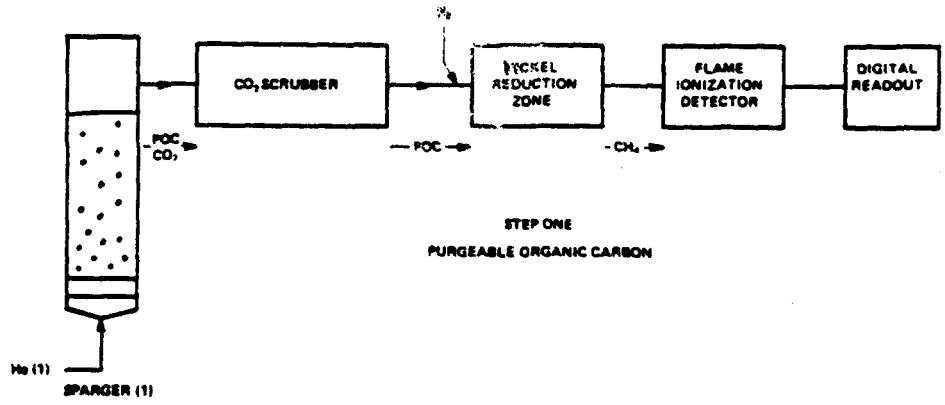
With respect to trihalomethane detection, some researchers are interested in measuring the POC to find out whether or not POC and total trihalomethanes are related.

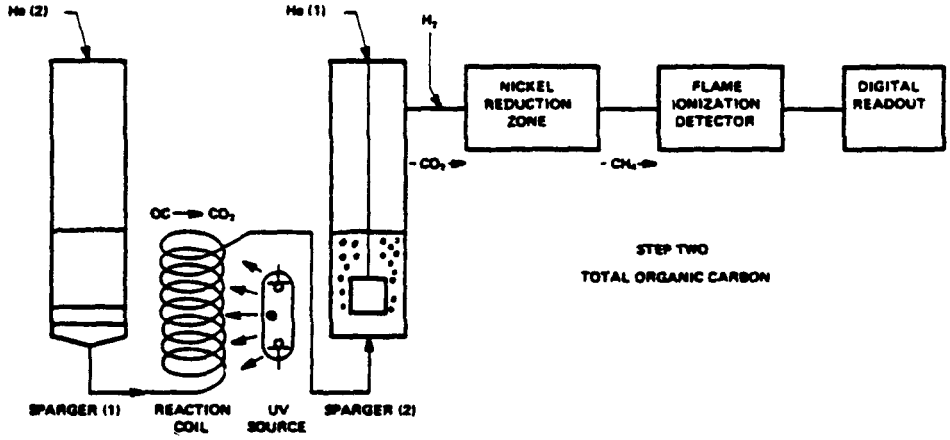
The POC produced by chlorination is 0.005 to 0.020 mg/l; typically the NPOC is 2 to 4 mg/l. Accordingly, a method to determine the POC at µg/l levels is needed along with a separate NPOC measurement.

Takahashi (11) developed a method to detect POC and NPOC sequentially with the detection limits of 1 and 10 µg/l, respectively.

The operation principle of this method is as follows. A 10 ml sample of water is mixed with an acidified potassium persulfate reagent. The sample is transferred to a glass sparge chamber where a flow of helium sweeps out carbon dioxide from inorganics and those organics that are purgeable (POC) under the temperature and flow conditions used. These materials are transferred by the carrier gas to a very efficient scrubber that removes the carbon dioxide but allows the POC to pass through. The POC is converted to methane and measured using the same catalytic reduction and flame ionization detector measurement procedure as described in reference (4). The water sample is then pushed through a quartz coil positioned around a very intense mercury discharge lamp. The combination of the persulfate oxidant and the intense ultraviolet light oxidizes the remaining organics to carbon dioxide. After oxidation, the sample passes to another glass sparge chamber where the resulting carbon dioxide is purged, converted to methane and measured. The final readout is the TOC content of the sample. The advantages of this procedure for low levels relate to use of a large water sample and a method background blank that is typically less than 0.03 mgC/liter (Figure 2).

The currently available techniques, UV or UV-promoted persulfate oxidation, satisfy most of the requirements for measuring trace TOC in drinking-water-related samples routinely and without highly skilled operators. The techniques are sensitive enough, for example, to distinguish the TOC in high





UV – PERSULFATE OXIDATION

Figure 2. UV - Persulfate Oxidation

quality deionized water from that in regular quality deionized water. TOC concentrations in selected water samples are summarized in Table 3.

Now the technology is available to utilize these photo-oxidation techniques to monitor the NPOC continuously.

Table 3
Typical POC and NPOC in Various Types of Water

SAMPLE	POC (μgC/l)	NPOC (mgC/l)
River Water	<2	2-6
Well Water	<2	0.1-2
Lake Water	<2	0.3-3
Drinking Water	1-15	0.3-3
GAC Effluent	<2	0.05-0.3
Deionized Water	<2	0.03-0.2
Distilled Water	<2	0.05-0.3
Reverse Osmosis	<2	0.05-0.3

It has been demonstrated that the NPOC in GAC column influent and effluent can be measured at constant intervals to indicate performance of a GAC column (Figure 3).

The TOC indicates the maximum organic concentration level in water but does not distinguish whether it is due to naturally occurring organics or to pollutants.

Studies have been made to increase the selectivity of TOC measurements to indicate the degree of pollution-oriented organics. This specificity was obtained by making carbon isotope measurements. The value of the $^{13}C/^{12}C$ ratio varies depending upon the nature of organics in water. Calder and Parker (18), and Games and Hayes (19) studied the variation of the $^{13}C/^{12}C$ ratios in the various water samples. Whether or not this type of additional information is indeed worthwhile remains to be seen.

ORGANIC HALIDE DETERMINATION

It has been well established that many halogenated organics are toxic to human health and some are carcinogenic. Many of these toxic substances have been found in drinking water supplies. The majority of halogenated organics in raw water are either chemicals discharged by various industries or are agriculturally related compounds, such as pesticides and herbicides leached from the soil. Naturally occurring halogenated organics in water are very limited. Thus, the total organic halides

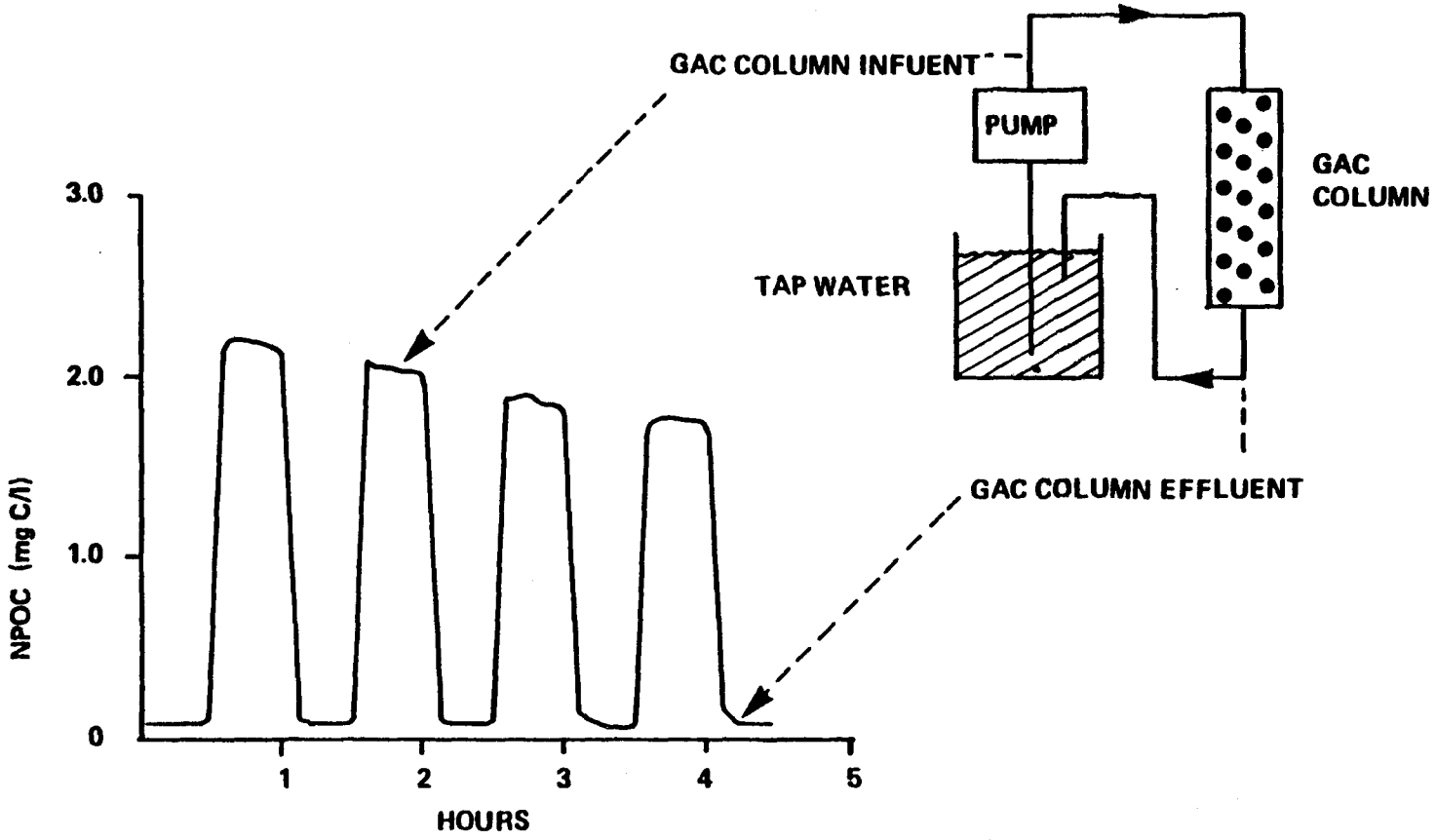


Figure 3. Continuous NPOC Monitor

(TOX) in raw water are closely related to manmade contaminants that are toxic.

Interest in measuring TOX was stimulated by finding chloroform in the drinking water of New Orleans, LA (33). Rook (34) traced the origin of chloroform in finished drinking water to the reaction between chlorine and naturally occurring fulvic and humic acids in water. Rook (35) also attempted to detect any significant amounts of intermediate chlorinated organics resulting from chlorination and found no other gas chromatographable compounds besides trihalomethanes. However, the question still remains whether or not any non-gas chromatographable chlorinated organics are produced and, if so, are they produced in any significant amounts.

TOX is still a relatively new water quality parameter, and the measurement is a little more difficult and time consuming than the TOC measurement. However, the technology of measurement has been improved lately to the point where routine measurement of TOX is feasible.

Difficulties with TOX measurements are mainly due to the following reasons:

1. The range of TOX in surface water is 1 to 100 µg/l. This requires a high sensitivity detector or the solution has to be concentrated.

2. None of the detection methods except neutron activation analysis, which requires highly sophisticated instrumentation, responds equally to all types of halogenated compounds. Thus, all halogenated organics have to be converted to a common species.

3. Inorganic halide (IX) concentration in surface water is 1,000 to 100,000 times higher than the TOX. Thus, the TOX method has to have an IX rejection ratio of at least 500,000 to one.

The following is a review of four TOX techniques presenting the advantages and disadvantages of each.

Liquid-Liquid Extraction Method

Liquid-liquid extraction is the simplest and most conventional technique to concentrate the TOX in an appropriate organic solvent and leave the IX in the aqueous phase. Wegmen and Greve (23) investigated extractable organic halides (EOX) in the Rhine River over the period of 1973 to 1975 (23), and later extended this work until 1977 (37), using the following extraction technique.

Organics from surface waters were extracted into petroleum ether more than three times. The combined extracts were dried and concentrated. A small aliquot of combined extracts was injected into a furnace and burned in an excess of oxygen. The hydrogen halides (HX) formed were passed into a titration cell where they were microcoulometrically titrated with silver ions in the cell electrolyte. The detailed discussion of the microcoulometric titration of HX is described elsewhere (39). In this method the EOX is concentrated by a factor of 1000 and the minimum detection limit is 1 μg/l.

Extraction efficiency of various organics from water and formation of microcoulometrically titratable species by this conventional combustion technique are discussed in this work. It was reported that a significant fraction of total organics were either not extracted or were evaporated along with the ether.

A variation of the liquid-liquid extraction technique is to use a small amount of organic solvent and avoid the evaporation step. This technique is commonly used to determine the trihalomethanes by GC (32). This kind of extraction is possible for the TOX determinations; however, the extraction may take a long time because of the slow kinetics to reach the partition equilibria. This is especially true for high molecular weight organics. Also, a solvent has to be selected by considering the most favorable partition coefficients for as many organics as possible between the solvent and water to achieve the highest extraction efficiency.

XAD Resin Method

Glaze, et al. (24) used a macroreticular resin (XAD) to adsorb organics from water and then eluted these organics with a small amount of ether.

In this method 200 mg of 100/120 mesh XAD is packed in a small glass column. About 120 ml of water is forced through the column at the rate of 25 ml/min. Then, the XAD column is washed with ether until 1 ml of ether is eluted. The organic halides in the ether are then determined by combustion and microcoulometric titration as described earlier.

XAD resin is expected to adsorb a greater fraction of organics than the fraction extracted by an organic solvent from water. In this technique the ether was not evaporated to concentrate the eluant, thus minimizing the loss of volatile organics. Furthermore, during the ether elution step, a gas-tight vial placed in ice water was used to collect the ether eluent. Therefore, overall recovery from water is expected to be better than the EOX.

By this method the organics in water are concentrated by a factor of 100, and the detection limit is 2 µg/l.

This method is free from IX interferences, but adsorption of organics into the XAD resin and the elution of adsorped organics from the resin by ether must be carefully evaluated.

Thurman, et al. (26), studied the relationship between solubility and adsorption capacity for selected organic compounds on the porous acrylic resin XAD-8. The adsorption capacity of the resin is important for predicting the optimum ratio of sample to column size in the preconcentration step. If the same relationship is applicable to XAD-2 resin, only a small fraction of organics will be retained on the column using the method described by Glaze, et al. (24). The adsorptivity of trace organics from natural water by the XAD-2 resin was also investigated by Suffet, et al. (25). The report indicated that granular activated carbon adsorbed nonpolar trace organics much more efficiently than XAD-2 on an equivalent bed volume basis.

Powdered Activated Carbon/Pyrohydrolysis Method

In 1973, Kühn and Sontheimer (27) reported on a method for organic chlorides based on powder carbon adsorption and pyrohydrolysis of carbon along with adsorbed organics. The pyrohydrolysis technique was first developed to study the efficiency of organic removal by pilot-scale or full-scale granular activated carbon (GAC) columns by measuring the TOX on the carbon at various depths in the column bed.

In this method two grams of powdered carbon is mixed with 20 l of sample, the pH is adjusted to 5, and the mixture stirred for 1 hour to adsorb the organics onto the carbon surface. After 1 hour of mixing, the pH is raised to 7 and some coagulants are added.

The carbon is then removed by filtration and saved. The solution is then mixed with another 2 g of powdered carbon to repeat the adsorption and filtration steps. The two portions of carbon are combined and transferred to a quartz boat for pyrohydrolysis.

In the pyrohydrolysis step a quartz boat is placed in the first section of a quartz pyrolysis tube. The second section of the tube is maintained at 1000°C. Oxygen and water vapor are passed through the pyrolysis tube and the pyrohydrolyzate is collected through the condenser. The temperature of the first section is programmed to 700°C.

The organic halide portion of the adsorbed organics is pyrolyzed to HX and X_2 and these are adsorbed in the pyrohydrolyzate. Halide concentration in the pyrohydrolyzate is then determined by an ion selective electrode (Figure 4).

To make the inorganic halide correction, the entire adsorption process is repeated and chlorides in the carbon are washed out using a nitrate solution. The chloride concentration in the nitrate solution is determined by an ion selective electrode.

Dressman, et al. (28), repeated the Kühn and Sontheimer method and reported some improvements. These improvements are:

1. Remove adsorbed Cl^- as well as the Cl^- in the pore water of the GAC by washing with nitrate solution prior to pyrohydrolysis. This is defined as "direct" carbon adsorbable organic halides (CAOX) method.

2. Use a microcoulometric detector to measure halides in pyrohydrolyzate. They found that the chloride selective electrode gave erroneously high Cl^- readings and was affected by addition of $CuSO_4$ and H_2O_2.

3. CAOX is applied to the nonpurgeable fraction only. Only 70 percent of the $CHCl_3$ was recovered.

Also, the chloride interferences were thoroughly investigated and it was found that nitrate ion effectively removed the sorbed chloride ion from the PAC.

The Kühn and Sontheimer method as modified by Dressman is an attractive method, but it still presents some difficulties. These are:

1. Lengthy carbon adsorption step,

2. Loss of purgeable organic halides such as $CHCl_3$,

3. Response to bromides has not been investigated.

Activated Carbon Column/Combustion Method

Takahashi and Moore (30) utilized a carbon column adsorption technique, but with shorter analysis time.

The analytical procedure consists of three steps. These are: 1) adsorption of organics from water into granular activated carbon (GAC) packed in a microcolumn; 2) desorption of inorganic halides by washing the GAC with nitrate solution; 3) combustion of sorbed organics along with the GAC, and coulometric titration of halides thus produced with silver ion. Water samples of 25 to 100 ml are used. Adsorption time is typically 15 to 30 min,

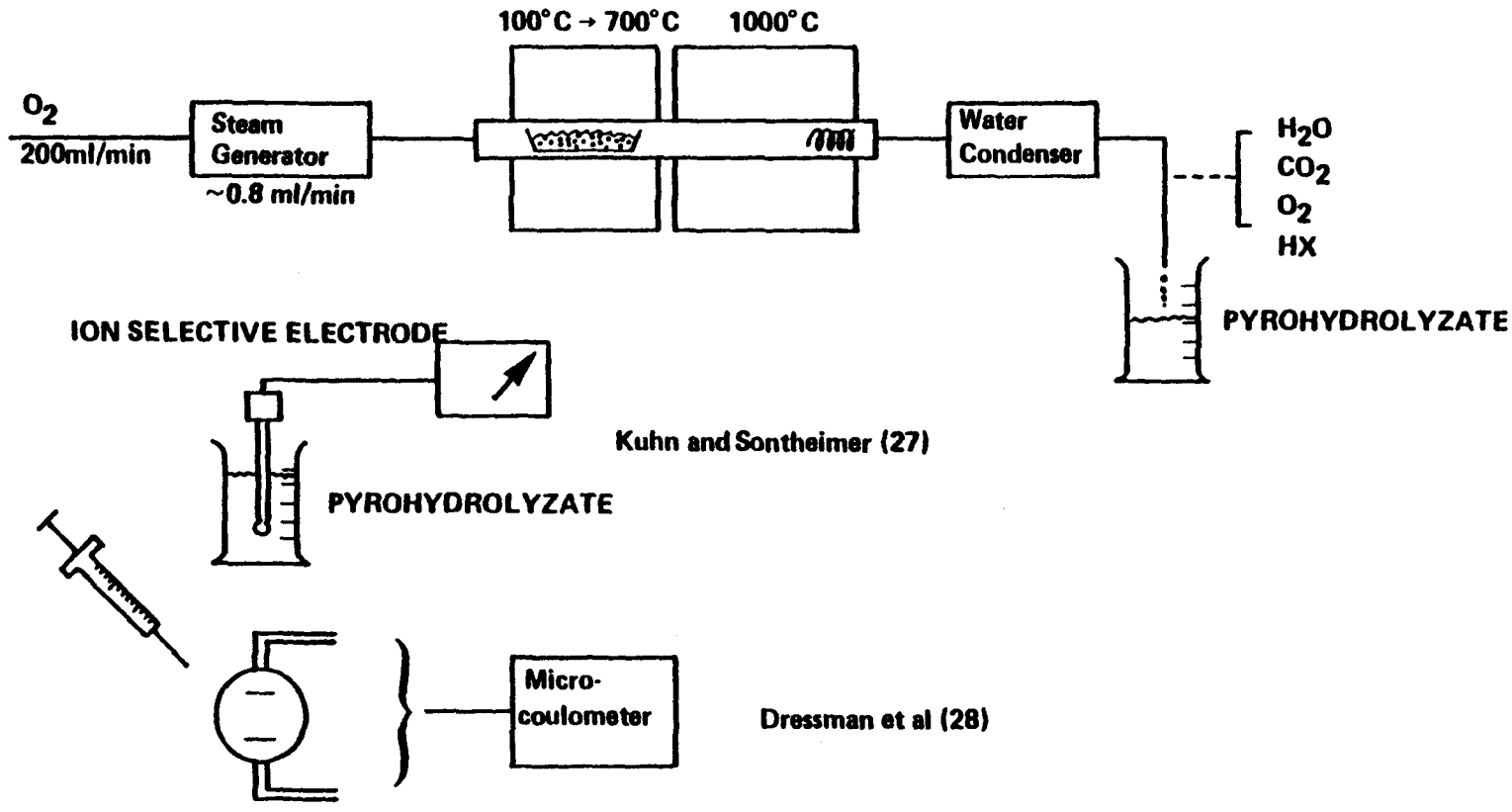


Figure 4. TOX Determination by Pyrohydrolysis

and combustion and determination time is typically 10 min. The detection limit of this method is 6 X 10^{-8} mole/l (or 2 µg/l of chlorine) and the apparent TOX from 100 mg/l of chloride ion was lower than the detection limit.

A schematic diagram of the adsorption apparatus is shown in Figure 5. One hundred to two hundred mesh GAC is packed in glass columns (2 mm I.D. x 5 cm long), and two columns are connected in series. A water sample is poured into the sample reservoir and is then forced through the GAC columns by pressurizing the reservoir. A typical sample flow rate is 2 to 3 ml/ min. Four samples are easily processed simultaneously.

The adsorption efficiency on the GAC in the first column is checked by measuring the TOX on the GAC in the second column.

The carbon is then oxidized along with sorbed organics from water, and the produced halides are coulometrically titrated.

It has been reported that, when using the conventional oxidation technique with O_2, the combustion products from brominated organics are not all titratable with silver ion. In this work, combustion is first carried out in an atmosphere of steam from water on the GAC and carbon dioxide. The GAC is then oxidized with oxygen.

This combustion technique provides not only the quantitative recovery from brominated organics, but also some information on the characteristics of the organic halides adsorbed on the carbon. Figure 6 shows the typical response from various samples. Peak X is obtained when the carbon is heated at 200°C with a CO_2 carrier gas. Here, low molecular weight organic halides which are weakly adsorbed on the carbon are vaporized. Peak Y is obtained when the carbon is heated at 800°C with CO_2 and the high molecular organics are vaporized. Finally, the GAC is completely oxidized along with residual organics with O_2 (Peak Z). Part of this combustion process is similar to the regeneration of GAC. Therefore, peaks X, Y, and Z may provide some information about regeneration of GAC after treating water. The relative contribution to peaks X, Y, and Z for selected organics is also shown in the Figure 6.

Similar results are expected with the two carbon adsorption techniques except for purgeable organic halides. However, no direct comparison has yet been done.

The organic halide fraction in water measured by these four techniques are graphically illustrated in Figure 7. There is uncertainty about the response to high molecular weight organics for each method. The solid adsorbents become less effective to adsorb large molecules due to unfavorable kinetics

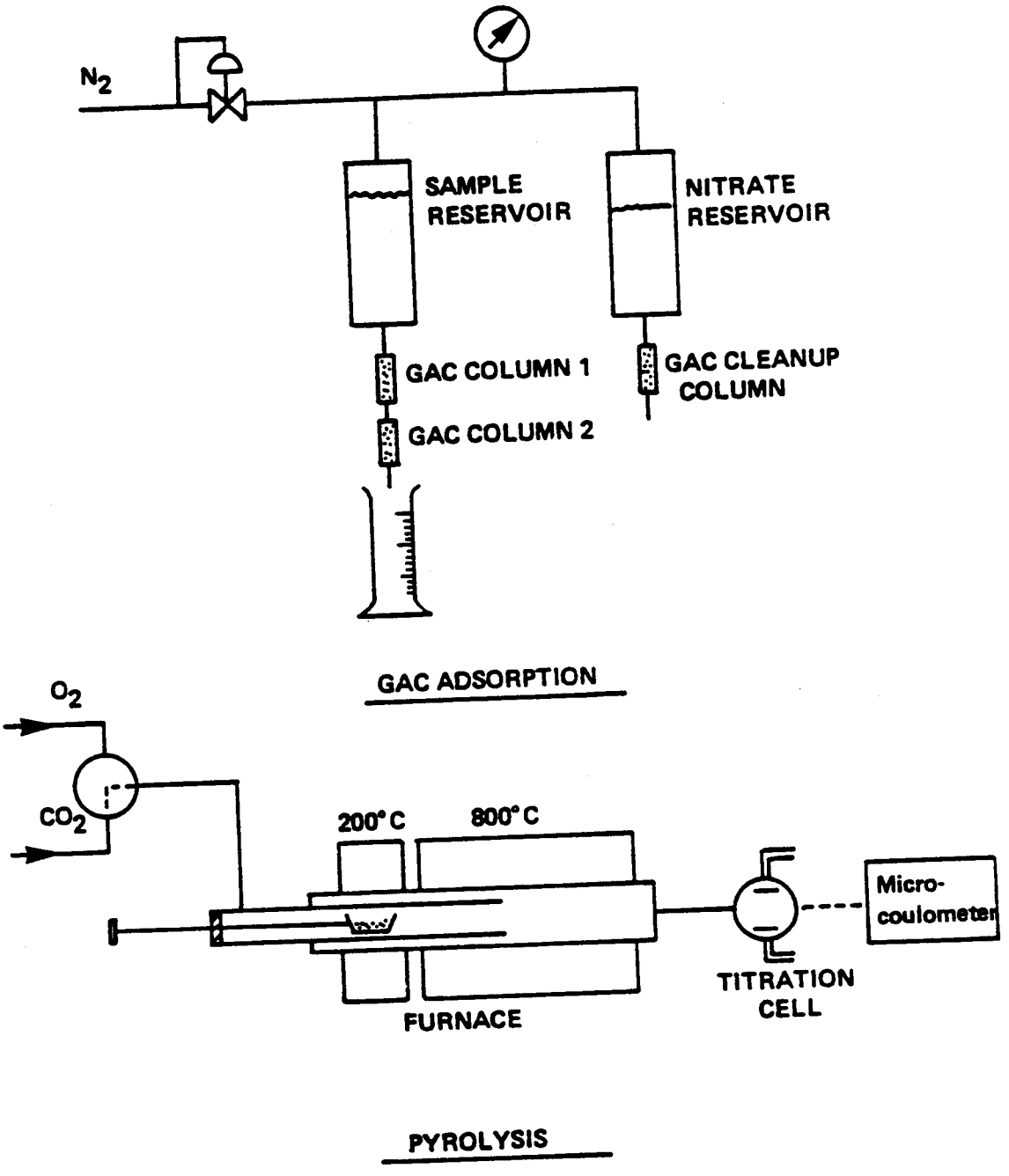


Figure 5. TOX by GAC Column Adsorption

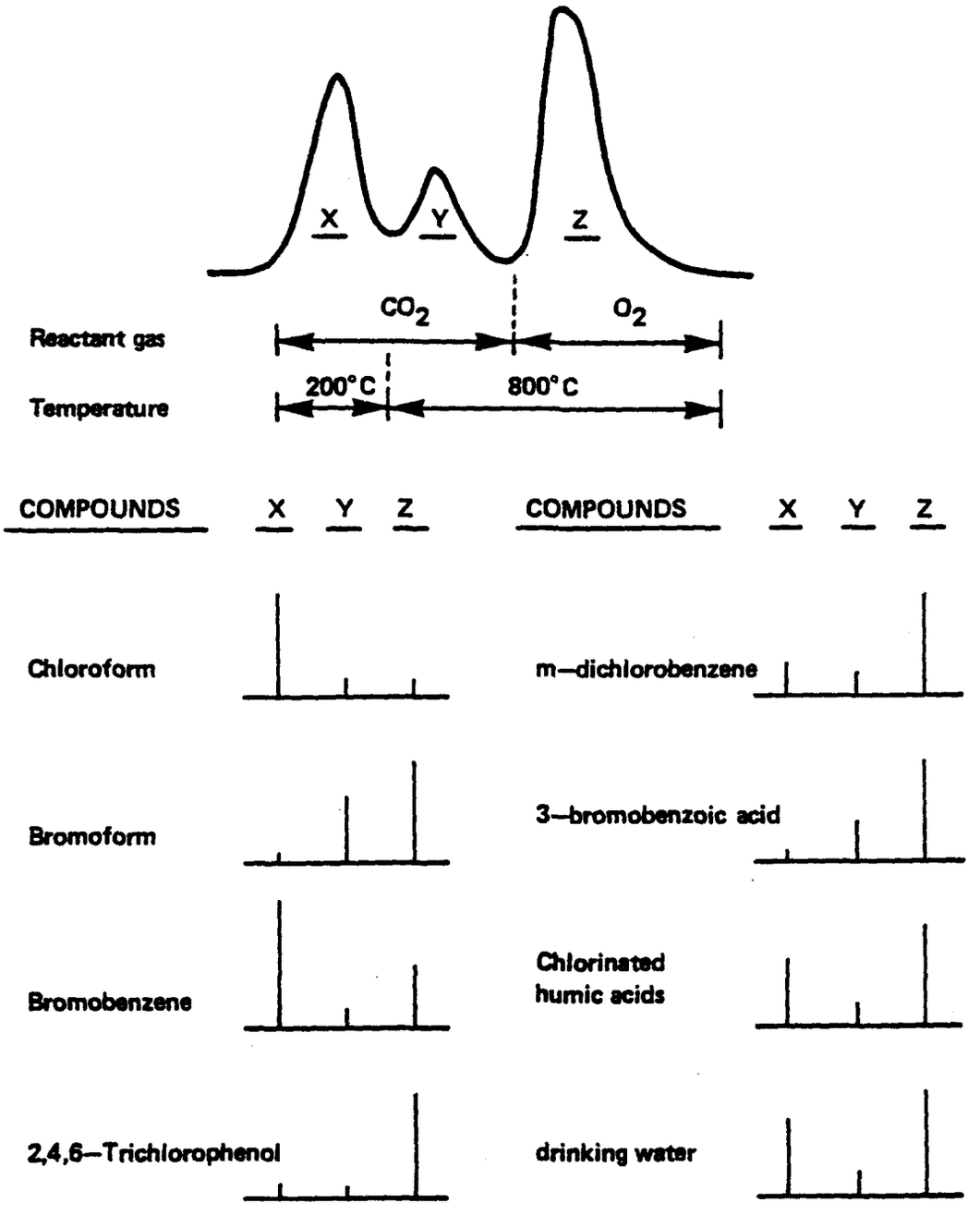


Figure 6. Pyrogram of Compounds Adsorbed on GAC

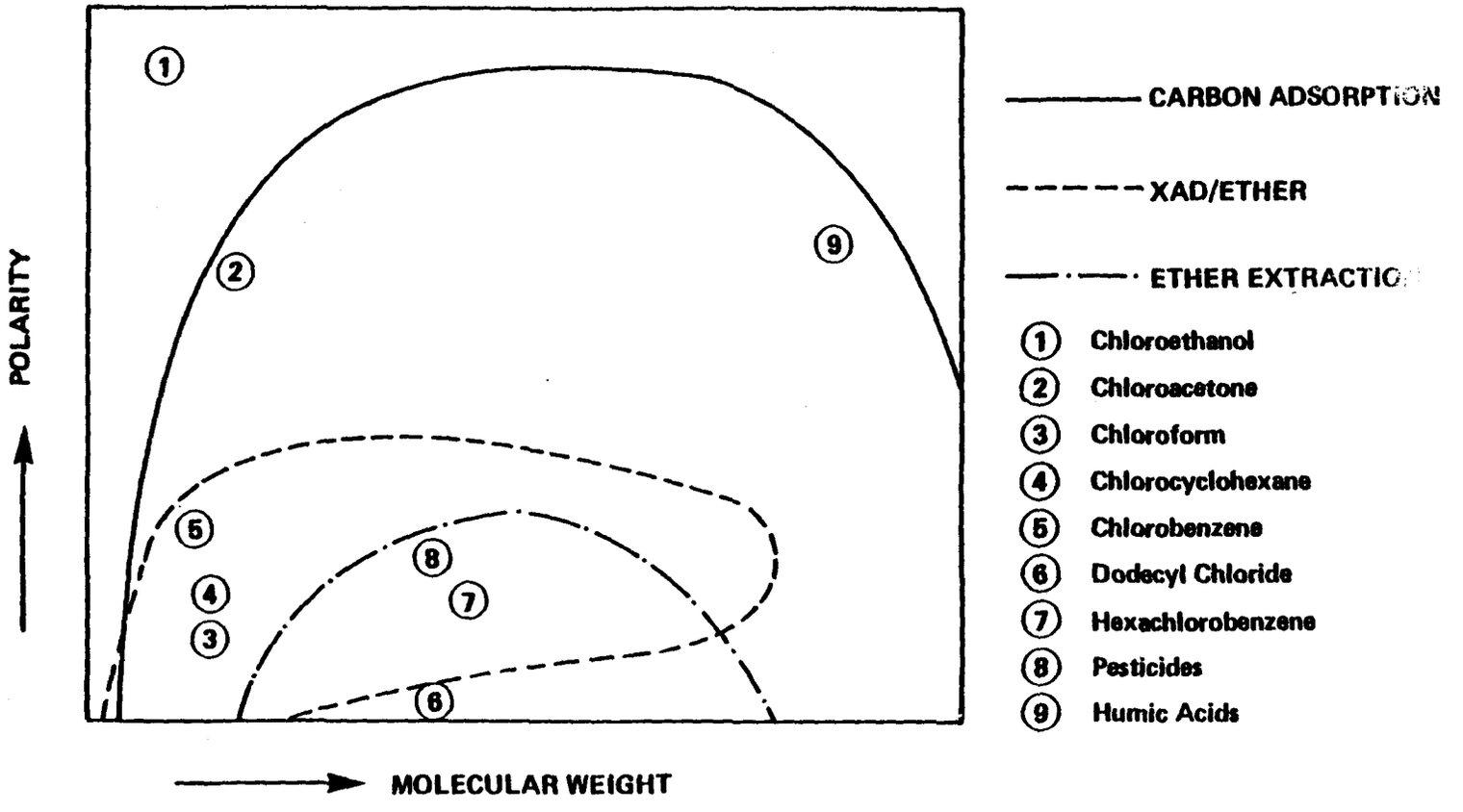


Figure 7. OX Determined by Various Methods

of adsorption. In liquid-liquid extraction methods, the partition coefficients and equilibrium kinetics of such large molecules are expected to be unfavorable.

Activated carbon adsorbs the largest fraction of total organics from water. The organic halides in natural waters determined by various methods are summarized in Table 4. Unfortunately, none of the samples were analyzed by all methods. Thus, the direct comparison of TOX values on these samples cannot be made. However, it is clear that TOX values by the carbon adsorption method are highest. Also, the high values are not due to inorganic halide interference.

There is no doubt that in the near future better TOX methods will be developed. Meanwhile, the TOX should be measured by the method which responds to the largest fraction of total organic halides. As one can see in Figure 7, the activated carbon will adsorb organics most effectively, and the carbon column adsorption technique can be performed routinely and conveniently.

The efficiency of the carbon adsorption has been evaluated by measuring the TOC in the sample before and after the adsorption, using various water samples. However, this area needs to be investigated more thoroughly.

In Table 5, the organic level in various waters is summarized. Four interesting results are found in this table. The TOX in many U.S. surface waters is less than 15 μgCl/l. After chlorination, the TOX increases as one might expect because of trihalomethane formation. However, the concentration of non-purgeable organic halides (NPOX) also increases.

Another example of organic levels in water is demonstrated in Figure 8. POX, TOX, and NPOC were measured at various stages of the drinking water treatment process including the GAC filter. The samples were obtained from the Philadelphia Water Department, Torresdale, PA.

There is potential for determining the TOCl and TOBr separately. Once the chloride ion is removed from the carbon, the TOCl and TOBr can be determined by neutron activation or perhaps by X-ray fluorescence without pyrolysis. Alternatively, after the pyrolysis of the carbon, the HCl and HBr, from the TOCl and TOBr, may be separately determined by ion chromatography (36).

It is generally agreed that TOX is a very important group parameter for drinking water. The carbon adsorption and microcoulometric detection technique offers a convenient method for closely approximating the true concentration of TOX in drinking water.

Table 4

Organic Halides by Various Methods

(µg/l as Cl)

SAMPLE		TTHM	EOX	XAD/ether	CAOX	REFERENCES
City 1	Raw	2.92		1.8		
	Finished	49.2		73.2(2.0)[a]		
City 2	Raw	0.88		5.5		
	Finished	152.7		113.4(11.0)[a]		Glaze, et al.,(24)
City 3	Raw	1.0		4.7		
	Finished	123.2		98.7		
Lake of Constance			3		6	Kuhn, et al.,(29)
Rhine above Basle			27		93	
Rhine of Cologne			37		192	Average value for 1974
Rhine at Duisburg			55		228	
Rhine at Lobith			18 (range 7.7-50)			Wegman & Greve (23) Average value for 1974

(a) Nonpurgeable

Table 5

Organic Levels in Various Waters

SAMPLE		POX (µg/l as Cl)	TOX (µg/l as Cl)	NPOC (mg/l)	REFERENCES
City A	Raw	1	6.0	2.99	Takahashi and Moore (30)
	Finished	59.5	178	2.14	
City B	Raw	1	11.5	3.29	
	Finished	98	312	2.25	
City C	Raw	1	21.0	6.50	
City D	Raw	ND	11		EPA Report (31)
	Finished	9.8	27		
City E	Raw	0.5	11		
	Finished	64	116		
City F	Raw	17.8	29		
	Finished	182	347		
City G	Raw	ND	11		
	Finished	26.6	125		
Untreated		1	6	2.99	Takahashi and Moore (30)
Chlorinated		76	356		
ClO_2 treated		1	23.5		
O_3 treated		1	4	1.94	
Ozonation followed by chlorination		-	154		
Rhine Water			78	4.60	Kuhn & Sontheimer (29)
Sandbank filtrate			17	0.90	
Chlorinated Sandbank Filtrate			85	1.00	
Activated Carbon Filtrate			2		

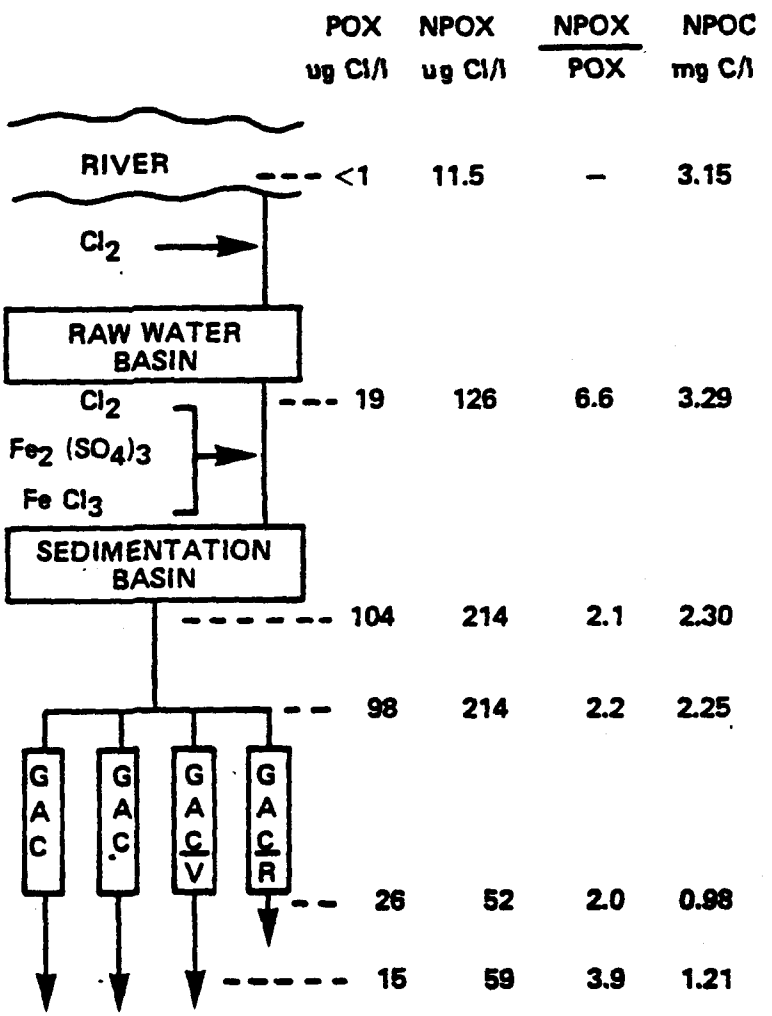


Figure 8. Change in Organic Carbon and Organic Halides During Treatment Process

ACKNOWLEDGMENT

The author thanks Jim Coyle of the Philadelphia Water Department for supplying a few samples for TOX measurements.

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USE OF ULTRAVIOLET (UV) ABSORPTION FOR CONTROL OF ADSORPTION PROCESSES

Friedrich Fuchs and Heinrich Sontheimer

One of the most important and difficult problems encountered when using activated carbon filters for drinking water treatment is the choice of the control method. The analytical criteria chosen for this purpose are crucial for carbon grade and quality, filter design, and for the operation conditions; e.g., regeneration frequency. As can be seen from other papers in this symposium, there are many different analytical methods used to control activated carbon filters. The most important and commonly used technique in Germany is ultraviolet (UV) absorbance.

UV-absorbance measurements are convenient and allow continuous, automatic control. In many waters, UV-absorbance correlates fairly well with the concentration of adsorbable organics and for this reason, has proven in many cases to be more practical for filter calculations than measurements of dissolved organic carbon (DOC) or chemical oxygen demand (COD).

However, UV-absorbance also has some important disadvantages. It does not give any information on toxic organic substances. It covers primarily aromatic organics such as humic and fulvic acids, which present no direct health problem apart from their role as precursors for haloforms and other chlorinated organic compounds.

Since humic substances constitute the bulk of total organics in most of our natural waters, a good correlation between UV and the total organics measurement, such as DOC, usually is observed.

Only a few seconds are needed to measure UV-absorbance and the measurements are very accurate. DOC measurements are more time-consuming and require more complex instruments. Thus, it seems reasonable to replace DOC by UV-absorbance measurements. For transforming UV-values to DOC-concentrations, a function derived from Rhine River data covering one year has been used (Figure 1).

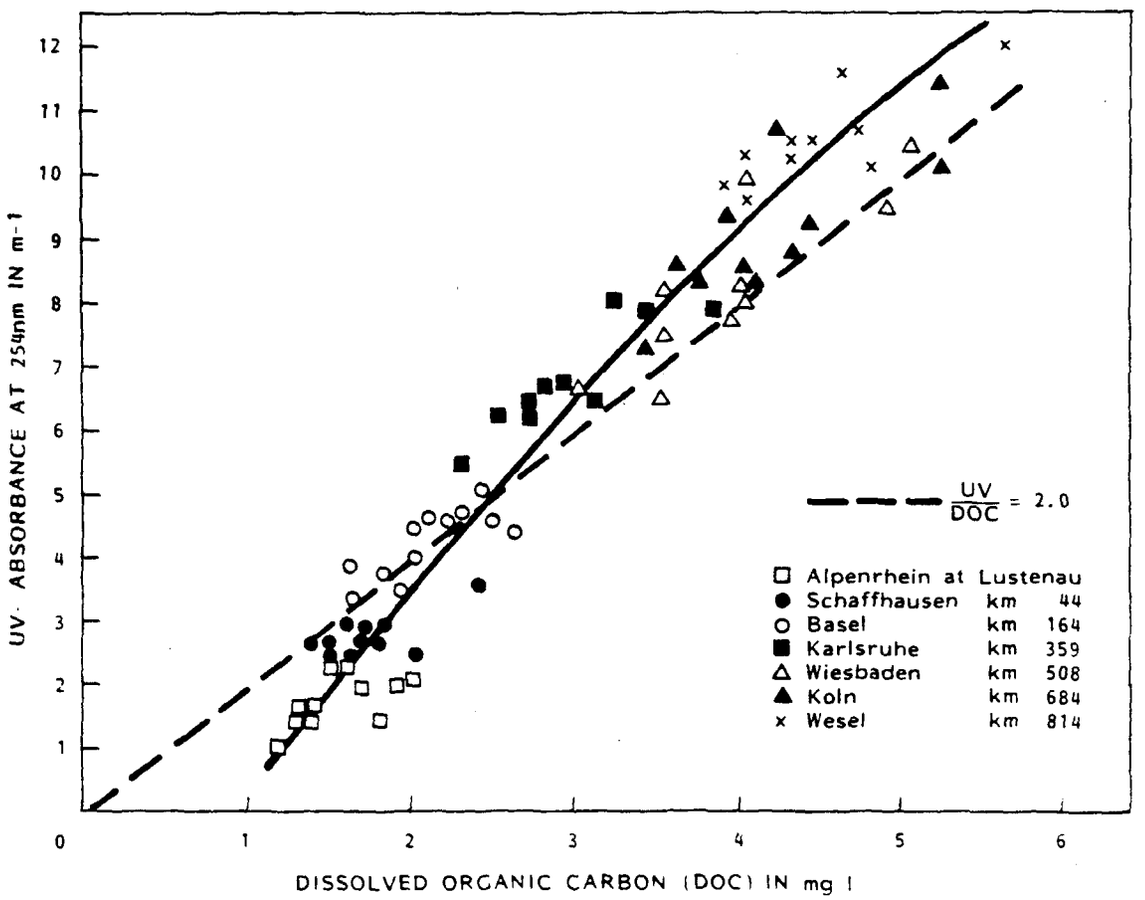

Figure 1. Correlation of UV-Absorbance and DOC Values for River Rhine

Figure 1 shows that there is a fairly good correlation between DOC concentration and UV-absorbance along the Rhine River. Some scattering appears which is to be expected since the Rhine water contains many different organics. Furthermore, there is no constant ratio between the two analytical measurements. This is shown by deviations from the constant UV/DOC ratio line of 2 in the diagram. The ratio is lower than 2 for less polluted waters, whereas with higher pollution, UV-absorbance increases to a larger extent than DOC does so that the ratio exceeds 2. The same observation is shown by Table 1, in which average values from different sources on the Rhine and other rivers are listed. These illustrations clearly point out that the higher the DOC, the higher the specific UV-absorbance.

Table 1

Typical DOC and UV-Absorbance Values
for River Waters in Germany

River	Place	DOC mg/l	UV m^{-1}	UV/DOC
Rhine	Au/Lustenau	1.5	1.8	1.2
Rhine	Schaffhausen	1.7	2.8	1.6
Rhine	Basel	2.3	4.4	1.9
Rhine	Mainz	4.2	8.3	2.0
Rhine	Düsseldorf	4.5	10.9	2.4
Danube	Leipheim	3.0	5.2	1.7
Kocher	Schwäb.Hall	5.0	10.3	2.1
Schussen	Lake of Constance	6.4	17.1	2.7

In many cases, we can observe a linear relationship between UV-absorbance and DOC with a positive intercept on the DOC axis. This indicates that a few organic substances exist that have some DOC but no UV-absorbance. This can be seen in Figure 2, based on data taken from control measurements in Wuppertal.

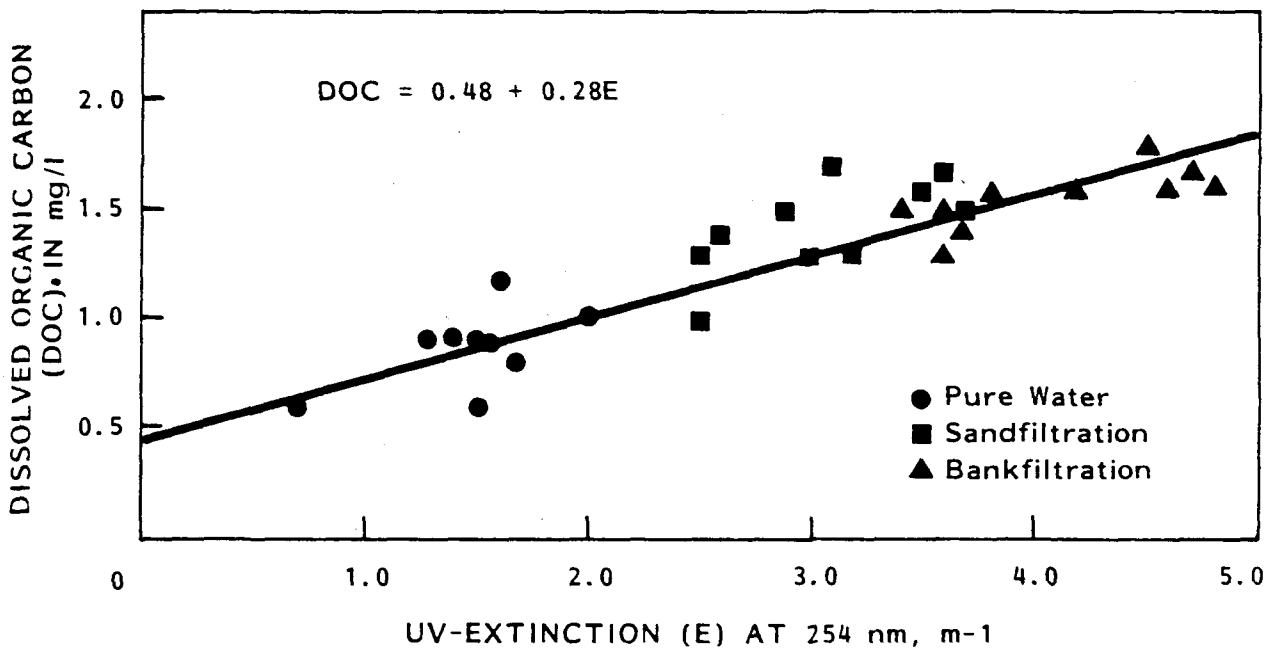

Figure 2. Relation Between UV-Absorbance and DOC at Wuppertal

In this special case, the UV and DOC values for the bank-filtered raw water as well as for the treated waters are on the same line, thus allowing a linear correlation between the two measurements. But this is not always the case, especially after other treatment steps. In order to understand this better, Figure 3 shows data from the plant in Düsseldorf which treats water from the Rhine River.

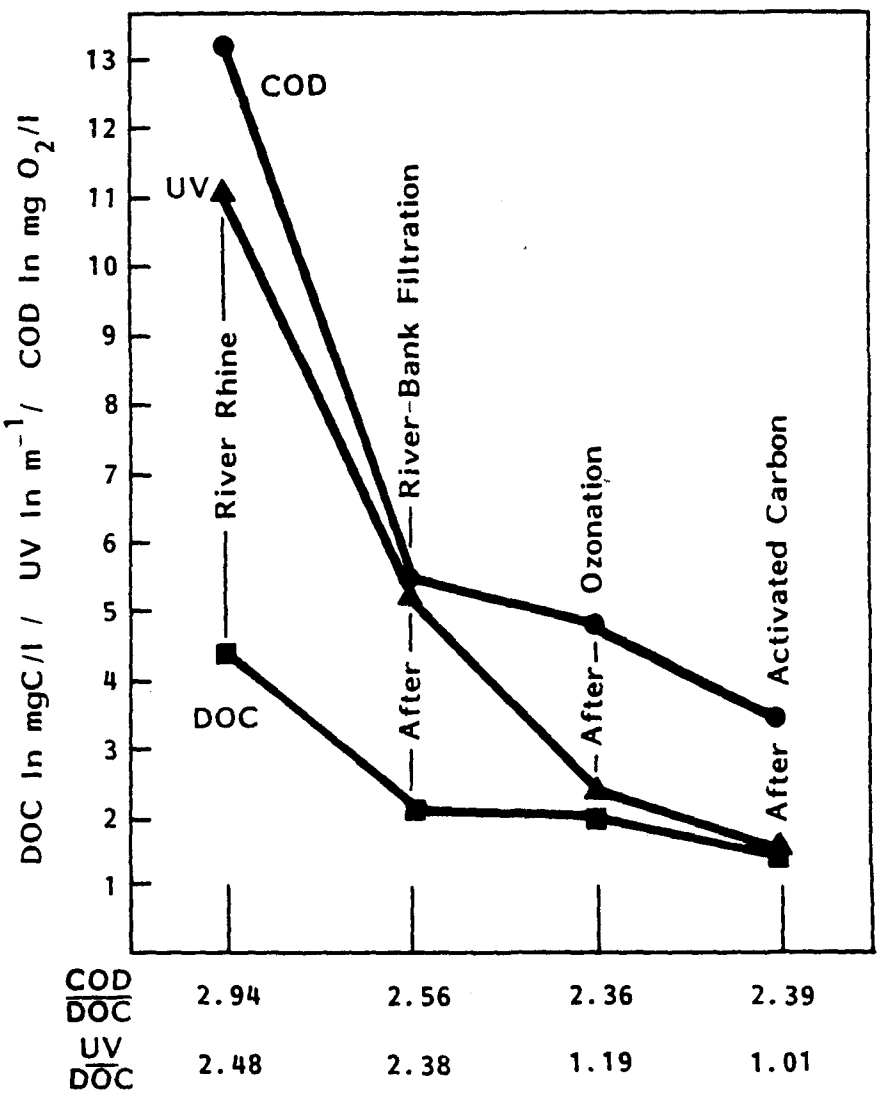

Figure 3. Changes in Collective Organic Parameters During Rhine-River-Water Treatment at Düsseldorf

The diagram includes data for DOC, COD, and UV-absorbance at 254 nm as well as the ratios COD/DOC and UV/DOC. The data are average yearly values for the different treatment steps. The results show that the UV/DOC and COD/DOC ratios decrease after ozonation. However, the COD/DOC ratio remains nearly constant after activated carbon filtration, whereas the UV/DOC ratio decreases further. This shows that UV-absorbance, combined with occasional DOC measurements, will help to shed light on the changes taking place in the organics during different treatment steps. Another application is in comparing data obtained during different years, as in Figure 4.

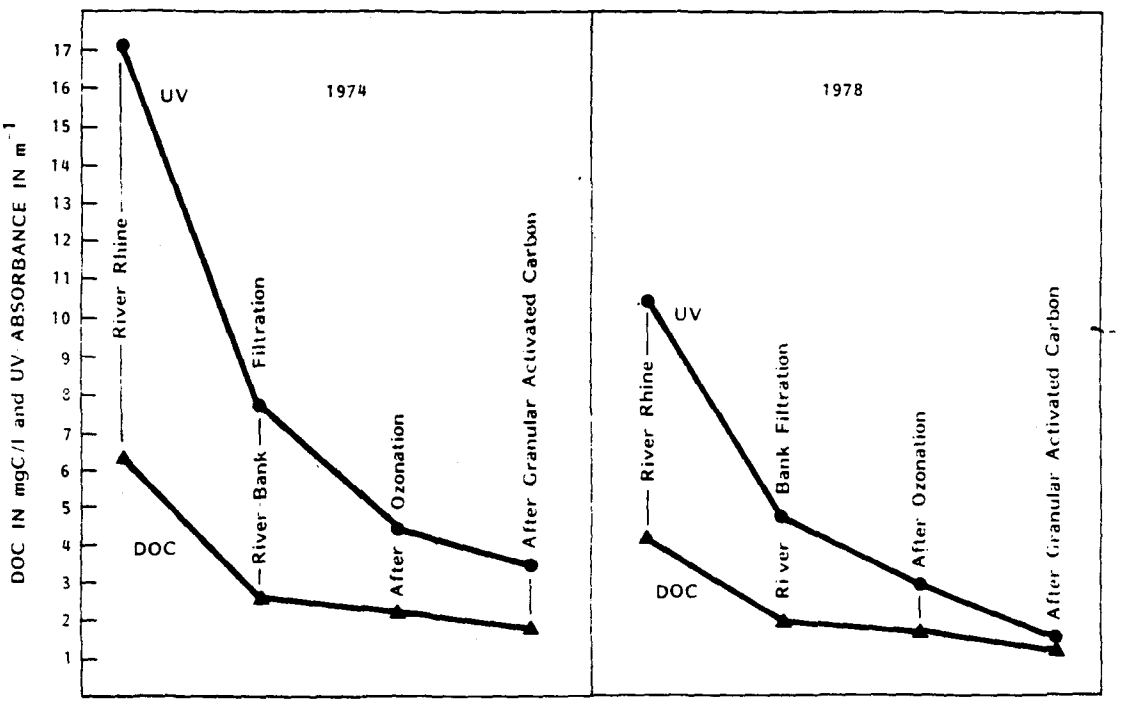

Figure 4. UV-Absorbance and DOC Values for Rhine-River-Water Treatment at Duisburg For Two Different Years

In 1974, the total organic pollution of the Rhine River had been much higher than in 1978. This is shown by the DOC and UV-absorbance measurements. The DOC and UV-absorbance values for drinking water were the same in 1978. This was not the case in 1974, due to the greater pollution of the untreated water. This example shows that UV measurements give information on the amount of the organics and the treatability of the polluted water similar to that obtained by DOC measurements.

This is especially true if we look at adsorption data, where DOC as well as UV measurements can be used to produce adsorption isotherms. As a typical example, such data are shown

in Figure 5 for two different carbons without pretreatment, and for one of the carbon grades before and after flocculation. UV-absorbance, measured at 254 nm wave length and calculated for a 1 m path, has been converted to an equivalent concentration of UV-active substances, calculated as mg/l.

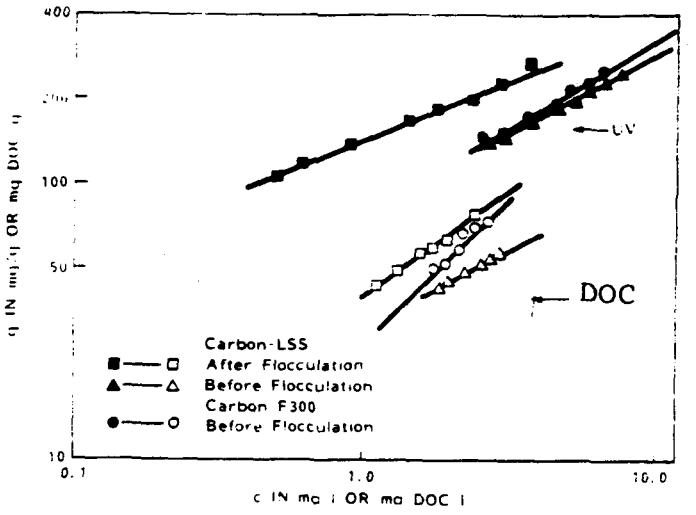

Figure 5. Adsorption Isotherms of Rhine River Water

Comparison between the two carbons reveals that the isotherms are similar when using UV values, but are different when using DOC values. Since UV data represent the better adsorbable organics, we find that the two carbons have similar capacities for these substances. However, this is not the case for all organic substances measured by DOC. Here the carbons and the isotherms are more different. At the same time we find steeper DOC than UV isotherms.

Preflocculation preferably removes polar organics otherwise competing with the less polar ones for adsorption sites on the carbon. Removing the more polar substances by flocculation prior to activated carbon adsorption will therefore reduce competition and lead to less steep and higher adsorption isotherms.

The slopes of the isotherms in Figure 5 explain why lower concentrations in the influent of the carbon filter will lead to lower loadings on the carbon too. This becomes obvious if we compare carbon loadings obtained in 1974 to values obtained in 1976-78, when the influent concentrations were somewhat lower. Some of these comparison data can be seen in Figure 6.

Figure 6 shows non-linear regression curves between loading and throughput for the high pollution level observed in 1974, compared to measured values for the period 1976-78. Here the

quantity of DMF extract has been used as a measure of the total organic concentration (Figure 6). It is quite evident that we now have lower loadings for the same volumetric throughput than we had before 1975. This allows a higher safety margin for the adsorption of undefined and possibly toxic organics for a larger throughput. It must not be forgotten that a decrease in the influent concentration of pollutant also implies a decrease in equilibrium adsorption capacity. The data in the lower half of Figure 6, showing the same comparison, represent the chlorinated organic loading. These data from the treatment of Rhine River water lead to the conclusion that the chlorinated organic compounds (Figure 6) are adsorbed with very similar results to those observed (Figure 6) for the overall organics for the changes in UV-absorbance.

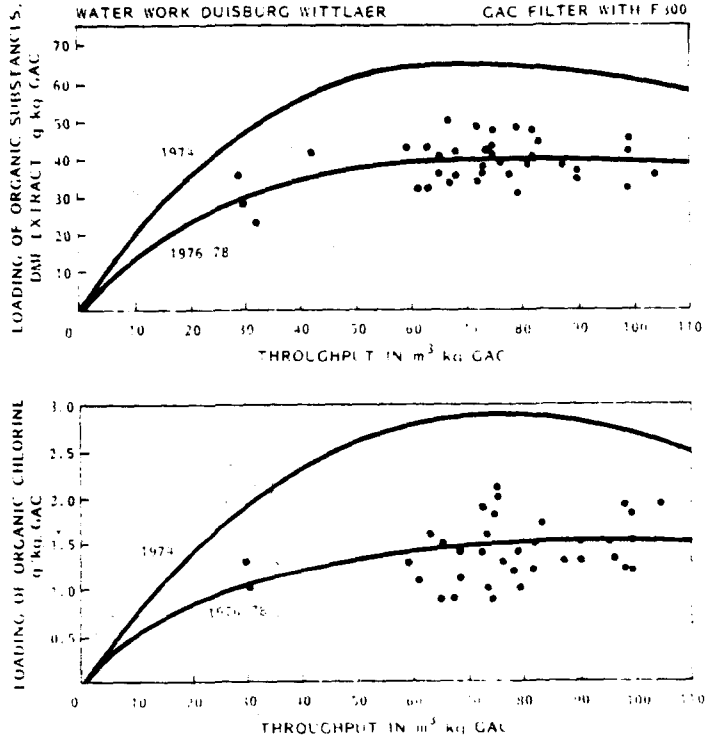

Figure 6. Comparison of Carbon Loadings with Higher (1974) and Lower (1976/78) Pollution in the River Rhine

While we can generally compare breakthrough curves in carbon filters by UV-absorbance as well as by using DOC, there are some differences, as illustrated in Figure 7. This diagram shows breakthrough curves measured at a carbon filter plant. The data suggest similar conclusions if we compare DOC or UV breakthrough curves, but there is a substantial difference

between the curves for the two parameters. The removal efficiency is always higher for the same throughput when measured by UV-absorbance rather than DOC values.

The curves also show that a temporary improvement of the water quality in the influent of the filter can cause desorption of organic substances on the carbon, whereupon the efficiency of the filter is reduced considerably. This is exemplified in Figure 7 by the incident that occurred at a throughput of approximately 23 m^3/kg. The amount of polar compounds covered by DOC is larger and because polar substances desorb more easily, the DOC values measured in the effluent are temporarily greater than the inlfluent values, resulting in a negative removal efficiency.

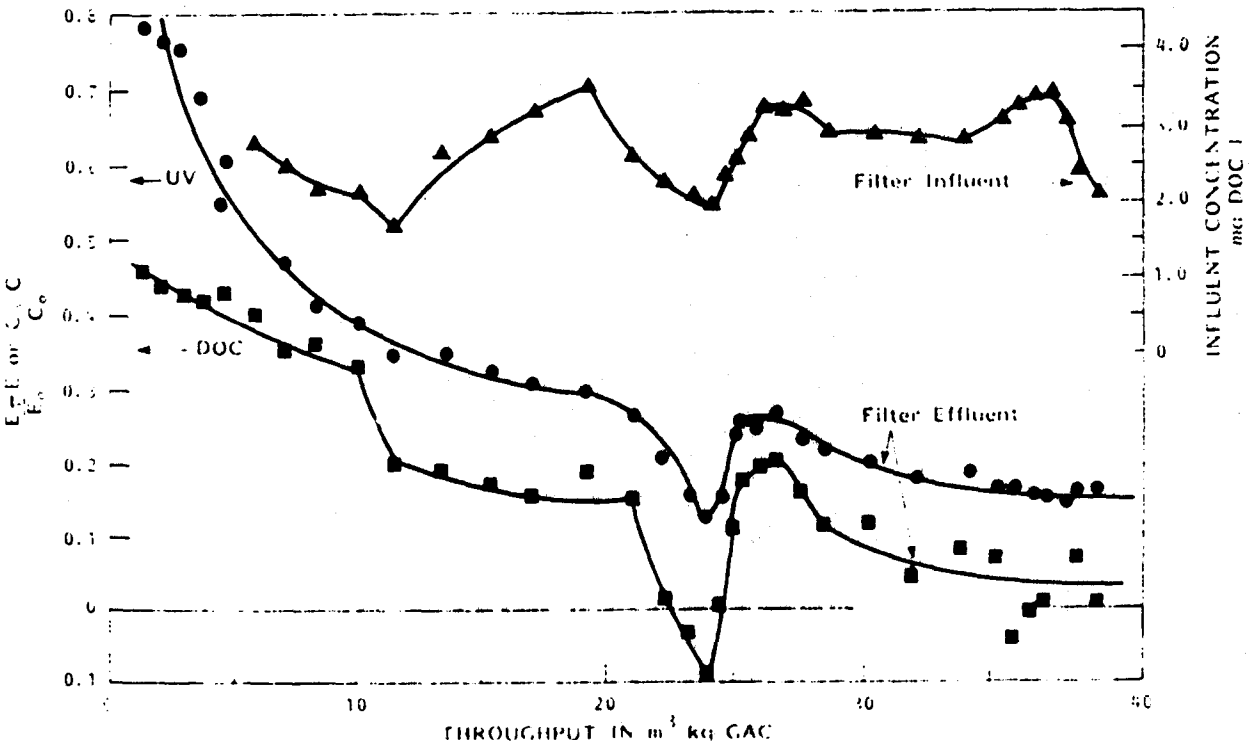

Figure 7. Removal Efficiency of an Activated Carbon Filter (River Ruhr Water). $\frac{Eo-E}{Eo}$ and $\frac{Co-C}{Co}$ are the fractional removals of UV-absorbance and DOC, respectively.

measurements explain the results fairly well, as the P630 carbon used in the first filter has a very flat isotherm and a high adsorption rate. With this we have to expect a small working zone in the carbon filter. One can conclude from the data that UV measurements are useful for easy, rapid control of activated carbon filters in operation. This also has been proven by experience in practice.

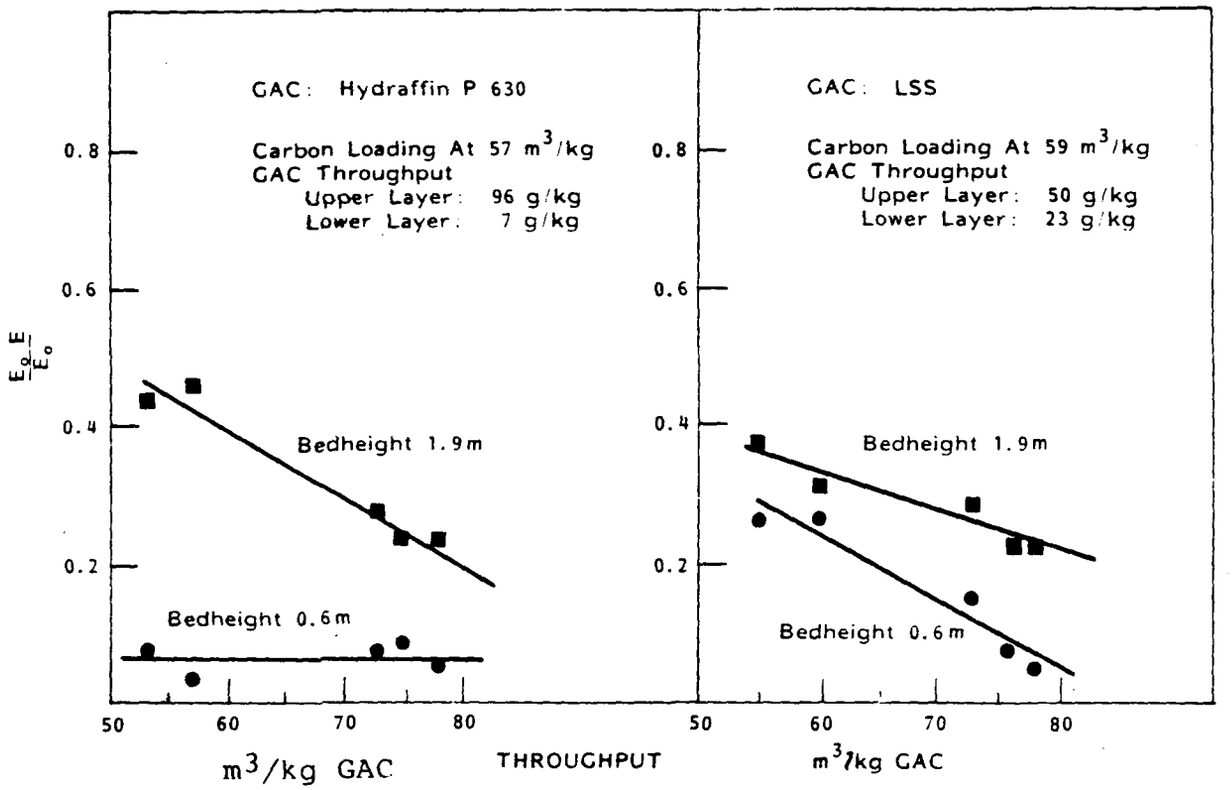

Figure 9. Filter Efficiency at Different Bed Heights in GAC Filters with Two Different Carbons (UV-Measurement)

SUMMARY

Summarizing all the available experience from different types of investigations, the following conclusions can be made:

1. UV-absorbance has proved useful as a control parameter for granular activated carbon filter performance. It is very easy to measure and very often runs parallel with other more significant but more difficult-to-measure criteria, such as dissolved organic chlorine.

2. Generally speaking, UV-absorbance can be used in those cases where parallel tests using other parameters and analytical methods have shown that the UV data correlate sufficiently well with other more important criteria. This is often, although not always, the case. There may be exceptions, for instance if the removal of pure substances like haloforms in small concentration is crucial for the carbon filter operation.

3. In most cases, carbon filter control can best be done by using a convenient method, such as UV-absorbance, for routine control of the filters and by comparing these data from time to time with the results of other more sophisticated methods. This will allow conclusions from easily obtainable data and will give information in such a short time that special tests could be made in case of unusual values and relationsips. In this respect, UV-absorbance measurements can be worthwhile and helpful for carbon filter control.

BIOASSAY TECHNIQUES FOR EVALUATING THE POSSIBLE CARCINOGENICITY OF ADSORBER EFFLUENTS

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INTRODUCTION

Considerable controversy exists concerning the efficacy of granular activated carbon (GAC) as a generally applied measure to protect the public health from the trace organic material that contaminates many surface and some groundwater sources of drinking water. Critics of proposed regulations that would mandate such treatment of drinking water argue that significant reduction of hazards, by GAC treatment, has not been sufficiently demonstrated to justify the capital costs of implementing such treatment.

A limited feel for benefits associated with GAC treatment of drinking water can be obtained by demonstrating the reduction of total organic carbon and removal of specific drinking water contaminants by such treatment. This approach is limited by the ignorance of the toxicological significance of the organic compounds removed by GAC and by the realization that most documented individual organic contaminants of drinking water occur at negligible concentrations in terms of acute toxicity to humans. Moreover, known contaminants of drinking water comprise a very small portion of the organic consitutents present. These difficulties have given rise to the suggestion that a more accurate indication might be obtained with biological testing of hazards associated with organic compounds in drinking water and a more comprehensive means of assessing the degree to which GAC might reduce these hazards.

CLASSICAL METHODS OF ASSESSING CARCINOGENIC RISKS

Carcinogenic and mutagenic activities of chemicals in drinking water are of particular concern because the risk from chemical carcinogens is generally believed to be linear with dose (Hoel, 1977). The traditional use of long-term carcinogenesis bioassays in experimental animals is limited in its application to the organics problem in drinking water for several reasons. First, to be of manageable size, whole animal experiments must deal with relatively high response rates

(Hartley and Sielken, 1977). To rule out the possibility of relatively low levels of risk, the concentration of very large volumes of water is required. Second, the experiments require a long time, either 2 years or for the lifetime of the animal. This limits the ability to take into account the periodic variations that occur in source waters. Third, the expense of this type of testing would considerably limit the ability to study varying source waters and thus leave questions about the generality of the results.

In recent years, considerable progress has been made in understanding certain phenomena which underlie carcinogenic and mutagenic responses. The somatic mutation theory of chemical carcinogenesis, and the demonstration that a large number of known chemical carcinogens could directly or indirectly (by activation with liver microsomal enzymes) induce point mutations in bacteria (McCann, et al., 1975), has led many to suggest that bacterial or in vitro mutagenesis testing could serve to assess the carcinogenic activity in drinking water. However, the relationship between carcinogenic activity and mutagenic activity does not appear to be quantitative (Bartsch, 1976; Meselson and Russell, 1977). To judge the efficacy of a treatment process one must be able to deal with reduction in risk. It is not clear that 50 percent reduction in mutagenic activity in a drinking water produced by GAC treatment can be interpreted as a significant reduction in carcinogenic risk.

The purpose of this presentation is to discuss this problem and outline the approach being taken by the Drinking Water Program of the U.S. EPA.

BACTERIAL AND IN VITRO SYSTEMS AS INDICATORS OF CARCINOGENIC RISK

The simplest and most broadly applied system for mutagenesis testing is the Salmonella tester strains developed by Ames (Ames, McCann and Yamasaki, 1975). Numerous other systems have also been evaluated utilizing other bacterial species, yeast, mammalian cell culture, and the classical Dosophila model. The endpoints employed in these alternative systems also differ from the reversion assay utilized in the Ames test.

The major shortcoming of bacterial and in vitro testing systems as risk assessment models is that they do not adequately take into account the critical role that absorption, distribution, metabolism, and excretion play in the development of toxicological responses in general (Gillette, 1977; Watanabe, Young and Gehring, 1977). The potency of a compound in vivo would be expected to be dependent on the kinetics of steps leading to the formation and destruction of the "active" metabolite as well as alternate pathways of metabolism (Gillette, 1974; Oesch, Raphael, Schwind and Glatt, 1977; Bentley, Oesch

and Glatt, 1977; Billings, McMahon, Ashmore and Wagle, 1977) which are not adequately taken into account with metabolic activating systems applied in vitro (Flesher, Harvey and Synder, 1976; Bigger, Tomaszewski and Dipple, 1978; Oesch, Bentley and Glatt, 1976; Baird, Dipple, Grover, Sims and Brookes, 1973). Similar reservations have been expressed even with pure compounds with respect to predicting risk of heritable mutation using bacterial and in vitro systems by the DHEW Working Group on Mutagenesis Testing (Flamm, et al. 1977). The absence of pharmacokinetic influences in bacterial and in vitro systems is self-evident and requires no further elaboration. It may be possible in the future to take such factors into account by fairly simplistic and short-term animal experiments when dealing with pure compounds. However, there is not even a clue as to how such variables might be taken into account when dealing with complex mixtures such as those found in drinking water.

It is apparent from work supported by our laboratory that drinking water devoid of mutagenic activity is not likely to be found. In Table 1 the mutagenic potency of organics isolated from six drinking waters are compared. Details of the sample preparation have been previously reported by Kopfler, et al. (1977) and the Ames test results by Loper and Lang (1978). The activities represent the total mutagenic activity that could be associated with the indicated drinking waters, excluding cytotoxic fractions, and normalized to recovered organic material. It is notable that the most potent mixture of chemicals was recovered from Seattle drinking water. Seattle obtains its drinking water from a protected watershed. New Orleans was considered to be one of the worst possible situations before this work was initiated, since it derives its water from the industrially impacted Mississippi River, yet it also ranks behind Tucson, where the concentration of total organic carbon is so low as to be unmeasurable. These data are placed in a somewhat different perspective if mutagenic activity is normalized by the volume of water from which they are obtained, however, Seattle still ranks ahead of New Orleans. These results have alerted us to possible carcinogenic hazards occurring in a number of drinking waters. But, can we relate these results to the relative carcinogenic risk posed by drinking water in these cities? We do not think so.

Several investigators have called attention to the fact that quantitative relationships between carcinogenic activity and mutagenic activity in the Ames test are difficult to achieve. These difficulties are evident within the major carcinogen classes such as the polycyclic aromatic hydrocarbons (Andrews, Thibault and Lijinsky, 1978a) and the nitrosamines (Meselson and Russell, 1977; Andrews, Thibault and Lijinsky, 1978b) as well as across chemical classes (Ashby and Styles, 1978a; Ashby and Styles, 1978b).

Table 1. Mutagenic Activity of Organic Compounds Found in Municipal Drinking Water (Adapted from Loper et al., 1978)

	Type of Water Supply	Presumed Source of Contamination	TA 100 Net Colonies/mg	TA 100 Net Colonies/l
New Orleans	Surface	Industrial	41.4	49.1
Miami	Ground	Natural and Industrial	46.4	240.2
Philadelphia	Surface	Natural and Industrial	193.0	181.5
Seattle	Surface	Natural	282.0	66.0
Ottumwa	Surface	Agricultural	6.9	10.0
Tucson	Ground	Uncontaminated	91.4	3.2

Meselson and Russell (1977) were able to obtain 14 chemicals for which the carcinogenic potency was sufficiently well established to compare with mutagenic potency in the Ames test. Without consideration of route of administration, a reasonably good correlation between carcinogenic and mutagenic potency could be made ($r^2 = 0.88$ for log potencies by linear regression) as long as 4 nitrosamines were removed from consideration. Inclusion of the nitrosamines reduced the correlation considerably ($r^2 = 0.12$ on linear regression). As an extension of this same data we have selected 13 of these 14 compounds which had been tested by the oral route. Where test results included multiple species the average carcinogenic potency was utilized and the results depicted in Table 2.

Table 2. Mutagenic and Carcinogenic Potency for 13 Compounds Tested by the Oral Route (Adapted from Meselson & Russell, 1977)

	Mutagenic potency M	Carcinogenic potency K
Aflatoxin B_1	230	405
4-Aminobiphenyl	1.8	0.31
Benzo(a)pyrene	4.8	5.5
Dibenz(a,h)anthracene	0.40	0.47
4-4'-Methylene-bis-2-chloroanaline (MOCA)	0.10	0.41
Methyl methanesulfonate (MMS)	0.057	0.032
2-Naphthalamine	0.59	0.083
1,3-propane sultone	0.54	1.4
Sterigmatocystin	28	21
Diethylnitrosamine	0.00093	9.3
Dimethylnitrosamine	0.0025	6.7
Di-N-butylnitrosamine	0.0097	0.32
N-nitrosomethylurea	0.43	0.10

$r^2 = 0.14$ based upon log potency

M = 1/μg required to produce 100 revertant colonies.
$K = [-\ln(1-I/Dt^{n+1})]$
I = single risk incidence of tumor
D = dose rate
t = time in 2 year intervals
n = 3

As can be seen the correlation between Ames test potency and carcinogenic potency is very low ($r^2 = 0.14$). It is apparent that the Ames test has not yet progressed to the point that changes in its activity can be taken to reflect comparable changes in carcinogenic risk. On the other hand, the qualitative

relationship between carcinogenic activity and mutagenicity in the Ames test indicates cause for concern.

SHORT-TERM IN VIVO BIOASSAYS FOR CARCINOGENIC ACTIVITY

The somatic mutation theory opens the way for shorter term in vivo assays for carcinogenic effects of chemicals as well as supplying a rationale for bacterial and in vitro systems. A number of experimental systems have been and are being developed which are capable in the short-term of addressing the relative carcinogenic potential of chemicals in vivo. These methods are of essentially two types, involving either measurements of DNA damage or cellular response (transformation). The former methods may or may not quantitatively relate to a carcinogenic response; the latter actually involve preneoplastic changes that should be proportional to carcinogenic potency. Consequently, there are certain advantages in interpretation in the latter case. The relationship between levels of DNA damage and carcinogenic potency is at present unresolvable because of questions relating to tissue specificity, repair processes, the large variety of eletrophilic intermediates generated with certain carcinogens, and the multiplicity of potential nucleophilic binding sites for such intermediates of DNA.

In Vivo Transformation Assays

Development of this group of bioassay methods have derived much of their impetus from evidence indicating there are two distinct stages involved in chemical carcinogenesis, first demonstrated in the mouse skin by Berenblum (Berenblum and Shubik, 1947). The stages are referred to as initiation and promotion. Initiation, the first stage, is the irreversible alteration of a cell to a potential cancer cell and can be accomplished by a single application of a chemical. This stage is hypothesized to result from a somatic mutation. Development of tumors could then be brought about or accelerated by continuous application of a second agent, referred to as a promotor. Some chemicals possess exclusively one property or the other. However, others possess both activities and are referred to as complete carcinogens. Higher total doses of an individual compound invariably are required for complete carcinogenesis than for initiation. These initial observations of Berenblum eventually resulted in the now classical bioassay system for tumor initiation and promotion in the mouse skin.

The mouse-skin system is a very convenient model. It is quite sensitive to certain classes of carcinogen and tumor development is quickly evident in the form of papillomas without sacrifice of animals. Papilloma formation appears as early as 5-6 weeks after beginning promotion, peaking at about 12-14 weeks. Development of carcinomas takes longer, approximately one year. However, there is a very high degree of correlation

between the initial development of papillomas and subsequent development of carcinomas (Burns, et al., 1978). The disadvantages of the system are that the skin is not the target organ for many classes of chemical carcinogens; and that it lacks the systemic pharmacokinetic influences. Thus, the data are of limited usefulness for risk assessment of chemicals involving the oral route of exposure.

Development of useful short-term systems for other target organs entailed finding the counterpart of the papilloma in these organs. These were first demonstrated by Farber (1973) as regenerating or hyperplastic nodules in the livers of animals fed different hepatocarcinogens. These nodules were shown to develop into carcinomas if treatment was continued, but many disappeared if treatment was terminated, a situation very similar to that observed with skin papillomas. It was subsequently shown that, although the nodule disappeared, transformed foci remained which could be appropriately stimulated to yield carcinomas (Farber, 1976). Prior to this finding (Friedrick-Freksa, Gossner and Borner, 1969) and subsequently (Solt and Farber, 1976; Farber, 1978), it has been shown that within a short time following initiating doses of hepatocarcinogens, small foci of altered cells can be demonstrated histologically. These cells possess alterations in morphology which appear identical to those served in fully developed carcinomas (Sherer and Emmelot, 1975). Subsequently, it has been demonstrated that the appearance of enzyme-altered islands and their development into hepatocellular carcinomas can be increased and accelerated by a variety of promoting agents (Peraino, Fry and Grube, 1978; Pitot, Barsness and Kitagawa, 1978; Farber and Solt, 1978). Phenotypic comparisons of foci and hepatocellular carcinomas are compatible with a progression of foci, to hyperplastic nodule, to tumor, and substantiate operation of a two-stage process of chemical carcinogenesis in the liver (Farber, 1973; Solt and Farber, 1976; Farber, 1976; Sirica, Barsness, Goldsworthy and Pitot, 1978).

The ability to promote lesions is extremely important to the development of short-term in vivo assays. The number of initiated cells produced does not vary between promoted and non-promoted systems, but the ability to detect initiation depends upon replication of the transformed cells. In the case of the liver, it has now been well demonstrated that promotion substantially increases the number of histochemically observable foci, the development of hyperplastic nodules, and ultimately the number of tumors developed in long-term experiments (Farber and Solt, 1978; Peraino, Fry and Grube, 1978; Pitot, Barsness and Kitagawa, 1978; Sirica, Barsness, Goldworthy and Pitot, 1978).

The enzyme-altered foci induced by carcinogens and subjected to promotion are easily detectable at low power magnifications within 3-4 weeks of carcinogen exposure. The sensitivity of a bioassay based upon such systems can be estimated by examining

the ratio of foci and tumors developed by such procedures vs. the responses obtained without such procedures. Farber and Solt (1978), using a promotion regimen involving subcarcinogenic doses of 2-acetylaminofluorene (2-AAF) in the diet for 1 week followed by partial hepatectomy, found approximately 10^3 foci/liver in fischer rats resulting from a dose of 200 mg/kg diethylnitrosamine (DEN). Seventy percent of animals so treated developed hepatocellular carcinomas in nine months. With the same dose of DEN and observation period no tumors were observed in Fischer rats which had not been subjected to 2-AAF and partial hepatectomy. In another study, 4.9×10^3 foci/liver were observed after 3 months in animals given 150 mg/kg DEN on a choline-deficient diet, whereas animals subjected to the same dose of DEN with a choline-sufficient diet displayed no foci. The effect of choline deficiency could be increased by another 25-fold by including partial hepatectomy in the experimental procedure (Lombardi and Shinozuka, personal comm.). These results indicate: measurement of foci is about 1000X as sensitive as long-term carcinogenesis studies conducted with the same treatments, even though results can be obtained within a month; and development of foci is predictive of subsequent tumor development.

Change in the target organ specificity of a chemical carcinogen is another feature of promotion. For example, dibenzanthracene and urethane are initiators, but not complete carcinogens in the mouse skin. However, the skin does become a target organ for these compounds; that is, tumors are developed if initiation by these compounds is followed by phorbol ester promotion. Recently, Shinozuka and Lombardi (1978) demonstrated that the choline-deficient diet greatly enhanced development of hepatocellular carcinomas and decreased evidence of pancreatic adenocarcinomas in rats exposed to azaserine. Without such promotion, pancreatic tumors predominate in azaserine carcinogenesis (Longnecker and Curphey, 1975). Consequently, it may be possible to base a short-term in vivo bioassay for carcinogenic potential on the basis of a single, or a few, target tissues. Despite this possibility the approach would be considerably enhanced if it could be applied to other target organs. Although not as yet extensively studied as the liver, identification of promoters active in other target tissues [e.g., colon (Reddy, Weisburger and Wynder, 1978), lung (Witschi and Lock, 1978), bladder (Hicks, Chouaniec, and Wakefield, 1978), and pancreas (Shinozuka, Popp and Konishi, 1976)] promises rapid progress in developing parallel assays in other target organs.

At the Health Effects Research Laboratory of EPA in Cincinnati, we are presently examining the utility of the two established initiation/promotion systems in assessing the hazards associated with organic chemicals in drinking water. In preliminary experiments we have found that treatment of coagulated, settled, and filtered Ohio River water with various disinfectants used in drinking water treatment increased the

carcinogenic potency of chemicals present in the mouse skin. These experiments were conducted by injecting a total of 1.5 ml of 100-180 fold reverse osmosis concentrates (celluose acetate) subcutaneously in SENCAR mice followed by promotion with phorbol myristate acetate (PMA). Preliminary results showing papillomas data obtained through 18 weeks of exposure are shown in Table 3. Ranking of the potency of the reaction products was ozone > chlorine = chloramines > chlorine dioxide. The specific activity of the compounds found in such water was approximately 1-2 percent of 7,12-dimethylbenzanthracene, based on the total organic carbon content of the original water. It is not possible to determine what this means in terms of potential human health hazard, although potencies of this magnitude are certainly not negligible. Ames tests of these concentrates were negative (Loper, personal comm.), most probably because of insufficient concentration of the material present. Similar concentrates are presently being used to confirm these results in mouse skin and to extend the analyses to enzyme-altered foci in the liver of rats in cooperation with Drs. Lombardi and Shinozuka of the University of Pittsburgh. An additional aspect in the present studies is to examine the influence of GAC removal of precursor substances on the carcinogenic responses induced by disinfectant treatment.

Table 3. Papillomas Resulting from Treatment of SENCAR Mice with Reverse Osmosis Concentrates[a] of Waters[b] Treated with Alternate Disinfectants and Promotion with PMA[c].

Treatment	Concentration Factor[d]	Number of Animals with Tumors/Number Treated.	Fraction	Total Number of Tumors
Non-disinfected	102	0/25	0	0
0.9% saline	-	0/25	0	0
7,12-Dimethylbenz-anthracene	-	16/25	0.64	35
ClO_2	168	0/25	0.00	0
Cl_2	106	4/25	0.16	5
$Cl_xNH_{(3-x)}$	142	5/25	0.20	8
O_3	186	7/25	0.28	9

[a] Dose of concentrate 6 x 0.25 ml s.c. injections over 2 weeks.

[b] Coagulated, settled and dual-media filtered Ohio River Water.

[c] PMA = phorbol myristate acetate 2.5 µg in acetone to the skin 3 x weekly for 18 weeks.

[d] Initial volume/concentrate volume.

A second study has been initiated using SENCAR mice which is attempting to determine the relative carcinogenicity of organics extracted from the drinking water of five cities. Concentration techniques were the same as indicated previously for Ames testing. Early results of this study are shown in Table 4. Although it is too early in the experiment to form any firm conclusions, it is interesting to note that to date an entirely different order of carcinogenic potency is emerging from this work than was obtained with Ames testing. Whereas Salmonella mutagenesis ranked the potency of chemicals derived from the five cities (in descending order) as Seattle > Philadelphia > Miami > New Orleans >Ottumwa, the initiating potency appears to be New Orleans > Miami > Ottumwa > Philadelphia > Seattle. Comparisons of the ROE and XAD fractions of the five cities also reveal marked inconsistencies with the mouse skin and Ames test in scoring relative potency. In fairness it must be pointed out that these assays were not run on identical samples, so that exact agreement is perhaps too much to expect. On the other hand, blind spots created in Ames testing of complex mixtures as a result of cytotoxicity may prevent direct comparisons from being made. We have yet to encounter toxicity problems in any of our SENCAR mouse studies.

DNA Damage

The somatic mutation theory of chemical carcinogenesis suggests that the initial (but not necessarily sufficient) event leading to cancer involves an alteration in genetic material, now known to be DNA. Consequently, if methods were available to assess the damage done to DNA as a result of carcinogen exposure, it should be possible to correlate such damage with the development of tumors. In point of fact, this assumption underlies all in vitro assays which utilize mutation as a measure of carcinogenic activity. If one assumes that the differences in potency of chemicals in vivo and in vitro is solely dependent upon pharmacokinetic and metabolic considerations, measurement of DNA damage in target tissues in vivo should rectify the differences. A number of factors prevent immediate adoption of available techniques for measuring nucleic acid damage in vivo as a simplistic answer to the short-term assessment of carcinogenic risk.

Chemical carcinogens or their metabolites interact with DNA at a variety of sites forming covalent bonds with purine and pyrimidine bases or the phosphodiester backbone of the DNA chain (see e.g., Singer, 1977, on nitrosamine adducts; Miller and Miller, 1977). Immediately after the damage is done, repair processes are initiated which may be of either high fidelity or error-prone. A question, the discussion of which is beyond the scope of this presentation, exists as to whether initial DNA damage, residual damage, or repaired damage would be the best measure of carcinogenic potency.

Table 4. Papillomas Resulting from Treatment of SENCAR Mice with ROE[a] and XAD[b] Fractions of Municipal Drinking Waters and Promotion with PMA for 16 Weeks

Sample[c]	Number of Animals with Tumors/Number Treated	Total Tumors	ROE + XAD
Miami			
ROE	4/40	4	
XAD	4/40	5	9
Ottumwa			
ROE	4/40	5	
XAD	2/40	2	7
Philadelphia			
ROE	2/40	2	
XAD	2/40	2	4
Seattle			
ROE	0/40	1	
XAD	1/38	1	2
New Orleans			
ROE	1/40	3	
XAD	3/40	7	10
Solvent	2/40	2	2
DMBA 25 µg	35/40	261	261

a = Reverse osmosis concentrate extracted sequentially with pentane, methylene chloride and acidified methylene chloride taken to dryness and combined (Kopfler et al. 1977).

b = Residual reverse-osmosis concentrate placed on XAD-2 and eluted with ethanol (Kopfler et al. 1977).

c = Doses 6 X 25 mg/Kg over a 2 week period for all ROE and XAD samples.

Only very limited attempts have been made to relate DNA-damage induced in vivo with subsequent tumor development. The alkaline elution method has been used to detect DNA damage induced by single doses of N-nitrosodimethylamine, N-methyl-N-nitrosourea, 1, 2-dimethylhydrazine, and cycasin (Parodi et al. 1978). This method measures the formation of breaks and/or alkaline labile sites within DNA. DNA strands are eluted from a filter paper under alkaline conditions in order of increasing molecular weight. The organ specific damage measured in this way was consistent with the target organ specificity of the above chemical carcinogens. In support of this observation, Petzold and Swenberg (1978) found similar target-organ-specific damage with dimethylnitrosamine, diethylnitrosamine, 4-nitro-quinoline-1-oxide, 2-acetylaminofluorene, N-hydroxyacetyl-amino-fluorene, aflatoxin B_1, 1,2-dimethylhydrazine, azoxymethane, benzidine, and 7,12-dimethylbenzanthracene. In this latter study, a number of direct acting alkylating agents demonstrated little organ-specificity in DNA-damage induced in vivo. It is expected that improvements in assay methods currently underway may improve the correlation with carcinogenic potency. Other methods of measuring similar damage or to recognize damaged sites other than the alkaline labile sites using endonucleases (Sheridan and Huang, 1977), and improved methods analysis of DNA molecular weight distributions (Koropatnick and Stich, 1976), are examples of technical improvements currently being investigated.

If quantitative correlations between DNA damage and carcinogenic potency can be established based on target organ specificity, sensitive and non-sensitive species, and carcinogenic potency we fully expect to apply such techniques to drinking water problems.

APPLICATION OF BIOASSAY METHODS TO DEFINING SAFETY OF DRINKING WATER

As outlined above there are several bioassay systems available for assessing the carcinogenic and mutagenic activity of organic chemicals occurring in drinking water. All of these methodologies have their place in the research effort necessary to determine what hazards are associated with drinking water and how such hazards may be reduced by varying water treatment practices. Advantages in terms of cost must be balanced with the quality of the information gained. Bacterial and in vitro systems have been applied widely and have basically established the point that there is reason for concern. They should be continued in this context. However, it must be recognized that they are not capable of defining the level of risk and by extension they are of limited usefulness in determining changes in the level of risk resulting from variations in the treatment process. Because of their limited performance as quantitative predictors of carcinogenic risk it cannot be concluded that a reduction in

in vitro mutagenic activity represents a proportionate reduction in carcinogenic hazard.

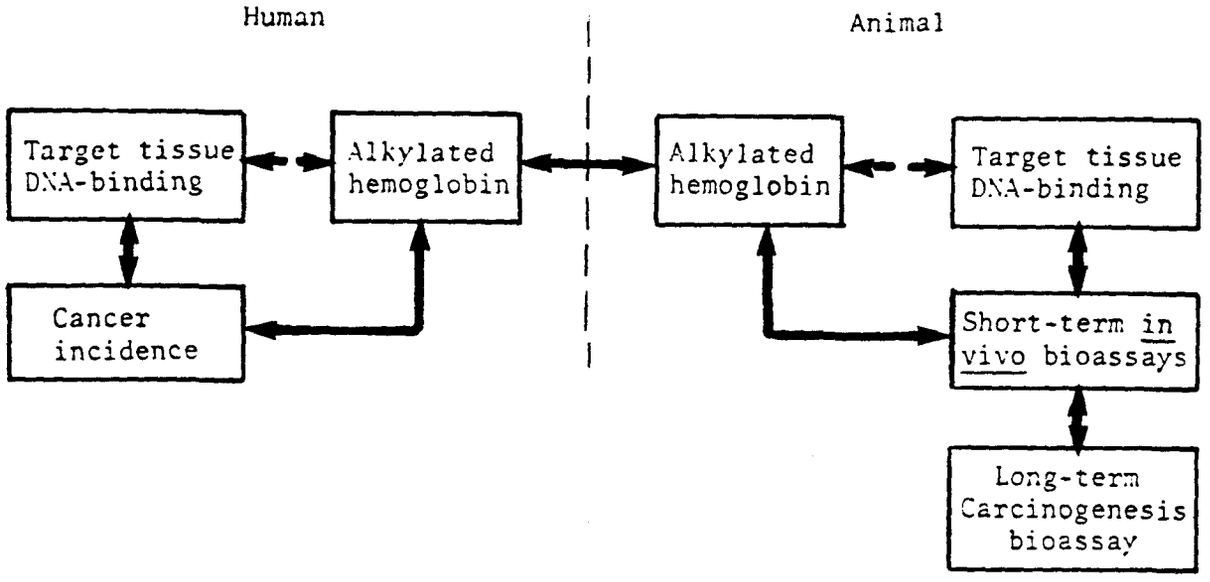
This fact has led us to the conclusion that evaluation of treatment processes for drinking water must involve in vivo methods. Consideration of the quantities of sample materials required and the high cost of long-term carcinogenesis bioassays precludes the use of these classical methods on a wide basis. Consequently, our Laboratory is concentrating its efforts on detecting the initiating activity of chemical carcinogens in short-term in vivo animal experiments. Many of these bioassays require less than 1 month to perform and approach in vitro techniques both in terms of quantity of sample required and in overall cost.

It is important not to be misled by the apparent simplicity and lower costs of bacterial and in vitro test systems for general screening of complex mixtures. In many instances, inexpensive in vivo systems, such as the mouse skin initiation/promotion assay, are likely to be more cost effective. This is particularly true where cytotoxicity prevents determination of activity by in vitro methods. The greater adaptive capabilities of the whole animal allows carcinogenic potency to be assessed where extensive fractionation, with the attendant problems of recovery and artifact, would be required for adequate Ames testing. The studies with SENCAR mice reported here indicate that sensitivity of such systems is not necessarily inferior to in vitro and bacterial systems, as is commonly supposed. Consequently, demands on the amount of sample required per mouse is certainly no more than that required per plate in the Ames test.

The in vivo methods available are not limited to those specifically addressed in this presentation. We have specifically chosen techniques which have high sensitivity to minimize the concentration of water samples. Extensive concentration magnifies problems of recovery and artifact. If required on a large scale, as would be required for long-term animal experiments, concentration of organic constituents from drinking water becomes the major cost involved. Although methods such as in vivo cytogenetic analysis and chromosome aberrations will undoubtedly be utilized, the sensitivity of such systems to low levels of risk in vivo are clearly limited (see e.g., Trzos, Petzold, Brunden and Swenberg, 1978).

Even using in vivo methods for determining carcinogenic potency, the extrapolation of risk from experimental animals to man is not without its difficulties (Schneiderman and Brown, 1978; Hartley and Sielken, 1977; Clayson, 1977). In some respects we see the utilization of short-term in vivo assays coupled with more adequate dosimetry as one means of improving the ability of cross-species extrapolation of carcinogenesis

data. If animal experiments and human epidemiology studies can be normalized by better dosimetry, much better comparison of carcinogenic potency may be realized in the context of the following scheme:



The proposed dosimeter, alkylated hemoglobin, is based upon the principle that the majority of chemical carcinogens appear to be, or are metabolized to, electrophilic agents which bind more or less indiscriminately with nucleophiles present within the body (Miller and Miller, 1977). Systemically administered carcinogens have been shown to bind to histidine and cysteine residues in hemoglobin (Osterman-Golkar, et al., 1976; Osterman-Golkar, et al., 1977; Segerback, et al., 1978, Calleman, et al., 1978; Pereira, unpublished results) in both man and experimental animals. Since the bound residues are potentially traceable to the exposure and represent an integration of both dose and metabolic activation, levels of alkylated hemoglobin can be adjusted both in man and experimental animals to take into account the influence of differing pharmacokinetic and metabolic factors. Thus, controlling the level of alkylated hemoglobin has the potential of being a powerful means of cross-species normalization of dose-response information. Given this tool, the ability to normalize initiating activity with eventual tumor incidence in experimental animals can be extended to human populations with documented and quantitated exposures to particular chemicals. This will allow direct comparison of results from animal experiments and human epidemiology.

The within-species validity of short-term in vivo assays can be easily established if there is a consistent relationship with tumor development in long-term carcinogenesis bioassays.

To a very large extent this can be done by comparing results in the short-term systems with already existing long-term data. Development of epidemiological data on the basis of comparisons of tumor incidence and levels of alkylated hemoglobin can then serve as the means of comparing man's sensitivity to particular carcinogens with that of animals. If this approach proves valid, we will be in a position to assess with confidence the hazards associated with chemically undefined mixtures found in drinking water.

In conclusion, it must be recognized that there are a wide variety of toxicological hazards potentially associated with drinking water. A combination of factors, ranging from public perception of the problems to the emergence of a critical level of fundamental knowledge, which allows development of appropriate short-term methods, has focused attention on the carcinogenic and mutagenic hazards found in drinking water. As imperfect as they are, these are the basis for the approach outlined here. There are limitations in the basic research information available to address other toxicological hazards such as potential developmental toxicities, cardiovascular disease risk, neurotoxic hazards, etc. resulting from organic chemicals in drinking water. As the ability to address such problems effectively is developed, these other toxicological endpoints will also have to become part of the assessment.

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SPECIFIC ANALYSIS OF TRACE ORGANICS IN WATER USING GAS CHROMATOGRAPHY AND MASS SPECTROSCOPY

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INTRODUCTION

Organic contaminants in water must be identified specifically and measured quantitatively if the mechanisms and efficiencies of their removal and formation in treatment processes are to be investigated. General parameters such as Total Organic Carbon, Chemical Oxygen Demand, and Total Organic Chlorine give a good indication of the overall performance of a process or a plant. However, they do not reflect the behavior of all the classes of organic compounds normally present in waste and polluted surface waters (1).

The need for specific compound analysis stems also from governmental, legal, and regulatory action. The "EPA Consent Decree" requires limitations or guidelines for as many as 129 pollutants, of which 114 are organic. The analytical implications and problems encountered in backing up these regulations have been discussed recently by L.H. Keith and W.A. Telliard (2). It is apparent that no straightforward approach is available today to measure all 114 pollutants.

This paper presents an approach for the analysis of a broad range of trace organic compounds, as it has evolved during a study on trace organics removal at the advanced wastewater treatment plant Water Factory 21 in Orange County (1). Four different extraction and chromatographic procedures have been combined in an integrated analytical scheme using gas chromatography for quantitation and gas chromatography/mass spectroscopy for qualitative analysis.

ENRICHMENT OF ORGANIC POLLUTANTS

The procedures for the extraction and enrichment of organic compounds from water samples are based on favorable thermodynamic equilibria. To predict their behavior in an analytical scheme, it is necessary to know the thermodynamic constants which control these equilibria. Constants for predicting the partitioning in a water/gas or water/solvent system include the Henry's Law constant and the n-octanol/water partition co-efficient (K_{oct}). In

Table 1 these constants are given for a set of representative compounds that are frequently found in water (3).

The Henry's Law constant relates the partial pressure of a volatile solute to its concentration in a pseudo-ideal dilute solution. The value of the constant can be approximated with reasonable accuracy from the ratio of the vapor pressure of the pure compound to the solubility limit of the solute in water [4]. The higher this constant, the better a compound volatilizes from water.

The n-octanol/water partition coefficient has been tabulated by Hansch and coworkers (5). The logarithm of the partition coefficient is the Hansch-parameter, P_{oct}. The higher the value of P_{oct} the more strongly a compound partitions into a hydrophobic organic solvent and the less solvent will be required for an efficient extraction.

Enrichment by Purge-and-Trap

A popular approach to concentrate volatiles from water samples is the purge-and-trap technique, where a continuous gas stream is bubbled through the water sample and the purged organics are trapped with a suitable adsorbent. The kind and amount of adsorbing material has to be chosen and optimized carefully. Bellar and Lichtenberg use TENAX^{R} adsorbent to measure the highly volatile compounds ranging from methylene chloride to chlorobenzene (6). Similarly, Grob and coworkers use milligram amounts of activated carbon (AC) to enrich a broad variety of compounds (7).

All compounds in Table 1 with a Henry's Law constant above 10^{-3} atm $\cdot$ mol^{-1} m^{3} are purged by gaseous stripping; we can assume that compounds with somewhat lower constants are at least partially stripped. However, compounds with constants below 10^{-6} are expected not to be recovered efficiently, as is the case for phenol (7). The overall recovery is affected not only by the stripping process, but also by the efficiency of the adsorption onto the AC filter and by the desorption from it. Highly volatile compounds are not well adsorbed (e.g., methylene chloride and chloroform) and therefore need to be trapped with an adsorbent having a relatively large surface. Desorption from a high-surface adsorbent with a solvent or by heating in a gas stream leads to a relatively high dilution and to a lesser concentration effect.

The Grob procedure uses the headspace of the apparatus (Figure 1) to purge the volatiles and a pump to recycle the air. Thus, no gas need be introduced from outside and contamination from gas supplies is eliminated. This is essential since

Table 1. Physical Constants of Representative Organic Pollutants[a]

Substance	Molecular Weight	Boiling Point (°C) 1 atm	Solubility in Water (mg/l) 20°C	Vapor Pressure (mm) 20°C	Henry's Law Constant atm·mol^{-1}·m^{3}[b]	P_{oct}[c]	Anal[h]
Dichloromethane	84.9	40	20,000	349	1.9×10^{-3}	1.59	(A)
Chloroform	119.4	62	8,000	160	3.1×10^{-3}	1.97	A
Benzene	78.1	80	1,780	76	4.4×10^{-3}	2.13	(B)
Toluene	92.1	111	515	22	5.2×10^{-3}	2.69	B
Tetrachloroethylene	165.8	121	140	76	2.2×10^{-2}	2.88	A
Phenol	94.1	182	82,000[d]	0.2[e]	$\sim 3 \times 10^{-7}$	1.46	E
Naphthalene	128.2	218	33	0.23	1.2×10^{-3}	3.20	B
Benzoic Acid	122.1	249	2,900	0.2[e]	1.1×10^{-6}	1.87	G
DDT[f]	354.5	-	1.2×10^{-3}	1×10^{-7}	3.9×10^{-5}	6.19[g]	C

[a] K. Verscheueren, Handbook of Environmental Data on Organic Chemicals, Von Nostrand Reinhold Co., Inc 1977.

[b] Approximated from the ratio of the vapor pressure of the pure compound to the solubility limit of the solute in water (4).

[c] P_{oct} = logarithm of n-octanol/water partition coefficient tabulated in Reference 5. (Underlined values are calculated based on substituent constants.)

[d] Value for 15°C.

[e] Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd ed., Wiley & Sons Interscience, New York, 1967.

[f] D. Mackay and P.J. Leinonen, Environ. Sci. Tech., 9(13), 1178 (1975).

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[h] See Table 2 for code of designations for analytical methods.

the purging time can then be extended so that slowly purged substances are trapped quantitatively at the activated-carbon filter.

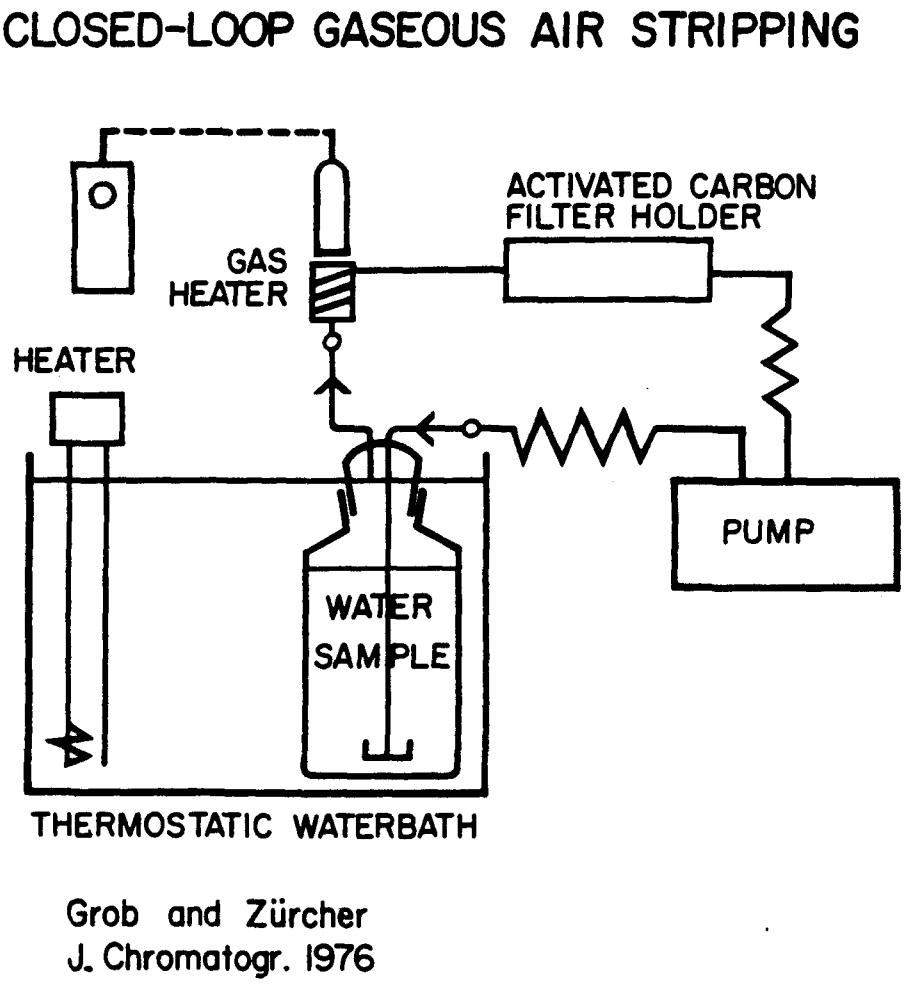

Figure 1. Schematic of Closed-Loop Stripping Apparatus

The flux J of a solute i across the phase boundary A, when liquid film resistance dominates, is given by Eq. 1 (4):

$$J_i = \frac{d(Q/A)}{dt} = K_{OL}\left(C_i - \frac{P_i}{H_i}\right) \qquad (1)$$

where Q is the mass of the solute removed, K_{OL} is the overall mass transfer coefficient, C_i the concentration of compound i in the liquid phase, P_i is the partial pressure in the bulk gas phase, and H_i is the Henry's Law constant of compound i. It is evident from this equation that if H_i becomes too small, the flux is reduced to such a degree that extremely long purge times would have to be applied to achieve a significant transfer. On the other hand, if the activated-carbon filter does not adsorb the volatiles from the headspace, they are recycled with the air into the water sample, and no significant removal occurs. K_{OL} is not known; however, it was found that smaller compounds of low molecular weight are removed within minutes when the purge gas is flowing.

To achieve optimum reproducibility, a number of measures have to be taken that are discussed by Grob and Zurcher [8]. These include temperature stabilization of the sample, preheating of the air stream prior to adsorption to reduce relative humidity, and preconditioning of the adsorbent filter. For quantitative determinations, recovery factors for each compound must be determined. This is particularly true for compounds which belong to a different compound class or differ considerably in their physicochemical constants from those for which the method has been calibrated previously.

For heavily loaded waters, smaller samples must be used since overloading of the AC filter may occur. Smaller samples are stripped in smaller flasks with equal headspace. Variations in the relative volume of the gas and liquid phases severely distort the recovery of the compounds. This is evident from Figure 2, which depicts the ratio of the peak areas of 1-chlorooctane ($Cl-C_8$) to 1-chloro-dodecane ($Cl-C_{12}$) as a function of increased headspace and decreased water volumes. It is evident that the recovery of the more volatile $Cl-C_8$ decreases as headspace increases. This effect is expected to be similar for all volatile compounds in the system and was, in fact, observed by Grob and coworkers. For benzene, these authors found a recovery of only 20 percent (7), presumably due to its insufficient recovery on the AC filter.

Elution of the organics from the AC filter has thus far been quantitative and has not been found to limit the range of the analysis if 20 µl carbon disulfide are used.

Enrichment by Solvent Extraction

Organic compounds partition from water into an immiscible organic phase in constant ratios. A comprehensive collection of such partition coefficients has been assembled by Leo, Hansch, and Elkins (5). They chose the partition coefficient in n-octanol/water, K_{oct}, as a reference and calculated incremental substituent constants. With these substituent constants it is

possible to estimate the partition coefficient for a compound when experimentally determined value for a parent compound is available. Log K_{oct} (or P_{oct}) is a measure of the lipophilic nature of a compound. The higher its P_{oct}, the more a compound will partition into a hydrophobic phase. DDT has a P_{oct} greater than 6 and is easily extracted from one liter of water with 2 x 15 ml hexane. In contrast, for the extraction of the more hydrophilic phenol, (P_{oct} = 1.46), repetitive extraction with approximately several hundred ml of methylene chloride is required. For acidic and basic compounds, the pH must be adjusted prior to extraction. This effect is used for a preseparation of the organics in acidic and basic fractions.

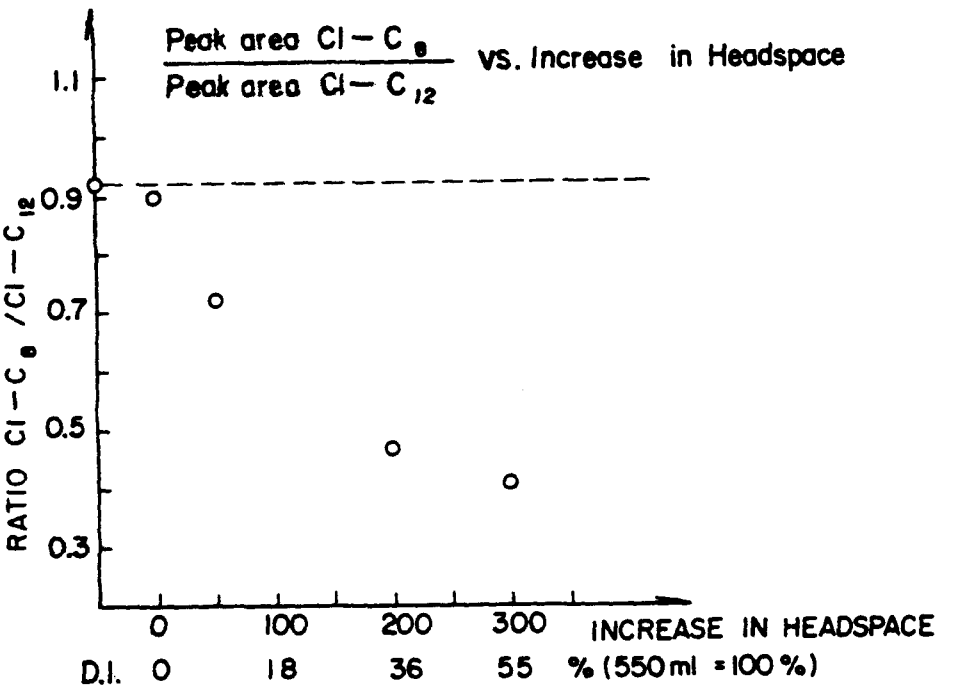

Figure 2. The Influence of the Headspace Volume (in ml) on the Relative Recovery of the Internal Standards Cl-C_8 and Cl-C_{12}. The dotted line represents the value of direct injection (D.I.) of standard solution.

THE ANALYTICAL SCHEME

These considerations and experiences have led to an integrated analytical scheme for the analysis of a broad range of compounds, in which four different extraction and enrichment procedures are combined (Figure 3). Highly volatile compounds are analyzed as 50-ml samples by pentane extraction. The analysis is termed volatile organic analysis (VOA) and is specific for the haloforms and chlorinated compounds with one and two carbons (Group A).

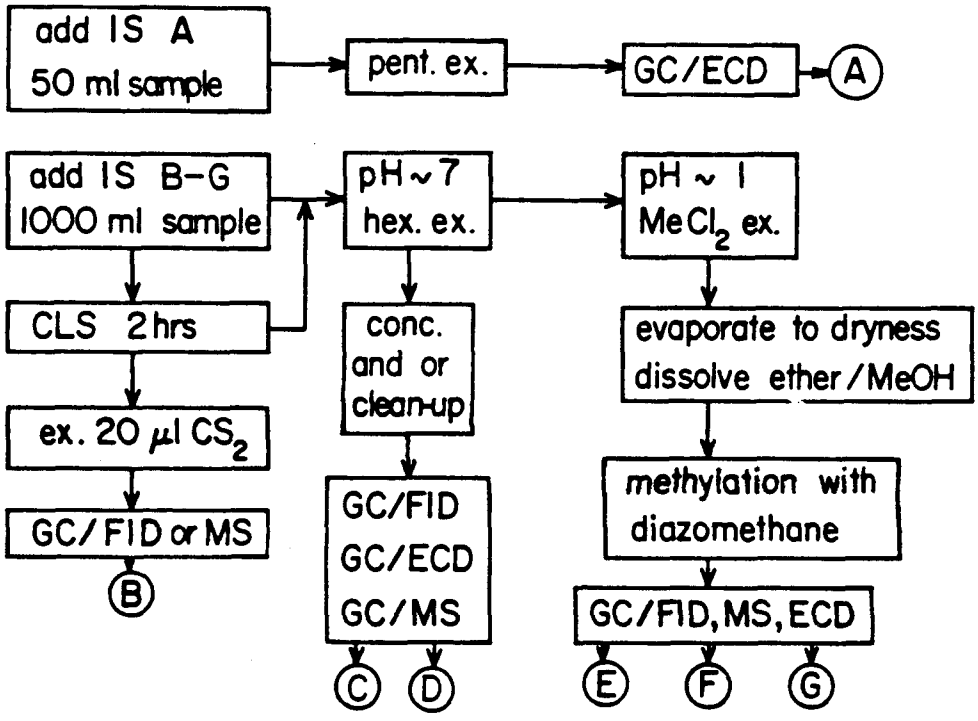

Figure 3. Analytical Procedures Applied for Compound Groups A through G (see Table 2)

Compounds of medium volatility and low water solubility (Group B) are measured by the Grob Closed-Loop Stripping Analysis (CLSA) utilizing 100-1000 ml samples. Heavier non-polar compounds (Groups C and D) are extracted with hexane at pH 7. Finally, the more polar and acidic compounds are extracted with methylene chloride after lowering the pH to 1. With this latter procedure, aliphatic and aromatic acids are extracted along with phenolic and other compounds having greater water solubility. For quantitation, the internal standards for Groups B through G are added to the water sample prior to closed-loop stripping if the entire analytical scheme is to be applied. Internal standards, groups of compounds analyzed, and procedures are summarized in Table 2. The applicability of this scheme depends on the type of water to be analyzed, other types of compounds present, and other factors. It is still preliminary and can by no means be considered final or universal.

EXPERIMENTAL

Group A: Volatile Organic Analysis (VOA)

The procedure to analyze volatile organics was adopted from Henderson, Peyton, and Glaze (10) without modifications. The

50-ml samples were shipped in sealed sample bottles and extracted in the same bottles after replacing 1 ml of the water by 1 ml of pentane. The pentane had been cleaned on an aluminum column (Woelm basic), activity I (ICN Pharmaceuticals, Inc., Life Sciences Group, Cleveland, Ohio 44128). 5 µl of the extract were then injected onto a 2 m x 4mm i.d. column packed with 10% squalane on Chromosorb W/aw (80-100 mesh) at 67°C. Argon/methane was used for a carrier gas and a linearized ^{63}Ni detector (Tracor, Austin, Texas 78721) with a Spectra Physics System I integrator was used for detection and quantitation.

Table 2. Summary of Procedures, Compounds, and Internal Standards

Group	Procedure	Compound	Internal Standard	Supplier	Reference
A	VOA	haloforms 1- and 2-carbon halogenated solvents	1,2-dibromoethane	M	[10]
B	CLSA	aromatic hydrocarbons	1-chlorooctane ($Cl-C_8$) 1-chlorododecane ($Cl-C_{12}$) 1-chlorohexadecane ($Cl-C_{16}$)	E E E	[8]
C	HEA	chlorinated hydrocarbon pesticides polychlorinated biphenyls	$\alpha,\alpha,\alpha',\alpha'$-2,3,5,6-octachloro-p-xylene	A	
D	HEA	polynuclear aromatic hydrocarbons	3,6-dimethylphenanthrene	AN	
E	MEA	aliphatic acids	6-bromohexanoic acid	A	
F	MEA	aromatic acids	m-bromosalicylic acid	A	
G	MEA	phenolic compounds	p-bromophenol	A	

Suppliers: M = MC/B, Norwood, Ohio 45212; E = Eastman, Rochester, New York 14650; A = Aldrich, Milwaukee, Wisconsin 53201; AN = Analabs, Inc., No. Haven, Connecticut 06437.

The compounds for which calibration factors, detection limits, and standard deviations have been determined are listed in Table 2.

The detection limits are near 0.1 µg/l. This has been shown to be sufficient to measure their removal in advanced waste treatment systems (1). The number of very volatile compounds that can be detected with this procedure is limited because of the interference of pentane. If, for instance, methylene chloride is to be determined by the VOA procedure, pentane is replaced by octane which elutes later, and thus makes the detection possible.

Group B: Closed-Loop Stripping Analysis (CLSA)

The closed-loop stripping analysis was adapted from Grob and coworkers (7,8). Gas-washing bottles, 100, 250, 500, and 1000 ml volumes were modified so that they could be connected to an all-steel or teflon diaphragm pump (Metal Bellows, Sharon, Mass. 02067) as shown in Figure 1. After placing the sample in the bottle and adding the appropriate amount of internal standards, an AC filter was placed into the filter holder and the headspace purged by running the pump for 30 seconds to remove contaminants from the headspace air. Following this, a clean AC filter was placed in the filter holder and proper air flow, approximately 1.5-1 min, was established. After two hours the AC filter was extracted sequentially with 3 portions of 7 ul carbon disulfide, approximately 14 µl of which could be recovered. Of this extract, 1.5 µl was then injected, splitless (9), for 42 seconds onto a 50 m UCON HB column (purchased from Jaeggi GC Laboratory, Trogen, Switzerland) at 40°C. After 4 minutes, the temperature was increased by 3°C per minute to 180°C and held there for 10 minutes. C_1-C_{12} was used as a standard for quantitation since this standard has shown the most reproducible recovery. The signal from the flame-ionization detector was recorded simultaneously by a strip-chart recorder (Linear Instruments 300 series) and a recording integrator (Perkin-Elmer, Sigma 10) for computer areas and concentrations.

Groups C and D: Hexane Extraction Analysis (HEA)

One liter samples were extracted in a 2 liter separatory funnel twice with 15 ml of redistilled hexane. The two phases were separated after allowing the extracted sample to stand for a minimum of 6 hours. The two extracts were then combined and dried over sodium sulfate. After concentration to one ml with a gentle nitrogen stream, the extracts were chromatographed on a small florisil column (10). Chlorinated hydrocarbon pesticides, PCBs, and similar compounds were eluted with 10 ml hexane/ether (85/15 v/v) and reconcentrated to 1 ml or less. The concentrated extract was then analyzed on a 50-m SE 54 glass-capillary column (same supplier as UCON HB) which was mounted in a GC (Finnigan 9610) equipped with a Grob injector (E.M. Becker Co., Bala Cynwyd, Pennsylvania) and a wide-range electron-capture detector (Valco Instruments, Houston, Texas). Samples from sufficiently clean water supplies did not require pre-separation on florisil and were analyzed directly after drying and concentration of the combined hexane extracts.

Aliquots of 1.5-2.0 µl were injected splitless for 42 seconds onto the 170°C column. After 13 min isothermal phase, the temperature was raised to 230°C and held at this temperature for four minutes. The injector temperature was held at 220°C and the detector temperature was set at 250°C. Helium was used as carrier gas with the column inlet pressure adjusted to 1 atm.

Detector scavenger gas was introduced by means of a heat exchanger, fabricated with 1/8 inch stainless steel tubing and a Swagelock^{R} fitting. The straightened capillary end was inserted all the way through the heat exchanger and into the detector cell. The ECD signal was recorded by an integrator (Perkin-Elmer, Sigma 10) for quantitation. Group D compounds (polynuclear aromatic hydrocarbons) were analyzed only qua litatively by GC/MS.

Groups E, F, and G: Methylene Chloride Extraction at pH 1 (MEA)

The samples were acidified to pH 1 or less by the addition of hydrochloric acid and then extracted four times with 20 ml redistilled methylene chloride. The amount of methylene chloride used for extraction has been increased in subsequent analyses in order to quantitatively extract the hydrophilic phenols. Emulsions which formed in heavily polluted water samples were separated by centrifugation. The extracts were combined and dried over anhydrous sodium sulfate, filtered through sintered glass, and evaporated to a volume of 10 ml in a rotary evaporator at a water-bath temperature of 30°C and a pressure of 1/2 atm. After transferring the sample to a 10-ml evaporative concentrator tube, it was taken to dryness by the airstream-water-bath method.

Diazomethane for methylation was produced from Diazald$^{(R)}$ (N-methyl-N-nitroso-p-toluenesulfonanide, Aldrich Chemical Co., Milwaukee, Wisc. 53233) by the following procedure:

An apparatus for downward distillation was constructed from a Diazald$^{(R)}$ Kit (Aldrich Chemical Co.), featuring Clean-Seal$^{(R)}$ joints, according to the configuration suggested by Aldrich. Approximately 2.15 g (10 mmoles) of Diazald were transferred to the 250-ml distilling pot along with a magnetic stirring bar, followed by the addition of 30 ml of ethyl ether. As the pot was cooled in an icewater bath, the Diazald was stirred into solution, and 13.0 ml of a 0.81N solution of KOH in 95% ethanol was slowly dropped into the yellow solution. Upon completion of the addition, the flask was allowed to warm to room temperature and the ethereal-alcoholic diazomethane solution was slowly distilled into the dry-ice-cooled receiving flask. The yield from 10 mmoles of Diazald is 320 to 350 mg or 7.6 to 8.3 mmoles.

The sample residue in the concentration tube was redissolved in one ml of a 50/50 (v/v) ether-methanol solution, and 0.5 ml of methanol was added to the reconstituted sample, followed by at least two Pasteur pipettes full of the reagent solution. After mixing, the sample was allowed to sit in the hood overnight, and the next day, the solution was concentrated to a volume of 100 ml by a steam-water-bath method. The volume was made up to 200 ml by the addition of 100 ml of methanol and after mixing, the sample was ready for analysis by GC and GC/MS. Approximately 2 ml were injected splitless for 42 seconds onto a 50 m SE 54

glass capillary column at 80°C. After 3 min, the temperature was programmed to 250°C at a rate of 3°C/min. The isothermal period was 20.0 min. The pressure of the carrier gas (helium) was adjusted to 1 atm.

RESULTS

Chromatographic Analysis

In general, the extracts obtained from polluted water samples are complex mixtures which require high resolution chromatography and/or specific detectors for the analysis of specific compounds. In many cases, even the combined application of high-resolution gas chromatography and specific detectors does not provide enough specificity, and combined gas chromatography-mass spectroscopy must be used for specific detection of individual compounds. The applicability of each separation and the detection method used depends on the type of water to be analyzed and must be adapted and tested in each case.

The VOA procedure uses packed columns with an electron-capture detector. The specificity of the method seems adequate for advanced treated wastewater as encountered in Water Factory 21. However, interferences from unknown peaks occasionally have been encountered.

For the CLSA extracts, high-resolution chromatography was deemed essential: Figure 4 depicts the chromatograms obtained from extracts of Water Factory 21 influent Q1, air-stripping tower effluent Q4, and the final chlorinated effluent Q9. Three internal standards were added (1-chloro-octane, 1-chlorododecane, and 1-chloro-hexadecane) prior to closed-loop stripping; the corresponding peaks are labeled in the chromatogram as IS-9, -15, and -20. The compounds listed in Table 3 have been quantified with respect to Cl-C_{12} as an internal standard.

Figure 5 shows a chromatogram of the standard mixture of compounds analyzed by the SEA method. The temperature was optimized such that all the compounds to be quantified were separated. The peaks labeled with letters belong to the profile of aroclor 1242. The internal standard used was $\alpha,\alpha,\alpha,\alpha'$ 2,3,5,6-octachloro-p-xylene. Figures 6 and 7 show the chromatograms from samples taken at the various treatment steps at Water Factory 21. In the extract from Q1, the peaks of the standard mixture coincide with peaks of the extract. The identity of the peaks was confirmed by GC/MS in Q1 for all peaks except lindane. One of the peaks which is not in the standard mixture has been identified as pentachloroanisole (peak #7), and some of the others were found to be lower chlorinated derivatives of anisole. The identities of these peaks remain to be ascertained. The chromatograms illustrate the effects of the various treatment processes

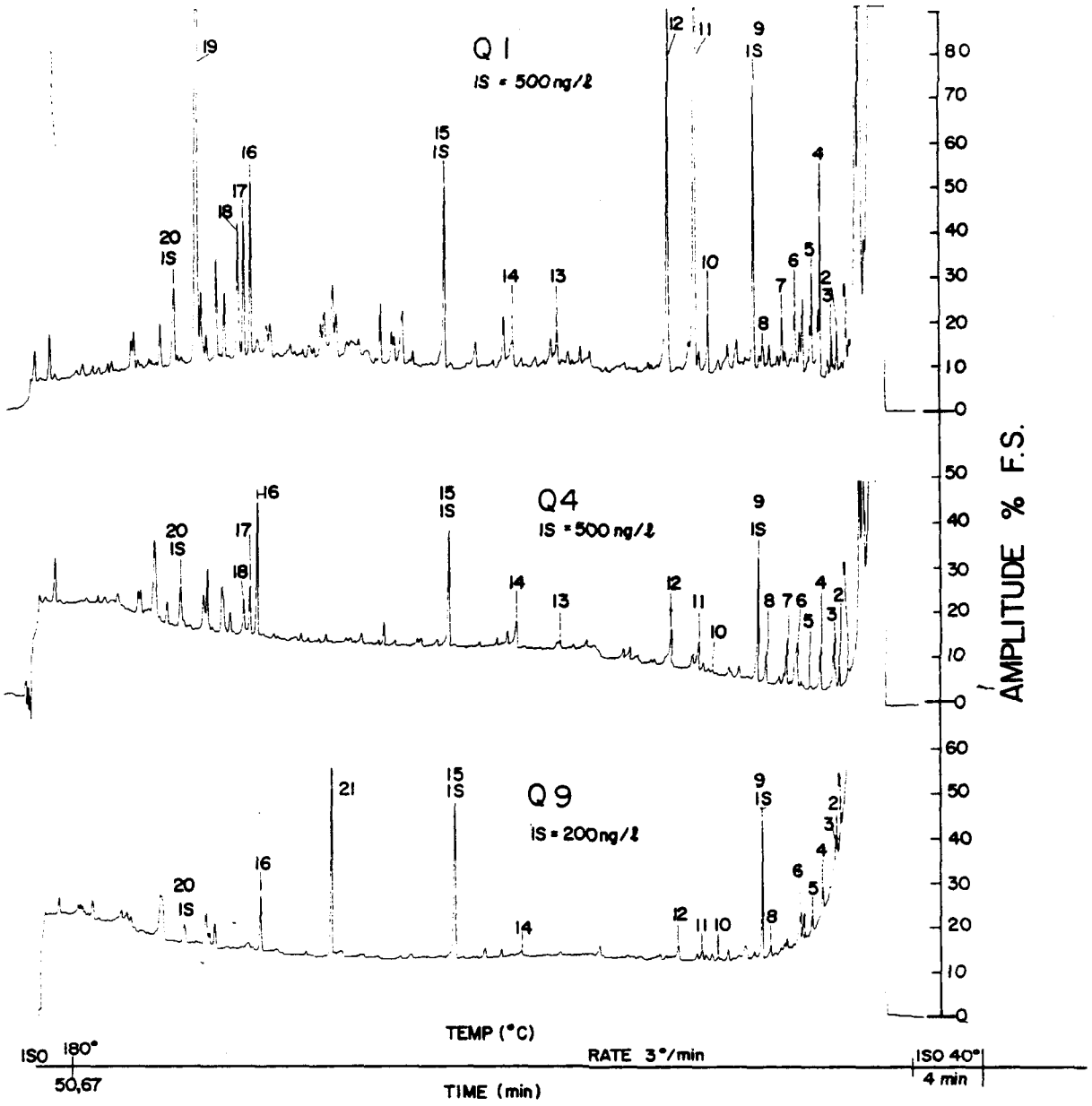

Figure 4. Chromatograms of CLS-extracts of Water Factory 21 waters (samples taken 11/14/78) (1): Q1, plant influent (secondary treated); Q4, stripping-tower effluent; Q9, chlorinated effluent. Quantified peaks are indicated in Table 3. Attenuation: 16 (top); 8 (middle and bottom).

Table 3. Detection Limits and Standard Deviations for Trace Organic Analysis, Groups A, B, C (12)

Compound	Detection Limit µg/l	Standard Deviation µg/l[a]	Applicable Concentration Range, µg/l	Number of Paired Samples Analyzed	Peak No.
A: VOA Components					
Trihalomethanes					
Chloroform	0.1	0.085C+0.25	0.1-10	95	
Bromodichloromethane	0.1	0.048C+0.09	0.1-8	114	
Dibromochloromethane	0.1	0.064C+0.06	0.1-5	115	
Bromoform	0.1	0.18C +0.2	0.1-19	98	
Other Volatile Organics					
Carbon tetrachloride	0.1	0.039C+0.05	0.1-1.5	58	
1,1,1-Trichloroethane	0.1	0.083C+0.09	0.1-20	95	
Trichloroethylene	0.1	0.085C+0.09	0.1-13	83	
Tetrachloroethylene	0.1	0.12C +0.05	0.1-8	89	
B: CLSA Components					Fig. 4
Chlorinated Benzenes					
Chlorobenzene	0.02	0.22C +0.002	0.02-3	21	4
1,2-Dichlorobenzene	0.02	0.15C +0.029	0.02-14	12	12
1,3-Dichlorobenzene	0.02	0.44C +0.002	0.02-5	16	10
1,4-Dichlorobenzene	0.02	0.19C +0.002	0.02-14	12	11
1,2,4-Trichlorobenzene	0.02	0.28C +0.014	0.02-3	9	13
Aromatic Hydrocarbons					
Ethylbenzene	0.01	0.94C +0.004	0.01-0.1	18	2
m-Xylene	0.02	0.87C +0.004	0.02-0.15	18	3
p-Xylene	0.02	0.87C +0.004	0.02-0.05	9	
Naphthalene	0.02	-	-	-	14
1-Methylnaphthalene	0.02	-	-	-	
2-Methylnaphthalene	0.02	-	-	-	
HEA Components[b]					Figs. 6 & 7
Dimethylphthalate	0.3	0.42C	0.3-6	9	1
Diethylphthalate	0.3	1.1C	0.3-3	6	4
Di-n-butylphthalate	0.5	0.83C	0.5-5	7	14
Diisobutylphthalate	0.3	0.66C	0.3-8	10	10
Bis-[2-ethylhexyl] phthalate	4.0	0.61C	4.0-17	5	24
Polychlorinated biphenyls (Aroclor 1242)	0.3	0.14C	0.3-0.6	4	6
Lindane	0.05	0.09C	0.05-0.15	6	8

[a] Values of the constants a_i and b_i for estimating the standard deviation according to Equation (2); C is the concentration of the compound in µg/l.

[b] HEA refers to Solvent Extraction Analysis.

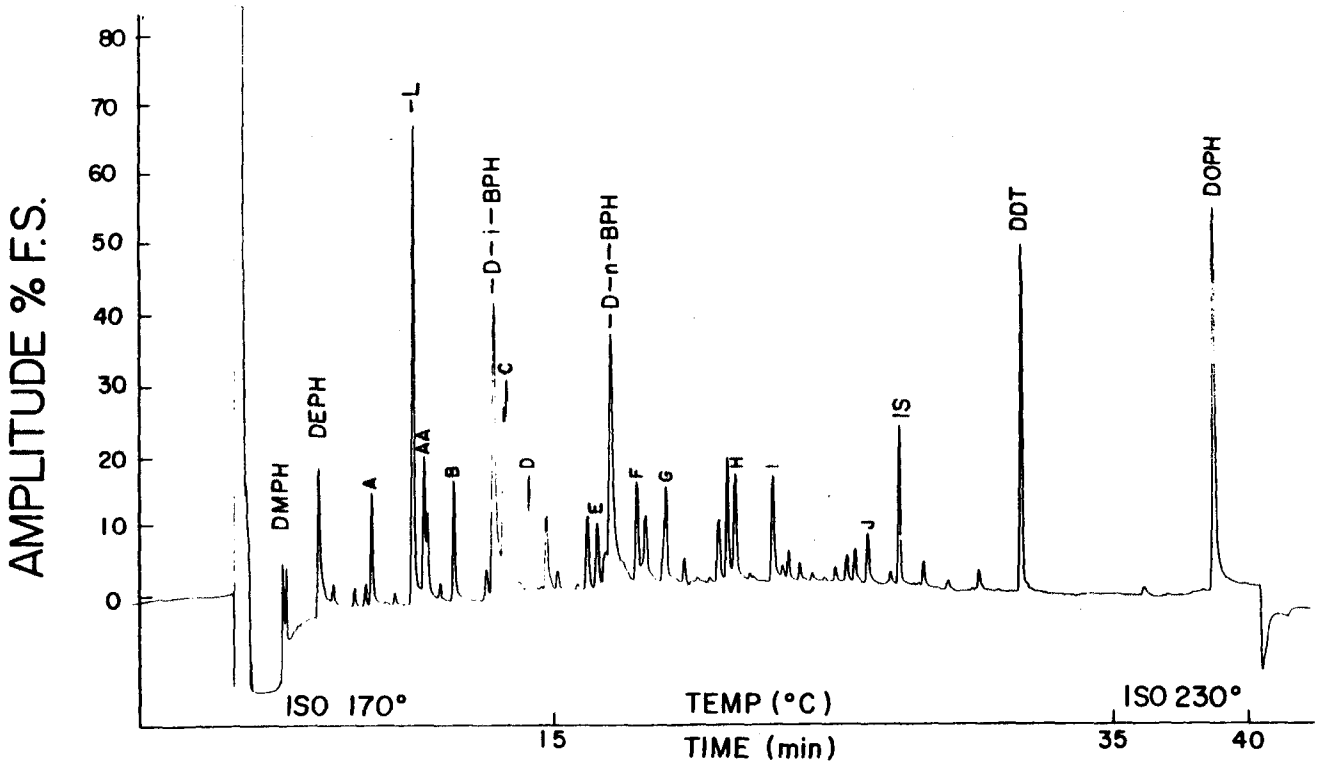

Figure 5. Standard chromatogram HEA, baseline setting 286, Attenuation: 2^3. DMPH: dimethylphthalate; DEPH: diethylphthalate; L: lindane; D-i-BPH: di-n-butylphthalate; DDT: 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane, (p,p'-DDT); DOPH: bis-[2-ethylhexyl]phthalate ("dioctylphthalate"). A-J: peaks of the Aroclor 1242 pattern.

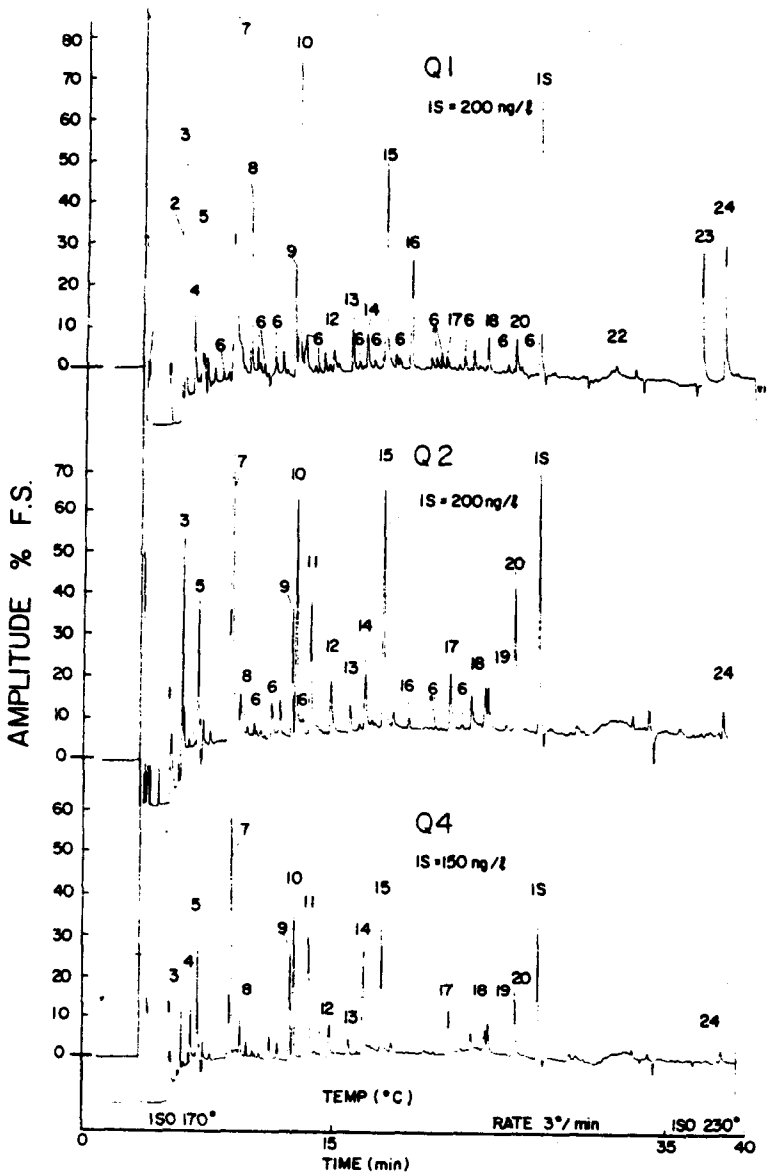

Figure 6. ECD chromatograms of hexane extracts, Water Factory 21 waters (1) (samples taken 11/3/78). Q1, AWT-plant influent; Q2, lime-treated effluent; Q4, stripping-tower effluent. Quantified peaks are listed in Table 3. Baseline setting: 350, Attenuation: 2^4.

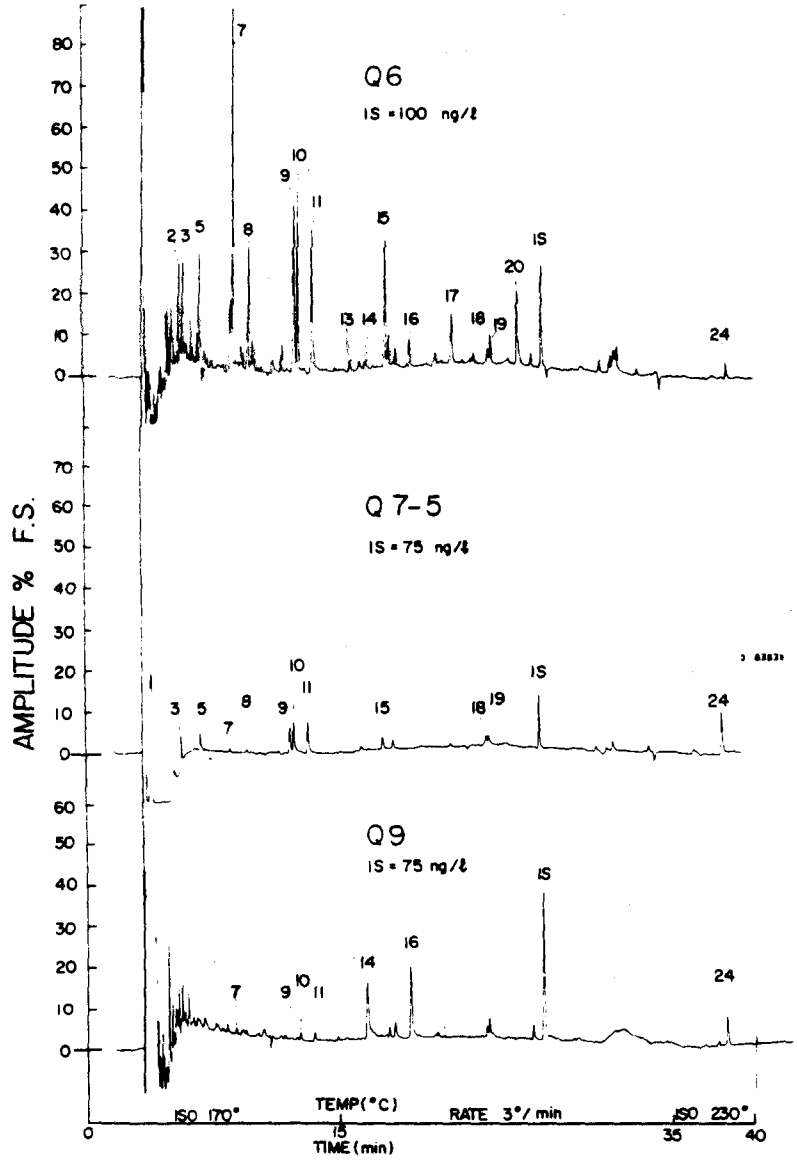

Figure 7. ECD chromatograms of hexane extracts, Water Factory 21 (samples taken 11/3/78). Q6, Q7-5, carbon column influent and effluent; Q9, chlorinated effluent. Quantified peaks are listed in Table 3. Baseline setting: 375, Attenuation: 2^3.

on removal of the compounds which are detected by this procedure: (1) PCB removal in lime treatment and ammonia stripping, (2) the effectiveness of activated carbon, and (3) formation of chlorination products following water chlorination as indicated by numerous peaks appearing early in the chromatograms of Q6 and Q9. More in-depth discussions on removal of these materials are given elsewhere (1,12,13,14,15).

Precision

The procedures described in this paper have been used to study the removal of trace organic material in an advanced waste treatment plant (1,11). The most prominent compounds of groups A, B, and C have been quantified; the remaining compounds were only qualitatively identified by GC/MS. To determine the precision of the analytical procedures, duplicate samples were analyzed for compounds of groups A, B, and C. Standard deviations were then calculated as a function of the contaminant concentration, the detection limits, and errors resulting from sampling and analysis (Table 3). The relative standard deviations (S_r) appeared to increase as compound concentrations approached their detection limits. The standard deviation could be described by a linear function of the form:

$$\text{standard deviation}(i) = a_i C_i + b_i \qquad (2)$$

where a_i and b_i are constants and C_i is the concentration of compound i. Values of a_i and b_i are given in Table 3 for selected compounds. The concentration range for which the relative standard deviation has been determined is given in column 4 of Table 3. Relative standard deviations may be lower at higher concentrations if no saturation effects are encountered. The upper limit of a concentration range was the highest value found in Water Factory 21 water samples.

Good results were obtained with the VOA procedure; S_r was less than 10 percent. Only the compounds eluting late in the chromatogram (e.g., bromoform and tetrachloroethylene) were measured with S_r above 10 percent.

For the compounds determined by the CLSA procedure, generally higher relative standard deviations were determined. The chlorinated benzene isomers were among the major contaminants: S_r ranged from 15 percent (1,2-dichlorobenzene) to 44 percent (1,3-dichlorobenzene). The nonchlorinated aromatic hydrocarbons were measured with much higher relative standard deviations. This is mainly due to the fact that the concentrations were closer to their detection limits and therefore quantification was affected by the failure of the integrator to calculate the correct area. For naphthalene and the methylnaphthalene isomers, no standard deviation could be calculated since not enough values were measured above the detection limit.

For the compounds extracted with hexane (HEA) and detected with the ECD, a simplified equation ($b_i = 0$) was found to describe the standard deviation satisfactorily. Only two chlorinated materials were quantified; Aroclor 1242 and lindane. Aroclor 1242 was identified based on its typical pattern and quantification was based on the more reliable peaks in this pattern. Since Aroclor 1242 is quantified as the whole mixture, but detected by individual components in this mixture, the total detection limit is approximately 20 times higher than the detection limit of one isomer.

Phthalate esters were detectable by the ECD due to their two ester functions. The response, however, was not very strong; hence, high detection limits result for this class of compounds. The relative standard deviations were large since all the values measured are relatively close to the detection limit.

Analysis by GC/MS

With the specificity of the mass spectrometer it is possible to overcome partially the limitations of gas chromatography as a separation technique. Figures 8 and 9 show a multimass-chromatogram (MMC) which is specific for certain groups of compounds. The chromatogram at the bottom represents the total ion or reconstructed gas chromatogram (RGC) in which all the major compounds are detected. The use of mass chromatograms enables the analyst to determine quickly various classes of compounds present in the sample. For example, in the MC 91, C_n-benzene isomers (alkylated benzene isomers with n aliphatic carbons) are detected along with the internal standards. MC 43 and 57 detects compounds of aliphatic nature and MC 35 is specific for some compounds containing chlorine atoms. To enhance the sensitivity for chlorine-containing compounds, m/e 35 was integrated for 64 milliseconds. In Figure 9, MC 104, 138, 83, and 127 have been selected to detect numerous compounds formed in chlorination. The chlorinated styrene isomers and styrene dichloride were formed upon chlorination of styrene, since these products are not present prior to chlorination.

The GC/MS analysis of the methylated methylene-chloride extracts has led to the detection of numerous substances. Among the most prominent are the higher fatty acids and many as yet unidentified compounds. Figure 10 shows the MMC of methylene chloride extract of activated sludge effluent (sample taken on 23 February 1979, at Palo Alto Water Pollution Control Plant). The MMC depicts the mass chromatograms of characteristic ions of long-chain, saturated, fatty-acid methyl esters (m/e 74, 83, 147) along with the total ion chromatogram (RGC). This analysis has been used for qualitative determinations only and the response factors of the compounds to be quantified remain to be established.

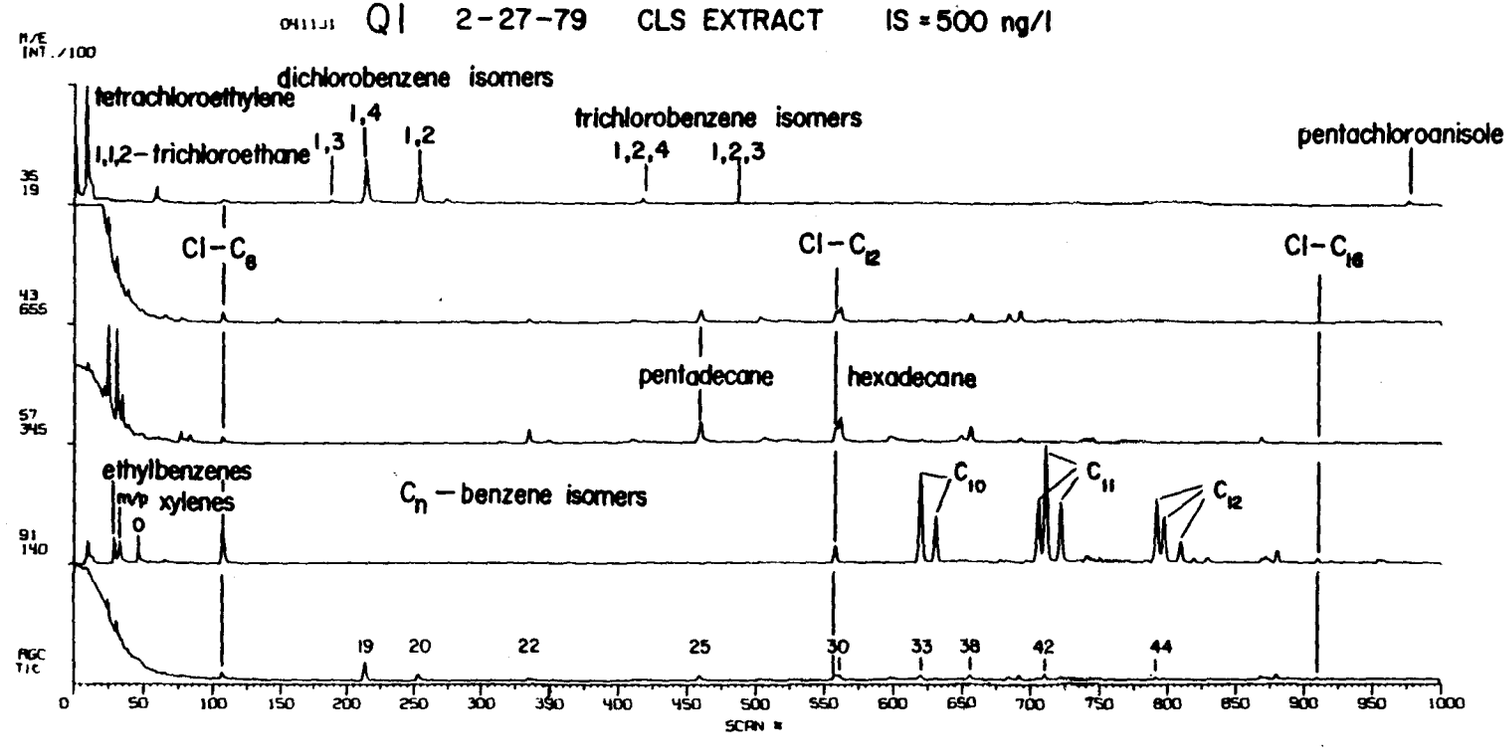

Figure 8. Multi-Mass Chromatogram (MMC) with Reconstructed-Gas-Chromatogram (RGC) (bottom) for detection of alkylated benzenes (m/e 91), aliphatic compounds (m/e 57, 43), and chlorinated compounds (m/e 35). MS conditions: EE, 70 eV; Mass Range, 29-31, 35-35, 36-135, 136-280; Integration Time, 4, 64, 4, 10. Substances identified are given in (1).

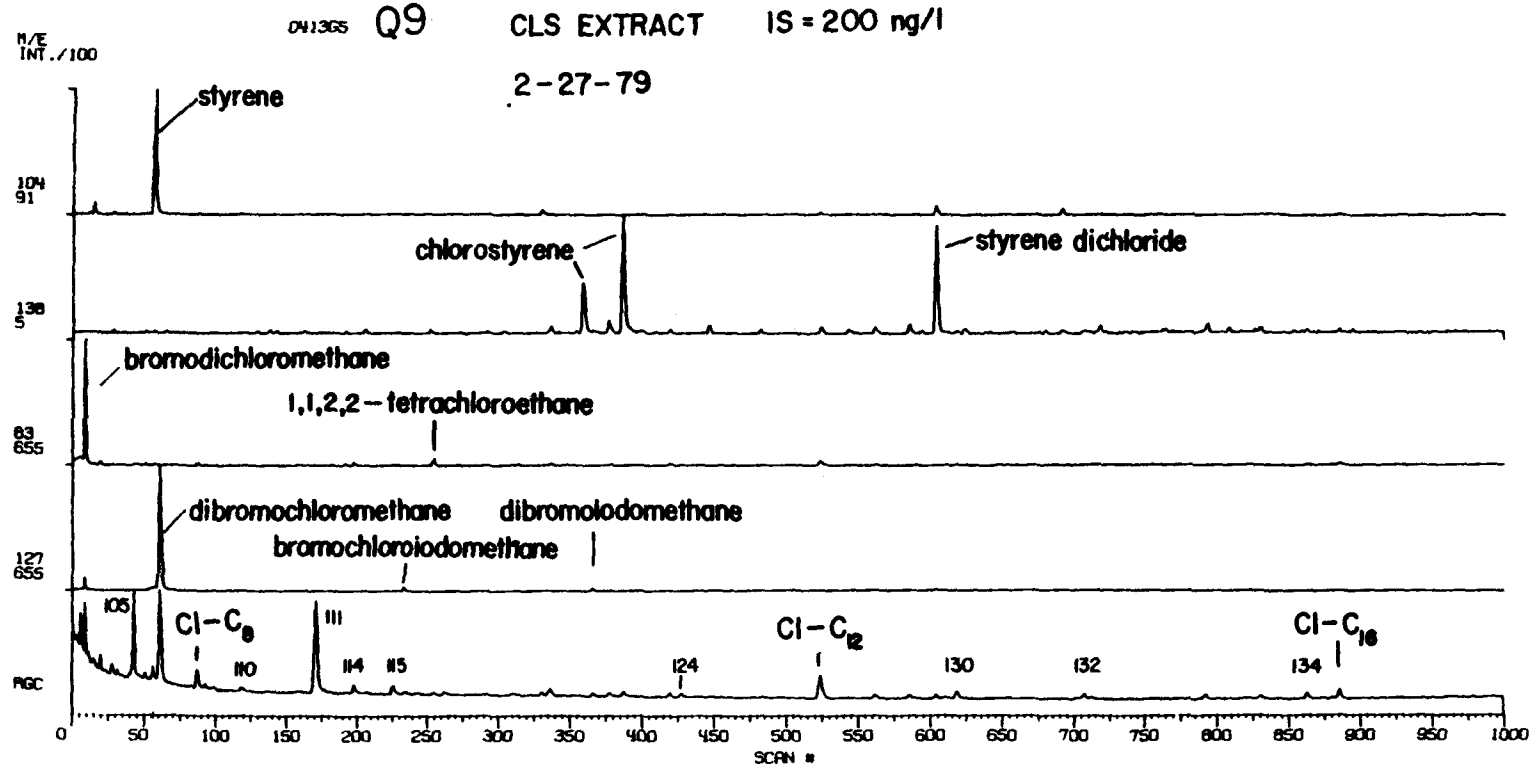

Figure 9. Multi-Mass Chromatogram (MMC) with Reconstructed-Gas-Chromatogram (RGC) (bottom) for detection of some chlorination products and styrene. MS conditions: EE, 70 eV; Mass Range, 29-31, 35-35, 36-135, 136-280; Integration Time, 4, 64, 4, 10. Substances identified are given in (1).

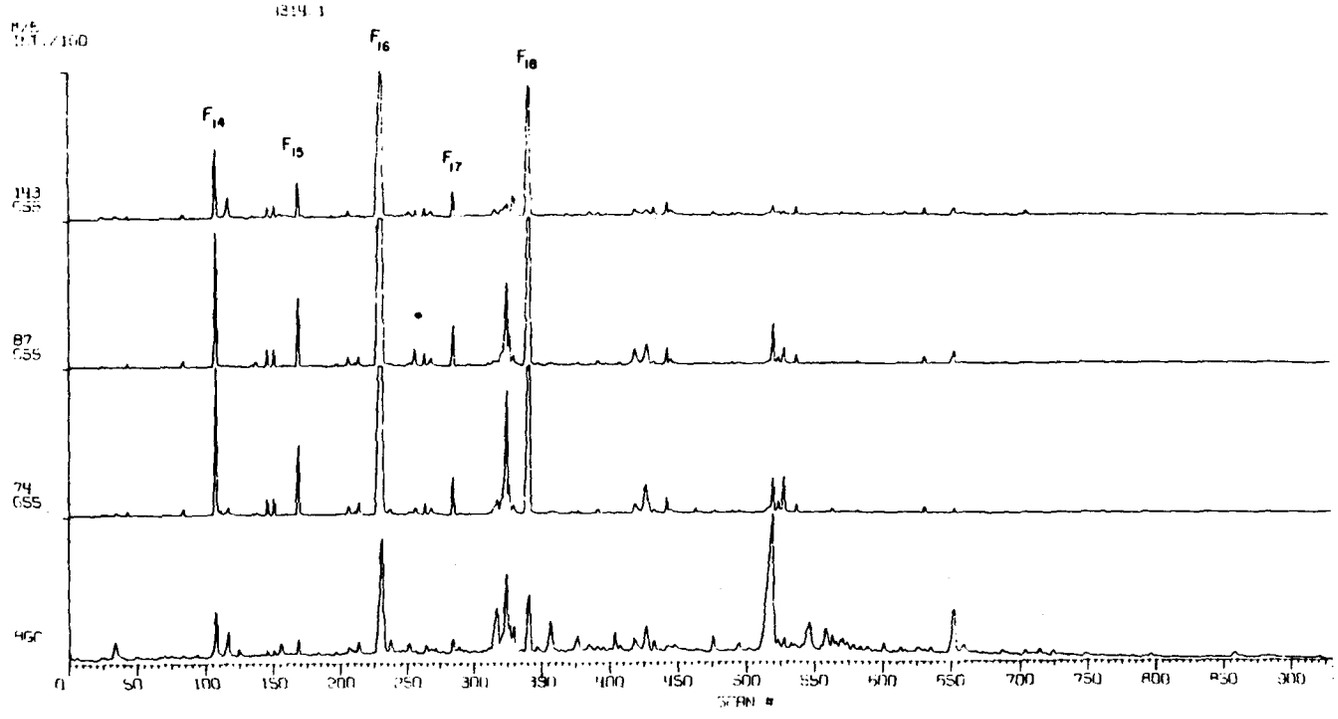

Figure 10. MMC for Specific Detection of Fatty Acids in MEA with RGC (Bottom) of Secondary Effluent (Palo Alto Wastewater Treatment Plant taken 2/23/79). For GC conditions, see text. MS conditions: EE 70 eV; Mass Range 30-31, 35-35, 36-235, 236-535; Integration Time 4, 64, 4, 6. Fatty acids are labeled with F_x (x = chain length)

SUMMARY AND CONCLUSIONS

For the characterization of a broad range of compounds in water, various methods have been combined into a procedure. The reliability and limitations of this approach have been discussed in this paper. This combined procedure represents only a preliminary solution to the problem of organic materials in water. Future improvements will be possible as new columns, instruments, and software become available. Physico-chemical constants of trace organic compounds have been used to predict and interpret their extraction and pre-separation in an analytical scheme where purge/trap and solvent extraction methods are combined to measure a broad range of organic materials. This approach is limited by the scarcity of thermodynamic data; such data must be generated if predictive models of pollutant behavior in analytical as well as environmental systems are to be developed.

In summary, the basic requirements for analyzing trace organic compounds in tertiary effluents and drinking waters include:

- The analysis must be based on a small sample size (up to 1 liter). Samples of one gallon or more are costly to ship and difficult to process and store. Samples of one liter or less can be shipped at moderate cost and stored in medium-sized refrigerators.

- The detection limit for most trace contaminants must be in the lower nanogram per liter range. At detection limits of 1 µg/l and above, the removal (or formation) of many contaminants cannot be determined precisely.

- For conclusive results, variabilities of the procedure, the compound, and concentration at a sampling point have to be considered and investigated. Generally, approximately 30 samples are needed to establish a concentration distribution (1).

ACKNOWLEDGEMENTS

This research was supported by: the Orange County Water District; the U.S. Environmental Protection Agency through Research Grants EPA-S-83873-011 and EPA-R-804431-01-0; the OWRT, U.S. Department of the Interior through Grant 14-34-0001-7003; and the California Department of Water Resources through Grant No. B52353.

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DISCUSSION

Tuesday Evening Session

DR. KÜHN: This evening's papers gave an overview about analytical control methods. We heard about some very practical parameters for routine monitoring. We heard about bioassay tests as a characterization method. Finally, we heard about a very complicated analysis scheme for specific compounds that is necessary for research work, legal cases, and cases of spills. I think the water chemists and water analysts use many instruments to control not only the water, but also the efficiency of activated carbon or other adsorption systems.

Q DR. COTRUVO: I have a couple of questions. When comparing the different group parameters, e.g., UV versus TOC, for measuring performance of the system or water quality, there is always a problem in trying to relate the parameter to an effect. I wonder if Dr. Bull sees a potential for using any of those techniques or indicators to justify the ultimate level of water quality that we are seeking, other than generally improving the quality of water.

A DR. BULL: I do not see any easy way of using group parameters for that purpose, at present, except to develop correlations on an empirical basis. Maybe by coupling samplings of water in a bioassay sense you could do a correlation, such as has been done with the relationship between the TOC and the UV, but I don't believe it would be easy.

Q DR. COTRUVO: Dr. Bull, I have another question related to the data that you showed on the slide that looked at different disinfectants, the laboratory mouse, and the number of papillomas produced. Let's assume that it's valid--I know that you haven't had a chance to reproduce that experiment yet. As I recall, the undisinfected water produced no tumors, and various disinfectants did produce some tumors: ozone, chlorine, and chloramines--and chlorine dioxide did not produce tumors. Do you think that provides sufficient evidence to conclude that the disinfection process is toxicologically more significant than raw water quality in terms of cancer risk?

A Dr. Bull: Well, within the realm of that one experiment the answer I suspect is yes, but the problem is that it was one instance on the Ohio River. I really don't think you can generalize from the one experience. I think that would have to be repeated a number of times before we reached the conclusion that the disinfectant byproduct problem is the most important problem in drinking water. I suggest that we ought to look at that aspect more carefully. One thing I didn't make clear in my presentation was that by reverse-osmosis concentration, using the aqueous concentrate, we get good recovery of the total organic carbon. But, it specifically excludes reaction products like the trihalomethanes. I want to emphasize that because low molecular weight compounds would not be concentrated by reverse osmosis. The cause is more complex than just trihalomethane formation, that's the point.

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ACTIVATED CARBON REACTIVATION AND COSTS

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THEORY AND PRACTICE OF REGENERATION

Dr. Jürgen Klein
and
Dr. Harald Jüntgen

INTRODUCTION

Liquid-phase and gaseous-phase adsorptive purification processes have been known for years and may now be regarded as classic. This technology is also used for dealing with the increasing problems of drinking water preparation and wastewater treatment. The practical use of adsorptive processes depends on the availability of suitable adsorbents and regeneration processes. Since activated carbon is a suitable adsorbent for water treatment, successful regeneration of loaded adsorbents is the key problem which ultimately determines the feasibility and cost-effectiveness of any adsorption process. Loaded activated carbon may undergo regeneration by distillation, extraction, or thermal treatment, depending on the material adsorbed (1-5). In Germany, thermal treatment in particularly advanced, fluidized-bed regeneration processes has become predominant.

DEFINITION

Regeneration may be defined as a process by which adsorbates are removed from the loaded adsorbent so that the latter can be reused (6).

In the case of physical adsorption the adsorbate is reversibly bound to the adsorbent's surface. As shown schematically in Figure 1, the adsorbate can be freed and removed completely (and recovered if necessary) by application of a desorption energy E_D, which is normally equal to the heat of adsorption, Q_A. For this process, called "desorption," not only thermodynamics, but above all kinetics are the key features. Normally, desorption is considerably slower than adsorption so that under industrial conditions complete removal of adsorbate is not achieved and a residual load remains.

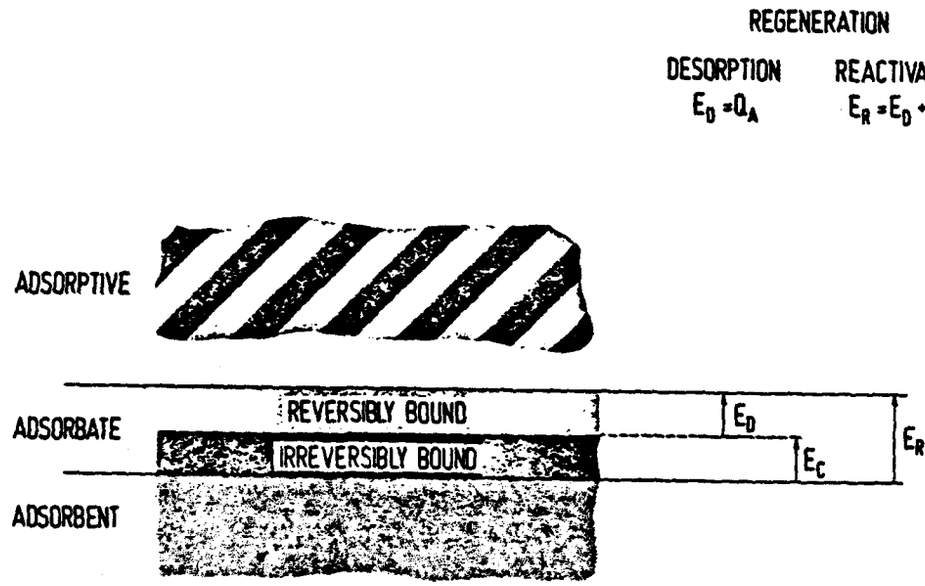

Figure 1. Terms of Regeneration

Residual load problems may be aggravated if a chemical reaction within the adsorbate or between the adsorbate and the solid adsorbent takes place. In such cases, the desired reversibility of the adsorption/desorption processes is lost. The desorption energy E_D (see Figure 1) enables only partial regeneration, so that the residual load consisting of a chemically changed adsorbate can only be removed by application of additional chemical energy Q_C. This chemical conversion process of irreversibly bound residual load is called "reactivation."

FUNDAMENTALS OF DESORPTION

In contrast to adsorption, desorption is a process which always requires activation energy. Desorption is a first-order reaction; its rate is proportional to the load q, at the time t (7).

The rate is given by:

$$\frac{dq}{dt} = -k \cdot q \qquad (1)$$

where k is the velocity constant, which is a function of temperature according to the Arrhenius-equation:

$$k = k_o \exp(-E_D/RT) \quad (2)$$

Where k_o = frequency factor and E_D = activation energy of desorption.

These processes may be investigated successfully by means of non-isothermal measuring methods (8). Thus a single test enables the calculation of the reaction-kinetic parameters E_D and k_o (see Figure 2). By means of this method, desorption was investigated for a number of systems (9). The measured desorption curves differed from the theoretically expected curves (Figure 2), as shown in Figure 3 for the desorption of phenol from activated carbon. In contrast to simple theory, it was found that desorption velocity is a function of the initial load. With increasing load, the temperature at which maximum desorption occurs is reduced to lower values. This permits the conclusion that desorption comprises overlapping processes with different activation energies. As adsorption heat depends on load, the activation energy of desorption increases with decreasing residual load. Calculation techniques were developed for the non-isothermal method presented here. This enables preliminary calculation of desorption curves for a number of systems, provided the adsorption isotherms are known.

For industrial practice it is important to know the influence of heating rate and adsorption temperature on desorption. The influence of the heating rate is shown in Figure 4 for the example of phenol-loaded activated carbon. According to the theory of non-isothermal reaction kinetics, the curves are shifted to higher temperature values with increasing heating rates. As shown in Figure 5 for phenol load, the adsorption temperature can be of utmost importance. The course of the desorption curve changes considerably with the adsorption temperature, due to the chemical conversion of the adsorbate during adsorption, which also implies a partial increase of desorption energy. Such conversion is in many cases the cause for the existence of a non-desorbable residual load. The presence of residual load means that, in subsequent adsorption cycles, the full adsorption area on the internal surface of the activated carbon is no longer available, which in turn means reduced adsorption capacity. In this case thermal desorption is no longer sufficient. As shown in Figure 6, activated carbons of different degrees of activation had been loaded with phenol and had subsequently undergone thermal desorption. After four adsorption/desorption cycles the adsorption capacity of A-38 and A-50 carbon was reduced by 50 percent and, after six cycles no further economical use of these carbons was possible. In such cases the original adsorptive capacity of activated

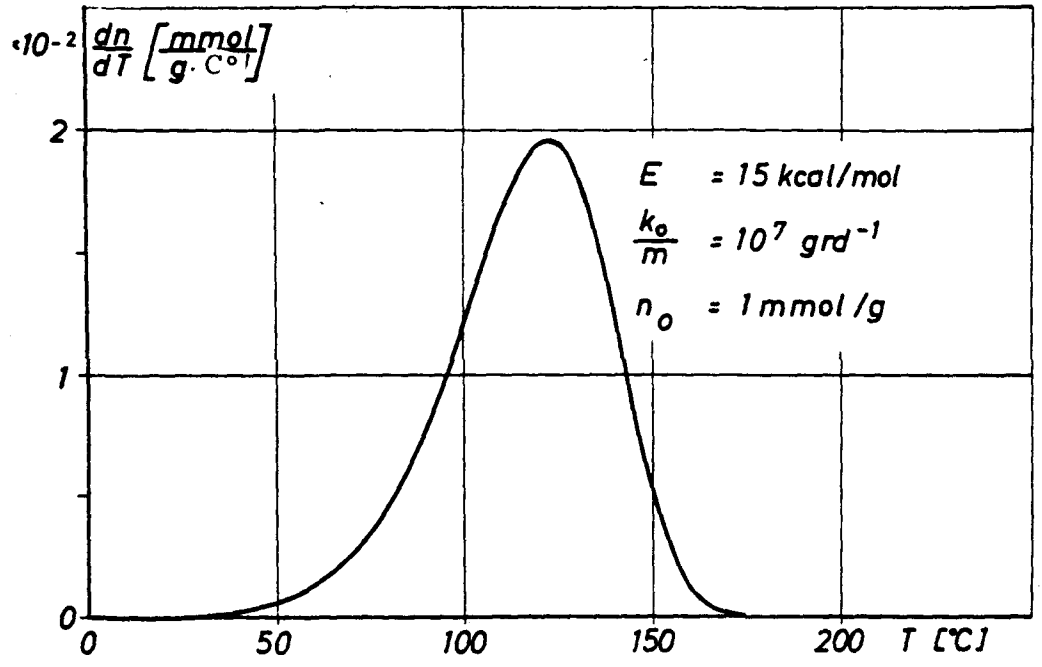

Figure 2. Desorption Curve Calculated Under Simplified Conditions

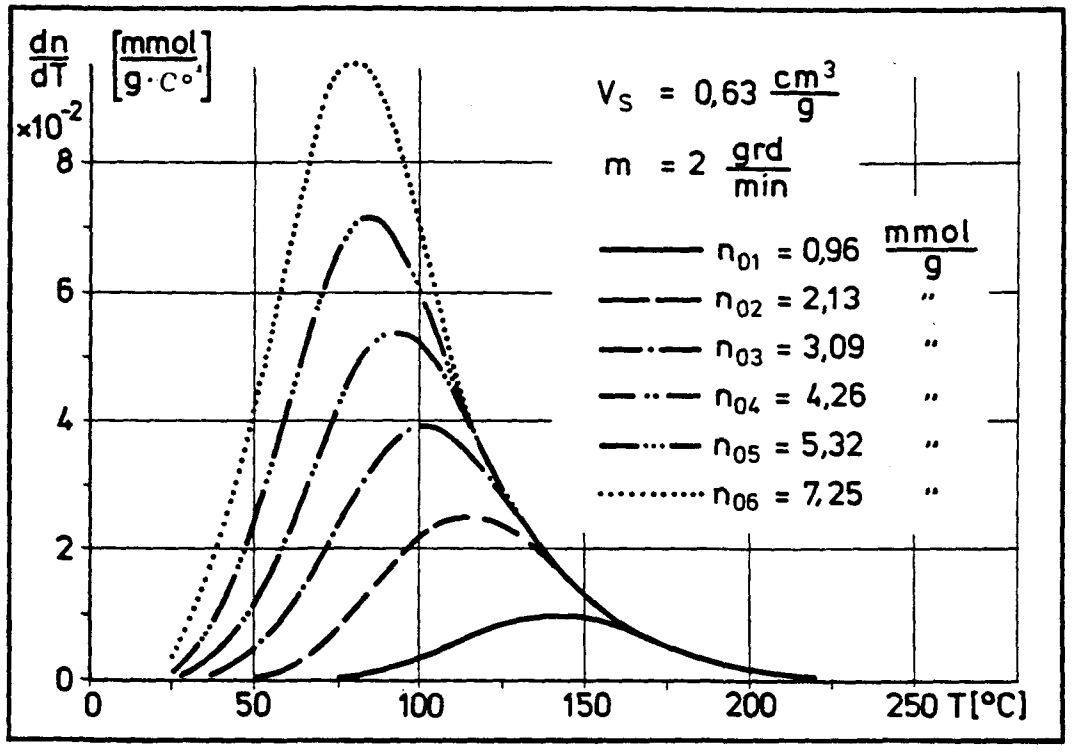

Figure 3. Non-Isothermal Desorption of Phenol as a Function of Adsorbate Loading

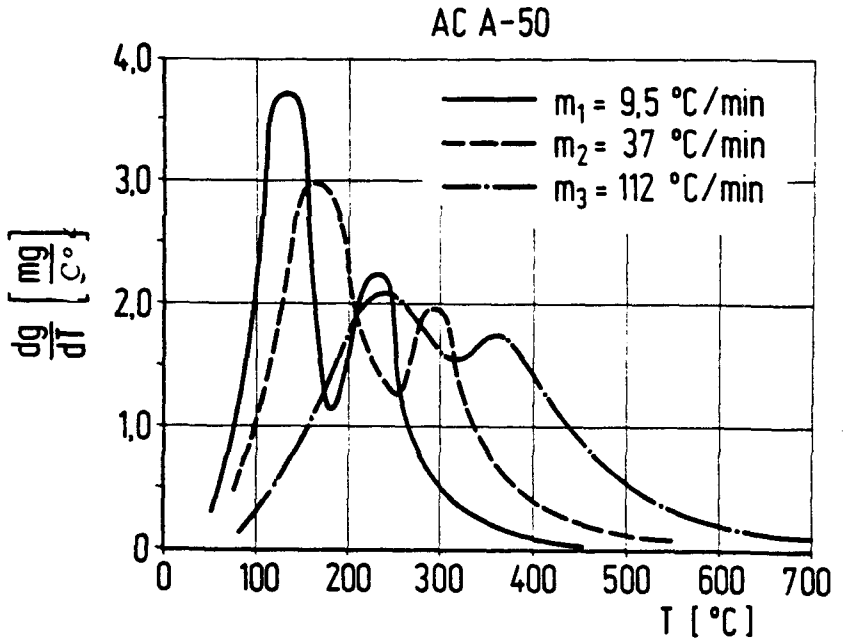

Figure 4. Influence of Heating Rate [m]on Desorption of Phenol

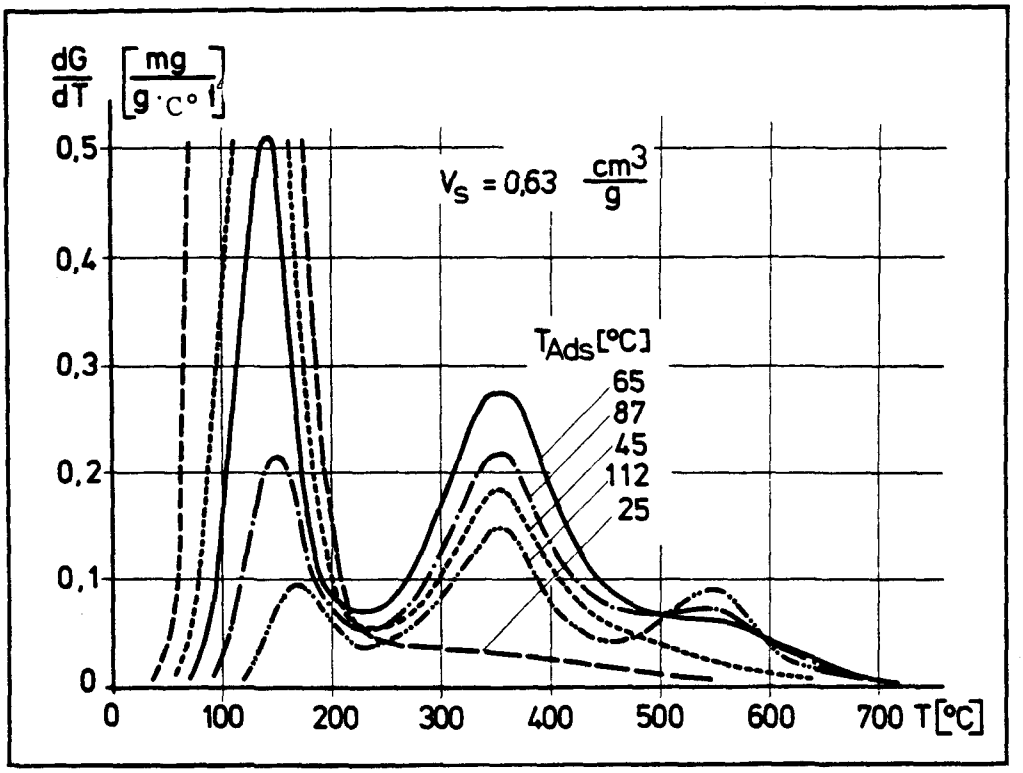

Figure 5. Influence of Adsorption Temperature on Desorption of Phenol

carbon can only be regained by chemical treatment; i.e., reactivation. Carbon type A-79 retained its original capacity over a greater number of regenerations than did types A-38 and A-50.

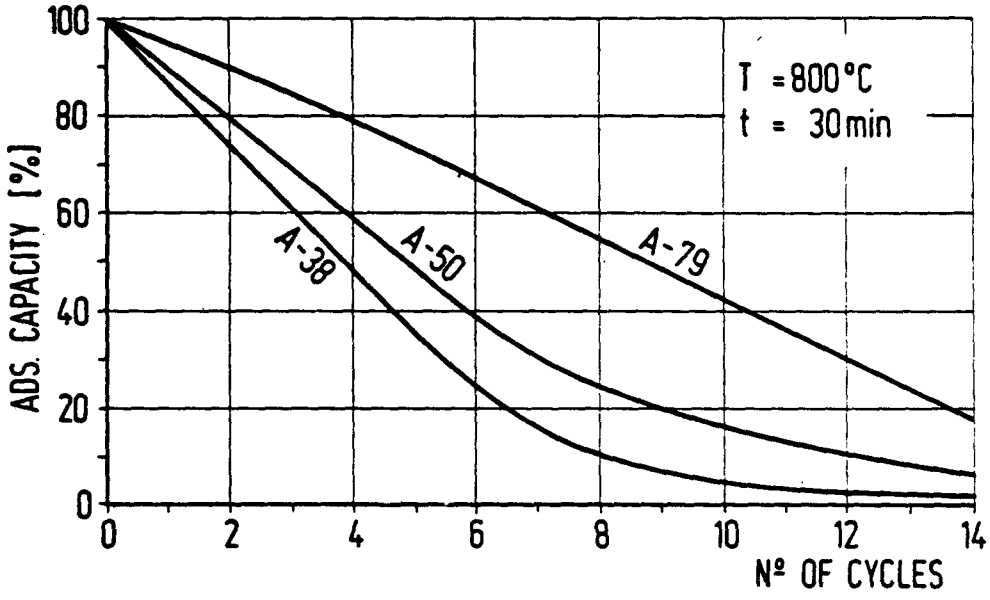

Figure 6. Change of Adsorption Capacity after Desorption

REACTIVATION MECHANISM

Thermal reactivation occurs by chemical reaction of the carbonaceous compounds constituting the residual load, by means of an oxidation process; e.g., partial steam gasification. If suitable conditions are achieved (i.e., temperature range of 700 - 900°C where only the chemical reactions control the velocity of the total reaction rate), a partial gasification reaction according to the overall equation can be achieved intentionally.

$$C + H_2O \text{ ------> } CO + H_2 + 31.4 \text{ kcal/mol} \qquad (3)$$

Detailed concepts of the mechanism of this chemical reaction have been developed (Wicke and Rossberg) (12). The basic proposed mechanism is shown in Figure 7. Steam is first adsorbed and then reacts with the carbon, resulting in disintegration of the H_2O molecules. The oxygen is bound to the carbon and forms a surface oxide which can react with an additional H_2O molecule, subsequently producing adsorbed H_2 and CO_2. The goal of regeneration is to gasify only the carbon contained in the residual load and not the carbonaceous adsorbent. Thus the reactivity of the several forms of carbon plays an important role.

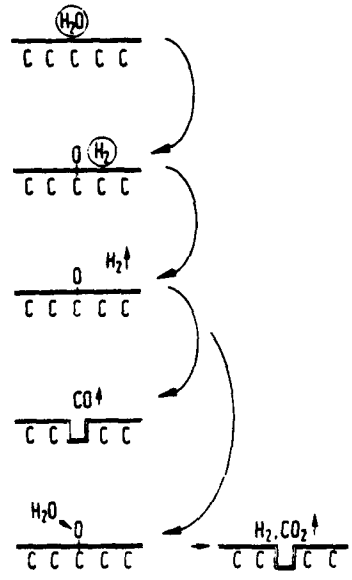

Figure 7. Mechanism of Steam Gasification

Carbon conversion can be described by the equation

$$r = k \cdot \Theta_{H_2O} \qquad (4)$$

where

$$k = k_o - \exp\ (-E/RT)$$

$$\Theta_{H_2O} = \left\{ \frac{K \cdot P_{H_2O}}{1 + K \cdot P_{H_2O}} \right\}$$

Our investigations (10,13) have shown that the dependence on the steam-partial pressure can be approached sufficiently by the following equation:

$$r = k' \, (P_{H_2O})^n \qquad (5)$$

where n ranges between 0 and 1. For partial pressures from 10 to 100 kPa (0.1 to 1 atm) the value of n is 0.5, so that under these conditions equation (5) is reduced to

$$r = k' \, (P_{H_2O})^{0.5} \qquad (6)$$

Investigation of activated carbon from different sources reveals that the raw material from which these carbons are produced appreciably influences reactivity. Figure 8 shows that hard-coal-based activated carbon is less reactive than activated carbon from coconut-shell or charcoal.

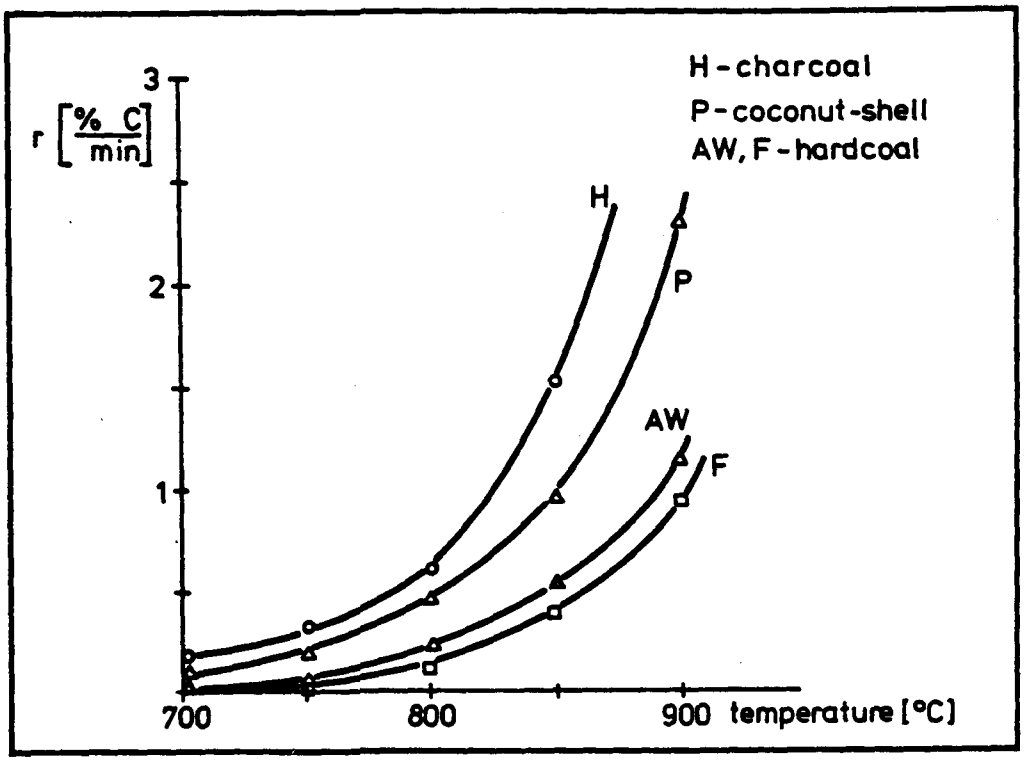

Figure 8. Reactivities of Activated Carbons Made from Different Materials

The conversion rates of virgin and phenol-loaded activated carbon are shown in Figure 9. It is evident that the loaded carbon has a higher reactivity than the virgin carbon. This permits the conclusion that steam reacts more easily with the compounds of the residual load. After a certain period of time, which depends on the reaction temperature (e.g., 20 minutes at 800°C), the conversion rate decreases to the corresponding value for the virgin carbon, suggesting that the total residual load is converted. This hypothesis is confirmed by investigation of the change in adsorption capacity and weight when varying this period. After 20 minutes at 800°C the change of weight is nearly zero and the adsorption capacity of virgin carbon is restored as shown in Figure 10. However, the results obtained for phenol-loaded carbon do not necessarily apply in general. The reaction conditions to achieve regeneration depend on the properties of the adsorbate and the quality of the carbon used. However, the above described technique enables investigation of regeneration conditions for any case in industrial practice.

REGENERATION PRACTICE

For industrial use of the regeneration process two essential conditions must be met: the activated carbon's original adsorption capacity must be restored; and the carbon losses caused by chemical reactions and attrition during regeneration should be minimized.

During liquid-phase adsorption the activated carbon takes up organic matter as well as considerable quantities of water, so that bulk density of the wet loaded carbon is double that of virgin dry carbon. Hence, the regeneration process comprises several steps: drying; desorption; decomposition; and steam-carbon reactivation.

The water on the external and internal surfaces of the carbon particles is evaporated at temperatures near 110°C. Approximately 60 to 70 percent of the total regeneration heat is spent for this step. After drying, temperature is increased for desorption of reversibly adsorbed compounds, which subsequently can be either destroyed or recovered. At higher temperatures, especially above 400°C, decomposition or cracking reactions may occur, forming a residual load of nearly irreversibly adsorbed matter; in the final step (i.e., reactivation) this residual load is removed by chemical reaction; e.g., with steam.

In industrial practice the following equipment is predominantly used: rotary kilns; multiple hearth ovens; and more recently, especially in Germany, fluidized bed systems (Figure 11.)

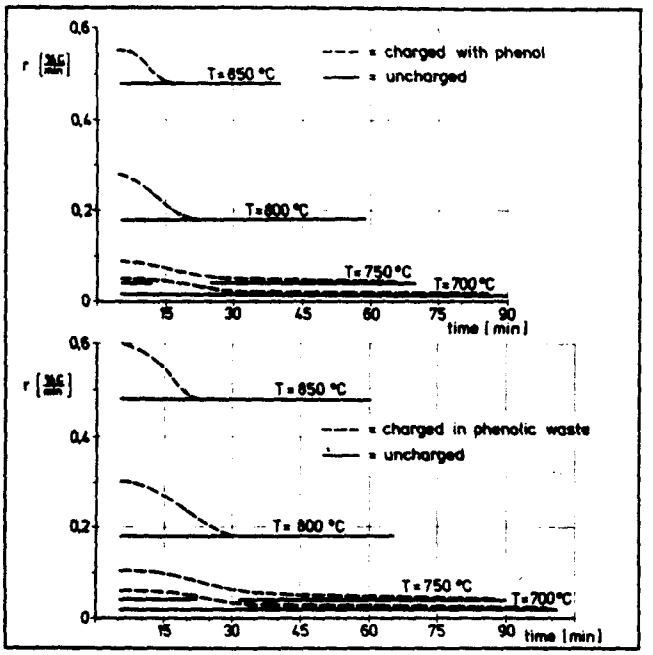

Figure 9. Reactivities of Virgin and Loaded Carbons

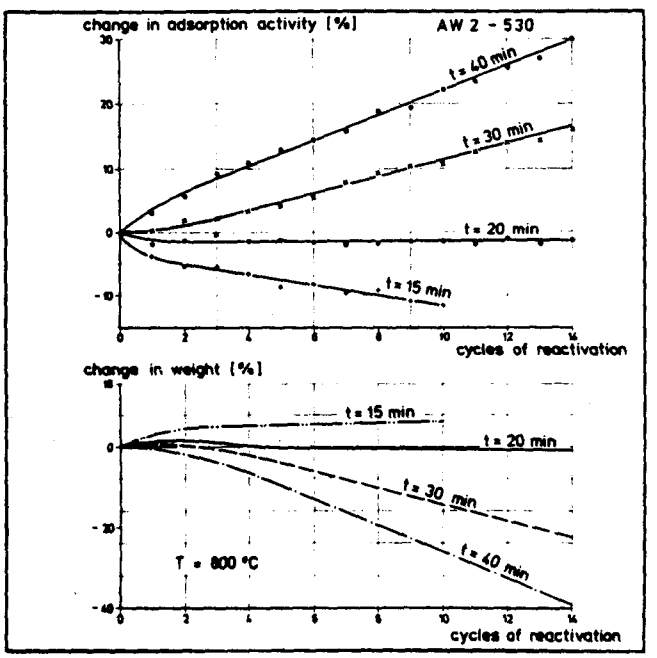

Figure 10. Influence of Residence Time on Success of Regeneration

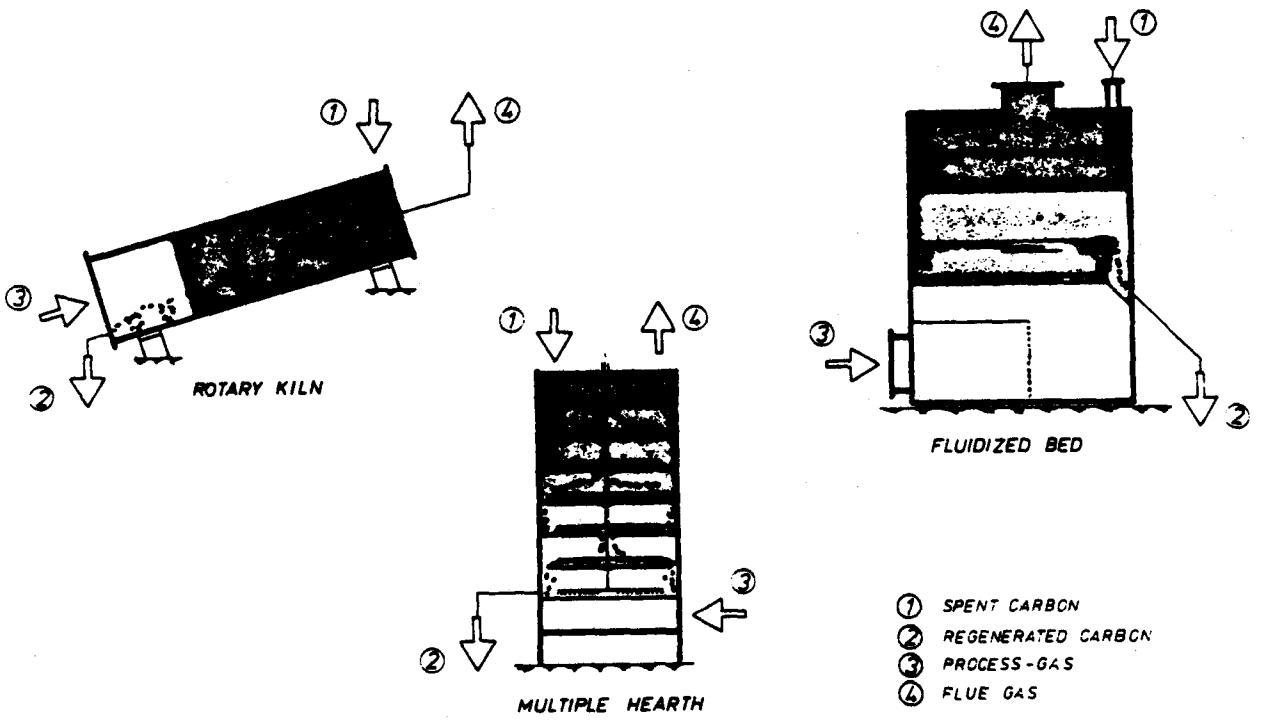

Figure 11. Equipment Used for Regeneration

Compared to rotary or multiple-hearth systems, the fluidized-bed system has the special advantages of improved heat and mass transfer, which result in smaller reactor volume and shorter residence times. In addition the fluidized-bed system results in less attrition and increased flexibility with respect to control of throughput and of reaction conditions.

An inherent disadvantage of the fluidized-bed when used in continuously operated plants is the wider range of residence time for the individual particles; however, this can be sufficiently mitigated by process-engineering improvements as discussed below.

The fluidized-bed principle developed by Winkler in the 1920's has since been adapted to a variety of technically important processes (14-17). Since 1955, Bergwerksverband has used a 15-stage cylindrical fluidized-bed system for production of activated carbon. Due to the increased use of activated carbon for drinking water preparation, Bergwerksverband began, in 1964 to regenerate spent carbon in a single - or two-stage fluidized-bed system. This technique was also applied directly by waterworks (18). The Düsseldorf, Germany waterworks operate a regeneration unit using this process (19), and our manufacturer has built eight additional plants abroad (20). Other fluidized-bed systems are used in the Wuppertal (21) and Zürich (22) waterworks.

Due to simplification and increased cost effectiveness, the process is significantly improved. Stringent regulations for treatment of industrial effluents gave impetus to further development of fluidized-bed systems. The conditions prevailing in this field, however are quite different from those in drinking water preparation with regard to pollutant concentrations and regeneration frequency. Pollutant concentrations in wastewater are orders of magnitude higher and thus require other regeneration conditions; e.g., higher temperatures, different heat-up conditions, and larger residence times for the solid particles. Moreover, in comparison to the adsorption cycles of 4 to 6 months that are common in waterworks, in wastewater treatment the carbon is spent after days or even hours. Thus, carbon losses are a considerably more important economic factor.

For the above-mentioned development work, particular importance is attached to the residence time distribution for the solid particles, which is to be kept as narrow as possible. For heterogeneous gas/solid reactions such as carbon regeneration, the solid particle's residence time in the reactor plays an important role. Only in case of ideal plug flow is each particle in contact with the reaction gas over the same period. In fluidized-bed systems, however, stream profiles, bubble formation, and back-mixing result in a distribution of residence times for the individual particles. Figure 12 displays such residence time distribution curves; n = 1 designates a one-stage fluidized-bed, whereas n = 4 and n = 10 signify fluid-bed systems with 4 and 10 theoretical stages, respectively ($\Theta = \frac{t}{\tau}$ is defined as reduced or dimensionless time).

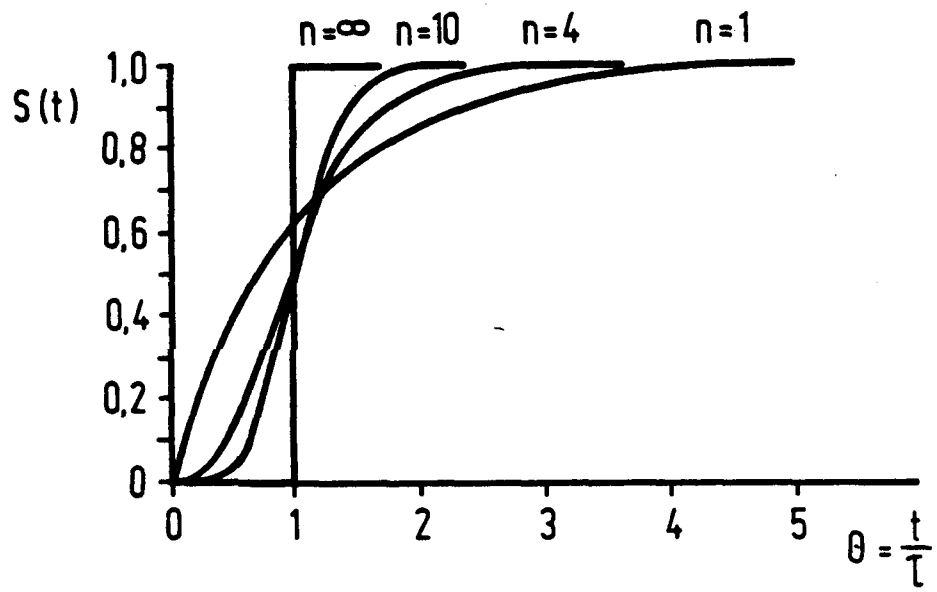

Figure 12. Residence Time Distribution Curve Ideal Plug Flow (n=00) Compared to Fluid Bed with n equivalent theoretical stages (n=1,4,10)
θ = Relative Residence Time
S = Fraction of input concentration in response to a step-change stimulus.

Laboratory-scale tests were conducted with a batchwise operated fluidized-bed. In this mode, the contact time is exactly defined for each solid particle, and the number of theoretical plates corresponds to $n = \infty$. It was found that activated carbon losses under the optimal process conditions investigated, as defined by the temperature T and mean residence time τ, are negligibly low and depend only on the carbon reactivity. In the upper diagram of Figure 13 the empirically determined correlation between T and τ for a loaded carbon used for purification of phenolic wastewater is shown. Under conditions defined by that characteristic curve, the carbon's original adsorption capacity is restored and the carbon loss is nearly zero. (13)

In continuous operation, therefore, the carbon losses to a large extent will be determined by the period of contact in the reactor beyond the desired mean residence time τ.

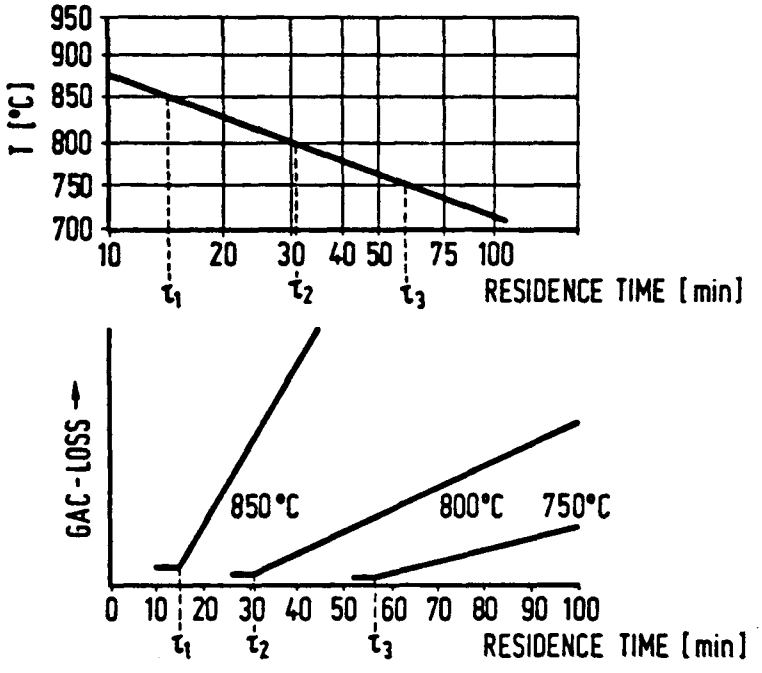

Figure 13. GAC Loss as Function of Residence Time and Temperature

As shown in the lower diagram of Figure 13, for a given temperature, chemical losses prior to the optimal τ_i are due to the reactivity of the remaining carbonaceous adsorbate towards the steam. After τ_i the carbon has no residual adsorbate and continued conversion affects only the carbon structure of the adsorbent. We may therefore expect that in continuous systems this carbon loss can be cut back by narrowing the residence time distribution; i.e., by increasing n, the number of theoretical plates.

The residence time distribution can be influenced significantly by design parameters (length/width ratio, multistage design, special built-in equipment, etc.) and furthermore is a function of fluidizing gas flow for a reactor of given design.

These considerations raise the question of the reasonable maximum investment in design features. Probably the cheapest improvements of the classic circular shaped reactor were the rectangular reactor (Figure 14) and the introduction of immersed weirs. Experimental runs of fluidized-bed models have shown that the rectangular design when compared to the circular type results in an improvement of residence time distribution which can be represented as n = 2 for the rectangular design versus n = 1 in a circular type. To optimize cost effectiveness, the length/width ratio (L/W) should be in the range : $2 < \frac{L}{W} < 6$.

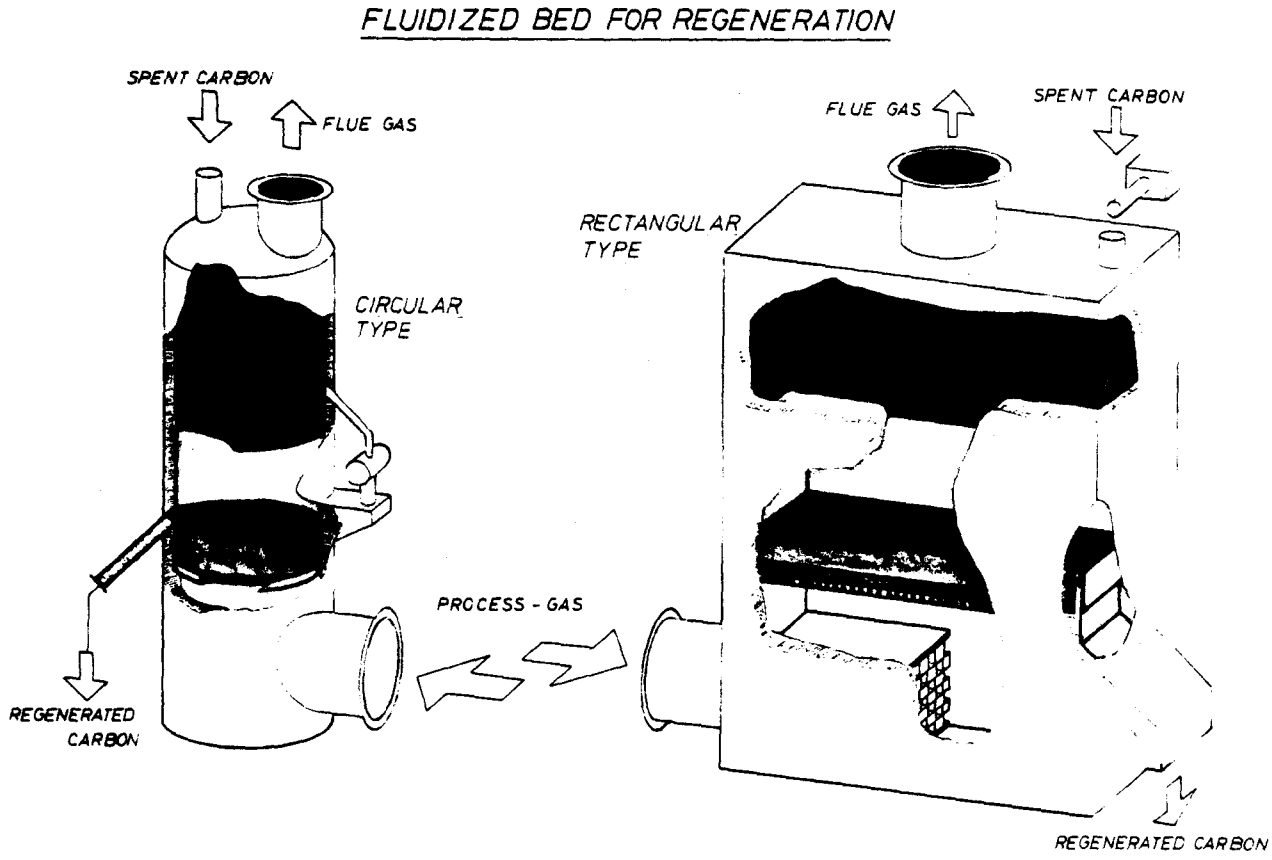

Figure 14. Types of Fluid-Bed Reactors for Regeneration

The installation of immersed weirs results in a considerable improvement of residence time distribution. A controlled flow is thus obtained for the majority of particles without affecting the desired optimum mixing in the chambers formed by the weirs. By suitable arrangement of the weirs, a backmixing of the solids between the individual chambers is largely avoided. In this way a single-stage reactor with a length/width ratio of 4 and with three immersed weirs yields the same results as a 4-stage reactor without weirs.

Hence, in view of the minimum carbon loss, the costs for the design features involved need not be extremely high. The probable carbon loss can be determined as a function of the number of theoretical plates n, on the basis of laboratory and pilot plant scale regeneration tests as well as from investigations on models. Figure 15 shows the total carbon loss as a function of n. If we suppose, for example, that under ideal process conditions a carbon loss of approximately 1 percent results when n = 4, it would not be necessary to increase n above a value of 6 considering the economics of such a regeneration process.

We found by model tests that an optimum value exists for the fluid gas velocity relative to the particle's minimum fluidization velocity. Given this value, the number of theoretical stages, dependent on the reactor design, can be reached. In case of lower or higher gas velocities the residence time distribution curve broadens again, implying lower values for n.

A rectangular reactor for carbon regeneration based on the design principles described above is shown schematically in Figure 16. The system may be adapted by means of suitable distribution plate design, to achieve the required temperature profile as well as optimal fluidization despite the changing physical states of the activated carbon during thermal treatment.

TECHNICAL APPLICATION

Rectangular reactors for GAC-regeneration developed as described above have been used in industrial applications. The first commercial plant was built for regeneration of about 104 kg GAC per day used in adsorptive treatment of plant effluents from the Friedrich Heinrich coke oven plant at KampLintfort (see Figure 17). Operation results confirmed that the above stated conditions for regeneration were met: i.e., restoration of the activated carbon's original adsorption capacity, and a minimization of the carbon losses during regeneration. The carbon losses could be reduced to less than 2 percent per cycle (18,23). This regeneration process has also been used at plants in Italy and Japan. The information given by the operators of these plants confirms the success of this regeneration process scheme.

The following is a brief discussion of the economics of fluidized-bed processes (24). Table 1 shows comparative figures for capital and operation costs of multiple-hearth ovens and rectangular type fluid-bed reactors for different carbon throughputs. The figures for multiple-hearth ovens refer to an American plant (25), those for the rectangular type are taken from plants using the Bergbau-Forschung (BF) process. According to these estimates the rectangular type appears more economic, especially for larger plants. It should be stated, in addition, that the lower carbon loss in the rectangular type (3 percent

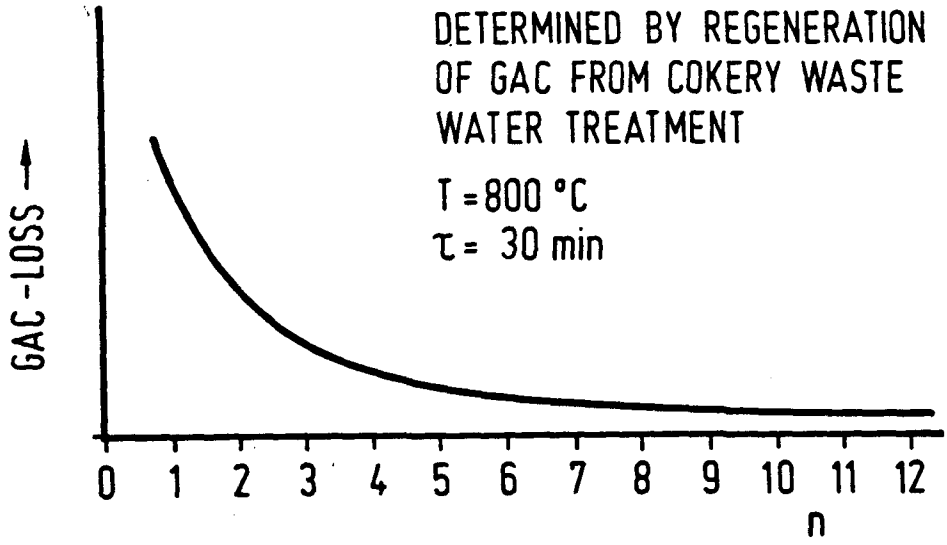

Figure 15. GAC-Loss as Function of Number of Theoretical Plates (n)

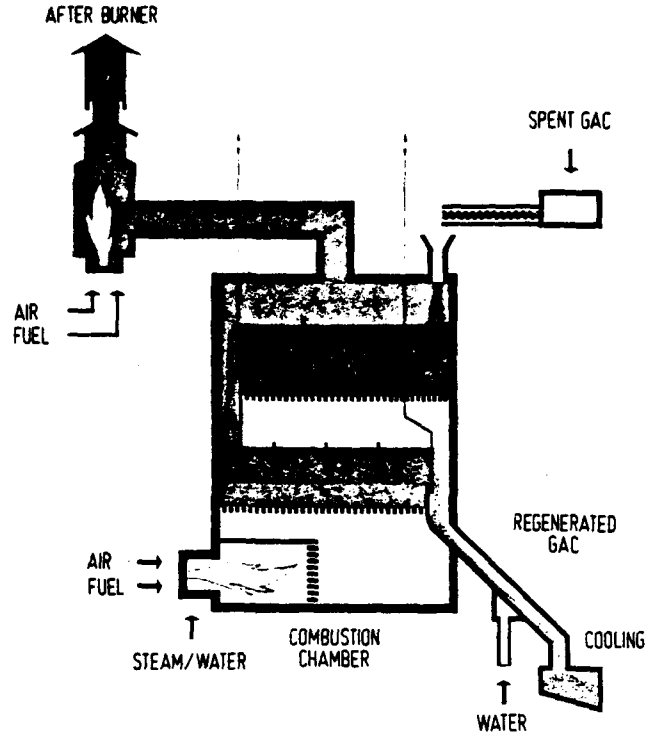

Figure 16. BF-Process for GAC-Regeneration by 2-Stage Fluidbed Reactor

compared to 7 percent for the multiple-hearth furnace) accounts for the greatest cost advantage.

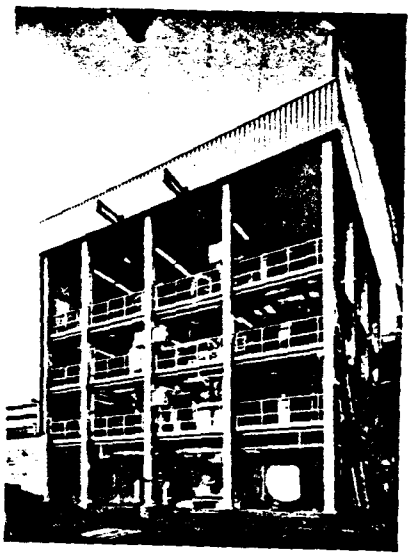

Figure 17. Photograph of Kamp-Lintfort Plant for Treatment of Coke Oven Effluents

		MULTIPLE HEARTH FURNACE [I]			FLUIDIZED BED [II]			
		a	b		c		d	
THROUGHPUT	[kg/h]	190	570		234		400	
CAPITAL COSTS (RELATIV) [DM]		100	211		55		60	
OPERATION COSTS	[%]			b:a		c:a		d:a
GAS [1]	(0,11 DM/m³)	15,60	20,02	15,31	21,58	16,47	19,43	7,41
ELECTRICITY	(0,06 DM/kWh)	3,47	3,78	2,89	2,99	2,28	3,49	1,33
STEAM	(22,16 DM/t)	2,60	3,40	2,60	2,38	1,82	0,81	0,31
GAC LOSS [2]	(2,64 DM/kg)	25,14	32,87	25,14	13,98	10,67	27,99	10,67
LAB / STAFF [3]		19,07	8,31	6,25	39,29	30,00	23,03	8,78
CAPITAL SERVICE	(15,5 %/a)	34,12	31,62	24,18	19,78	15,10	25,25	9,63
		100,00	100,00	76,47	100,00	76,36	100,00	38,14

1) Hu = 4100 kcal/m³
2) a and b = 7 VOL%
   c and d = 3 VOL%
3) a,b and d = 1 MAN/YEAR
   c = 2 MAN/YEAR

I) CHEM.-ENG. SEPT 12 1977 S 95
II) c: DETERMINED AT BF-PROTOTYPE-PLANT KAMP LINTFORT
d: CALCULATED FOR A PLANT UNDER CONSTRUCTION

Table 1. GAC Regeneration Costs Multiple Hearth/Fluidized-Bed-Oven

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OPERATIONAL EXPERIENCES WITH THE CARBON REGENERATION FURNACE AT CHURCH WILNE

D.J. Osborne and C.A. Kennett

INTRODUCTION

The decision to build a regeneration furnace at Church Wilne was made on economic grounds since it represented the least cost alternative among throw-away use of powdered or granular carbon, regeneration at the manufacturer's works, and on-site regeneration. The bid specification did not state that regeneration of the carbon had to be on site; it could be transported to the manufacturer's works if this proved economic.

COST COMPARISON

The 1973 costs* for a 91,000 m^3/day flow and 20 mg/l equivalent dose rate were as follows:

Operating:

Offsite regeneration (including 250 miles transportation)	£3.28/1000 m^3	£164/tonne
On-site regeneration	£0.73/1000 m^3	£36.5/tonne

Capital:

Extra capital cost of the regeneration system	£60,000

A discounted cash flow calculation using a write-off period of 15 years and an interest rate of 8 percent, with a water flow increasing from 45,500 m^3/day to 91,000 m^3/day over the period, gave the following results:

Present (1973) investment to buy the regeneration plant and operate for 15 years	£211,000

*Costs are given in British pounds (£), 1 £ = $US 2.40.

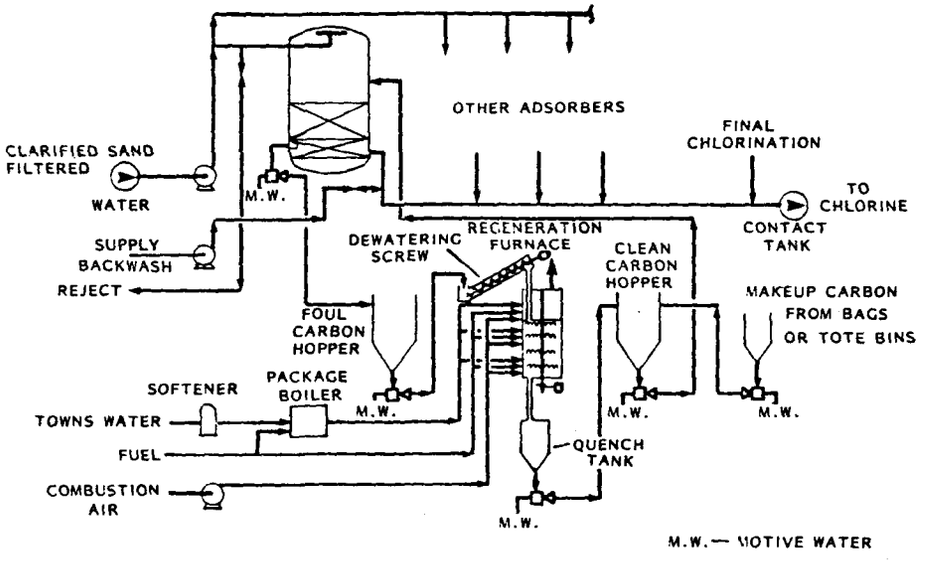
Present (1973) investment to provide funds for offsite regeneration for 15 years	₺724,000

These costs have increased considerably, but a similar differential for on-site over off-site regeneration exists today (1979) where an expected regeneration rate of between 0.5 and 0.75 tons/day is exceeded.

REGENERATION SYSTEM

On becoming spent, one full charge of carbon is transported hydraulically by eductor from the adsorber to the spent or "foul" carbon hopper (See Figure 1). The carbon in both clean and exhausted (foul) carbon hoppers is kept permanently under water. At the base of the foul hopper, a timer-operated ball valve controls an intermittent carbon flow to the suction side of an eductor. The carbon slurry is lifted to an Archimedean screw-type dewatering device at the top of the furnace. The dewatered carbon falls vertically from the screw onto hearth 1 of the furnace.

Figure 1.
Carbon Adsorption and Regeneration System



The 1.37 m (54") diameter furnace is a seven-hearth, Herreschoff type with rotating rabble arms. It is sized for

a maximum throughput of 3 tons per day dry carbon, but normally operates at 2 tons per day. Carbon is rabbled from the outside of hearth 1 to a circular annular hole at the center and then falls to hearth 2. Here it is rabbled to the outside and falls through holes to hearth 3. This system is continued until the carbon emerges at the outside of hearth 6 and falls down a chute into the quench water. There are two burners on hearths 2 and 4 and two on the top hearth (hearth zero). The zero hearth contains no carbon, but is a strongly oxidizing afterburner stage for the flue gases. Carbon from the quench tank is educted to the clean carbon hopper.

On hearths 1 and 2, the wet carbon is dried by the rising hot gases; on hearth 3, regeneration begins at approximately 600°C. Here easily volatile compounds are driven off. On hearths 4, 5, and 6, the temperature is gradually increased and steam is injected. The excess oxygen content at the oil-fired burners is kept to controller maximum, around 2 percent O_2. Extra air can be injected on the hearths without burners 3 and 5, as necessary. By hearth 6, all adsorbed organics have been pyrolised to carbon within the granule and with a controlled oxygen input this outer layer of carbon can be preferentially burnt before the carbon of the granule structure. The temperature of the final hearth is 950 to 975°C.

The maximum fuel input to each burner is 6.2 kg per hour. In operation, it was found that hearth 4 burners require about 4.3 kg per hour each, that only one hearth 6 burner is necessary at 4.1 kg per hour and that the zero hearth burners are both operated at maximum rate (6.2 kg per hour).

The furnace consumes about 230 kg per hour of steam at 310 kPa (45 psia) from an oil-fired boiler installation. Steam is used for direct injection, center shaft cooling, and non-operating burner cooling duties.

The boiler is provided with feedwater treatment including a base exchange softener and tannin and polyelectrolyte dosing.

All excess water in the furnace area from the eductor operations is collected in a furnace area sump and then pumped into the main dirty backwash water sump. This water is pumped back to the raw water reservoir, thereby utilizing any carbon fines as a rough pretreatment.

Commissioning

The first run of the furnace in January 1976, was plagued with minor mechanical and constructional problems. However, these were overcome as they arose. The decreasing carbon losses on each subsequent regeneration show the improvements; 25 percent

on the first run, 6 percent on the second, and the current routine losses of 4-1/2 to 5 percent.

The main problem, initially, was defective alignment of the rabble system center shaft. This led to two problems; an air inleakage at the bottom seal (subsequently corrected by realignment and a different packing material), and a cooling air inleakage through a flange half way up the hollow center shaft. This second problem was difficult to solve, but was eventually alleviated by using steam for center shaft cooling. There were also many instances of high torque cut-out caused by the rabble tines touching the hearth bricks as these expanded upwards; many tines were cut and ground to give sufficient clearance.

One persistent problem was encountered on the burners. Those on hearths 4 and 6 are at 950°C in an often slightly reducing atmosphere. They have removable caps and jets that require fairly frequent cleaning. The cap threads are about 50 mm from the burner tips and were often found to be completely seized. This problem was not overcome until the whole burner was redesigned to put the cap threads well down the body and thus removed from the hottest zone. At normal throughputs, it was found necessary to close down one hearth 6 burner. A system was eventually designed to allow steam to be passed into the atomizing air line to any burner to keep it cool while not in use without using the atomizing air, which would burn carbon unnecessarily. Any burner left in the furnace with no cooling flow was rapidly and permanently made inoperable by carbon, from pyrolysis of the residual fuel, causing changes in the high temperature steel structure.

These experiences have convinced the design engineers (H&G) that, where possible, future installations should be fired by pipeline natural gas or site-stored LPG. The difficulties in using fuel oil in this small but very hot burner have been overcome, but the 2:1 mechanical ratio turndown system on the oil burners causes more operating difficulties than a fully modulating 10:1 turndown system which is available for natural gas burners.

On a new installation, it should also be possible to use a water seal at the bottom of the center shaft and so eliminate the frequent need to repack the bottom gland to prevent air inleakage.

Carbon Quality

At the time of writing, some 550 tons of carbon have been regenerated with no deterioration in quality.

The regenerated carbon quality is controlled by three tests; the apparent density, the methylene blue number, and the iodine

number. The apparent density of fresh F 200 carbon is about 570 g/l; the density at regeneration averages 640 g/l and after regeneration 560 g/l. The pore size distribution is an important feature in the adsorption capacity of the carbon. On repeated regenerations, the small-sized pores tend to enlarge. The iodine number gives a measure of the smaller pores and the methylene blue number the somewhat larger ones. The iodine number of fresh F200 carbon is about 950. This slowly drops on each regeneration; after three or four regenerations it is around 800 to 850. The methylene blue number of fresh F200 is approximately 220 and the regenerated carbon has always been between 195 to 230, so it seems that the subsequent adsorption of taste and odor compounds can be related to the methylene blue number. The routine control of regeneration is by apparent density and iodine number. A sudden increase of iodine number during a regeneration run with no change in apparent density has been correlated with increased oxygen in the furnace atmosphere. A recent addition has been the inclusion of zirconia-type, continuous recording oxygen probes in several hearths of the furnace. These are very useful when setting up the furnace at the start of a regeneration campaign. Many manual Orsat analyses were previously required to ensure that the furnace box was airtight and the burners correctly adjusted to give a 1-1/2 to 2 percent oxygen atmosphere before introduction of the carbon feed. When operating, no readings of oxygen are given; any inleak is indicated by abnormally high temperature on the leaking hearth.

Some quality parameters for regenerated carbon are:

F200	Apparent density g/ml	Iodine No.	Methylene Blue No.
Fresh	0.556	950	220
Fouled	0.610	666	165
After 3 regenerations	0.554	827	230
F400			
Fresh	0.520	1,000	270
Fouled	0.584	821	182
After 1 regeneration	0.525	1,020	260

The 15 tons of F400 was mixed with the main plant F200 carbon after this one regeneration.

Control System and Alarms

The furnace alarm and trip system developed for Church Wilne allows the furnace to be left unattended. An alarm in the main plant control room calls an operator to deal with any emergency.

A trip system shuts down the furnace for:

flame failure at any burner;
fuel oil low pressure;
high hearth temperature (any hearth above 1000°C);
high torque on the furnace rabble arms;
or build-up of carbon in the quench tank.

The control feature which has given the regenerator the most problems has been the interrupted flow on/off ball valve at the foul carbon hopper eductor. This valve has Teflon seats which require changing every few months owing to abrasion. The complete stainless steel valve requires changing every year. One unnecessary feature was an alarm on the valve actuator to indicate seizure; the downstream eductor suffers more blockage problems and the consequent furnace carbon feed failure is seen some few minutes later as a rapid rise in the normally very stable hearth 3 temperature of 675°C.

The one measurement problem has been the setting of the furnace carbon feed rate. This is done manually using a clear plastic tube to measure the carbon volume in a 2 minute catch sample of the intermittent slurry feed. An instrumental method would be preferable. If a rubber pinch suction valve were used to control a constant flow of slurry, a density meter (ultrasonic or gamma ray) could be used to measure the feed rate. A normal low flow could be interspersed with a full open period to clear bridging or blockages as required. The fouled Church Wilne carbon does not have the same sticky nature and tendency to form clumps as fouled sugar industry carbon.

Carbon Exhaustion Rate, and Furnace Utilization

The carbon exhaustion rate predicted for the design 20 mg/l equivalent dose rate at 91,000 m^3/day was 1.82 tons/day. The furnace is capable of 3 tons per day throughput, but was set up at 1.92 tons/day and has always been operated at this rate.

Initially, seven or nine adsorbers were on line at flow rates ranging from 35,000 to 45,000 m^3/day giving 6 to 8 min. contact time. (This number has to be on line to cope with the flow surges from the gravity filters.) The equivalent dose rate for taste and odor (T and O) in practice was in the range 7.6 to 9.7 mg/l giving an exhaustion rate of only about 0.32 tons/day and furnace operation was required only some 60 days/year.

Since 1977, all 12 adsorbers have been operated to deal with the trace organics problem. The equivalent dose rate has risen to 15 mg/l and the exhaustion rate for these trace organics, rather than taste and odor control, has risen to 0.68 tons/day, requiring 130 days per year for furnace operation. The furnace

is normally operated in two regeneration campaigns of 130 tons each at 6-monthly intervals.

Costs

Base costs for a plant similar to Church Wilne are given in Table 1 using as many real data from the plant as could be abstracted from the records. The following aspects deserve special mention:

Labor is estimated as that necessary in excess of requirements to run the main works. When the furnace is in operation, shifts are extended from 8 to 12 hours to leave one man free to attend the furnace at any time if required. This is not strictly the time spent at the plant, which is nearer 6 man-hours per day.

The fuel cost is high because of the use of steam from the boiler used to cool the center shaft. If the air inleakage problem had not arisen this steam demand would be 150 kg/hr lower.

The wastewater includes a generous 10 min. backwash of all adsorbers every day although this is only necessary in summer. In winter, wastewater usage on the adsorber section is approximately 1.1 percent while in summer, it is up to 2.2 percent.
The carbon is, in theory, as good at year 15 as at year 1 and so perhaps should not be 'written off' in this way.

The maintenance materials cost is high because the cost period taken included purchase of many spares which have not yet been used.

Wastewater is assigned a cost of £0.045 (4.5p) per m^3. It is in fact recycled to the raw water reservoir and is not lost, but passes again through the main plant.

With benefit of hindsight, the regeneration cost on the 1977 basis could probably be reduced to around £150 per ton.

COST SUMMARY

It can be seen that the GAC plant adds about 20 percent to the cost of the water leaving the treatment plant but adds only some 10 percent to the cost of water to metered consumers.

Costs to metered consumers in 1977 were 10 to 12p per m^3 comprising of 4 to 5p for water treatment and 5 to 7p for distribution and administration.

Table 1

Cost Experience

	Adsorber Section	£/day	Regeneration	£/day
Throughput per day	45,500 m^3		2 tons	
Electric Power Adsorbed				
To overcome head loss	19 KW		-	
Furnace drives/fans & dewatering screw	-		6KW	
Carbon fluid transport system			3KW	
Total at 1.6p per KWh	19KW	7.3	9KW	3.5
Labor				
Analytical services	0.5h/day		2.0h/day	
Supervisor	2.0		3.0	
Shift Operator	3.0		12.0	
Instrument fitter	0.25		0.5	
Mechanical fitter	-		1.25	
Total at average £7 per manhour	5.75	40.25	18.75	131.3
Maintenance Materials				66.0
Waste Water	1000 ^{3}m/day	45.0	770m^3/day	34.7
Fuel Oil for Burners, Afterburner & Boiler at 8.84p per Kg			941Kg/day	83.0
Make-Up Carbon 6% Losses			120Kg/day	96.0
Boiler Chemicals			0.33l/day	0.7
Total Daily Cost		£92.55		£415.2
Cost per ton regenerated				£208

Capital Cost

The capital cost on a 1977 basis for a plant similar to Church Wilne would be approx. £730,000 including the regeneration facility and initial carbon change but excluding Civil Costs.

Operation Costs

Using an interest rate of 10%, a write-off period of 15 years, a flow of 45,500m^3/day at 9.7 min. contact time and 250 tons/year regeneration rate gives:

Total Costs (pa = per annum)

Debt Charges (Factor 0.1315pa)	95,995pa
Adsorption plant	33,781
Regeneration plant	52,000
	£181,776pa

£ 0.01094 per m^3, or approximately $0.083 per U.S. gal.

SUMMARY AND CONCLUSION

From the commissioning and operating experience at Church Wilne we are confident that carbon regeneration at a waterworks site is a completely feasible proposition for the normal personnel, who were very quick to assimilate techniques new to the industry.

The costs of the use of GAC for taste and odor removal, or for removal of specific organic compounds where contact times of up to 10 minutes are necessary, are not as high as is generally supposed.

If total organics removal to a 1 mg/l TOC standard were required, the GAC treatment costs would perhaps be multiplied by a factor of 2 to 3. The use of such a broad parameter is no substitute for knowledge of the specific nature of organic micropollutants of industrial origin and their biodegradability, toxicity, and adsorption properties.

If industrial discharges are causing a micropollutant problem at a drinking water works, it is probably best from an environmental as well as a cost point of view to use GAC first at the industrial discharge, and then as a final clean-up or emergency safeguard as the last treatment stage before supply to consumers.

Consider a hypothetical example (Figure 2) of a complex organic industrial effluent, or 1000 m^3/day, containing 10 mg/l of a non-biodegradable micropollutant, being discharged to a sewage works of 100,000 m^3/day throughput, which then discharges to a river of 1 x 10^6 m^3/day total flow, of which 100,000 m^3/day is withdrawn downstream for drinking water.

For total equivalent costs, alternative plants could probably be built and operated as follows:

1) At the industrial site, 40 m^3 carbon with a contact time of 1 hr needing a 5 ton/day regeneration rate to give removal from 10 mg/l to 0.5 mg/l.

2) At the waterworks, 700 m^3 of carbon with a contact time of 10 min. needing a 1 ton/day regeneration rate to give removal from 10 µg/l to 1 µg/l.

The industrial plant alternative removes 9.5 kg/day and a level of 0.5 µg/l is found in the drinking water. The water works plant removes only 900 g/day, 9.0 kg/day passing on down the river and 1 µg/hr is present in the drinking water.

In both of these examples, the compounds of interest would be in a small minority compared with the total of adsorbable

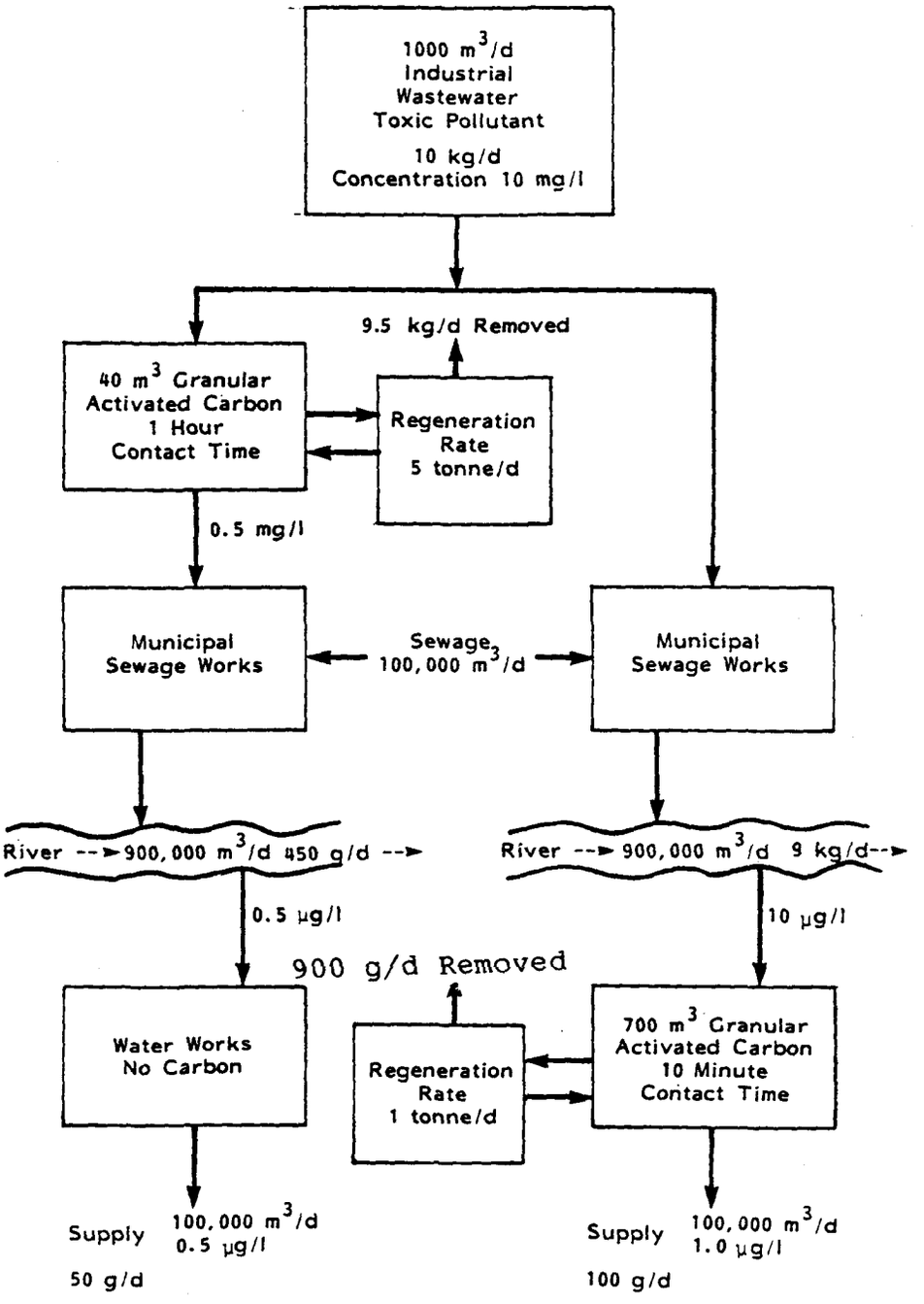


Figure 2. Basis for Hypothetical Total Cost Example

species and complex, competing adsorption would occur. Full pilot scale investigations are always necessary before any design work can be undertaken for such systems, but the examples are of the right order of magnitude for many real situations.

It is probably a good insurance policy to construct a GAC plant at the waterworks with a 5 to 10 minute contact time to act as a safeguard against unknown taste and odor problems and pollutants or spillage, but removal of non-biodegradable organics from known source industrial discharges should be done at the highest concentration possible.

ACKNOWLEDGEMENTS

This paper is given by kind permission of W.H. Richardson, C. Eng, MICE, Mi. Mun. E, MRTPI, Dip. TP, Divisional Manager Lower Trent Division of the Severn-Trent Water Authority and of Humphreys and Glasgow Limited. The authors would like to thank the operations and scientific staff of Severn-Trent and commissioning staff of H&G, on whom the successful running and careful monitoring of the plant depended and whose work is reported in this paper. The comments made and conclusions drawn are those of the authors alone and not those of Severn-Trent W.A. or H&G.

EXPERIENCE ON THE REACTIVATION OF ACTIVATED CARBON WITH A DOUBLE-STAGE FLUIDIZED-BED FURNACE AT THE HOLTHAUSEN TREATMENT PLANT, DÜSSELDORF, FRG

Wilhelm Poggenburg

INTRODUCTION

The Stadtwerke Düsseldorf AG are treating Rhine River bank filtrates with ozone and activated carbon in the waterworks of Staad, Flehe, and Holthausen (Figures 1 and 2). The daily capacity is about 400,000 m^3. Granular activated carbon is capable of eliminating from the water many organic compounds as well as substances causing taste and odor.

In recent years, the number, concentration, and danger of the pollutants and contaminants have increased. Some of the resulting effects have been:

- Today activated carbons are exhausted faster than 20 years ago
- Activated carbons of much higher quality are needed in order to achieve a drinking water of constant quality
- As a rule, the contact time has to be extended and hence, the carbon quantity increased.

The resulting demand for larger quantities of higher quality and therefore more expensive activated carbons does not permit only one-time use. The activated carbons must be reactivated and then reused. Initially, this was done in the manufacturer's works; however, there are now several waterworks which operate their own reactivation plants. The studies revealed that, in addition to economic considerations, the following factors are of major importance:

- The waterworks must be independent of the available reactivation capacities of the manufacturing companies.
- Carbon quality can be adapted to the requirements of each individual type of drinking water treatment. Reactivated carbons usually differ in quality, and

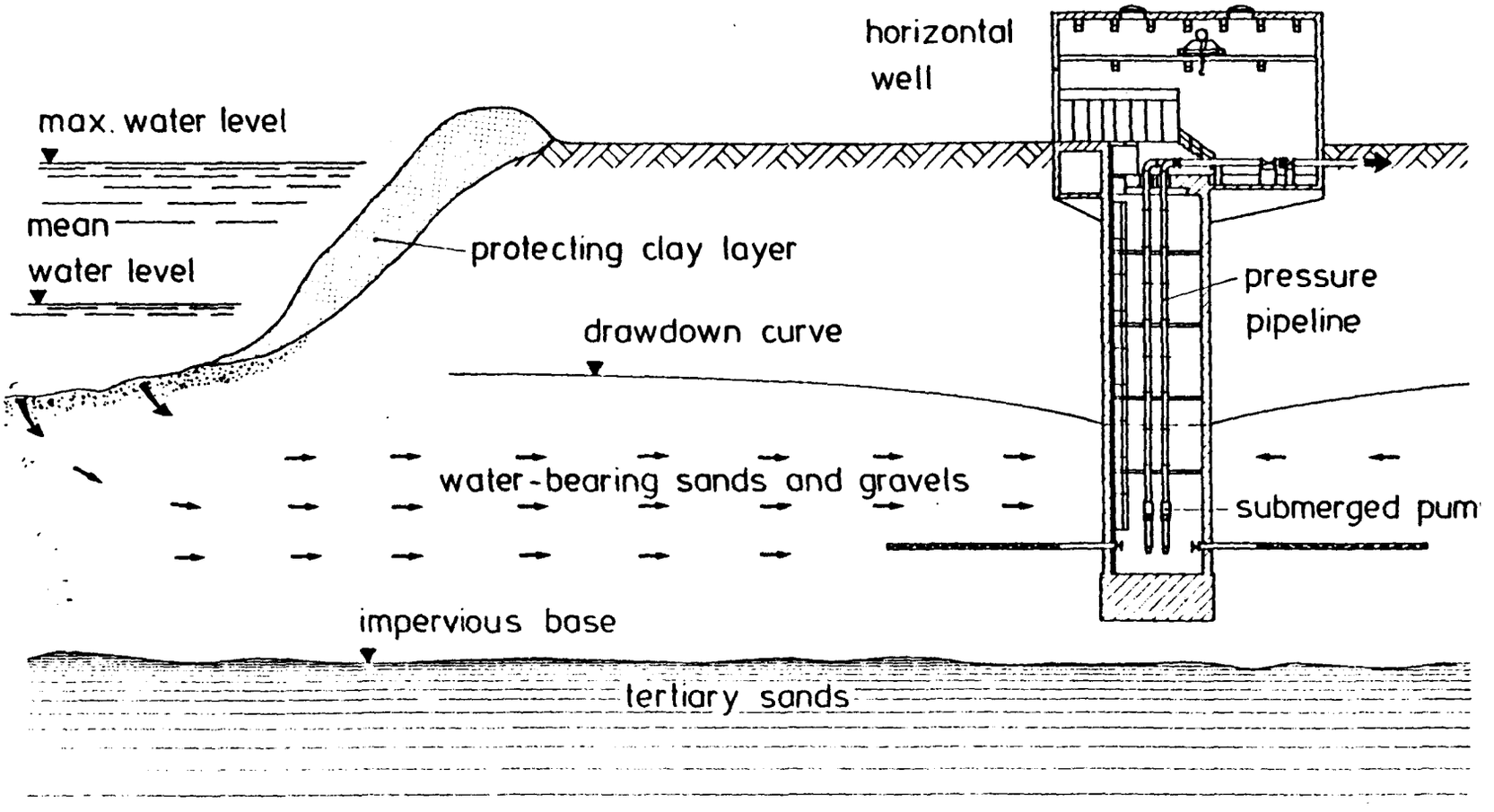


Figure 1. Water Collection in a Horizontal Well Near River Rhine

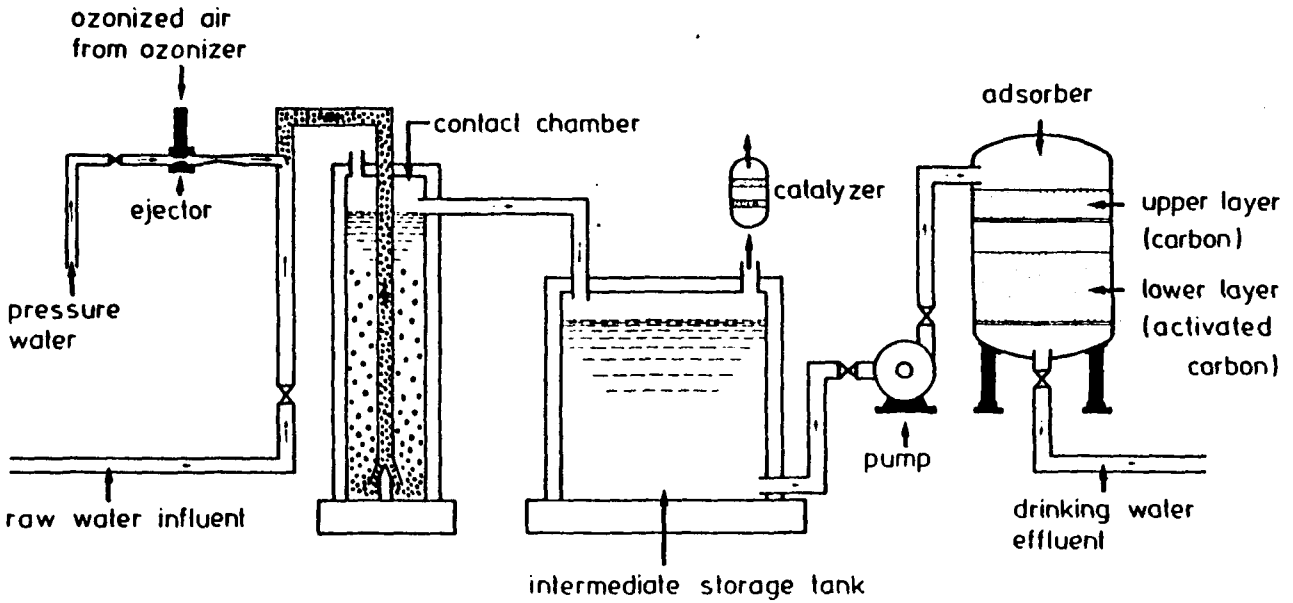


Figure 2. Flow Diagram of Water Treatment Plant

often the quality is unsatisfactory when regeneration has been performed at the carbon manufacturing plant.

REACTIVATION OF ACTIVATED CARBON FOR WATER TREATMENT

Saturated activated carbons can be regenerated by chemical or thermal means. Thermal reactivation is the only process used, to a large degree, in the waterworks. This involves the following process steps: drying, desorption, and pyrolysis.

Drying is achieved by evaporation of absorbed and pore water from the carbon particles at temperatures up to 100°C. Subsequently, highly volatile compounds are desorbed at temperatures up to about 300°C. Finally, irreversibly adsorbed organic compounds are pyrolyzed, while the cracking products escape as gases. This results in pyrolyzed coke as residue on the carbon which can be eliminated only by oxidation in the presence of H_2O, CO_2, or O_2 at temperatures starting from about 700°C.

The following furnace types are available for the thermal reactivation:

Shaft furnace
Rotary kiln
Multiple hearth furnace
Single-step fluid-bed reactor
Two-step fluid-bed reactor
*Fluidizing launder

THE REACTIVATION PLANT AT DÜSSELDORF

A total of approximately 900 t (t = metric ton = 2200 lbs) of activated carbon, which must be reactivated up to three times per year, are used in 42 adsorbers.

In the adsorbers, granular carbons of varying quality, with grain size of 0.5 to 2.5 mm and with apparent densities of between 360 and 480 kg/m^3, are predominant. Lesser quantities of shaped carbons with a diameter of about 0.9 mm and about a 2 mm length are also used.

A two-stage, fluid-bed reactor was erected directly adjacent to the largest of the three treatment plants in Holthausen. More than half of the total 2,100 m^3 of activated carbon is used here.

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*Single-stage fluid-bed reactor where the carbon is flowing in a channel (Wirbelrinne).

The reactor (Figure 3) is the main part of the reactivation plant. Its daily capacity is rated at approximately 6 t of reactivated product. The reactor has an outside diameter of 1.6 m and is approximately 4 m high. With an inside diameter of 0.9 m, the grate surface area is 0.636 m^2.

A pulse-controlled screw feeder, in an inclined position for preliminary dewatering, feeds the wet saturated carbon with a water content of 45 to 55 percent from the inlet tank to the upper part of the reactor. Here the carbon is dried at temperatures between 200 and 300°C and passes through a rotary valve into the reaction chamber where it is reactivated at temperatures between 700 and 800°C. The red-hot, reactivated carbon flows through a discharge pipe into a water-filled quench tank. The average residence time of the carbon in the reactor is about 20 minutes.

The process gas is generated in a combustion chamber underneath the reaction chamber. Natural gas serves as fuel. The desired process gas temperature of 900°C is controlled by water addition. There must always be sufficient steam for gasification. A substoichiometric combustion prevents oxygen from getting into the reaction chamber, thus guarding against combustion of carbon.

The process gas flows from the combustion chamber through the perforated bottom plate of special steel into the reaction chamber. With sufficient flow velocity, the activated carbon bed is raised and fluidized intensively. Although the temperature in the fluid-bed is generally maintained at about 780°C, it always can be adjusted to the specific properties of carbon and adsorbate.

The temperature of the reactivated carbon coming from the reactor and its residence time can be varied for a given process gas temperature by changing the carbon feed rate. Relatively uniform residence time of the carbon particles is achieved by weirs on the lower perforated bottom plate in the reaction chamber which avoids intermixing.

The process gas passes through the upper perforated plate with a temperature of about 700°C, enters into the drying chamber and fluidizes the wet carbon. During this drying phase, the gas temperature drops to the range of 200 to 300°C. The process gas is then cleaned in a special unit.

The material flows in the plant are shown in Figure 4. Spent activated carbon from the Holthausen treatment plant is flushed into the storage tank through a system of pipes. The storage tank of concrete with plastic lining has a capacity of 45 m^3. From this tank, the carbon to be reactivated comes

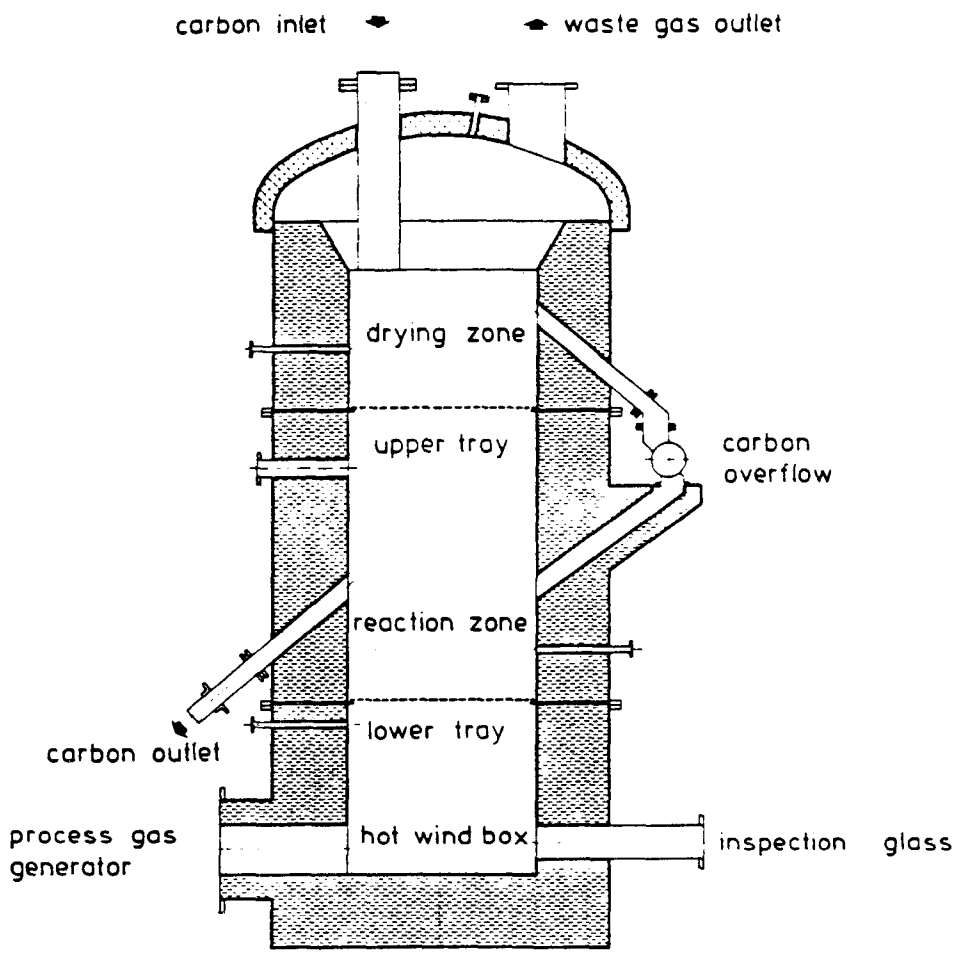

Figure 3. Two-Stage Reactor

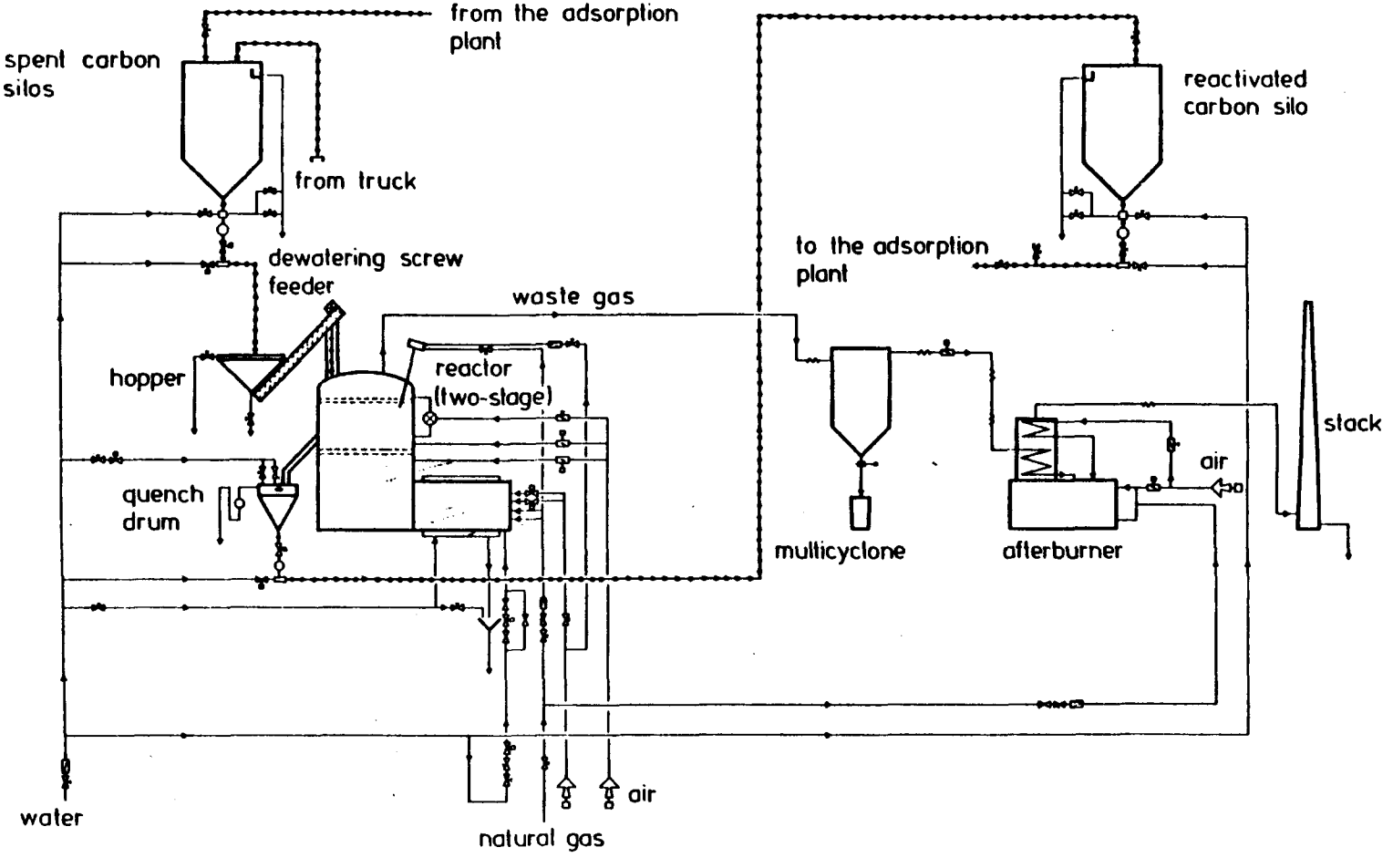

Figure 4. Flow Diagram of Düsseldorf Reactivation Plant

through the PE-pipes into a 0.85 m^3 stainless steel holding tank, from which the screw feeder charges the reactor. The reactivated carbon coming out of the reactor is transported from the quenching tank through the pipe system into another 45 m^3 storage tank.

Carbons from the treatment plants Flehe and Staad are moved in bulk by trucks.

For the hydraulic transportation of the carbon, by ejector pumps, the ratio of water to carbon is adjusted to about 3 : 1; the flow velocity of this water-carbon mixture is about 1.3 m/s. The mechanical controls in the pipe system consist of stainless steel ball valves.

The process gas is emitted from the reactor at a temperature of 200 to 300°C; it contains carbon dust and the materials discharged during reactivation. The dust is separated in a multicyclone and drawn off with the aid of a water-jet pump. The odorous materials partly contained in the process gas are burned in a post-combustion chamber at about 900°C. The hot gas leaving the chamber passes through two heat exchangers. The first serves to preheat the process gas from the reactor, the second, to preheat the combustion air for the post-combustion chamber. The cleaned waste gas, having a temperature of approximately 640°C, is released into the atmosphere through a 16.5 m high steel stack. This relatively expensive waste gas treatment guarantees that the standards of environmental protection, as laid down by legislation and regulatory agencies, will be met at all times.

The operation of a continuous process without constant attendance requires the complete automation of the reactivation plant. A part of this automation is the automatic "shut-down" of the plant to a safe condition in case of failure. Facilities for manual operation are included for the purposes of maintenance, tests, and troubleshooting.

In fully automatic operation, a process computer monitors and controls the startup and shutdown, the operation of the reactor, and the handling of the carbon in the reactivation plant.

A mosaic panel in the control room, manned only part-time, shows all important parts of the plant in a flow diagram. Optical signals of the plant condition and faults, switches and buttons for possible manual operation, and the most important readings are integrated in this control panel, which indicates at all times the actual state of the process.

The following conditions were specified for the planning of the reactivation plant:

- In several fluid-bed reactors, which are independent from each other, a total of up to 500 kg of reactivated product must be obtained per hour.

- The plant is to be operated continuously and is to be staffed by personnel only during working days.

- The storage and handling system must permit charging the reactors from all three treatment plants.

- The waste gas cleaning must meet the anti-pollution air requirements of the authorities concerned.

Since no experience on the operation of a two-stage fluid-bed reactor with fully automatic process control was available to the waterworks, the expansion was arranged in two phases.

The possibility of erecting the equipment without housing was rejected for reasons of environmental protection and in the interests of humane working conditions. All equipment is housed in a building of steel frame construction finished with a light sheeting of shaped metal.

The construction of the plant started in Spring 1975; the first activated carbon was reactivated in August 1976. Since then, 2,000 t, or about 5,000 m^3, of carbon have been reactivated in one two-stage, fluid-bed reactor. Table 1 shows some technical data for the reactivation plant.

Table 1
Technical Data of the Reactivation Plant

Capacity	
First stage of completion	250 kg/h
Final completion	500 kg/h
Reactor (first stage of completion)	
Natural gas consumption (fuel value: 9.7 kWh/Std. m^3)	Approx. 60 m^3/h
Power requirement	490 kW
Water requirement	Approx. 50 l/h
Afterburner (first stage of completion)	
Natural gas consumption (fuel value: 9.7 kWh/Std. m^3)	Approx. 21 m^3/h
Temperatures	
Process gas	850 - 950°C
Reaction zone	700 - 800°C
Drying zone	200 - 300°C
Afterburner	Approx. 900°C
Stack	Approx. 640°C

For plant safety, the monitoring, measuring and control equipment, and the "EMERGENCY-OFF" controls all work independently of the computer.

FIELD EXPERIENCE

It was not expected that such a plant would go into operation without any difficulties. Considerable efforts and constant readiness of the staff of contractors and plant personnel have led to the result that, after about 2 years, the reactivation plant is giving satisfactory service in automatic operation and is supplying a reactivated product of quality that consistently meets specifications.

On the basis of this past experience, only one additional fluid-bed reactor is planned for future installation to reactivate all spent activated carbon arising from the three waterworks. Furthermore, fresh activated carbon of low quality can be up-graded by the fluid-bed reactivation, although only with higher losses.

The performance test in the second half of 1976 showed an extraordinarily high failure rate although only proven standard material had been used. Because of frequent plant failures it was still impossible, one year later, to sustain sufficient continuous operation to allow the determination of optimum reactivation conditions. However, substantial knowledge and experience on function and service life of all equipment was gained during this time, and large quantities of spent activated carbon were reactivated. Surprisingly, the failures occurred most frequently in those parts of the plant which had proved to be particularly successful in other applications under similar conditions. Considerable changes were also necessary in the reactor itself and in the control program.

IMPROVEMENTS IN THE REACTOR

With the original internal components in the bottom of the reaction chamber, it was impossible to obtain a uniform retention time for the carbon. Widely varying and often unsatisfactory qualities of the reactivated product were the result. The high initial adsorption capability of the carbons declined very rapidly in operation, probably because the micro-pore system was insufficiently reactivated. Various reactor internal configurations had to be tested until a complete recovery of quality was obtained in combination with only mild attacks on the activated carbon structure. With the current solution, there is only a small deviation in the retention times of the various carbon particles. The presently established thorough exchange of mass and heat enables a precise temperature control of the process.

No significant effect upon the hardness of the carbon can be detected, although the screen distribution is gradually shifting toward smaller particle sizes.

The originally installed ceramic nozzle bottoms have not met expectations. After a short time of service, the slots in the nozzle heads were clogged by sediment from the water, by material from the brick lining, and by foreign matter in the carbon resulting in an unacceptable pressure increase. Perforated bottom plates of heat-resistant, alloy steel therefore have been installed in the drying and reactivation chambers. They can be run for months without cleaning. Their service life until now has been satisfactory.

An early test of water injection for control of the process gas temperature in the burner space revealed considerable operating problems. The water with a carbonate hardness of 100 to 110 mg/l as $CaCO_3$ and with a maximum chloride content of 250 mg/l is now softened and introduced by way of a cascade. Current experience indicates no need for further treatment.

At first, minor quantities of gravel inadvertently charged into the reactor together with the carbon were found to interfere with the reactivation process. Sintering on the trays resulted very quickly in constriction of the slots or perforations. The result was that it was no longer possible to achieve the gas flow rate needed for fluidization and reactivation after a short time of operation. Bar grates in the feed system to the reactor are now retaining the gravel. Danger to the feeding screw is thus eliminated and the sintering on the trays is satisfactorily minimized.

EXPERIENCE WITH CARBON TRANSPORT

No problems are encountered in the pipe system if the hydraulic transportation of the carbon is carried out correctly. An insufficient water-to-carbon ratio or an excessively high flow velocity will lead to clogging or increased wear. Pre- and reflushing with water are important prerequisites for trouble-free carbon handling.

Stainless steel, plastic, and shaped steel pieces with inside enamel coating or cement mortar lining were used for the transport lines on a test basis. All these materials gave satisfactory service when properly made and assembled.

Originally installed, cast iron ball valves were removed because of severe erosion and replaced by ball valves of stainless steel. With tanks and pipelines it was found that, in case of improper execution or insufficient quality, stainless steel in this unusually corrosive environment will fail within a very short time.

A particular problem is the reliable determination of the filling level of activated carbon under water, especially under corrosive conditions or high temperatures. Improved methods of measuring and indicating filling level are presently under trial.

THE WASTE GAS SYSTEM

The ceramic nozzle bottoms installed originally in the reactor cause higher pressure losses than the current perforated bottom plates. In order to avoid excessive stress of the reactor shell by over-pressure and to prevent the leakage of gas, a waste gas fan was installed which produced a slight suction of about 500 Pa (0.07 psi) at the reactor top. This waste gas fan was extremely susceptible to failure and caused numerous total breakdowns.

After the perforated bottoms had been installed, the reactor was run successfully at a slight over-pressure without utilizing the waste gas fan. The fan was therefore removed and an over-pressure of about 6 kPa (0.9 psi) now exists in the burner chamber in normal operation.

During commissioning there were occurrences of undesirable dust deposits on the heat exchanger pipes after extended operation. A cleaning device consisting of chains, which are operated intermittently by an electric motor, was later installed and is now removing these deposits.

VERIFICATION OF THE GUARANTEES

The manufacturers' guarantees were verified by tests in June 1978.

Guarantees:

1. Reactivation of 250 kg/h granular activated carbon with a bulk density of virgin carbon (unsaturated) of about 430 kg/m^3 and a grain size range of 0.5 to 2.5 mm, or shaped carbon with about 0.9 mm diameter and about 2 mm length. This guarantee applies at a discharge temperature of 720°C.

2. The quality of the reactivated product must at least meet the standard of service reactivation presently offered by carbon manufacturers.

3. The loss in the reactor must not amount to more than 5 percent by volume for the activated carbon grades F300, LSS, and ROW 0.8. The undersize fraction (<0.5 mm) fed into the reactor is disregarded in calculating the loss.

4. Energy and process water requirement:

Natural gas consumption (H_u = 7,600 kcal/std. m^3)	130 m^3/h
Electric energy consumption	50 kW
Process water consumption	10 m^3/h

Results:

1. The carbons defined here are all reactivatible. In the case of granular carbons, the guaranteed throughput of 250 kg/h was achieved and often exceeded. Further tests are necessary to determine whether the throughput can also be achieved in the reactivation of shaped carbons.

2. The reactivation quality is uniform and satisfactory. It matches or exceeds the qualities obtained in contracted reactivations. The quality of the reactivated products are, in some cases, even better than those of virgin carbon. Further tests are necessary to determine the optimum operating conditions of the reactor.

3. The losses in the reactor are not easily determined. As yet, this problem has not been solved satisfactorily. The contractor's reactivations show widely fluctuating losses; the total losses (operating, handling, and reactivation losses) are between 12 and 25 percent. In the instance of on-site reactivation, losses are currently 11 to 12 percent and relatively constant. Between the storage silo holding the material to be reactivated and the silo holding the reactivated carbon, the losses amount to about 9.5 percent; approximately 2 percent of the carbon is lost during transport and backwashing in the filter plant. A first test, with a loss balance in the various parts of the reactivation plant, leads to the conclusion that the losses in the reactor are below 5 percent by volume. A significant change of the mean particle diameter was not detected here.

   Common knowledge indicates that it should be possible to achieve further reduction of the reactivation losses and especially of the handling losses. Tests of these possibilities are planned. This program will also try to monitor the loss rate in the various parts of plant with more accuracy than before.

4. The consumption of gas and electric energy is much lower than the guaranteed values. Hence, the operation of the proprietary reactivation plant is much more economical in terms of energy costs than calculated originally (Figure 5). The process water consumption is higher than expected and therefore must be reduced, although it does not significantly influence the economy. An essential portion of the process water is that used for transport.

REACTIVATION COSTS

The reactivation costs consist of the carbon losses, the energy consumption, costs for personnel, and the depreciation as listed in Table 2.

Table 2

Reactivation Costs at Holthausen

		Cost Basis	Cost DM per 10^3 kg AC
1.	Natural gas	75 m^3/h	132
2.	Electrical power	35 kW	14
3.	Water for transport, etc.	14 m^3/h	17
4.	Manpower and maintenance		67
5.	Capital interests, etc.		264
	Reactivation costs		494
6.	Carbon losses		
	a) Reactivation furnace	<5%	
	b) Transport in the reactivation plant, multiclone discharge	Approx. 4.5%	
	c) Transport and backwashing in the filter plant	Approx. 2%	
	Total losses	Approx. 11.5%	345
	Total costs including carbon replacement		839

The reactivation costs may be reduced still further after the second reactor is installed.

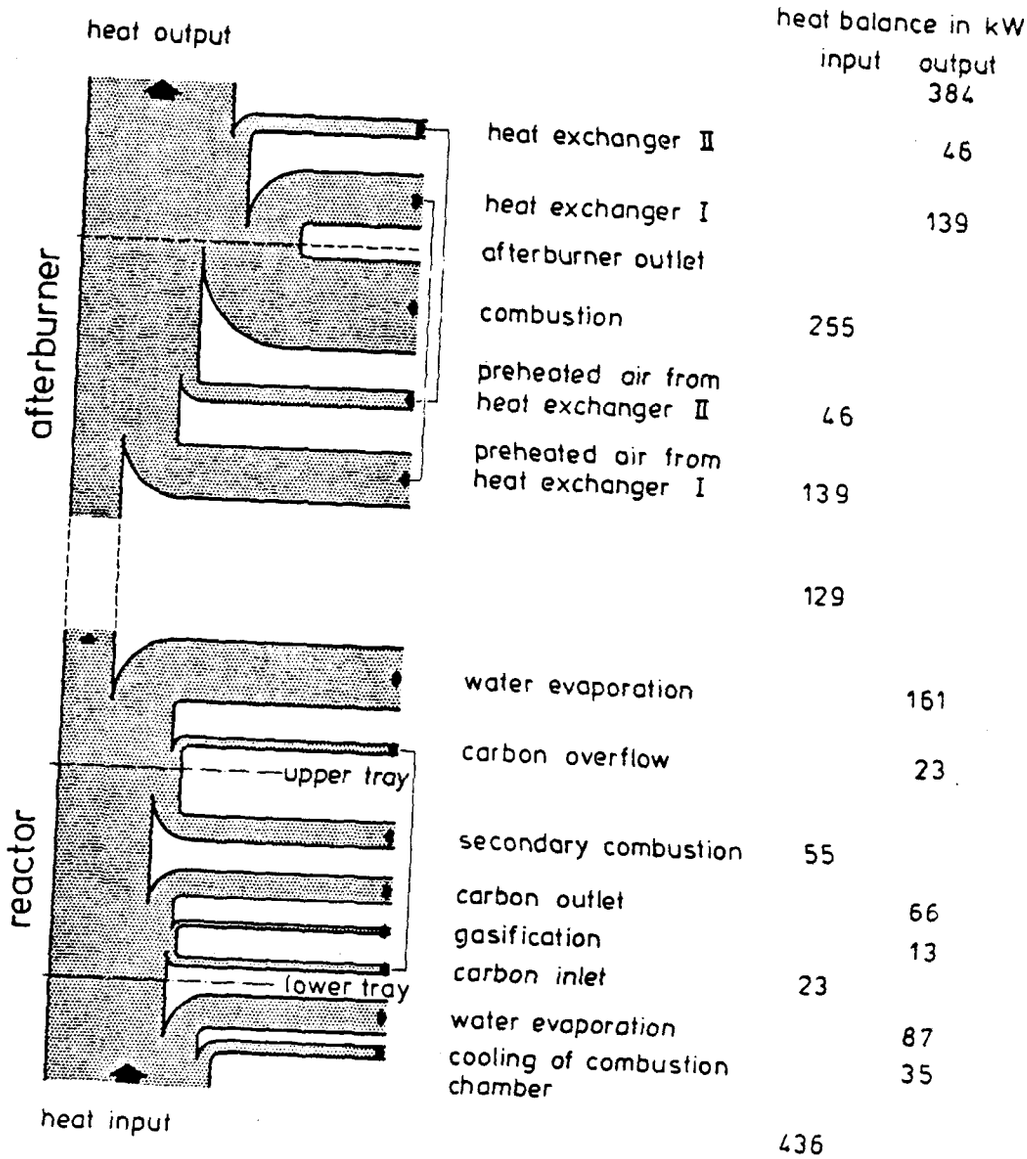

Figure 5. Heat Diagram

SUMMARY

The thermal reactivation of activated carbon in the waterworks has been successful in satisfying widely varying requirements. Most importantly, reactivation plants can today be reliably operated fully automatically. The on-site reactivation plant has come to be a valuable element in guaranteeing the supply of safe, palatable drinking water at all times, even under adverse conditions.

EXPERIENCE WITH A FLUIDIZED BED FURNACE AT BENRATH TREATMENT PLANT

Dr. B. Strack and H. Martin

DESCRIPTION OF THE PLANT

Benrath waterworks have been delivering drinking water from the river banks of the Rhine for the town of Wuppertal for exactly 100 years. Raw water from the sand banks of the Rhine River requires careful treatment, which has been done with ozone and granular activated carbon filtration since 1967. The carbon must be replaced or reactivated between two or three times per year, depending on output and water quality. The sixteen filters yield about 1,000 metric tons yearly of spent carbon to be reactivated.

The activated carbon was formerly reactivated by the carbon manufacturer; since 1977, our own activated carbon reactivation plant with a capacity of 5 metric tons per day has been in operation. Such a plant in the waterworks area offers the advantages that the filter carbon can be exchanged quickly, there are short lines of transfer, and the manager of the waterworks is independent from forwarder and carbon manufacturer. The fluidized bed furnace employed for reactivation allows fast starting as well as changes of reactivation conditions during its operation. Furthermore, it is possible to achieve the carbon qualities required for adsorption of the impurities present in water.

A flow diagram of the Benrath reactivation plant is shown in Figure 1. Spent carbon from the filters is hydraulically transported into a rectangular storage tank made of concrete. Underneath the tank is a separating vessel in which heavy impurities such as gravel, which could cause troubles in the furnace, are separated.

The carbon is transported via an intermediate tank to a conveyor screw, which feeds the furnace continuously.

The superficially dewatered but still wet carbon is fed into the fluidized bed (Figure 2) and is reactivated for about 45 minutes at a temperature of 600°C. The furnace is fired with natural gas. The temperature is controlled by injection of

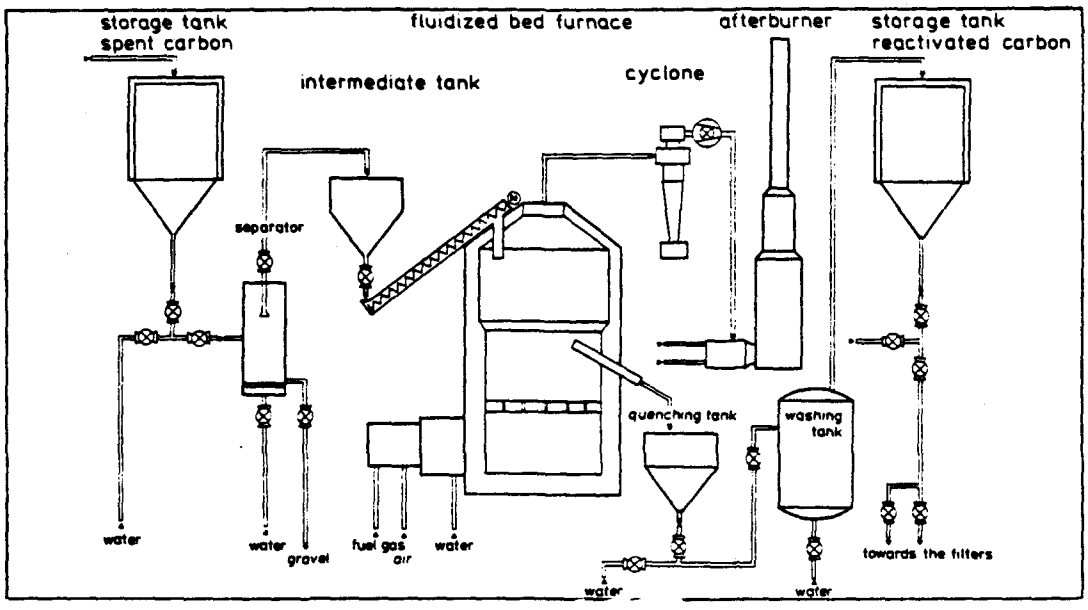

Figure 1. Flow Diagram of the Benrath Reactivation Plant

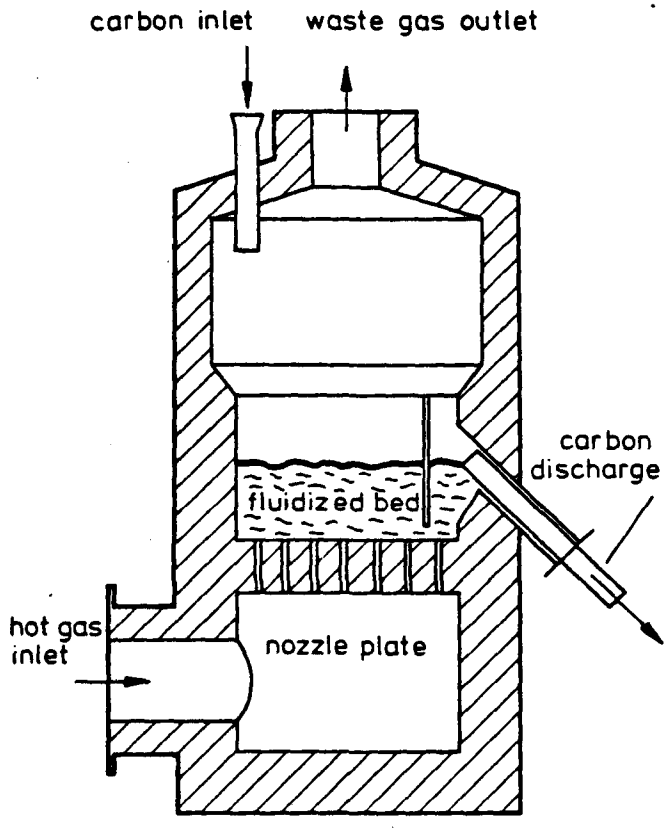

Figure 2. Cross-Section of the Fluidized Bed Furnace

water. Afterwards the carbon is quenched and washed with water, then stored in a tank, and transported back to the filters as needed.

The exhaust gas from the furnace passes a cyclone which removes dust and is purified in a combustor to meet air pollution control requirements. Thus, less than 20 mg/m^3 of dust and 3 ppm of carbon monoxide escape as pollutants.

During the time this plant has been operating, extensive experience has been gained in estimating the quality of the reactivated carbon and in identifying and solving operational difficulties. This is discussed in more detail below.

QUALITY OF THE REACTIVATED CARBON

The activated carbon has several simultaneous tasks in the process used at Benrath. The water treated with ozone and filtered over gravel is passed through the carbon filter primarily for removal of dissolved organic matter by adsorption. In addition, microorganisms in the carbon bed remove ammonium and some of the organic substances. Furthermore, residual ozone is decomposed in the top layer of the carbon filter and a small amount of manganese, not completely removed in the preceding sand bed, is retained.

The experience of many years shows that the granular activated carbon filters perform these simultaneous tasks if a good quality of carbon is used. Hence, quality control at the reactivation step is important. During recent years, detailed investigations have been carried out with the support of the German Federal Minister for Research and Technology.

The total concentration of the dissolved organic substances is often determined as DOC. Measurement of the UV-adsorbance on the other hand is faster, simpler, and gives similar information. Table 1 illustrates mean values of DOC and UV absorbance for Rhine River water, river bank filtrate, and drinking water.

Table 1. Mean Values of Dissolved Organics

	Rhine River	River bank filtrate	Drinking water
UV (m^{-1})	10.1	3.5	1.0
DOC (g/m^3)	3.9	1.6	1.0

Because of its advantages the UV method is used for continuous surveillance of the filters at Benrath waterworks. In this manner the efficiency of the filters can be monitored and decisions made as to the necessity of carbon replacement. Both the efficiency and frequency of replacement depend on the quality of the carbon and the composition of the raw water. The filters should be operated so that a DOC value of 1 g/m^3 in the drinking water reservoir is not exceeded; this will ensure that all undesirable substances are removed.

The efficiency of a filter is a practical criterion for evaluating performance at the waterworks. It is defined by the ratio of the amount of matter removed by the filter to the amount being initially present. It is determined by UV measurements at the inlet and the outlet of a filter. The efficiency decreases continuously as more water is treated, eventually reaching a specified lower limit at which the carbon in the filter is exchanged with reactivated or fresh carbon.

The speed of the deterioration depends on the quality of the carbon, since a carbon with a high adsorption capacity will treat more water before the efficiency limit is reached than one with low capacity. Of practical interest is how much water can be treated with a given type of carbon in the present filters. This measure of quality must also be valid for the reactivated carbon.

As an example, Figure 3 shows the efficiency of different filters recorded over the throughput. It is evident that efficiency can be described as a function of throughput or time of operation. The data, though somewhat scattered, seem to be log-linearly related. One of the tests with our own reactivated carbon yields a somewhat better efficiency at low throughput, suggesting the possibility of a more suitable quality. However, as throughput continues our two reactivated carbons behave essentially the same as the virgin carbon and the carbon reactivated by the producer.

At the waterworks it takes a relatively long period for the adsorption behavior of the carbon to be recognized. Therefore a rapid test of the quality of the reactivated product is needed to allow prediction of the behavior of the filters in practice. Conventional tests such as Iodine Number, Methylene Blue Number, and benzene loading were assessed. These methods can supply some indirect information about the porous structure, but no regular relation to the behavior of the filters in the waterworks could be found. Only the Iodine Number gave, in some cases, useful hints for predicting the performance of the carbon.

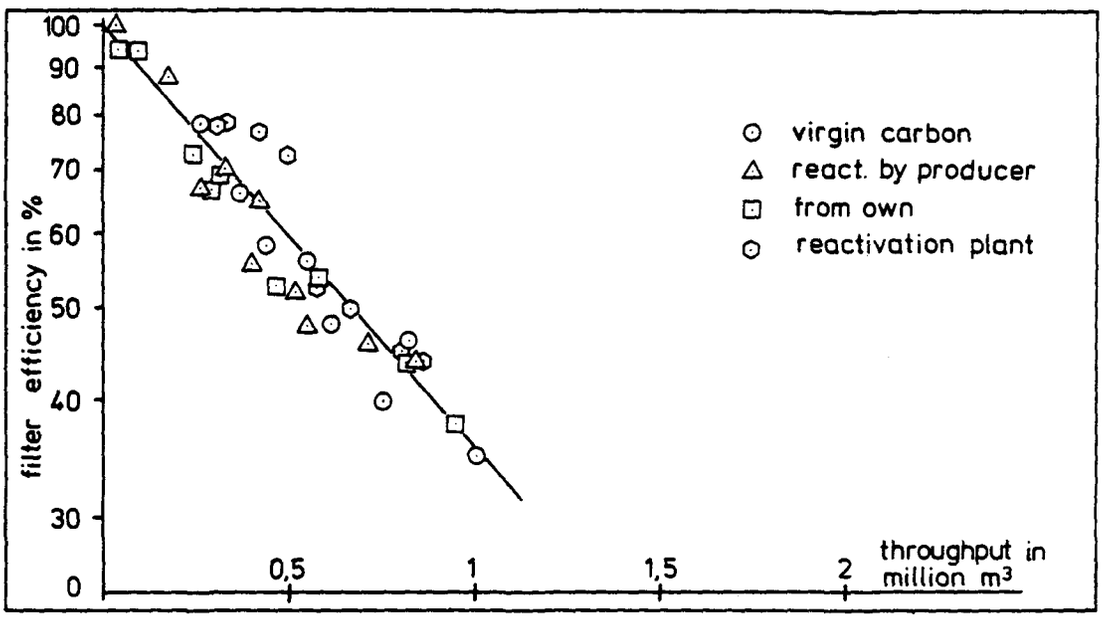

Figure 3. Breakthrough of UV-Absorbing Substances in Benrath AC Filters

After these negative results, a practical test proposed by the study group of Prof. Sontheimer was further developed and applied in our research program. In this method the adsorption equilibrium between organic matter in the water to be treated and a carbon sample is investigated using a UV-measurement. One obtains isotherms as shown in Figure 4a. To calculate the adsorption capacity in practice, or the amount of water which can be treated before equilibrium is reached, it is necessary to assume an acceptable residual concentration or a ratio of organic compounds to be removed.

As a second part of the method, paranitrophenol (PNP) is added to the raw water, since PNP is thought to adsorb in a manner similar to some chlorinated organic compounds. The isotherms of raw water and PNP (Figures 4a and 4b) show that carbon sample 1, which behaves least favorably in raw water, is the best with PNP. Thus selection of a carbon and operating conditions for removal of chlorinated organics cannot be based solely on isotherms describing overall organic compound removal from raw water. Instead, it is necessary to consider the adsorption behavior of both raw water and of PNP and then select operating conditions which yield satisfactory overall results.

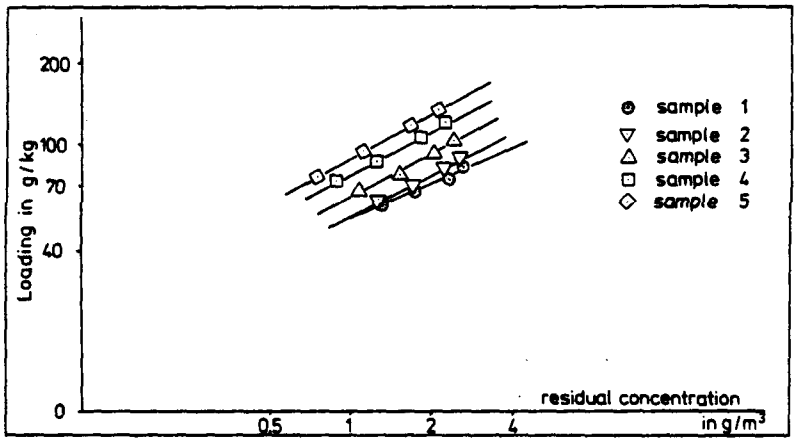

Figure 4a. Isotherms of Raw Water with Several Carbon Samples

note: The residual concentration is based on UV-extinction in m^{-1} which, in this case, corresponds nearly exactly with the total concentration of organic matter in g/m^3. The latter concentration units are used to be consistent with the units of g/kg used for loading.

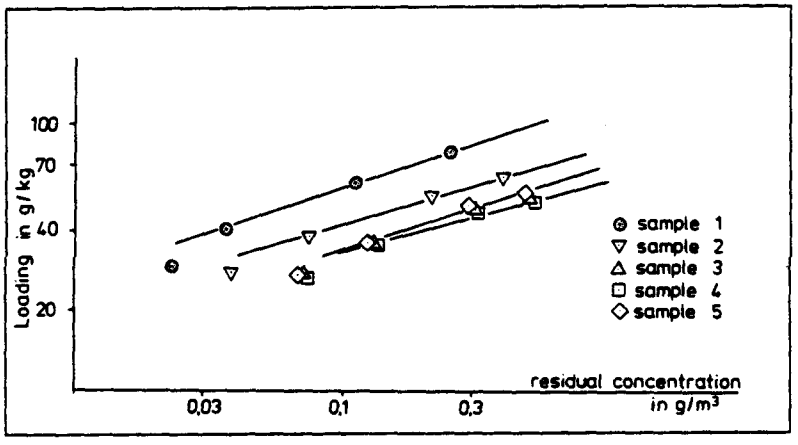

Figure 4b. Isotherms of PNP with Several Carbon Samples

A new method has been evaluated for the analysis of the raw water isotherms which has proven very useful. In this method the activated carbon filter is assumed to be a completely mixed reactor in which equilibrium is always attained during the passage of the water. In this manner a theoretical prediction based on the isotherms can be made for the filter efficiency as a function of the treated quantity of water. Furthermore, a comparison of the theoretical prediction with the standard sample can be made, the behavior of which is known in the filter. In Figure 5, the calculated and observed efficiency are plotted versus specific throughput in m^3 water per kg carbon. The efficiency values shown are for total organic substance in the raw water, inferred from UV-absorbance measurements. It is evident that the actual data agree well with the prediction resulting from this rather simple approximate method.

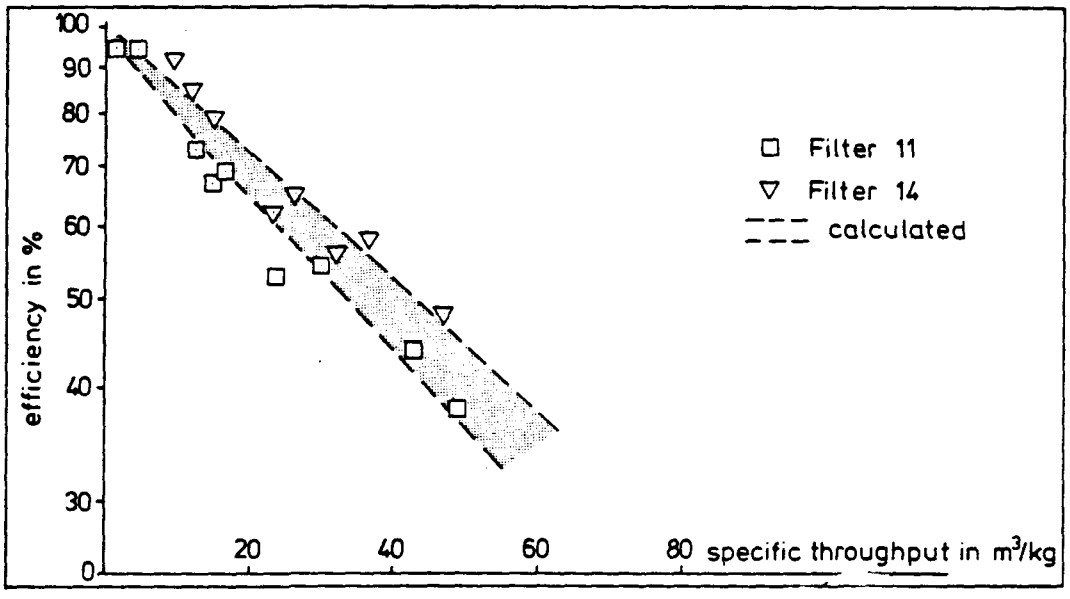

Figure 5. Measured and Calculated Breakthrough of Filters with Reactivated Carbons

Hence the adsorption test using the actual raw water is a fast and practical method, at least for the conditions in Benrath waterworks. With this method it is also possible to calculate the amount of carbon that can be saved if a better quality is achieved through reactivation.

Further investigations are planned to determine how the described method must be changed or extended to ensure useful results under other presuppositions and boundary conditions. For example, the effect of biological processes occurring on the carbon will also be taken into consideration.

Another important aspect of the quality of the reactivated carbon is its mechanical strength. The carbon grain is stressed during backwash, hydraulic conveyance, and reactivation.

Consequently every grain becomes smaller by attrition. Figure 6 shows, for example, the screen analysis for virgin, spent, and reactivated carbon. The fine grain fraction increases with time, which results in carbon loss when the very fine particles are rinsed out of the filter. Therefore care has to be taken to ensure that this decrease of the grain size is minimized. Past experience indicates the carbon loss depends mainly on hardness. Thus, the virgin carbon must be as hard as possible. Presently the overall loss, including conveyance to and from the filters, separation of heavy particles, thermal reactivation, and washing, totals about 15 percent. Efforts are still being made to reduce this carbon loss.

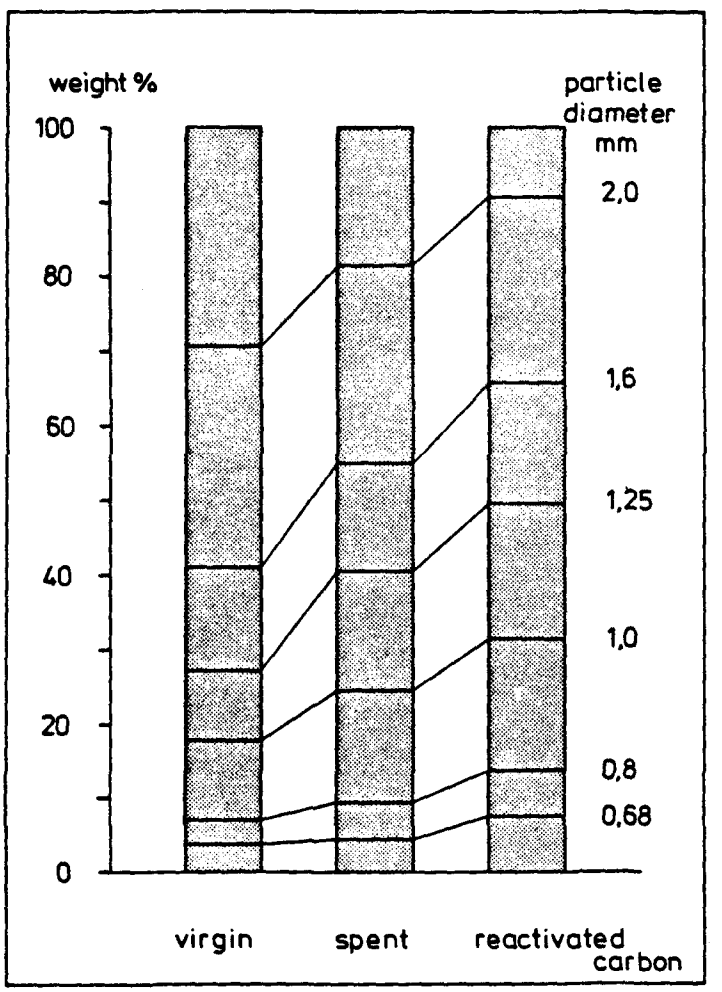

Figure 6. Screen Analysis of Activated Carbon

PRACTICAL EXPERIENCE WITH PARTICULAR PARTS OF THE PLANT

The reactivation plant has been operating since 1977. During that time, we modified the plant to deal with some of the problems that were encountered. They are summarized in Table 2.

Table 2. Summary of the Improvements at Benrath

1.	Problems resulting from water hardness a. Desalination of injected water b. Quick exchange of quenching water
2.	Process gas composition control
3.	Distribution of wet carbon
4.	Use of special injectors
5.	Use of special steel quality

PRETREATMENT OF PROCESS WATER

One problem concerned the quality of the water used for the reactivation process and for conveyance. The process gas contains a considerable portion of steam originating from liquid water sprayed into the burner chamber. Originally, softened water was used. However, the remaining salts, mainly sodium carbonate, reacted with the fine sand taken in with the carbon and formed a slag which gradually obstructed the nozzles. Now the water is completely demineralized by a reverse osmosis plant and the described troubles no longer occur. Another problem arose in quenching the carbon after the reactivation to fill the pores with water. The hot reactivated carbon causes both an increase of the pH of the water into the alkaline range and a rise in temperature. As a result, calcium carbonate precipitates, depositing itself as a dense layer on the wall and the nozzles or the rinsing vessel. Remedial measures included changing the water frequently and inserting less easily fouled nozzles.

GAS PRESSURE

According to past experience, the composition of the process gas must be held constant to allow optimum conditions for the reactivation process. Variation of supply pressure can result in different quantities of fuel gas and air being delivered, which is undesirable since excess oxygen burns the carbon and causes unnecessary losses. Therefore a control vent for the exhaust gas was installed to hold the pressure constant and a supplementary gas analyzer was included to allow simple control of the gas composition.

CONTROL OF RESIDENCE TIME

The wet heavy carbon coming from the conveyor screw can fall through the fluidized bed and stay on the bottom. Therefore the wet carbon has to be spread by a simple device so that it is at once thoroughly mixed. By this means the distribution of the temperature in the bed and the residence time of the carbon is more steady and therefore the reactivation is better.

EJECTOR DESIGN

For hydraulical conveyance, jet ejectors are installed at several places. The carbon flows from above into the horizontal driving water jet. This results in attrition at the water nozzle. However, there are better ejectors designed especially for hard solids in which the nozzle is retracted out of the carbon stream and the diffuser consists of an exchangeable shell made of a hard alloy.

CONSTRUCTION MATERIALS AND FABRICATION

Considerable corrosion has occurred in the plant where stainless steel 1.4571 (equivalent to AISI 316 Ti) was not used or where the welding was poor. The presence of spent carbon and water containing chloride resulted in pitting corrosion at the welding seams and crevice corrosion at the flanges. Consequently, some of the welding seams had to be rewelded as well as etched and passivated. The welding operator must be very familiar with handling stainless steel. The flanges should be absolutely plane and the seal must stay elastic and tight so that no hollow space is formed. In summary the use of high quality materials, and very careful design and manufacturing, are necessary to prevent problems of corrosion under the conditions experienced at Benrath.

SUMMARY

The encountered difficulties were overcome during the first 2 years of operation. Our present results show that the compact and not very complicated reactivation plant, based on a single stage fluidized bed type furnace fed with wet carbon, works successfully. The reliability of the waterworks performance has improved, thereby enabling optimization of plant operation so that a good water quality can be achieved in an economic manner.

EXPERIENCE WITH AN INFRARED FURNACE FOR REACTIVATING GRANULAR ACTIVATED CARBON

O. Thomas Love, Jr.
and
Wendell R. Inhoffer

Granular activated carbon is a broad-spectrum adsorbent that must be kept in an "active" state to be effective. One method of achieving this is with thermal reactivation. The status of an EPA sponsored research project to evaluate an infra-red tunnel furnace for reactivating granular carbon used in drinking water is the topic of this report.

WHY AN ELECTRIC FURNACE?

Two reasons why an electric furnace might be an attractive option for reactivation are:

1. Some water utilities in the United States have limited fossil fuels available, yet adequate electric power. Some of this power may be hydroelectrically generated at the waterworks.

2. An electric furnace may be started or shut down without long warm-up or cool-down periods.

Further, a tunnel furnace conveys the adsorbent on a traveling belt and this gentle handling should reduce mechanical attrition losses in reactivation.

LOCATION AND DESCRIPTION OF STUDY SITE

The utility selected for this study is the Little Falls Filtration Plant in Totawa, New Jersey. This facility is owned and operated by the Passaic Valley Water Commission; the source of water is the Passaic River.

This location has a history of trace organic contamination (1) (the Passaic River has hundreds of industrial discharges upstream of the Little Falls intake). Furthermore, in recent

years several experiments have been conducted using granular activated carbon adsorption (2). Thus, detailed characterization of both the source and the treatment plant existed.

The Little Falls Filtration plant employs prechlorination, alum coagulation, settling, filtration (anthracite coal over sand), and at times dechlorination. The average flow is 55 mgd (208,000 m^3/day). A side stream of treated water [2.2 mgd (8,300 m^3/day)] was diverted to three pressure vessels, each containing a different type granular activated carbon, with an empty bed contact time (EBCT) of approximately 8 minutes. The granular activated carbon adsorbers filled with virgin adsorbents were operated continuously without backwash from March to May 1978, and then reactivated.

FURNACE

The furnace selected is by Shirco, Inc.* of Dallas, Texas. Design characteristics are given in Table 1 and the unit is shown in Figure 1.

Table 1. Electric Furnace, Little Falls Filtration Plant

Dimensions	4 feet (w) x 20 feet (l) (1.2m x 6m)
Activated Carbon Residence Time	20 to 25 minutes
Temperature	
drying zone	1,150°F (620°C)
activation zone	1,650°F (900°C)
Power required	100 kW
Warm-up time	30 minutes
Weight	17,000 lbs (7727 kg)
Reactivation capacity	100 lb/hr (45 kg/hr)

*Mention of commercial products does not constitute approval or endorsement by the U.S. EPA.

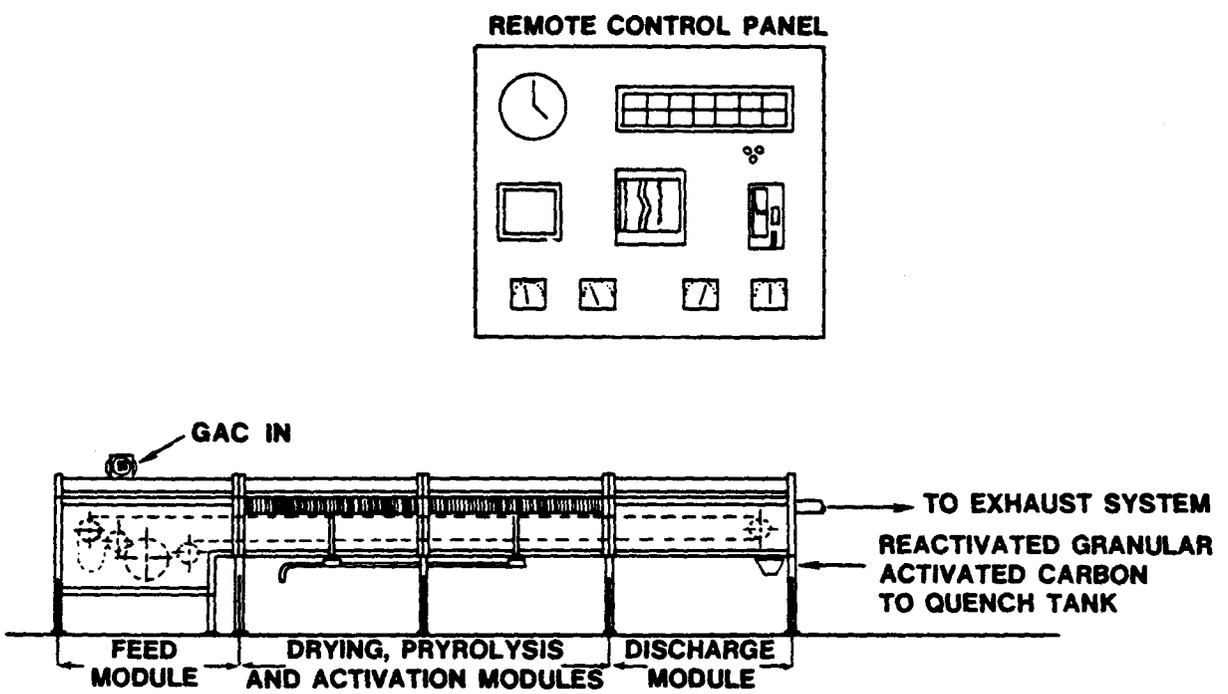

Figure 1. Cross Section of Infra-Red Tunnel Furnace

The adsorbents were then sequentially educted into a storage bin, fed into the furnace, and returned to the adsorbers for quenching. As of May 1979, the granular carbon has been reactivated twice; plans call for at least two more exposure/reactivation cycles before the project is completed.

Adsorption and reactivation performance is being judged on the parameters shown in Table 2. Additionally, data are collected on power consumption, labor, and adsorbent attrition losses.

Table 2. Performance Parameters

Parameter	Analyzed by	Procedure Used
Total Organic Carbon (TOC)	A	Dohrmann DC-54 (3)
Total Organic Halogens (TOX)*	B	Pyrolysis, microcoulometric detector (4,5,6)
Specific organics (39 total)	C	GC/MS
UV absorbance	A	254 nm (7)
Fluorescence	A	Rapid fluorometric method (8)
Iodine Number	B,D	AWWA Standards (9)
Apparent Density	B,D	
Phenol Number	B,D	
Bacteriological	A	Standard plate count 35°C coliform analysis (10)

A - Passaic Valley Water Commission
B - Havens and Emerson, Consulting Engineers
C - Rutgers University
D - Shirco, Inc.

*Includes influent and effluent to adsorbers, plus top and bottom GAC samples.

For the initial reactivation, the contact time for the granular carbon within the furnace was 20 minutes at a temperature of 1,650°F (900°C). These conditions were selected by the furnace vendor on the basis of thermographic analysis and Iodine Numbers.

The first carbon to be reactivated in this system was the lignite-based HD-1030 (a product of ICI America, Inc.). Unfortunately, because of inexperience, problems were encountered in handling the adsorbent and in operating the furnace resulting in atypical losses. Further, performance of the lignite activated carbon could not be equitably judged. The characteristics of the two coal-based granular carbons (Westvaco WV-W and Calgon F-400) before and after reactivation are shown in Table 3. Iodine numbers were restored to within 12 percent of the virgin granular carbon and apparent densities increased about 3 percent through the cycle.

Table 3. Comparison of Virgin To Reactivated Granular Carbon
Cycle 1

	Virgin	Exhausted	Reactivated
Iodine Number			
HD-1030	601	416	(See text)
WV-W	850	711	761
F400	1,023	790	890
Apparent Density			
HD-1030	0.44	0.44	(See text)
WV-W	0.57	0.61	0.57
F400	0.47	0.51	0.49

The real test was how the granular activated carbon performed during actual treatment of Passaic River water. The total organic carbon (TOC) concentration in the influent to the virgin activated carbon ranged from 1.5 mg/l to 3.9 mg/l with a mean of 2.7 mg/l. When the adsorbents were reactivated and put back into service, the TOC had a mean concentration of 4.4 mg/l. Because of the different loadings, the comparison of virgin to reactivated carbon is obscured, but if these differences are neglected, the decline in TOC removal is approximately 12 percent for the 11 weeks in service after reactivation (Figure 2). Subsequent cycles should allow for more direct comparisons.

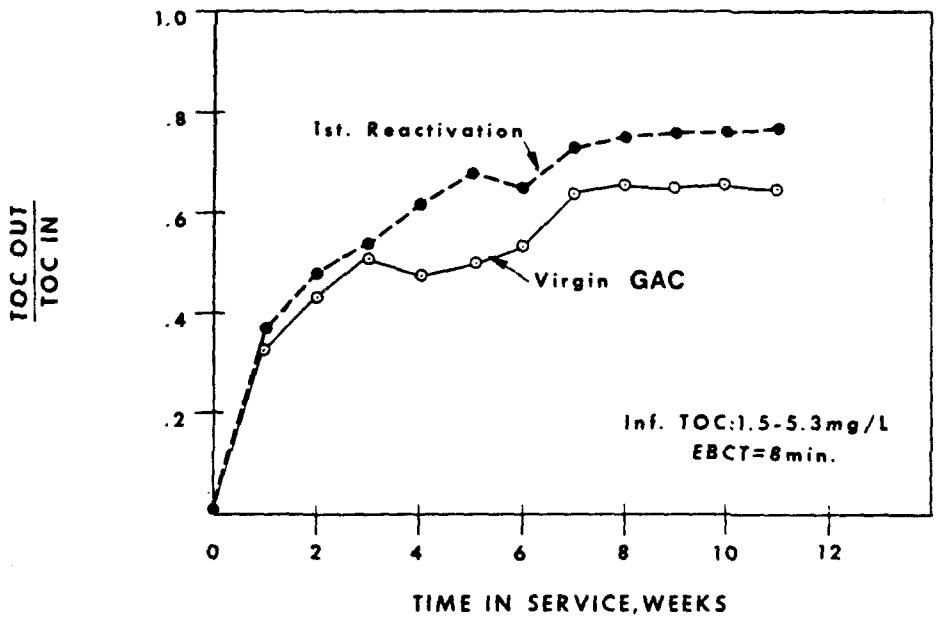

Figure 2. Effectiveness of Reactivation Measured by Total Organic Carbon

Organic halogen (TOX) concentrations on samples of activated carbon collected from the top and bottom of each adsorber were averaged, with the results shown in Figure 3. Again, the reactivated carbon was about 10 percent less effective than the virgin material. Because of a modification in the TOX analysis the influent and effluent TOX concentrations before and after reactivation cannot be compared directly. For perspective, however, the nonpurgeable organic halogen concentrations applied to the adsorbents after reactivation ranged from 106 µg/l to 260 µg/l and the breakthrough pattern was very similar to the TOC curve.

Although both UV absorbance and fluorescence data were collected, the latter parameter is more consistent and is potentially a good operational monitor for this system. Figure 4, a plot of fractional removal of fluorescence, shows about 4 percent difference between virgin and reactivated granular carbon.

DISCUSSION OF RESULTS

The study by the Passaic Valley Water Commission at the Little Falls Filtration Plant is providing very useful information for understanding the handling and reactivating of granular carbon. The infrared furnace in the first reactivation restored the adsorptive properties to within 85 to 96 percent of virgin, depending on which parameter performance is judged on.

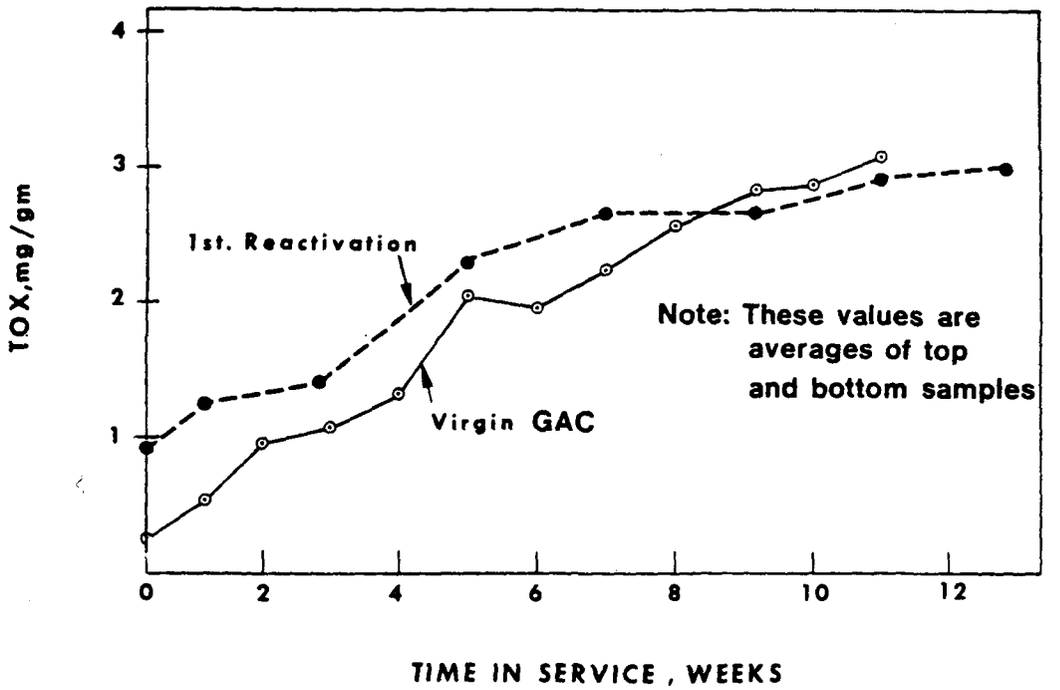

Figure 3. Effectiveness of Reactivation Measured by Total Organic Halogen (TOX)

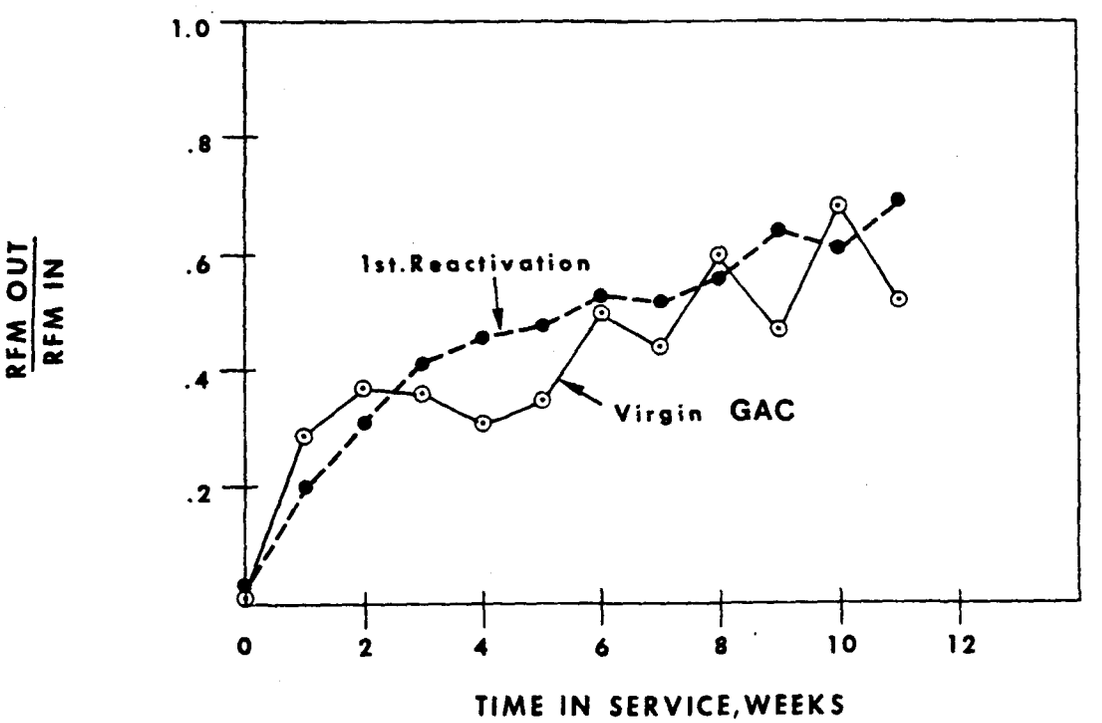

Figure 4. Effectiveness of Reactivation Measured by Fluorescence. RFM = Rapid Fluorometric Method (Ref. 8).

Most of the published reactivation data from European installations use UV absorbance as a measure of performance. As an example, Weissenhorn (11) showed that virgin activated and reactivated carbon were nearly equivalent. Interestingly, the parameter showing the least change in performance in the Little Falls study is fluorescence, so any surrogate measurement will be closely examined during the remainder of this project.

The second reactivation has been completed and currently (May, 1979) the twice reactivated carbon is being exposed to filtered water. Furnace conditions were slightly changed for the second reactivation. The temperature in the activation zone was raised to 1,700°F (926°C) and the retention time lengthened to 25 minutes. the Iodine Numbers and apparent densities improved and when compared to the first reactivation, these preliminary results indicate that the removal of other parameters, such as TOC and TOX, will also improve.

PROBLEMS

The methods used to transfer the exhausted carbon from the adsorbers to the storage hopper are somewhat archaic and cumbersome. The greatest problem has been the discharge of activated carbon from the hopper because of arching within the sloped sides of this unit causing erratic feed rates into the furnace. The storage system is being redesigned to include an internal vibrator. This should minimize, if not eliminate, the feed problem. With improvements in the feed system, the capacity of the furnace could be fully utilized; presently the throughput is only about one-half the rated capacity.

Since the infrared furnace is still in the development stage, assessing its mechanical durability at this time would be unrealistic. Corrosion has been troublesome where #304 stainless steel was in contact with either the wet activated carbon or the scrubber water. This should be solvable with a different type stainless steel (probably #316), or possibly a liner or coating as a preservative.

SUMMARY AND FUTURE WORK

The performance of the electric furnace at the Little Falls Filtration plant (Passaic Valley Water Commission) is very encouraging. Problems with activated carbon handling and corrosion have occurred, but these are minor and are being corrected. Information currently (May, 1979) available on the operation of this unit is summarized in Table 4. The preliminary data indicate that the second reactivation is improved from the first. Monitoring attrition losses in discrete processes is not possible;

hence, the losses shown are aggregate values. These losses can perhaps be reduced as more experience is gathered on operating the system. The power requirements are also reassuring. Assuming a power cost of $0.03/kW-hr the cost of running the furnace would be slightly over 2 cents/lb ($0.045/kg) of carbon reactivated. This compares very favorably with the reported power costs from installations using other type furnaces (12).

Table 4. Comparison Summary for Virgin and Reactivated Carbon

	Cycle 1 Percent Change	Cycle 2 Percent Change
Iodine Number	-12	-6
Apparent Density	+ 3	+1
Total Organic Carbon	-11	Not yet available
Flourescence	- 4	Not yet available
Total Organic Halogen	-10	Not yet available
Attrition Losses*	7%	4%
Power Required**	0.7 kW/lb	0.7 kW/lb (1.6 kW/kg)

*This is the entire system -- sum of losses from initial backwash through transporting, reactivation, and quenching.
**This is the electrical power for the furnace only.

Steps are now being taken to improve the activated carbon handling. Also an effort will be made to monitor off-gasses before and following an afterburner. This effort is part of a much broader program within the U.S. EPA to study reactivation of granular carbon used in drinking water applications. Other sites in various stages of study are shown in Table 5. Details on any of these projects are available from either the project officer or the principal investigator.

ACKNOWLEDGEMENTS

The authors thank Dr. F.K. McGinnis of Shirco, Inc. and Mr. Fred Menzenhaur and his staff at Havens and Emerson for their help. Particular thanks is expressed to Mr. Dick Roby and William Reed as well as their coworkers at the Little Falls Filtration Plant for their assistance.

TABLE 5

ONGOING REACTIVATION STUDIES

SITE	FURNACE TYPE	FURNACE SIZE, lb/hr	(kg/hr)	AMOUNT REACTIVATED lb	(kg)	FIRST REACTIVATION	EPA PROJECT OFFICER	PRINCIPAL INVESTIGAT(
Little Falls, New Jersey	Shirco Infrared	100	(45)	45,000	(20,500)	June 1978	Love, T.	Inhoffer, W
Manchester, New Hampshire	Westvaco Fluid Bed	500	(225)	320,000	(145,500)	May 1979	DeMarco, J.	Kittredge, D.
Cincinnati Ohio	Westvaco Fluid Bed	500	(225)	350,000	(159,000)	Sept. 1979	DeMarco J.	Miller, R.
Evansville, Indiana*	Shirco Infrared	100	(45)	1,500	(680)	June 1979	Lykins, B.	Mills, D.
EPA Lab Cincinnati	Several processes on a bench scale			40	(18)	July 1979	Love, T.	Love, T.

*Exhausted GAC will be reactivated using furnace located at Little Falls, New Jersey

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COST OF GRANULAR ACTIVATED CARBON ADSORPTION TREATMENT IN THE U.S.

Robert C. Gumerman, Russell L. Culp
and Robert M. Clark

The use of granular activated carbon (GAC) as a means of treating drinking water was proposed by the U.S. Environmental Protection Agency (EPA) in January 1978 (1). Since that time arguments both for and against the use of GAC as a treatment method have been widely published (2). Serious challenges and questions have been raised regarding EPA's cost estimates for GAC use.

In order to respond to some of these questions, EPA's Drinking Water Research Division initiated a carefully designed study to establish water supply unit process cost curves on a consistent and understandable basis (3). The study focused on processes for the removal from potable water of contaminants included in the National Interim Primary Drinking Water Regulations (NIPDWR) and on the development of construction, and operation and, maintenance cost curves for these processes. The final report for this project contains cost curves for 99 different unit processes. These cost curves were divided into two categories: (1) large water treatment systems applicable to flows between 1 and 200 mgd (3,785 and 757,000 m^3/d), and (2) small water treatment systems applicable to flows between 2,500 gpd and 1 mgd (9.46 and 3,785 m^3/d). A computer program for retrieving, updating, and combining the cost data was also developed as a part of this study. This paper reports on that portion of the study related to cost curves associated with GAC applications.

COST CURVES FOR ACTIVATED CARBON APPLICATIONS

Twelve of the 99 cost curves included in the final report are specifically for activated carbon applications. Eleven of the processes discussed are applicable to large systems (1 to 200 mgd); the package GAC columns pertain to small systems (2,500 gpd to 1 mgd).

Gravity Carbon Contactors - Concrete Construction

Concrete gravity carbon contactors are essentially the same as concrete gravity filtration structures. Costs were developed for carbon bed depths of 1.5 and 2.6 m (5 and 8.5 ft), which

provide empty bed contact times (EBCT) of 7.5 and 12.5 min respectively, at an application rate of 3.4 mm/s (5 gpm/sq ft). The contactors were assumed to be completely housed. The costs incorporated are for the contactor only, and exclude surface wash and backwash pumping facilities, the initial carbon charge, and carbon handling equipment outside of the pipe gallery.

Gravity Carbon Contactors - Steel Construction

Steel gravity carbon contactors are large diameter, field-erected structures. Costs were developed for 6.1- and 9.1-m (20- and 30-ft) diameter contactors which were 10.7 m (35 ft) deep and were suitable for a carbon bed depth of 6.1 m (20 ft). The contactors were sized for downflow operation and an application rate of 3.4 mm/s (5 gpm/sq ft), which provides a 30-min EBCT. Spent carbon is removed from the contactors through multiple carbon drawoff pipes in the underdrain support plate. Regenerated carbon is returned to the top of the contactors, which are completely housed. The costs exclude surface and backwash pumping facilities, the initial carbon charge, and the carbon handling equipment outside of the building.

Pressure Carbon Contactors

Pressure carbon contactors are shop-fabricated, cylindrical pressure vessels having a diameter of 3.7 m (12 ft). Costs were developed for contactors with carbon bed depths of 1.5, 3, and 6.1 m (5, 10, and 20 ft) that give EBCTs of 7.5, 15, and 30 min at application rates of 3.4 mm/s (5 gpm/sq ft). The contactors were designed for downflow operation and employed a nozzle type underdrain system for rapid spent carbon removal. The contactors were completely housed. The costs exclude backwash and surface wash pumping facilities, the initial carbon charge, and carbon handling equipment outside of the building.

Conversion of Sand Filters to Carbon Contactors

An inexpensive, but temporary method of providing carbon contact is afforded by removing the sand media and replacing it with activated carbon. Generally the underdrain and support gravel design can be retained without modification. The installation of a spent carbon collector and transport system and a return system for regenerated carbon are the only additions required. Extensive piping replacement and alteration of existing filter rate controls and instrumentation are usually necessary if the application rate is to be increased beyond the original filtration rate.

Granular Activated Carbon - Material Cost

Virgin granular activated carbon is required for both the initial carbon charge and to replace carbon lost during

regeneration. For quantities weighing less than 18,145 kg (40,000 lb), carbon is normally purchased in 0.056-m^3 (2-cu ft) bags; larger quantities are purchased in bulk.

Multiple Hearth Granular Carbon Reactivation

Multiple hearth reactivation uses a multiple hearth furnace operated under closely controlled conditions of temperature, oxygen, and moisture content. The required furnace size is a function of the required reactivation frequency, carbon dosage (which is a function of the nature of the organics adsorbed), allowable hearth loading, and anticipated downtime. The costs that were developed include the basic furnace, cooling fans, spent carbon storage and dewatering equipment, regenerated-carbon handling system, quench tank, exhaust scrubbing system, and all necessary instrumentation. The furnace was assumed to be housed. Operation and maintenance cost curves are based on continuous operation, and adjustment must be made for operation times falling below 100 percent.

Infrared Granular Carbon Reactivation

Granular carbon can be reactivated by using infrared energy to generate heat. The principal advantage of infrared reactivation is the ability of the furnace to be rapidly put into or taken out of operation without furnace damage or excessive operational cost. The carbon moves through the furnace on a conveyor belt, and reactivation time is varied by changing the conveyor speed and varying the depth of the carbon on the belt. The cost curve includes the furnace, spent carbon storage and dewatering facilities, quench tank, afterburner and scrubber, all required electrical equipment and controls, and an enclosure for all equipment. The operation and maintenance cost curves assume operation 100 percent of the time, and adjustment must be made for lesser operation times.

Fluid Bed Granular Carbon Reactivation

This type of reactivation uses hot gases both to fluidize and reactivate carbon. No inert heat source such as sand is required. Reactivation rates as high as 342 kg/hr/m^2 (70 lb/hr/sq ft) can be accomplished. The cost curve includes spent and reactivated carbon storage, carbon dewatering equipment, the fluid bed reactor, fluidizing air blower, quench tank, particulate scrubber, instrumentation, and controls. All facilities were assumed to be housed. The operation and maintenance cost curves are developed on the basis of 100 percent operation; adjustment must be made for less operational time.

Atomized Suspension Powdered Carbon Reactivation

The atomized suspension process operates by spraying a carbon slurry through a spray nozzle, where the slurry is atomized with steam, into the top zone of a three zone reactor. In the top zone of the reactor all water is evaporated, in the middle zone the organics adsorbed on the carbon are pyrolyzed to a residual char deposit, and in the third zone the residual char deposit is removed. The reactor diameter can vary from 0.3 to 0.9 m (1 to 3 ft) and the height can vary from 3 to 15.2 m (10 to 50 ft), depending upon the reactivation capacity. The cost curves developed include a spent carbon slurry storage tank, the basic reactor, a feed pump, exhaust scrubbing, reactivated carbon recovery equipment, and all required instrumentation and controls. The operation and maintenance curves are for 100 percent operation, and adjustment must be made for lesser percentages of operation.

Fluidized Bed Powdered Carbon Reactivation

Powdered carbon can be reactivated in a fluidized bed of graded silica sand that is maintained at 704°C (1,300°F). The fuel source and fluidizing air are added at the bottom of the reactor. Wet spent carbon is added from above the sand layer and reactivated carbon is separated from the fluidizing sand and withdrawn at the base of the reactor. The costs developed include the fluidized bed reactor, fluidizing air blower, carbon feed and removal equipment, and required instrumentation and controls. The operation and maintenance cost curves assume 100 percent operation, and adjustment for operating time less than 100 percent is required.

Off-Site Regional Carbon Reactivation

Small water treatment plants employing activated carbon may find reactivation at a large plant (or a regional reactivation facility) more economical than purchasing virgin carbon to replace spent carbon or providing on-site reactivation. The construction costs include only granular carbon dewatering-storage bins. The costs do not include the cost of reactivation at the regional site. The operation and maintenance curves include the cost of hauling to the regional reactivation location but do not include the cost of reactivation.

Package Granular Activated Carbon Columns

Factory-assembled package GAC carbon columns may be used in small water treatment applications. Costs were developed for pressurized, downflow steel contactors designed for manual operation. The columns are skid-mounted and both supply and backwash pumps are included, as is housing. Typical carbon bed depths are 1.5 m (5 ft); application rate is 3.4 mm/s (5 gpm/ sq ft).

DERIVATION OF COST CURVES

Relating Costs to Design Parameters

The construction cost for each unit process is presented as a function of the process design parameter which was determined to be the most useful and flexible under varying conditions such as loading rate, detention time, or other conditions that can vary because of designer's preference or regulatory agency requirements. For example, the contactor construction cost curves are presented in terms of cubic feet of contactor volume, an approach that allows various empty bed contact times to be used. Contactor operation and maintenance curves are presented in terms of square feet of surface area since operation and maintenance requirements are more appropriately related to surface area than to contactor volume. Reactivation facility cost curves are presented in terms of square feet of hearth area for the multiple hearth furnace and pounds per day of reactivation capacity for the other reactivation concepts. This allows the loading per square foot of hearth area to be varied for the multiple hearth furnace (and other furnaces) for carbon reactivation rates less than the maximum capacity for which the system is designed. This approach provides greater flexibility in the use of the cost curves than if the costs were related to water flow through the treatment plant.

Methods Used to Develop Cost Curves

The construction cost curves were developed using equipment cost data supplied by manufacturers, cost data from actual plant construction, unit takeoffs from actual and conceptual designs, and published data. The costs developed* then were checked by a second firm**, using an approach similar to what would be utilized by a general contractor in determining the construction bid. Any discrepancies that existed between the initial estimate and the second estimate were then resolved.

Construction Cost Components

The costs for eight principal construction components were developed and then aggregated to give the construction cost for each unit process. The eight components are (1) excavation and sitework, (2) manufactured equipment, (3) concrete, (4) steel, (5) labor, (6) pipe and valves, (7) electrical and instrumentation, and (8) housing. These categories also provide enough detailed information to permit accurate cost updating.

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*Culp/Wesner/Culp, Santa Ana, Calif.
**Zuheide-Herrmann, Inc., St. Louis, Mo.

The construction cost curves are not the final capital cost for the unit process. The construction cost curves do not include costs for general contractor overhead and profit, administration, engineering and legal fees, fiscal determinations, and interest during construction. These items are more directly related to the total cost of a project than to the cost of the individual unit processes. Therefore, they are more appropriately added following summation of the cost of the individual unit processes, if more than one unit process is required. Four example calculations are presented in Tables 1 to 8 to illustrate the recommended method for the addition of these costs.

Operation and Maintenance Cost Components

Operation and maintenance requirements were developed for building-related energy, process energy, maintenance material, and labor. The separate determination of building energy allows for regional variations. Energy requirements are presented in kilowatt-hours per year for electricity, standard cubic feet per year for natural gas, and gallons per year for diesel fuel. Labor is presented in hours per year, allowing local variations to be incorporated into the operation and maintenance cost calculations. Maintenance material cost is given in dollars per year, but does not include the cost of chemicals. Chemical costs are added separately as shown in Tables 1 to 8.

EXAMPLE COST CURVES

For the majority of the unit processes, three separate figures were used to present construction and operation and maintenance curves. The first graph presents the construction cost, the second graph presents energy (electrical, natural gas, and diesel fuel) and maintenance material requirements, and the third graph presents labor requirements and total operation and maintenance cost. Figures 1, 2, and 3 present the cost curves that were developed for pressure carbon contactors.

UPDATING COST CURVES

For many engineering purposes a single cost index such as the Engineering News Record (ENR) Construction Cost Index (CCI) can be used to update construction costs. When this approach provides sufficient accuracy, a single index is certainly the simplest and easiest approach. In the case of water treatment construction costs, especially those for carbon treatment, use of the CCI is not recommended because the construction components used in its development are not related to those required for water treatment plants. For example, the CCI does not include process equipment or electrical equipment for instrumentation and control. For water treatment plants, the use of several indices is recommended. For example, this could include the Bureau of

Table 1
Cost Calculation and Operation and Maintenance Requirements for a 2 mgd Pressure Granular Activated Carbon Plant

System and Design Criteria	Design Parameter	Construction Cost	Operating Parameter	Energy (kW-hr/yr)	Natural Gas (acf/yr)	Diesel Fuel (gal/yr)	Maintenance Material ($/yr)	Labor (hr/yr)
Pressure Carbon Contactors - 18 min. E.B.C.T., 5 gpm/ft^2	1670 ft^3/ contactor	$ 225,770	226 ft^2 total area	133,900	0	0	1,860	1,057
Initial Carbon Charge - 26 lb/ft^3	86,890 lb	53,720	—	0	0	0	0	0
Backwash Pumping - 12 gpm/ft^2	1356 gpm	43,810	—	0	0	0	0	0
Off-Site Regional Reactivation Transportation - 20 miles	3342 ft^3	60,730	434,450 lb/yr	0	0	1,680	170	141
Off-Site Regional Regeneration*	880 sq ft	111,350	530 sq ft	38,110	3,973,960	0	530	424
Make-up Carbon - 6%/regen., 5 regen./yr	—	0	26,067 lb/yr	0	0	0	16,840	0
Subtotal	—	495,380	—	172,010	3,973,960	1,680	19,400	1,622
Site-Work, Interface Piping, Roads @ 5%	—	24,770	—	—	—	—	—	—
Subsurface Considerations	—	0	—	—	—	—	—	—
Standby Power	—	0	—	—	—	—	—	—
Total Construction Cost		520,150						
General Contractor's Overhead and Profit	—	62,420	—	—	—	—	—	—
Subtotal	—	582,570	—	—	—	—	—	—
Engineering @ 10%	—	58,260	—	—	—	—	—	—
Subtotal	—	640,830	—	—	—	—	—	—
Land, 2 acres $2,000/acre	—	4,000	—	—	—	—	—	—
Legal, Fiscal, and Administrative	—	12,060	—	—	—	—	—	—
Interest during Construction - 8%	—	24,830	—	—	—	—	—	—
TOTAL CAPITAL COST	—	681,720	—	—	—	—	—	—

*Assumes this plant uses 5% of the regional regeneration facilities, and that the regional facilities operate at 70 percent of full capacity using multiple hearth granular carbon regeneration.

Table 2
Annual Cost for 2 mgd Pressure GAC Plant

Item:	Total Cost/year
Amortized Capital @ 8%, 20 years	$ 69,430
Labor, 1,622 hr, @ $10/hr (total labor costs including fringes and benefits)	16,220
Electricity, 172,010 kW-hr @ $0.03/kW-hr	5,160
Natural Gas, 3,973,960 scf @ $0.00175/scf	6,950
Diesel Fuel, 1,680 gal @ $0.45/gal	760
Maintenance Material	19,400
TOTAL ANNUAL COST*	$117,920

*Cents per 1,000 gal treated = $\frac{\$117,920\ (100)}{1,400\ (365)}$

= 23.1 ¢/1,000 gal

TABLE 3
Cost Calculation and Operation and Maintenance Requirements
for a 20 mgd Pressure Granular Activated Carbon Plant

System and Design Criteria	Design Parameter	Construction Cost	Operating Parameter	Energy (kW-hr/yr)	Maintenance Material ($/yr)	Labor (hr/yr)
Pressure Carbon Contactors - 18 min. E.B.C.T., 5 gpm/ft^3	2,089 ft^3/ Contactor	$ 1,961,850	1,810 ft^2 total area	618,660	8,890	2,308
Initial Carbon Charge - 26 lb/ft^3		523,550	--	0	0	0
Backwash Pumping - 12 gpm/ft^2	1,356 gpm	43,810	--	0	0	0
Infrared Carbon Reactivation	4,000 lb/day	339,460	4,000 lb/day	1,198,100	10,640	2,519
Make-up Carbon - 6%/regen., 5 regen/yr	--	0	260,690 lb/day	0	158,810	0
Subtotal	--	$ 2,868,670	--	1,816,760	178,340	4,828
Sitework, Interface Piping, Roads @ 5%	--	143,430	--	--	--	--
Subsurface Considerations	--	0	--	--	--	--
Standby Power	--	0	--	--	--	--
Total Construction Cost	--	$ 3,012,100	--	--	--	--
General Contractor's Overhead and Profit	--	301,210	--	--	--	--
Subtotal	--	$ 3,313,310	--	--	--	--
Engineering @ 10%	--	331,330	--	--	--	--
Subtotal	--	$ 3,644,640	--	--	--	--
Land, 5 acres @ $2,000/acre	--	10,000	--	--	--	--
Legal, Fiscal, and Administration	--	35,240	--	--	--	--
Interest during Construction - 8%	--	238,010	--	--	--	--
TOTAL CAPITAL COST	--	$ 3,927,890	--	--	--	--

Table 4
Annual Cost for 20 mgd Pressure GAC Plant

Item:	Total Cost/year
Amortized Capital @ 8%, 20 years	$400,060
Labor, 4,828 hr, @ $10/hr (total labor costs including fringes and benefits)	48,280
Electricity, 1,816,760 kW-hr @ $0.03/kW-hr	54,500
Maintenance Material	178,340
TOTAL ANNUAL COST*	$681,180

*Cents per 1,000 gal treated = $\frac{\$681,180\ (100)}{14,000\ (365)}$

= 13.3 ¢/1,000 gal

Table 5
Cost Calculation and Operation and Maintenance Requirements
from a 75 mgd Gravity, Steel Granular Activated Carbon Plant

System and Design Criteria	Design Parameter	Construction Cost - $	Operating Parameter	Energy (kW-hr/yr)	Natural Gas S.C.F/yr	Maintenance Material ($/yr)	Labor (hr/yr)
Gravity, Steel Contactor - 18 min. E.B.C.T., 30' dia., 5 gpm/ft^2	12,533 ft^3/ Contactor	$ 3,029,620	125,330	2,596,330	0	16,460	5,971
Initial Carbon Charge - 26 lb/ft^3	3,258,690 lb	1,907,800	—	0	0	0	0
Backwash Pumping - 12 gpm/ft^2	7,520 gpm	101,710	—	0	0	0	0
Multiple Hearth Carbon Reactivation Furnace	800 ft^2	2,151,230	800 ft^2	909,700	109,446,800	11,630	10,956
Make-up Carbon, 6% regen., 5 times/yr.	—	0	yr	0	0	588,130	0
Subtotal	—	$ 7,190,360	—	3,506,030	109,446,800	616,220	16,927
Site-work, Interface Piping, Roads @ 5%	—	359,520	—	—	—	—	—
Subsurface Considerations	—	0	—	—	—	—	—
Standby Power	—	0	—	—	—	—	—
Total Construction Cost	—	$ 7,549,880	—	—	—	—	—
General Contractor's Overhead and Profit	—	754,990	—	—	—	—	—
Subtotal	—	$ 8,304,870	—	—	—	—	—
Engineering @ 10%	—	830,490	—	—	—	—	—
Subtotal	—	$ 9,135,360	—	—	—	—	—
Land 15 acres @ $2,000/acre	—	30,000	—	—	—	—	—
Legal, Fiscal, and Administrative	—	65,100	—	—	—	—	—
Interest during Construction - 8%	—	742,550	—	—	—	—	—
TOTAL CAPITAL COST	—	$ 9,973,010	—	—	—	—	—

Table 6
Annual Cost for 75 mgd Gravity, Steel GAC Plant

Item:	Total Cost/year
Amortized Capital @ 8%, 20 years	$1,015,750
Labor, 16,927 hr, @ $10/hr (total labor costs including fringes and benefits)	169,270
Electricity, 3,506,030 kW-hr @ $0.03/kW-hr	105,180
Natural Gas, 109,446,800 scf @ $0.00175/scf	191,530
Maintenance Material	616,220
TOTAL ANNUAL COST*	$2,097,950

*Cents per 1,000 gal treated = $\frac{\$2,097,950\ (100)}{52,500\ (365)}$

= 10.9 ¢/1,000 gal

Table 7

Cost Calculation and Operation and Maintenance Requirements for a 110 mgd Gravity, Steel Granular Activated Carbon Plant

System and Design Criteria	Design Parameter	Construction Cost - $	Operating Parameter	Energy (kW-hr/yr)	Natural Gas S.C.F/yr	Maintenance Material ($/yr)	Labor (hr/yr)
Gravity, Steel Contactor - 18 min. E.B.C.T., 30' dia., 5 gpm/ft^2	11,489 ft^3/ Contactor	$ 4,503,440	183,824 ft^3	3,720,810	0	21,590	8,362
Initial Carbon Charge - 26 lb/ft^3	4,779,400 lb	2,746,810	—	0	0	0	0
Backwash Pumping - 12 gpm/ft^2	7,520 gpm	101,710	—	0	0	0	0
Multiple Hearth Carbon Reactivation Furnace	1,173 ft^2	2,467,640	1,173 ft^2	1,111,310	158,149,050	12,740	13,824
Make-up Carbon, 6% regen., 5 times/yr.	—	0	1,433,820 lb/yr	0	0	857,740	0
Subtotal	—	$ 9,819,600	—	4,832,120	158,149,050	892,070	22,186
Site-work, Interface Piping, Roads @ 5%	—	490,980	—	—	—	—	—
Subsurface Considerations	—	0	—	—	—	—	—
Standby Power	—	0	—	—	—	—	—
Total Construction Cost	—	$10,310,580	—	—	—	—	—
General Contractor's Overhead and Profit	—	927,950	—	—	—	—	—
Subtotal	—	$11,238,530	—	—	—	—	—
Engineering @ 10%	—	1,123,850	—	—	—	—	—
Subtotal	—	$12,362,380	—	—	—	—	—
Land 20 acres @ $2,000/acre	—	40,000	—	—	—	—	—
Legal, Fiscal, and Administrative	—	79,070	—	—	—	—	—
Interest during Construction - 8%	—	1,108,240	—	—	—	—	—
TOTAL CAPITAL COST	—	$13,589,690	—	—	—	—	—

Table 8
Annual Cost for 110 mgd Gravity, Steel GAC Plant

Item:	Total Cost/year
Amortized Capital @ 8%, 20 years	$1,384,110
Labor, 22,186 hr, @ $10/hr (total labor costs including fringes and benefits)	221,860
Electricity, 4,832,120 kW-hr @ $0.03/kW-hr	144,960
Natural Gas, 158,149,050 scf @ $0.00175/scf	276,760
Maintenance Material	892,070
TOTAL ANNUAL COST*	$2,919,760

*Cents per 1,000 gal treated = $\frac{\$2,919,760\ (100)}{77,000\ (365)}$

= 10.4 ¢/1,000 gal

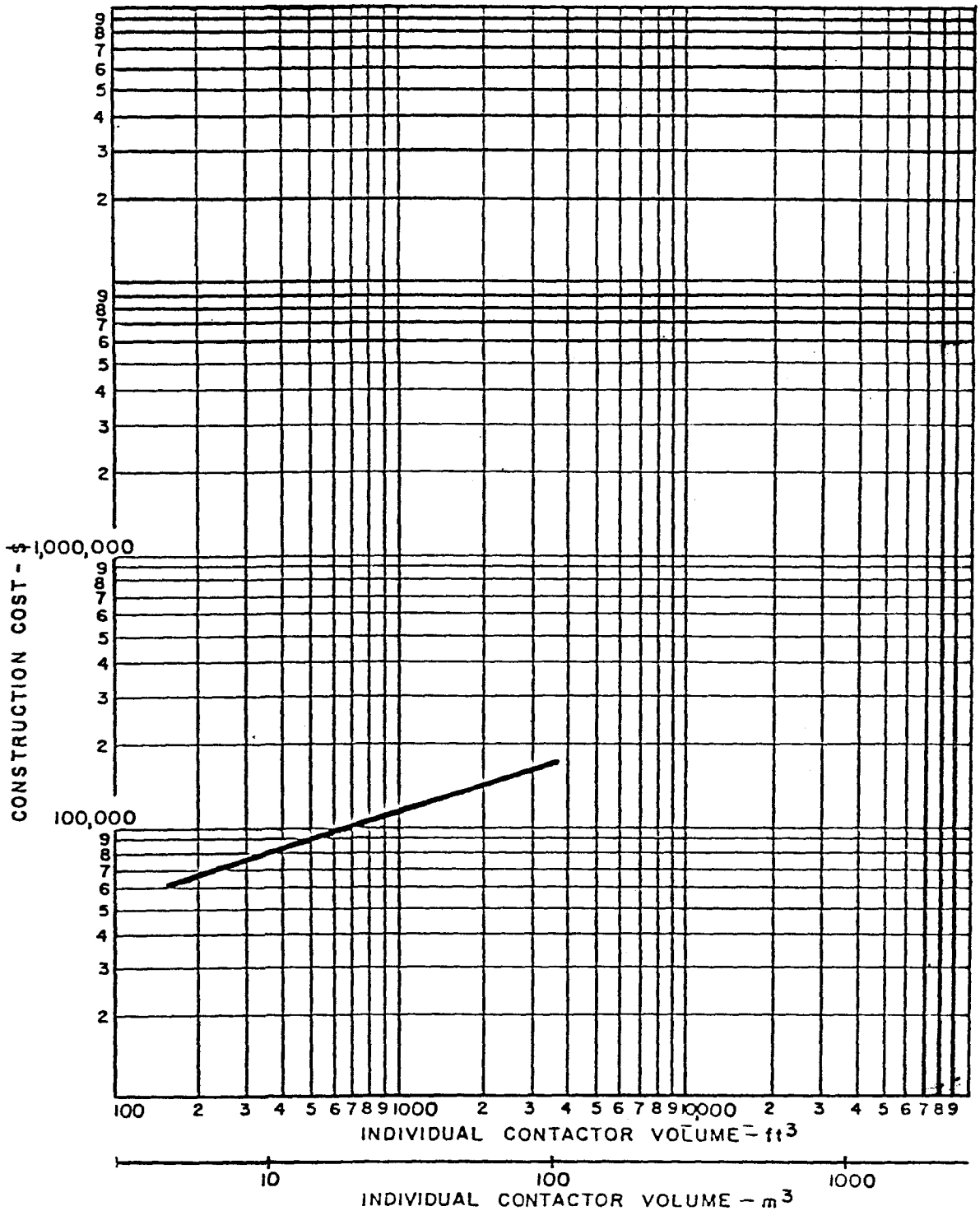

Figure 1. Construction Cost for Pressure Carbon Contactors

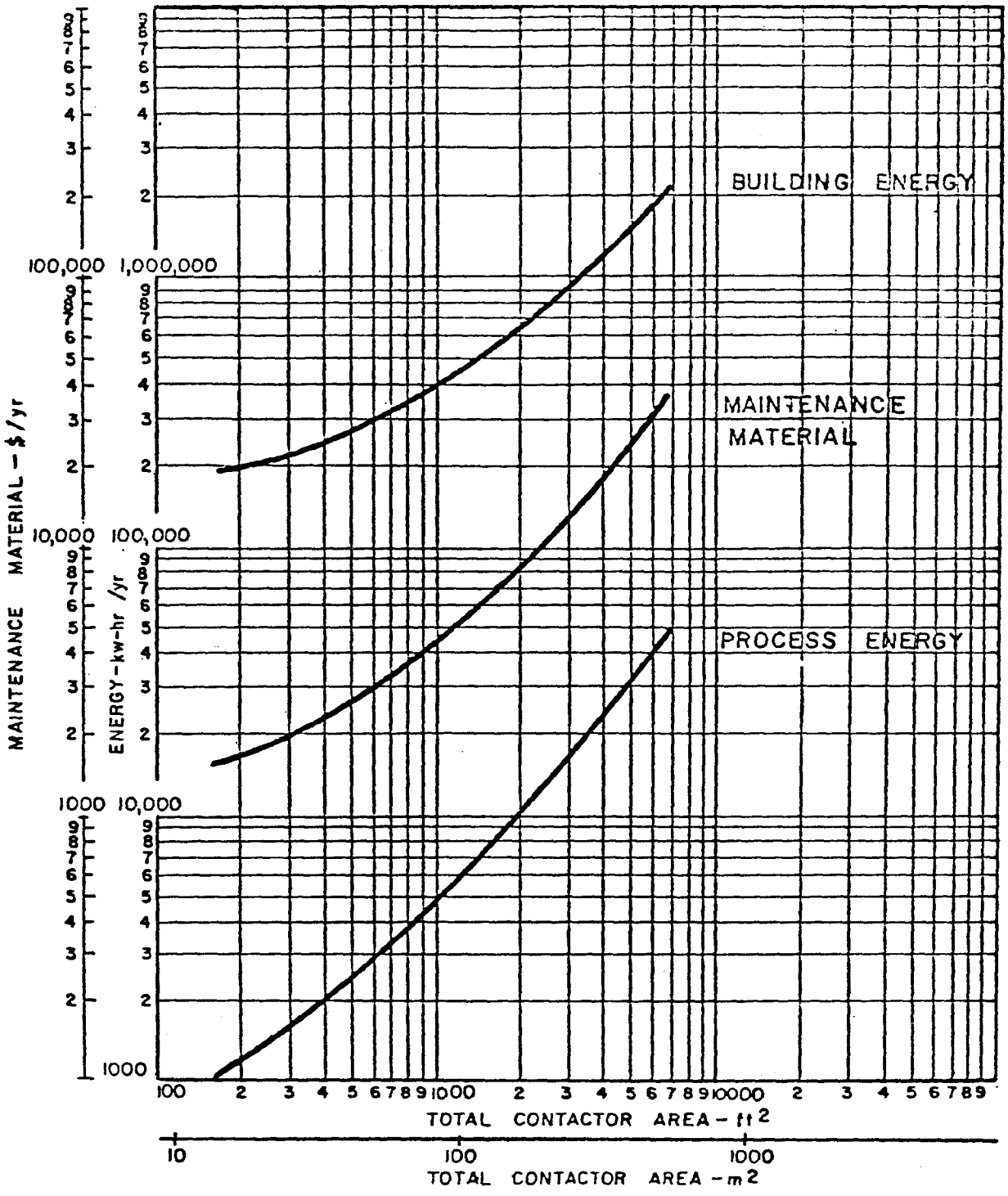

Figure 2. Typical Activated Carbon Column Installation

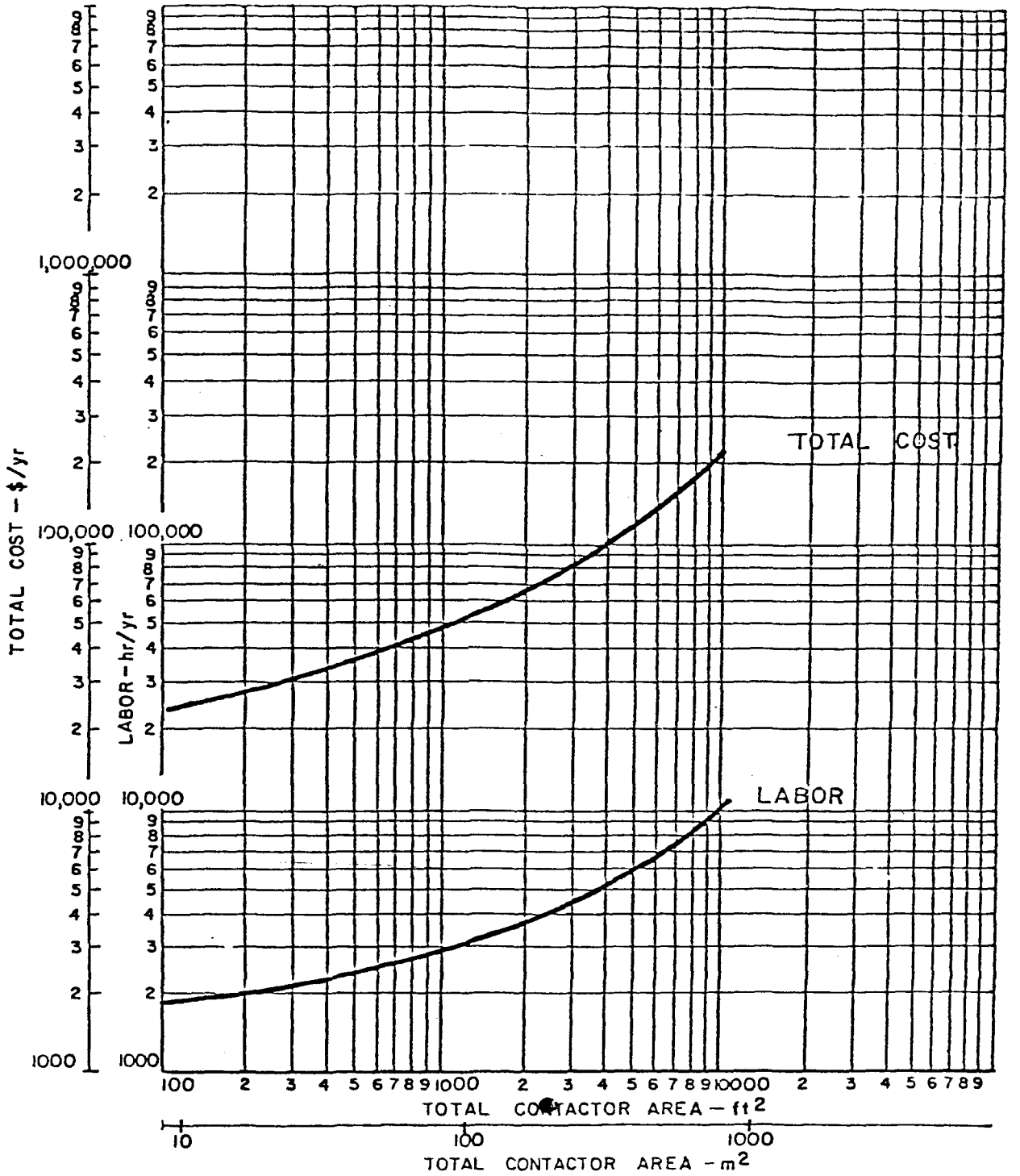

Figure 3. Operation and Maintenance Requirements for Pressure Carbon Contactors - Labor and Total Cost

Labor Statistics (BLS) (4) indices in conjunction with the ENR Building Cost Index and Skilled Labor Wage Index.

Table 9 shows the indices recommended for application to each of the eight categories used to derive construction costs. This approach allows updating to be done proportionally to changes in the cost of each component. The eight construction cost components represent the major items of material and labor affecting the cost of water treatment plant construction.

The principal disadvantages of this approach are the lack of geographical specificity of the BLS indices and the additional effort involved in the use of seven indices rather than a single index. The approach that was used to develop the cost data provides the user of the data with a choice of updating procedures to be used. The individual cost indices can be applied to the components and component costs then added to obtain the unit process cost. As an alternative, the total unit process cost can be updated in a single step by applying the ENR Construction Cost Index to the sum cost of the eight components.

UPDATING OPERATION AND MAINTENANCE COSTS

Operation and maintenace (O&M) costs are updated somewhat differently. Energy requirements are presented in terms of kilowatt-hours per year for electricity, standard cubic feet per year for natural gas, and gallons per year for diesel fuel; labor is presented in hours per year. Therefore, updating of energy and labor costs is accomplished simply by using prevailing unit costs for energy and labor. Maintenance material costs, which do not include chemicals, are best updated using the new Producer Price Index for Finished Goods. The maintenance material costs presented in the final report are based on October 1978, Producer Price Index for Finished Goods of 199.7 (4).

THE COMPUTER PROGRAM

A computer program was developed as a portion of this project. This program and data file that contain the construction costs as well as operation and maintenance requirements are presented in the final report. The purpose of the computer program is to allow costs to be retrieved, updated, and analyzed.

The program allows a number of other factors to be varied in addition to the indices used for updating. Other factors that can be varied to examine their impact on project costs are: (1) the operating parameter for the process; (2) sitework and interface piping costs; (3) special subsurface requirements; (4) standby power requirements; (5) general contractors overhead and profit percentage; (6) engineering costs; (7) land cost; (8) legal, fiscal, and administrative costs; and (9) interest during construction and capital cost amortization.

Table 9
Recommended Indices for Derivation of Construction Costs

Construction Cost Components	Indices
Excavation and sitework	ENR wage index (skilled labor)
Manufactured equipment	BLS general purpose machinery and equipment code 114
Concrete	BLS concrete ingredients code 132
Steel	BLS steel mill products code 1013
Labor	ENR wage index (skilled labor)
Pipes and valves	BLS valves and fittings code 114901
Electrical and instrumentation	BLS electrical machinery and equipment code 117
Housing	ENR building cost index

EXAMPLE CALCULATIONS FOR GRANULAR ACTIVATED CARBON PLANTS

To demonstrate the application of the construction and operation and maintenance cost curves that were developed for granular activated carbon and other processes, examples were developed for four different capacity GAC postadsorber systems. These examples use varying concepts for the carbon contactor design and for the method used to reactivate spent carbon. The four example GAC plants and their capacities are: (1) 2-mgd plant - pressure carbon contactors and off-site carbon reactivation at a regional facility; (2) 20-mgd plant - pressure carbon contactors and on-site infrared carbon reactivation; (3) 75-mgd plant - gravity, steel carbon contactors and on-site multiple hearth furnace carbon reactivation; and (4) 110-mgd plant - gravity, steel carbon contactors and on-site multiple hearth furnace carbon reactivation.

The design criteria, capital cost calculation, and operation and maintenance requirements for these examples are presented in Tables 1, 3, 5, and 7, respectively. The annual cost calculations for the examples are presented in Tables 2, 4, 6, and 8, respectively. Construction costs are in October 1978 dollars. Unit costs used to calculate operation and maintenance costs were $0.03/kWh (electricity), $10.00/hr (labor), $0.00175/scf (natural gas), and $0.45/gal (diesel fuel).

The examples are only for hypothetical conditions. The design criteria and costs presented are general, and are not necessarily applicable to all plants with the same capacity and operating conditions.

As expected, economy of scale plays a major factor in the calculation of the unit cost of water produced. As shown in Tables 2, 4, 6, and 8, the unit cost of water produced by the example plants ranged from $0.23/1,000 gal treated for the 2-mgd plant to $0.10/1,000 gal for the 110-mgd plant.

FACTORS INFLUENCING CAPITAL AND OPERATION AND MAINTENANCE COSTS

In addition to deriving detailed capital and operation and maintenance costs, the data can be used to study the sensitivity of unit process costs to changes in specific design parameters. For example, if it is desired to perform a sensitivity analysis for a specific set of design variables, unit process costs can be set at predetermined levels and then varied individually over an appropriate range. The following analysis for postfilter adsorption systems illustrates this technique.

Assume a set of design variables for a postfilter adsorption system (contactor plus multiple hearth reactivation furnace) as given in Tables 10 and 11. Table 10 contains the levels assumed

Table 10
Design Parameters for Post-filter Adsorption

Design Parameter	Level
Activated carbon cost	$ 0.60/lb
Activated carbon loss per reactivation cycle	6%
Fuel cost	$ 1.75/mil Btu
Electric power cost	$ 0.03/kW hr
Construction cost index	265.4
Producer price index	199.7
Direct hourly wage index	$ 10/hr
Amortization rate	8%
Amortization period	20 years
Loss in adsorptive capacity	0%
Design capacity	70%
Empty bed contact time	18 min
Reactivation frequency	Every 2.4 months

Table 11
Assumptions for Separate Post-filter Adsorption

Item	Design Capacity (mgd)				
	1	5	10	100	150
Number of contactors	3	6	12	40	60
Diameter of contactors (ft)	8	12	12	20	20
Depth of contactors (ft)	13	13	13	14	14
Volume of GAC per contactor (ft^3)	653	1,469	1,469	4,396	4,396
Minimum empty bed contact time (min)	18	18	18	18	18

as input variables and Table 11 contains assumed design configurations for various sized systems. Table 12 contains the amortized capital and operating and maintenance costs in ¢/1,000 gal resulting from these assumptions.

An important variable related to both cost and quality of finished drinking water is the period between carbon reactivations. Figure 4 depicts the cost in ¢/1,000 gal versus frequency of reactivation. The total production costs rise exponentially as the period between reactivations decreases. It is obvious from this analysis that systems requiring short periods between reactivations to maintain water quality will face extremely high costs. Such a situation might force consideration of other options such as pretreatment to reduce total costs.

SUMMARY AND CONCLUSIONS

Concern has been expressed among utility managers, designers, and regulators regarding the use of GAC as a drinking water unit process. Many of these concerns are related to the cost of GAC operations. This project was initiated to study and develop cost curves for GAC-related processes and also for other unit processes. A portion of the results are reported in this paper.

The cost curves resulting from this study have been developed so that they can be easily used. Costs have been related to specific design parameters such as volume of process, square feet of surface area, or feed rate. The cost curves were formulated to allow for updating and adaptation to regions of the U.S. via the use of indices. Special curves were prepared to estimate costs that must be added to the construction cost to derive the capital cost. A computer program has been developed to facilitate ease of computation and updating of the cost curves. These curves can also provide insight into the influence of changes in design configurations upon costs, and they allow for comparisons between processes by sensitivity analysis.

ACKNOWLEDGEMENT

This study was sponsored by the Drinking Water Research Division of EPA under Contract No. 68-03-2516.

Table 12
Amortized Capital and Operating and Maintenance
Cost for Post-filter Adsorption
(cents/1,000 gallons)

Item	Design Capacity (mgd)				
	1	5	10	100	150
Amortized capital cost:					
Filter adsorber	29.4	12.7	9.8	4.9	4.6
Operating and Maintenance Cost:					
Filter adsorber	22.1	12.6	10.8	7.4	7.1
Total Cost:					
Filter adsorber	51.5	25.3	20.6	12.3	11.7

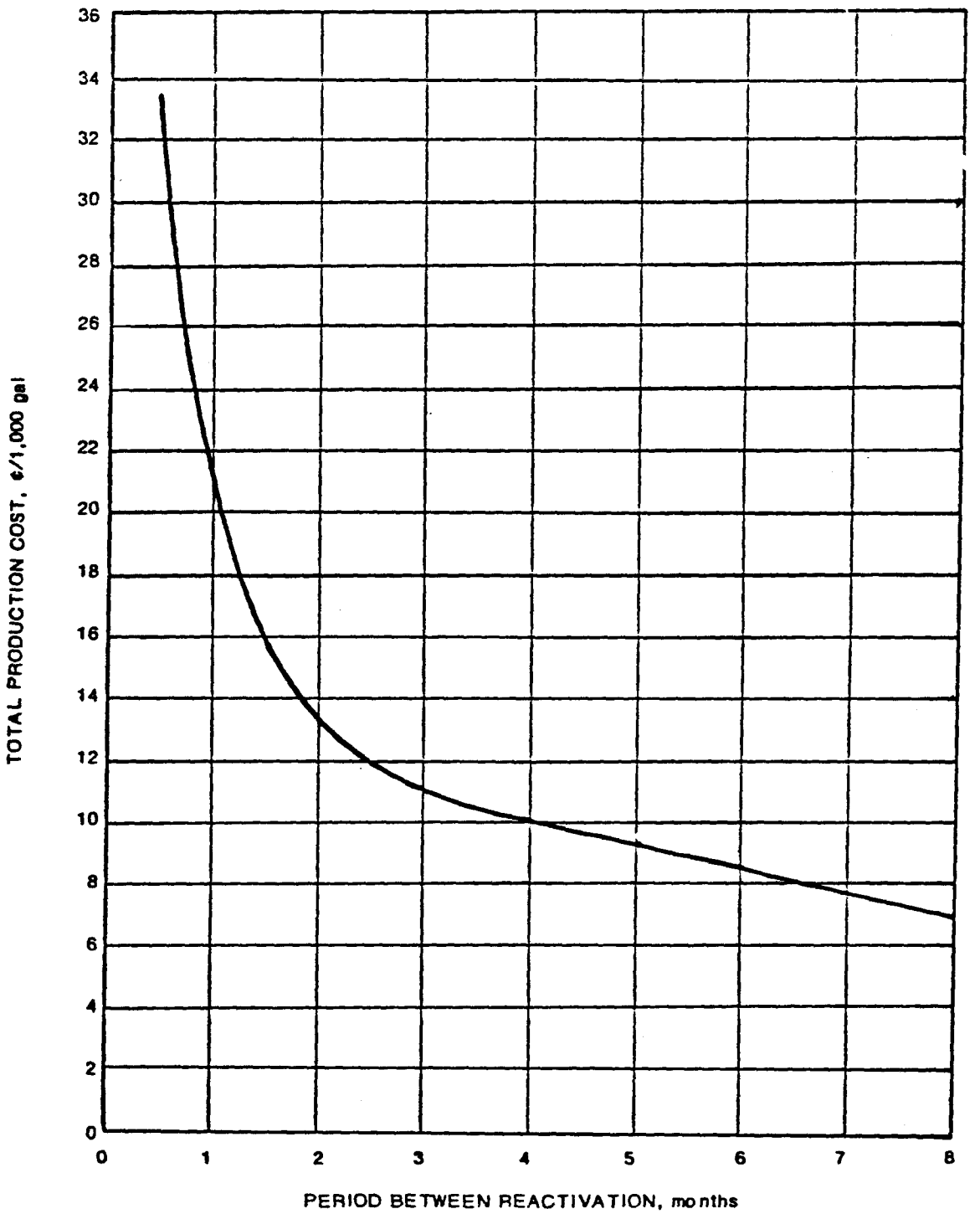

Figure 4. Production Cost for Post-filter Adsorbers versus Period Between Reactivation (100 mgd design capacity)

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INFLUENCE OF OPERATING VARIABLES ON THE COST OF GRANULAR ACTIVATED CARBON TREATMENT

by
Robert M. Clark and Paul Dorsey

On January 9, 1978, the Environmental Protection Agency (EPA) proposed a regulation designed to protect the public from organic chemical contaminants in drinking water (1). The proposed regulation consists of two parts: Part A, a maximum contaminant level (MCL) of 0.10 mg/l (100 parts per billion) for total trihalomethanes (TTHM) including chloroform, and Part B, a treatment technique requiring the use of granular activated carbon (GAC) to keep synthetic organic chemicals associated with industrial pollution and urban and agricultural runoff from contaminating drinking water supplies.

Much concern over these regulations has been expressed by the potentially affected water supply utilities. The general focus has been on the costs and benefits associated with the utilization of GAC as a water treatment process (2). To clarify GAC economics, a study was undertaken to obtain the best possible information regarding the construction and operation of GAC systems (3). Data from this study has been utilized in this paper to examine the influence of changes in the level of operating variables on the cost of GAC treatment.

GAC USE IN WATER TREATMENT

Treating water with granular activated carbon involves two major and separate process operations: filtration and reactivation (4). The water comes in contact with the activated carbon by passing through a structure filled with activated carbon granules. Impurities are removed from the water by adsorption when sufficient time is provided for this process. The structure can be either a water treatment filter shell in which the filter media has been replaced with GAC, or an independent activated carbon adsorption system. A separate activated carbon adsorption system usually consists of a number of columns or basins used as contactors and connected to a reactivation system. When the activated carbon's adsorptive capacity is exhausted, it is taken out of service and either replaced with new activated carbon or reactivated by combustion

of the organic adsorbate. Activated carbon is routinely added to the system to replace that lost during hydraulic transport and reactivation. These losses include those due to physical deterioration and burning during the reactivation process.

This economic analysis will include both the use of GAC as a replacement for existing filtration media (sand replacement) and as a separate adsorption system (post-filter adsorption). In the first part of this analysis, on-site multiple hearth reactivation will be assumed. The economics of using truck transport combined with regional or centralized reactivation furnaces will also be considered. Standard levels of key design parameters will be set at predetermined levels and then one variable at a time will be changed to determine its effect on system cost.

The need to consider the cost of separate GAC contactors is eliminated if GAC is assumed to replace sand in existing filters. For the purposes of the sand replacement analysis, a water treatment plant is assumed to consist of an integral number of 1-mgd (4000 m^3/d) filters with an effective volume of 18.5' (5.6 m) X 18.5' (5.6 m) X 2.5' (0.8 m) or 856 ft^3 (24.4 m^3). Design parameters assumed for the sand replacement systems are shown in Table 1 and design assumptions for post-filter adsorber systems are shown in Tables 1 and 2.

For sand replacement, a GAC loss of 10 percent per reactivation cycle is assumed, but a GAC loss of only 6 percent per cycle is assumed for post-filter adsorbers. These two assumptions are intended to reflect differences in the operation of the two systems. Sand replacement systems are labor intensive and increase the possibility of GAC loss because the activated carbon is changed manually. In post-filtration systems, the activated carbon is assumed to be changed hydraulically, leading to fewer possibilities for handling losses. Table 3 shows the unit costs for both types of systems for 1, 5, 10, 100 and 150 mgd plants (4,000, 20,000, 40,000, 400,000 and 600,000 m^3/d) at 70 percent capacity.

The costs shown in Table 3 can be further divided into reactivation costs for sand replacement systems and into reactivation and contactor costs for the post-filter adsorbers. Table 4 contains amortized capital and operations and maintenance costs for sand replacement and post-filter adsorption systems. As can be seen, a large portion of the capital cost for both processes is associated with reactivation. Post-filter adsorption is more capital intensive in general than is the sand replacement mode.

Table 1

Design and Cost Parameters for Granular Activated Carbon

Design Parameter	Level
Sand replacement:	
Activated carbon cost	$ 0.60/lb ($1.32/kg)
Activated carbon loss per reactivation cycle	10%
Fuel cost	$ 1.75/million BTU ($1.66/kJ)
Electric Power Cost	$ 0.03/kw hr
Construction cost index	265.4
Producers price index	199.7
Direct hourly wage rate	$10/hr
Amortization rate	8%
Amortization period	20 yrs
Volume per filter	856 ft^3 (24 m^3)
Loss in adsorptive capacity	0%
Design capacity	70%
Empty bed contact time	9 min
Reactivation frequency	Every 1.2 months
Post-filter adsorption:	
Activated carbon cost	$ 0.60/lb ($1.32/kg)
Activated carbon loss per reactivation cycle	6%
Fuel cost	$ 1.75/million BTU ($1.66/kJ)
Electric Power Cost	$ 0.03/kw hr
Construction cost index	265.4
Producers price index	199.7
Direct hourly wage rate	$10/hr
Amortization rate	8%
Amortization period	20 years
Loss in adsorptive capacity	0%
Design capacity	70%
Empty bed contact time	18 min
Reactivation frequency	Every 2.4 months

Table 2

Assumptions for Separate Post-Filtration Systems

Item	Design capacity (mgd) (m^3/day)				
	1 (4,000)	5 (20,000)	10 (40,000)	10 (400,000)	150 (600,000)
Number of contactors	3	6	12	40	60
Diameter of contactors (ft)	8	12	12	20	20
(m)	(2.4)	(3.7)	(3.7)	(6.1)	(6.1)
Depth of contactors (ft)	13	13	13	14	14
(m)	(4.0)	(4.0)	(4.0)	(4.3)	(4.3)
Volume of GAC per contactor, (ft^3)	653.1	1469.5	1469.5	4396.0	4396.0
(m^3)	(18.5)	(41.6)	(41.6)	(124.4)	(124.4)
Minimum empty bed contact time (min)	18	18	18	18	18

Table 3.

AMORTIZED CAPITAL AND OPERATING AND MAINTENANCE COST FOR GAC SYSTEMS

Cost (¢/1,000 gal)*

Item	Design Capacity (mgd) (m^3/day)				
	1 (4,000)	5 (20,000)	10 (40,000)	100 (400,000)	150 (600,000)
Amoritized Capital cost:					
Sand replacement	24.8	9.0	6.2	2.0	1.7
Filter adsorber	29.4	12.7	9.8	4.9	4.6
Operating & Maint. Cost:					
Sand replacement	19.5	13.0	11.7	8.7	8.4
Filter adsorber	22.1	12.6	10.8	7.4	7.1
Total Cost:					
Sand replacement	44.3	22.0	17.9	10.7	10.1
Filter adsorber	51.5	25.3	20.6	12.3	11.7

*To convert from ¢/1000 gal to ¢/m^3 multiply by 0.26

Table 4

Amortized Capital and O&M Costs for GAC Systems (¢/1,000 gal)*

		Plant Capaciy (mgd) (m^3/day)									
		1 (4,000)		5 (20,000)		10 (40,000)		100 (400,000)		150 (600,000)	
		Capital	O&M	Captial	O&M	Capital	O&M	Capital	O&M	Capital	O&M
Sand Replacement	Reactivation	24.0	27.6	8.3	13.0	5.4	11.7	1.4	8.7	1.1	8.4
	Activated carbon fill	0.8	0.0	0.7	0.0	0.7	0.0	0.6	0.0	0.6	0.0
Filter-Adsorbers	Reactivation	24.0	17.1	8.4	10.0	5.5	9.3	1.4	6.6	1.1	6.3
	Contactor	3.7	5.1	2.9	2.9	2.9	1.5	2.4	0.8	2.4	0.8
	Activated carbon fill	1.8	0.0	1.5	0.0	1.4	0.0	1.2	0.0	1.2	0.0

*To convert from ¢/1,000 gal to ¢/m^3 multiply by 0.26

SENSITIVITY ANALYSIS

In this section, the effect of changing variable levels will be considered. Standard values shown in Table 1 and the resultant unit costs shown in Tables 3 and 4 will be assumed. The effect of changing the design parameters around the standard values will be examined for GAC sand replacement and post-filter adsorbers separately (5). A comparison will be made between 100 mgd (400,000 m^3/day) sand replacement and filter-adsorption systems. Mathematical equations describing these systems will be presented.

Figure 1 shows the cost of both sand replacement and post-filter adsorption systems versus plant capacity,* based on the assumptions in Tables 1 and 2. Figures 2 and 3 show the O&M and amortized capital costs for both system types respectively. Significant economies of scale exist with respect to plant capacity. Similar relationships hold with respect to loading rate as well. Unit costs will rise dramatically for a plant of given capacity as loading rate decreases. Figure 4 shows the effect of reactivation frequencies on a total production cost for both post-filter adsorption and sand replacement systems. As can be seen, cost rises dramatically with increased reactivation.

O&M Cost Effects

Some operating variables influence only operating and maintenance cost, some only amortized capital cost, and some variables affect both O&M and capital cost. The first set of variables to be examined are those that influence O&M cost only. These variables are: hourly wage rate in $/hr; activated carbon loss per reactivation cycle in percent; fuel cost in $/therm; producers price index; and electrical power cost in $/kWh. This analysis is performed for 1, 5, 10, 100, and 150 mgd (4,000, 20,000, 40,000, 400,000 and 600,000 m^3) systems operating at 70 percent of capacity.

Figure 5 shows that changes in hourly wage rate have a greater impact on O&M cost in small plants than in larger plants. For example, it can be seen that as the hourly wage rate increases from $6/hr to $10/hr, the O&M cost for a 1 mgd

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*Note: The proposed regulation (Part B) was to apply to utilities serving 75,000 people or more [approximately 10 mgd (40,000 m^3/d)] (1).

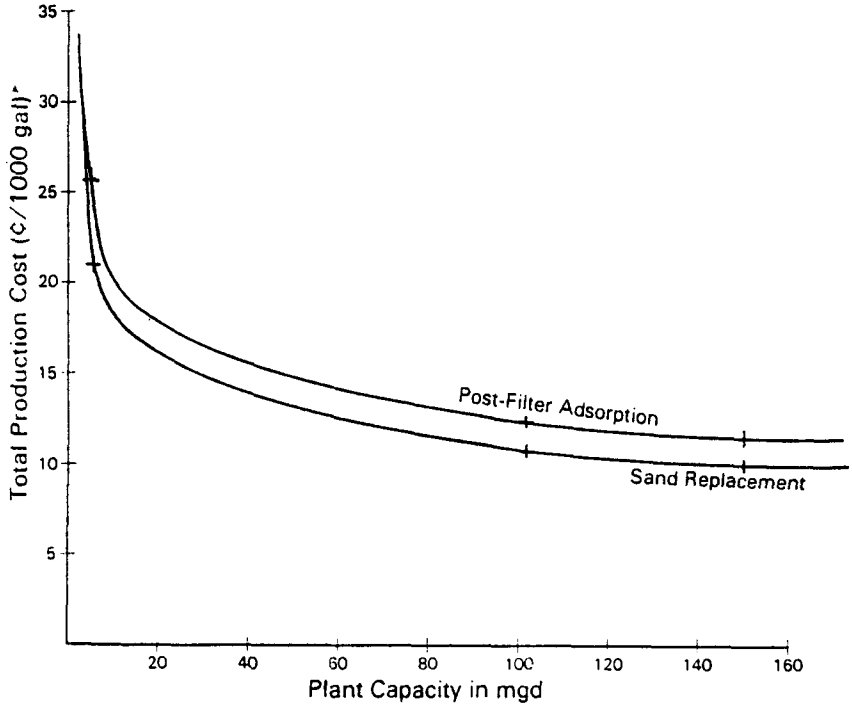

Figure 1. Total Production Cost Versus Plant Capacity for Post-Filter Adsorption and Sand Replacement Systems

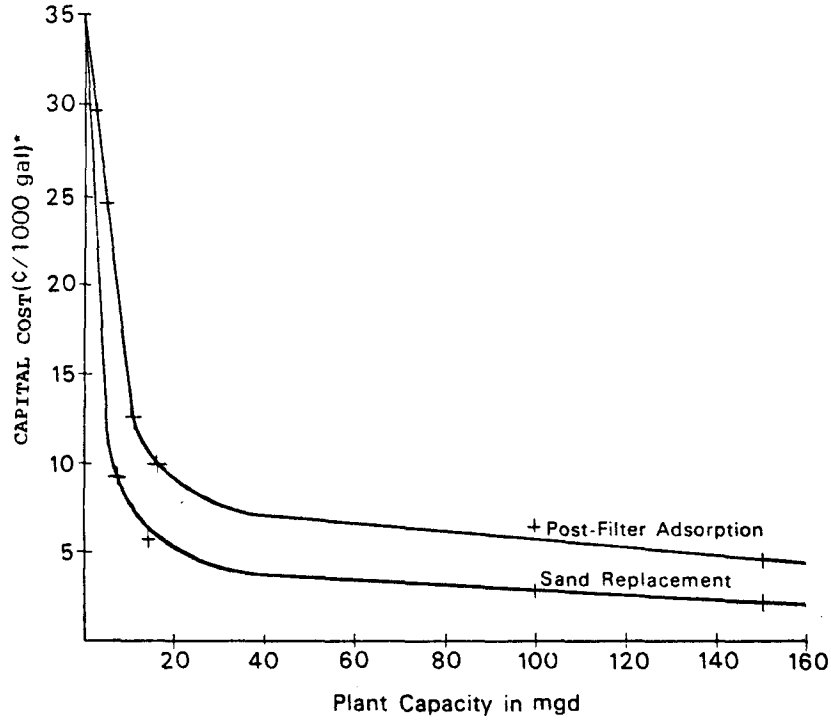

Figure 2. Capital Cost Versus Plant Capacity for Post-Filter Adsorber and Sand Replacement Systems

*To convert from ¢/1,000 gal to ¢/m^3 multiply by 0.26

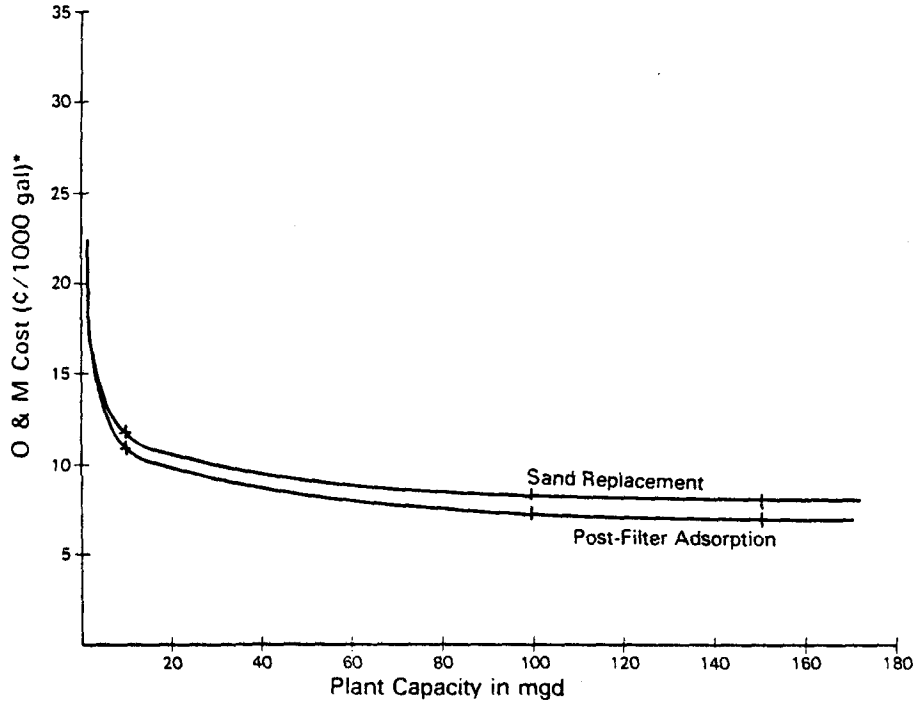

Figure 3. O & M Cost Versus Plant Capacity for Post-Filter and Sand Replacement Systems

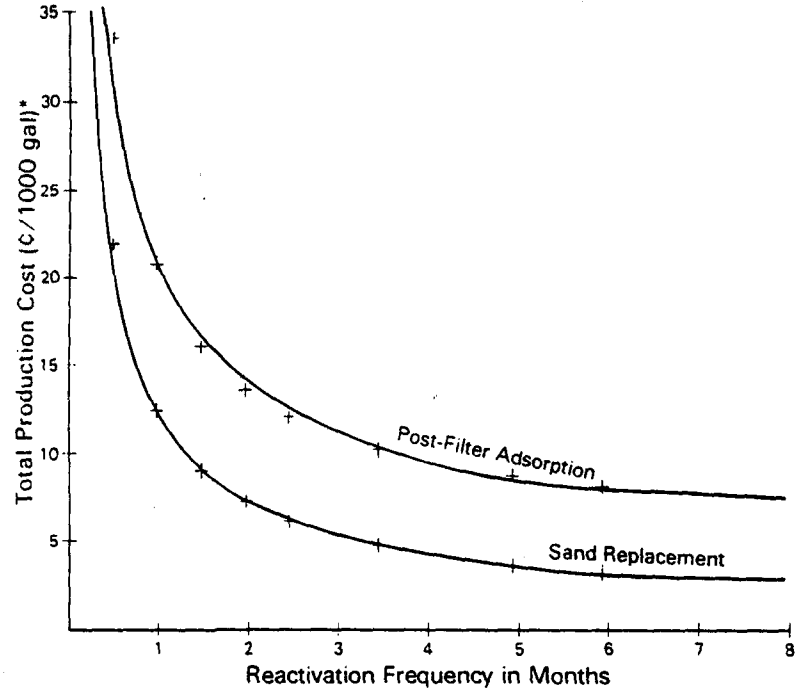

Figure 4. Total Production Cost Versus Reactivation Frequency in Months for Post-Filter Adsorption and Sand Replacement Systems (100 mgd)

*To convert from ¢/1,000 gal to ¢/m^3 multiply by 0.26

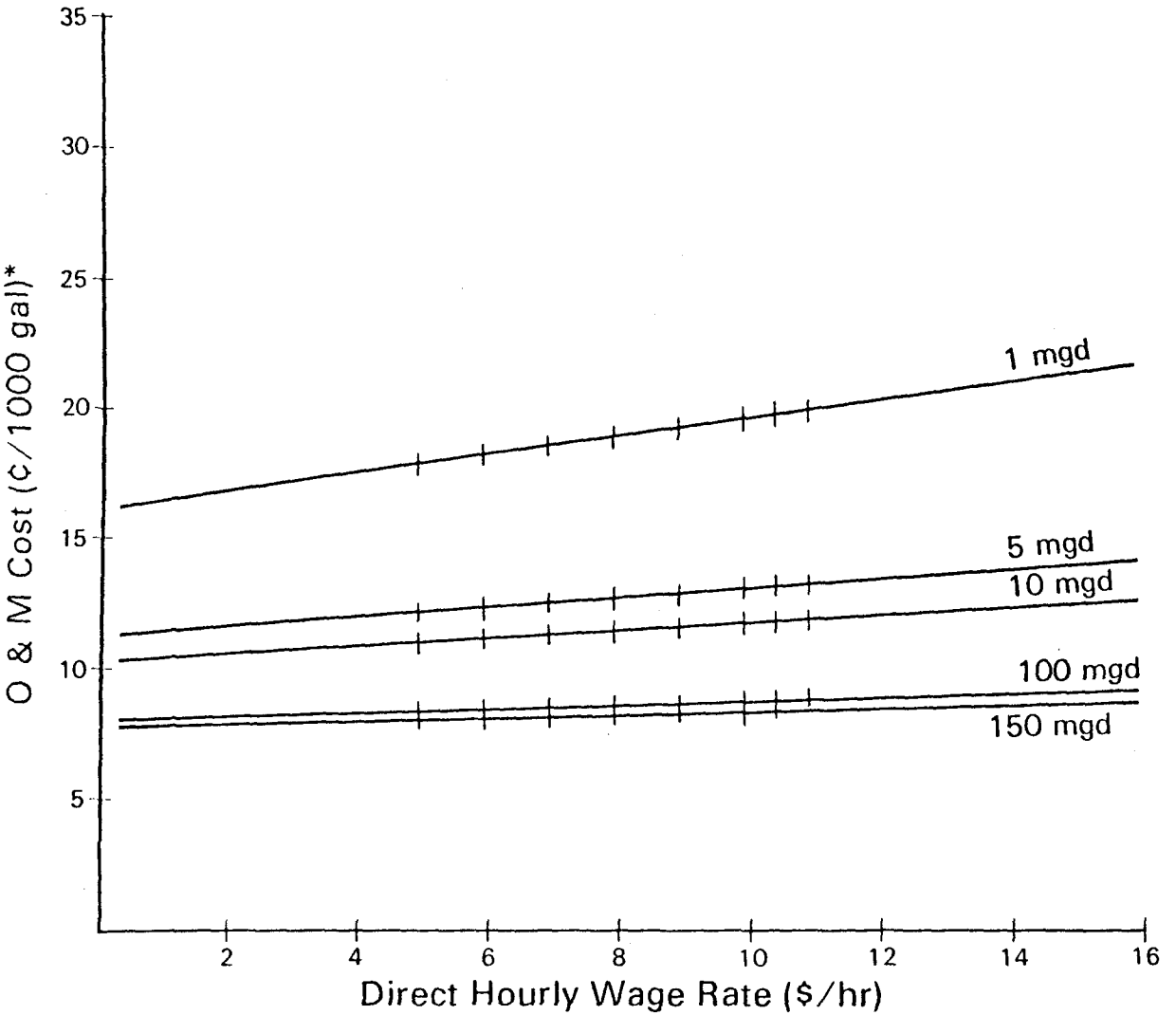

Figure 5. O & M Cost Versus Wage Rate for 1,5,10,100, and 150 mgd Sand Replacement Systems

*(To Convert from ¢/1000 gal to ¢/m^3 Multiply by 0.26)

plant (4,000 m^3) increases from slightly over 17¢/1,000 gal (4.4 ¢/m^3) to slightly less than 19.5¢/1,000 gal (5.1 ¢/m^3). The same wage rate changes in a 10 mgd plant (40,000 m^3) increases the O&M cost from approximately 11¢/ 1,000 gal (2.9 ¢/m^3) to 11.6¢/1,000 gal (3.0 ¢/m^3). Figure 6 shows the changes in O&M cost resulting from increases in activated carbon loss per reactivation cycle. Figures 7 through 9 show changes in O&M resulting from changes and wage rates, fuel cost, wholesale price index, and electrical power cost.

Capital Cost Effect

The group of variables that influence amortized capital cost are as follows: construction cost index; amortization interest rate; amortization period in years. Figure 10 illustrates the impact of varying construction cost index on amortized capital cost in ¢/1,000 gal. Figure 11 shows the effect of changing interest rates on amortized capital cost. Figure 12 shows the effect of changing amortization period. As can be seen, the impact of changing these parameters is also greater for small than for large plants.

O&M and Capital Cost Effect

Several of the standard design parameters affect both amortized capital and O&M cost. These parameters are activated carbon cost and reactivation frequency. Figures 13 and 14 show the effect of activated carbon cost variations on capital and O&M cost and Figures 15 and 16 show the effect of changing reactivation frequency.

Key Variables

Our previous analyses show that the cost of GAC systems are more sensitive to some variables than to others. Most variables have a greater impact on smaller than on large systems. The only exception is the impact of reactivation frequency on capital cost.

O&M Effects--

The variables having the most effect on O&M costs are system size, reactivation frequency, activated carbon loss, and activated carbon cost. Small changes in these variables may have large effects on system cost. Fuel cost and wage rate have a smaller effect on system cost. System cost is relatively insensitive to power cost and producers price index. Power cost has a greater impact on smaller systems than do some of the other variables.

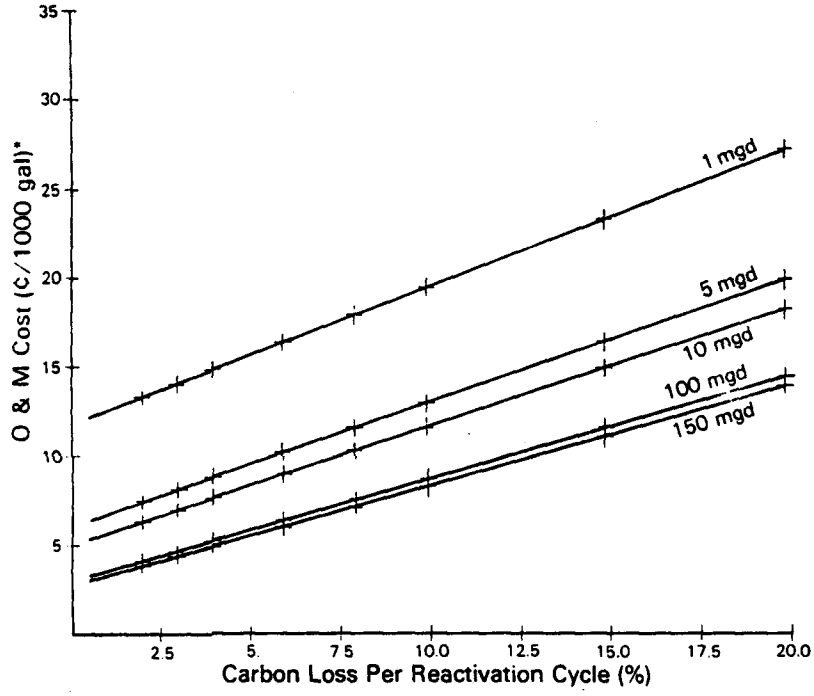

Figure 6. O & M Cost Versus Carbon Loss Per Reactivation Cycle for 1, 5, 10, 100, and 150 mgd Sand Replacement

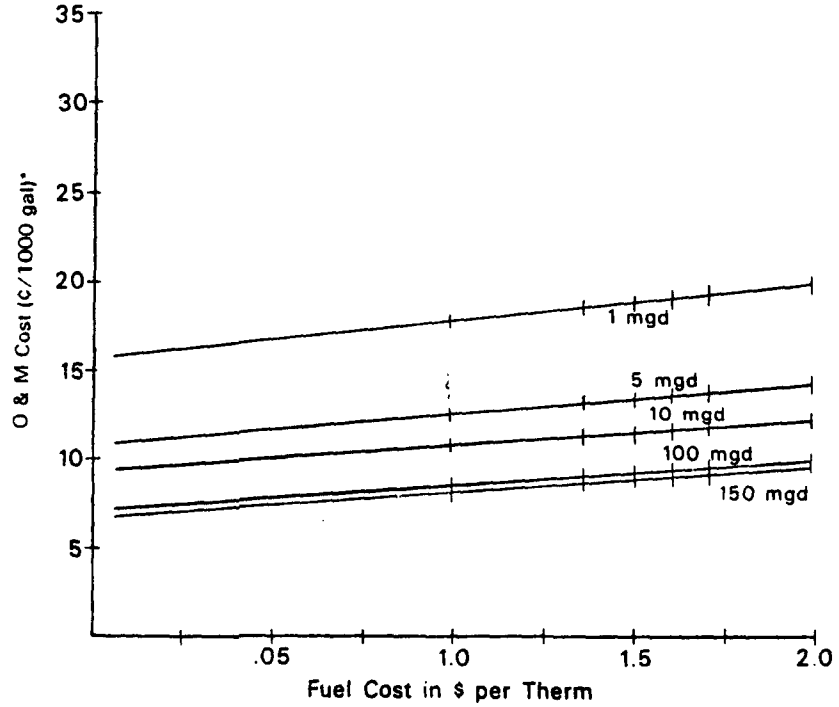

Figure 7. O & M Cost Versus Fuel Cost in $/Therm for 1, 5, 10, 100, and 150 mgd Sand Replacement Systems

*To convert from ¢/1,000 gal to ¢/m^3 multiply by 0.26

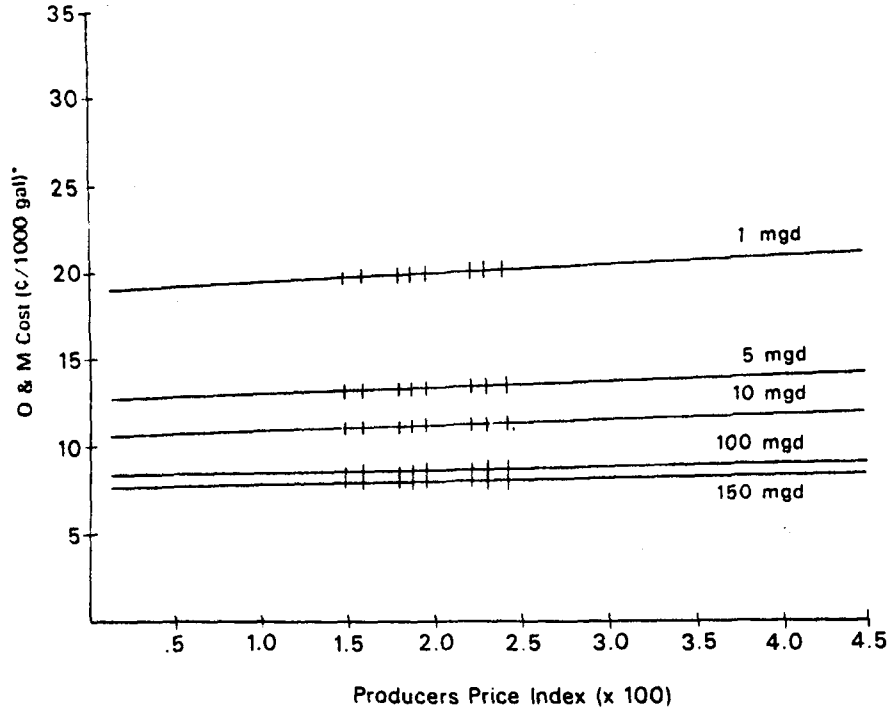

Figure 8. O & M Cost Versus Producers Price Index for 1, 5, 10, 100, and 150 mgd Sand Replacement Systems

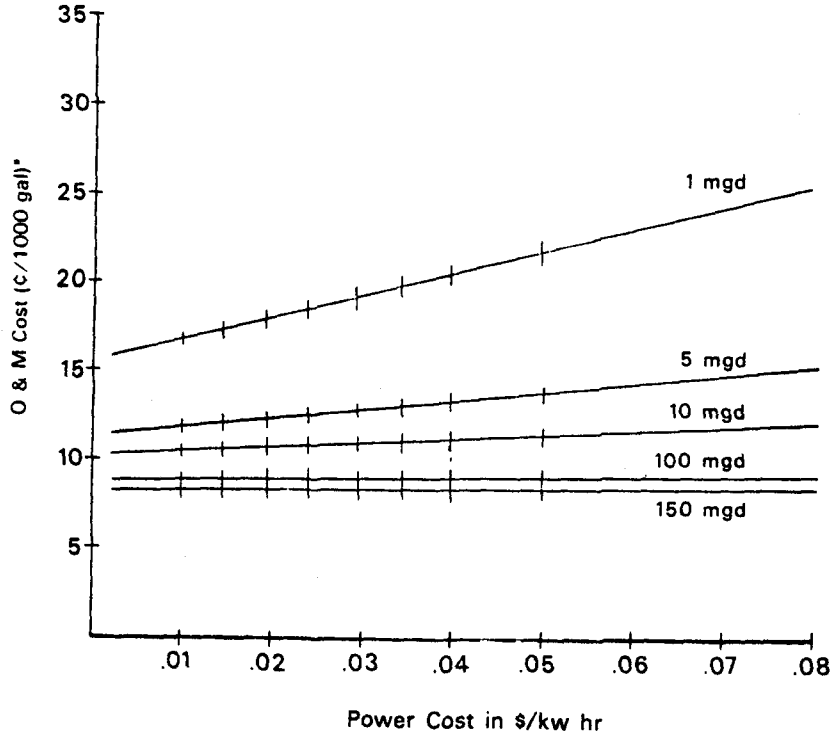

Figure 9. O & M Cost Versus Power Cost for 1, 5, 10, 100, and 150 mgd Sand Replacement Systems

*To convert from ¢/1,000 gal to ¢/m^3 multiply by 0.26

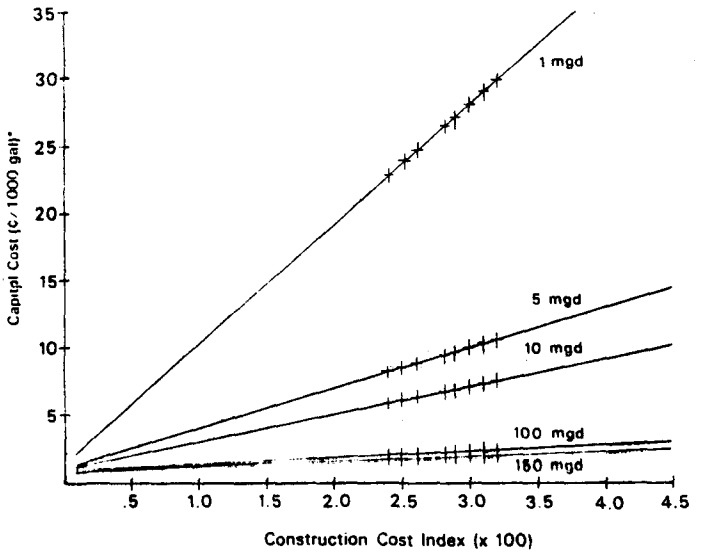

Figure 10. Capital Cost Versus Construction Cost Index for 1, 5, 10, 100, and 150 mgd Sand Replacement Systems

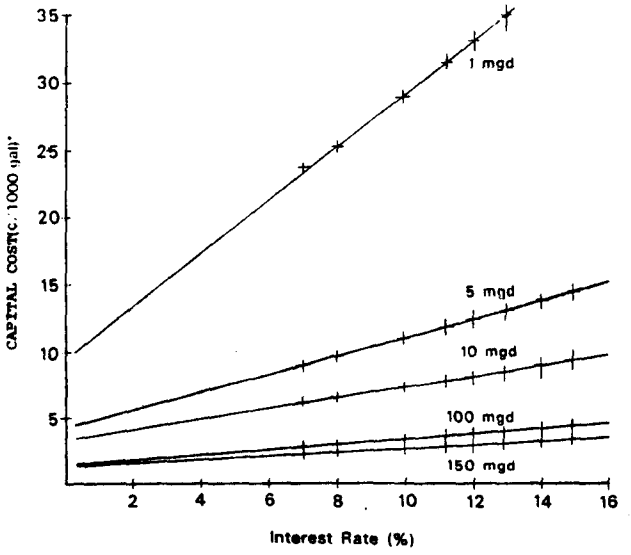

Figure 11. Capital Cost Versus Interest Rate for 1, 5, 10, 100, and 150 mgd Sand Replacement Systems

*To convert from ¢/1,000 gal to ¢/m^3 multiply by 0.26

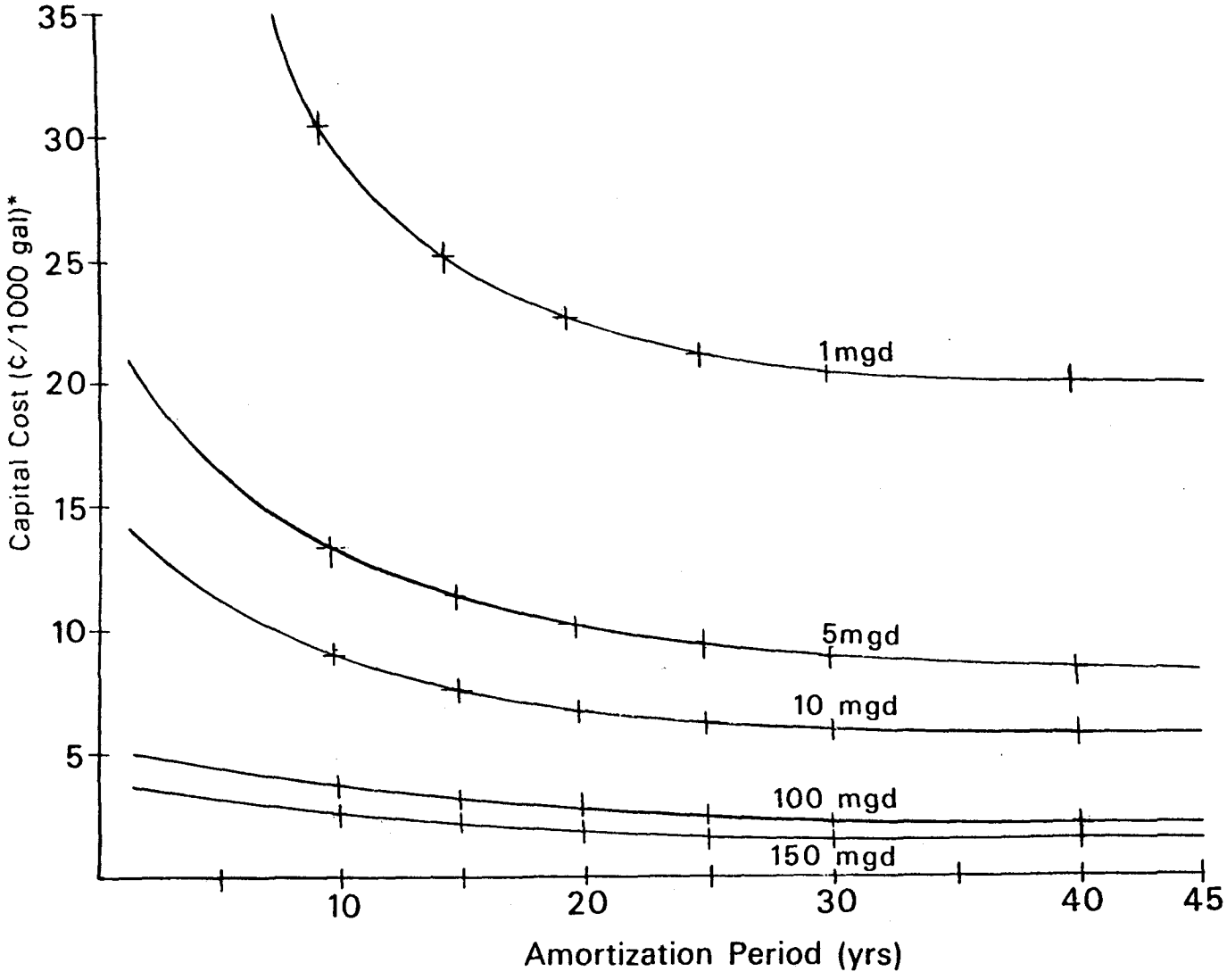

Figure 12. Capital Cost Versus Amortization for 1,5,10,100, and 150 mgd Sand Replacement Systems

*(To Convert from ¢/1000 gal to ¢/m^3 Multiply by 0.26)

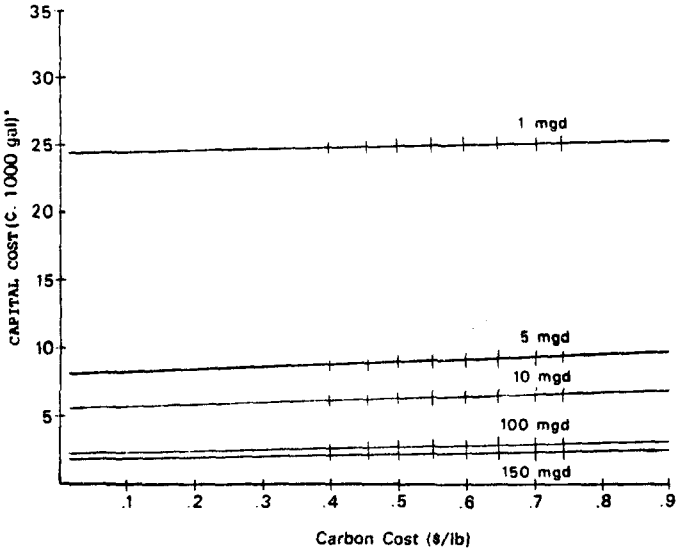

Figure 13. Capital Cost Versus Carbon Cost for 1, 5, 10, 100, and 150 mgd Sand Replacement Systems

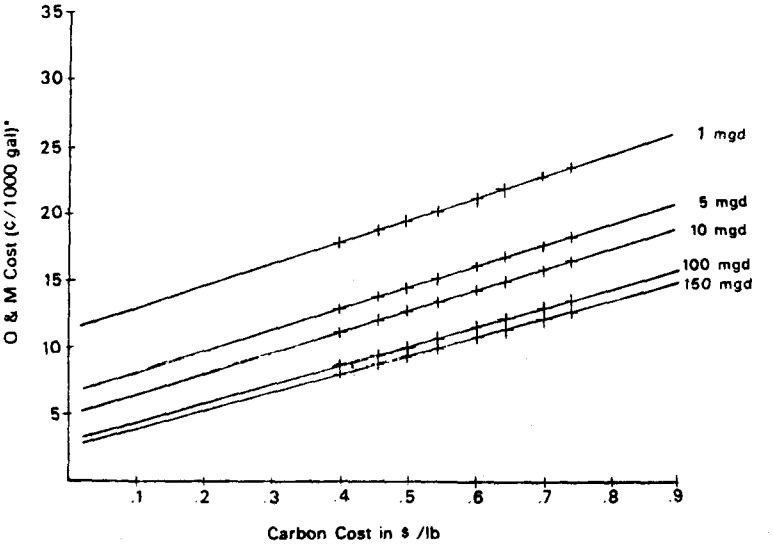

Figure 14. 0 & M Cost Versus Carbon Cost for 1, 5, 10, 100, and 150 mgd Sand Replacement Systems

*To convert from ¢/1,000 gal to ¢/m^3 multiply by 0.26

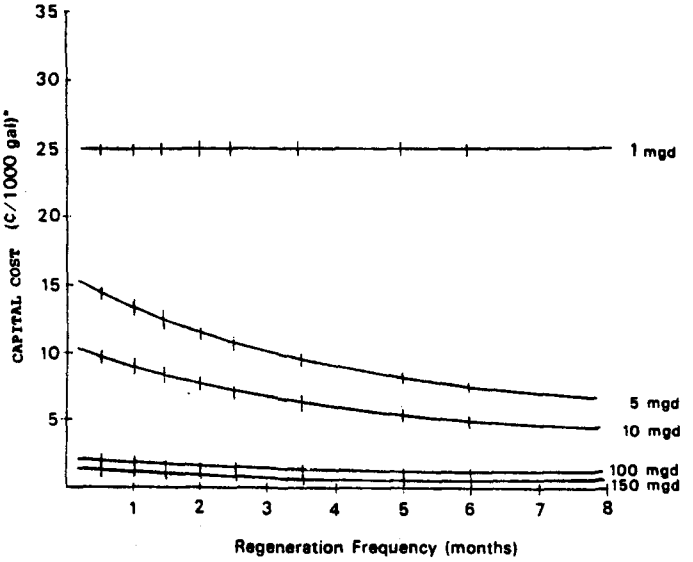

Figure 15. Capital Cost Versus Regeneration Frequency for 1, 5, 10, 100, and 150 mgd Sand Replacement Systems

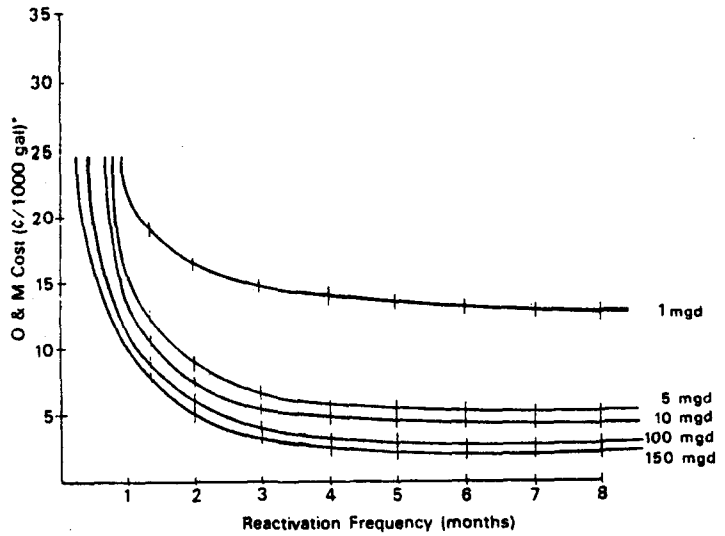

Figure 16. 0 & M Cost Versus Reactivation Frequency for 1, 5, 10, 100, and 150 mgd Sand Replacement Systems

*To convert from ¢/1,000 gal to ¢/m^3 multiply by 0.26

Capital Cost Effects--

Plant capacity, amortization period, construction cost index, and interest rate have a significant impact on system cost. System costs are relatively insensitive to activated carbon cost. Capital costs are moderately sensitive to reactivation frequency.

Cost Equations

From the previous analysis, some variables have a greater impact on cost than do others. For example, both O&M and capital costs are extremely sensitive to plant capacity and loading rate. Reactivation frequency also has a significant impact on cost.

In the previous sections, the effect of changing individual parameters was studied. Some of these variables may change simultaneously, however, complicating the relative impact of each variable on total cost. Individual regression equations have therefore been developed relating key design variables to annual cost. For capital cost, these calculations have been made in terms of dollars per year at 8 percent over a 20-year amortization period. Conversion to another base, such as ¢/1,000 gal, or to a different annualized cost, is a simple calculation.

These equations were derived by performing a regression analysis on key design variables (3). The variables were randomized and several hundred points chosen in order to arrive at each equation. The O&M and Capital Cost equations for steel downflow gravity contactors and multiple hearth reactivation furnaces follow:

Contactor O&M Cost--

$$CV_o = 92.2\ TVOL^{0.66} PR^{0.40} DHR^{0.44} PPI^{0.15} \quad (r^2 = 0.98) \qquad (1)$$

where

CV_o = annual operating and maintenance cost for steel downflow gravity contactor vessels in $/yr

TVOL = total contactor volume in ft^3

PR = power cost in $/kW hr

DHR = direct hourly wage rate in $/hr

PPI = Producers Price Index divided by 100

Contactor Capital Cost--

$$CV_c = 9.6\ CNTN^{0.99} VOL1^{0.81} CCI^{0.99} \quad (r^2 = 0.99) \qquad (2)$$

where

CV_c = annual capital cost for steel downflow gravity contactor vessels in \$/yr

CNTN = the number of individual contactors

VOL1 = the effective volume in ft^3 of a single contactor

CCI = Engineering News Record Construction Cost Index divided by 100

Reactivation O&M Cost--

$$RE_o = 1008.1\ RRTE^{0.86} CRBC^{0.67} CRBL^{0.65} \quad (r^2 = 0.99) \qquad (3)$$

where

RE_o = annual reactivation operating and maintenance cost in \$/yr for a multi-hearth furnace

RRTE = reactivation rate in lbs/day

CRBC = carbon cost in \$/lb

CRBL = carbon loss in percent per reactivation cycle

Reactivation Capital Cost--

$$RE_c = 1991.7\ RRTE^{0.38} CCI^{0.99} \quad (r^2 = 0.99) \qquad (4)$$

where

RE_c = annual reactivation capital cost in \$/yr for a multi-hearth furnace

RRTE = reactivation rate in lbs/day

CCI = Engineering New Record Construction Cost Index divided by 100

Initial Carbon Fill Cost--

The capital cost for the initial carbon fill is given by the following:

$$CF = (TVOL)(UN)(AM) \qquad (5)$$

where

CF = annual capital cost for carbon fill in \$/yr

TVOL = total initial volume of carbon in lbs

UN = unit cost in $/lb

AM = capital recovery factor

Design Implications

This analysis can provide some guidance for design. One can consider the most sensitive variables when making both design and operating decisions. Examples of how these data might be used are provided in the following sections.

REGIONAL REACTIVATION

The previous analysis shows that unit costs associated with smaller capacity plants are extremely high (Figure 1). A significant portion of the amortized capital costs are for on-site reactivation facilities, which suggests the possibility that for small plants some alternative to on-site reactivation such as regional reactivation should be explored. To illustrate the economic trade-offs considered with a regional reactivation site, the following case study is hypothesized.

Case Study

The case study consists for four water utilities of various sizes. Three options are considered for each site as follows:

1. establish a granular carbon reactivation system at each utility;

2. establish a centralized or regional granular carbon reactivation system;

3. discard the spent activated carbon and replace it with virgin GAC.

Costs associated with the three options will be calculated on the basis of $/yr. Activated carbon requirements for the various water treatment plants are in tons/yr and furnace sizing is based on lb/day of granular carbon reactivated. Table 5 contains the utility identification number, average water flow, and demand for activated carbon in tons/yr.

Three cost components are normally considered in a regional system. These components are the cost of on-site storage, the cost of transportation, and the cost of reactivation. The cost of on-site storage is given below.

Table 5

Design Assumptions for Case Study

Utility No.	Average Flow mgd	Average Flow (m^3/d)	Reactivation Demand tons/yr	Reactivation Demand (t/yr)
1	40	(16,000)	3114	(2,825)
2	5	(20,000)	389	(353)
3	100	(400,000)	7785	(7,062)
4	20	(80,000)	1557	(1,412)

TABLE 6

Variable Levels for Equation 8

Design Parameter	Level	
TSVOL	34,126 ft^3	(966 m^3)
CCI	265.4	
TCRB	207,600 ft^3	(5,875 m^3)
DI	$0.65/gal	($0.17/L)
DHR	$10/hr	
PPI	199.7	
RRTE	70,384 lb/day	(31,919 kg/day)
CRBC	$0.60/lb	($1.32/kg)
CRBL	6%	
Z	0.24	

$$OS_S = 1.35\ TSVOL^{0.98} CCI^{0.98} \quad (r^2 = 0.99) \tag{6}$$

where,

OS_S = Annual storage cost in \$/yr

TSVOL = Total storage volume in ft^3

CCI = Engineering News record construction cost index divided by 100

Transportation cost is given by the following equation:

$$TRC = 0.006\ TCRB^{0.99} MIL^{0.75} DI^{0.57} DHR^{0.33} PPI^{0.082} \quad (r^2 = 0.99) \tag{7}$$

where,

TRC = Transportation cost in \$/yr

TCRB = Total Volume of carbon transported in ft^3/yr

DI = Cost for diesel fuel in \$/gal

MIL = Distance to reactivation site in miles

DHR = Wage rate in \$/hr

PPI = Producers price index divided by 100

Reactivation costs are given by equations 3 and 4. Combining equations 3 and 4 with equations 6 and 7 yields an equation for total cost to a utility as follows:

$$\begin{aligned} REGC = {} & 1.35\ TSVOL^{0.98} CCI^{0.98} \\ & + 0.006\ TCRB^{0.99} MIL^{0.75} DI^{0.57} DHR^{0.33} PPI^{0.082} \\ & + Z(1008.1\ RRTE^{0.86} CRBC^{0.67} CRBL^{0.65} \\ & + 1991.7\ RRTE^{0.38} CCI^{0.99}) \end{aligned} \tag{8}$$

where,

REGC = the cost to a given utility in \$/yr for regional reactivation

Z = the portion of the reactivation cost charged to the utility

Given the levels assigned to the variables in equation 8 (Table 6), the costs associated with off-site regeneration as a function of distance are shown by equation 9.

$$REGC = 583{,}000 + 1{,}950\ MIL^{0.75} \tag{9}$$

Equation 9 was plotted as shown in Figure 17 and compared against on-site reactivation and disposal of spent activated carbon. Off-site reactivation can be a cost-effective solution particularly for small utilities. As the utility becomes larger the advantages of off-site reactivation diminish.

DESIGN IMPLICATIONS

The sensitivity analysis performed for operating variables has some important design implications. To illustrate these implications, the following examples will be considered: trade-off between contactor volume and number of contactors, activated carbon quality and cost, contact time and activated carbon use rate.

Contactors--Volume and Number

The annual capital cost for contactors is represented by equation 2, as follows:

$$CV_c = 9.6\ CNTN^{0.99} VOL1^{0.81} CCI^{0.99} \tag{2}$$

The partial of equation 2 with respect to CNTN is:

$$\frac{\partial CV_c}{\partial CNTN} = 9.50\ CNTN^{-0.01} VOL1^{0.81} CCI^{0.99} \tag{10}$$

The partial of equation 2 with respect to VOL1 is:

$$\frac{\partial CV_c}{\partial VOL1} = 7.78\ CNTN^{0.99} VOL1^{-0.19} CCI^{0.99} \tag{11}$$

If a constant total volume is to be maintained a minimum cost solution will result from fewer contactors of larger volume. The cost for additional increments of volume is lower than for increased number of contactors (equations 10 and 11). To illustrate this effect, assume two design configurations for contactors and volume as shown in Table 7. Figure 18 is a plot of equation 2 assuming the values in Table 7. As can be seen, configuration 2 (fewer contactors, larger volumes) is always less expensive even though the total volume of activated carbon is the same for both design configurations.

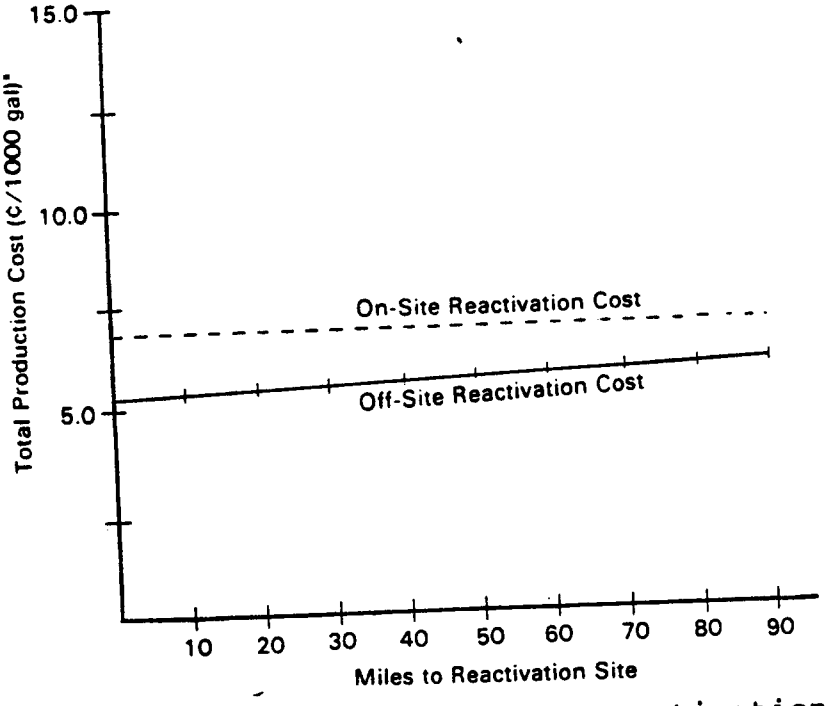

Figure 17. Off-Site Versus On-Site Reactivation for a 40 mgd System - Throwaway Cost is 30 ¢/ 1,000 gal

*To convert from ¢/1,000 gal to ¢/m^3 multiply by 0.26

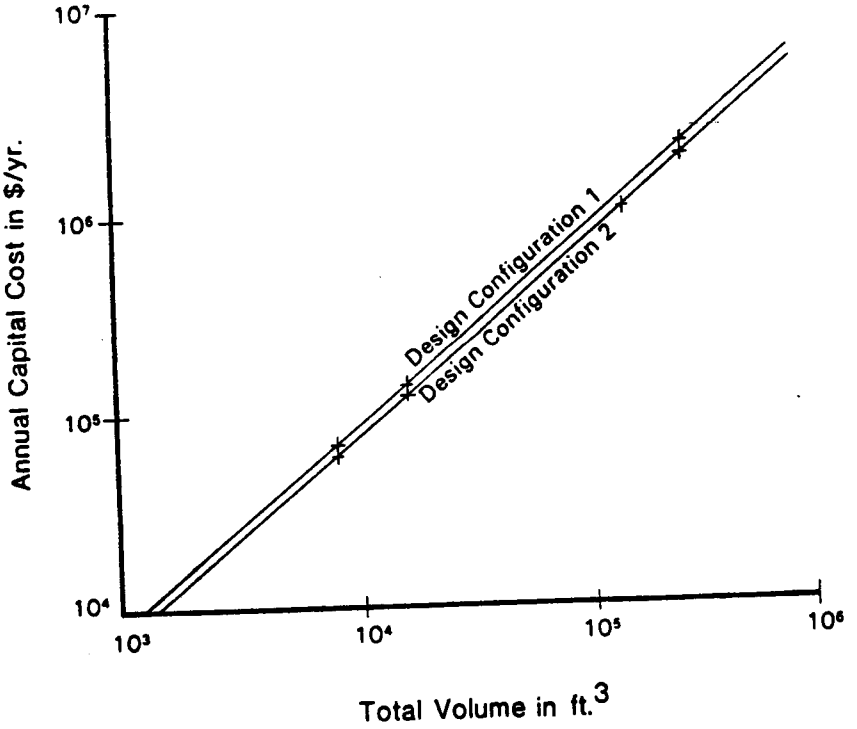

Figure 18. Comparison Between Design Configurations

Table 7

Assumed Design Configurations

Item	Design Configuration							
	1	2	1	2	1	2	1	2
Number of Contactors	6	3	12	6	40	20	60	30
Volume per Contactor in ft^3	1500	3000	1500	3000	4400	8800	4400	8800
(m^3)	(457)	(914)	(457)	(914)	(1341)	(2682)	(1341)	(2682)

Carbon Cost and Quality

The previous analysis shows that carbon cost, carbon loss, and reactivation frequency have a significant impact on cost. A manager interested in minimizing total system cost might choose to purchase the minimum cost activated carbon. Figure 19 shows total system cost versus reactivation frequency for a 100 mgd (400,000 m^3) post-filter adsorption system for three different carbon costs. Assuming 60¢/lb carbon for the system being reactivated at a frequency of 1.1. months the total system cost is approximately 16¢/1,000 gal (P_1) (4.2 ¢/m^3). If carbon cost is increased from 60¢/lb (132.3 ¢/kg) to 80¢/lb (176.4¢/kg), the reactivation period would have to increase from 1.1 to 1.7 months (P_2), for costs to remain constant. If the reactivation period increased beyond 1.7 months as a result of the more expensive carbon, system cost would be lowered. Equation 3 can be used to study the trade-off between reactivation frequency, carbon cost, and carbon loss per cycle. The annual reactivation O&M cost equation is as follows:

$$RE = 1008.1\ RRTE^{0.86}\ CRBC^{0.67} CRBL^{0.65} \qquad (3)$$

Taking the natural log of both sides of equation 3 yields:

$$\ln RE_o = \ln 1008.1 + 0.86 \ln RRTE + 0.67 \ln CRBC + 0.65 \ln CRBL \qquad (12)$$

To illustrate how CRBC and RRTE vary assuming cost remains constant, one can take the partial of equation 12 as follows:

$$\frac{\partial \ln RE_o}{\partial \ln CRBC} = 0.86 \frac{\partial \ln RRTE}{\partial \ln CRBC} + 0.67 + 0.65 \frac{\partial \ln CRBL}{\partial \ln CRBC} \qquad (13)$$

If one assumes that change in cost is zero, and activated carbon loss is constant, then equation 13 can be set equal to zero and the changes in reactivation frequency vs. carbon cost studied. This relationship would show the elasticity of substitution between CRBC and RRTE. These elasticities are summarized in Table 8.

Table 8

Elasticities for Equation 12 ($\partial Y/\partial X$)

	ln RRTE	ln CRBC	ln CRBL
ln RRTE	-	- 0.78	- 0.76
ln CRBC	- 1.28	-	- 0.97
ln CRBL	- 1.32	- 1.03	-

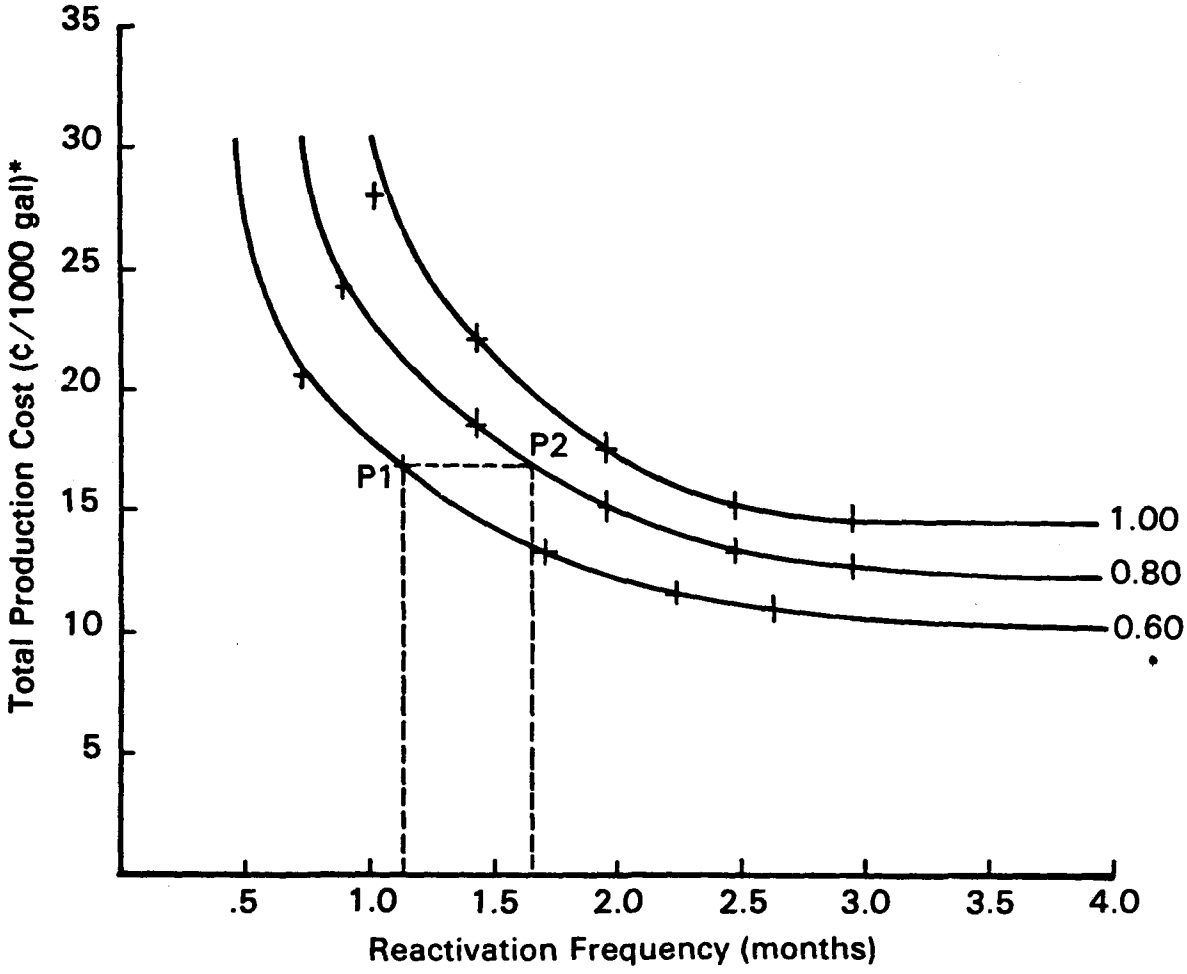

Figure 19. Total Production Cost Versus Reactivation Frequency for 0.60, 0.80, and 1.00 Dollar per Pound Carbon for a 100 mgd Post-Filter Adsorption System

***(To Convert from ¢/1000 gal to ¢/m³, Multiply by 0.26)**

Table 8 shows the changes in independent variables required to keep costs constant. For example, if the cost of activated carbon increased by 10 percent, the reactivation rate (lbs/day) has to decrease on the average by 12.8 percent or, correspondingly, the period between reactivations has to increase by 12.8 percent. This value will, of course, vary depending on the initial point on the curve in Figure 19. If one wishes to use a more expensive carbon, the decrease in reactivation frequency and/or activated carbon loss must be sufficiently great to offset the increased cost.

Contact Time and Use Ratio

In design of GAC systems the number of contactors should be minimized and the volume per contactor maximized. One might also conclude that, the greater the total volume of carbon or Empty Bed Contact Time (EBCT) the more efficient the organic removal process and the lower the unit cost.

Figure 20 shows the relationship between system size, cost, and empty bed contact time for a 100 mgd (400,000 m^3) post filter adsorption system. From Figure 20, if the required EBCT of 18 minutes at a reactivation frequency of 2.4 months were increased to 22 minutes, the reactivation frequency would have to be increased to 3.4 months (P_2) or greater to achieve a favorable economic trade-off. Therefore, to maintain the same cost if the EBCT were increased by 22 percent, the period between reactivations would have to increase by at least 42 percent.

This result appears to be "counter-intuitive." Conventional wisdom leads one to believe that deeper beds are more efficient in their removal of organic material (6). If, however, the use ratio of activated carbon is constant, that is the "lbs of carbon per million gallons of water loaded on the bed" remains constant with increasing bed depth, then a shallower bed is more cost effective. The excess activated carbon in the deeper bed is only so much excess inventory, not contributing to system performance until the end of a cycle but constantly costing more.

To properly understand this nonproportionality relationship, one should carefully consider the adsorbent use rate vs. EBCT. Data from pilot columns and field scale studies can be used to calculate the use ratio of activated carbon per unit volume to meet a controlling criterion for any empty bed contact time. Adsorbent use ratio is calculated by dividing the dry weight of adsorbent for a given empty bed contact time by the total volume of water passing through the column until a performance criterion is exceeded.

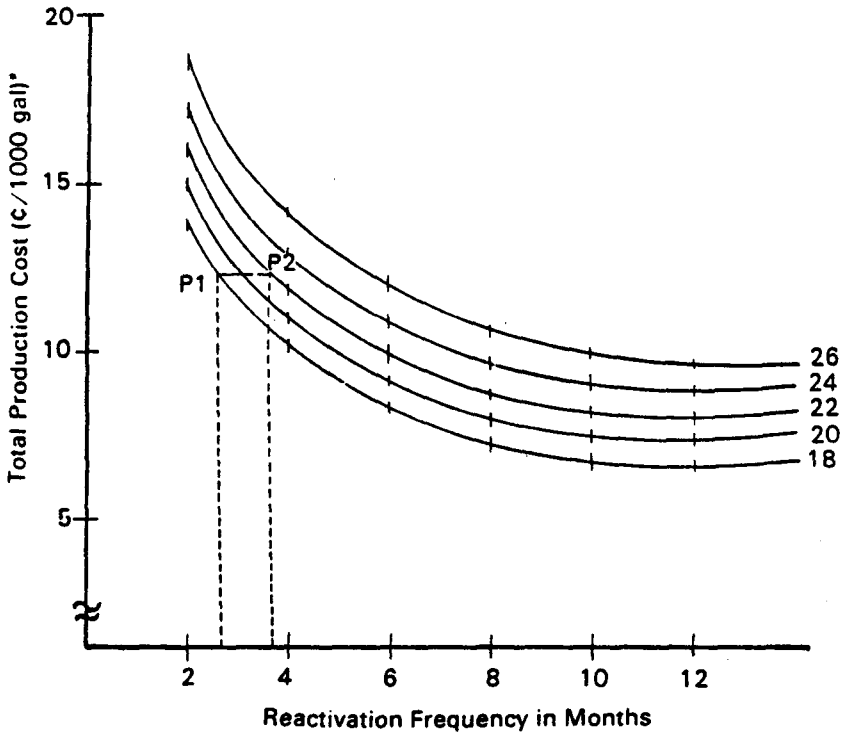

Figure 20. Effect of changing EBCT on Production Cost

*To convert from ¢/1,000 gal to ¢/m^3 multiply by 0.26

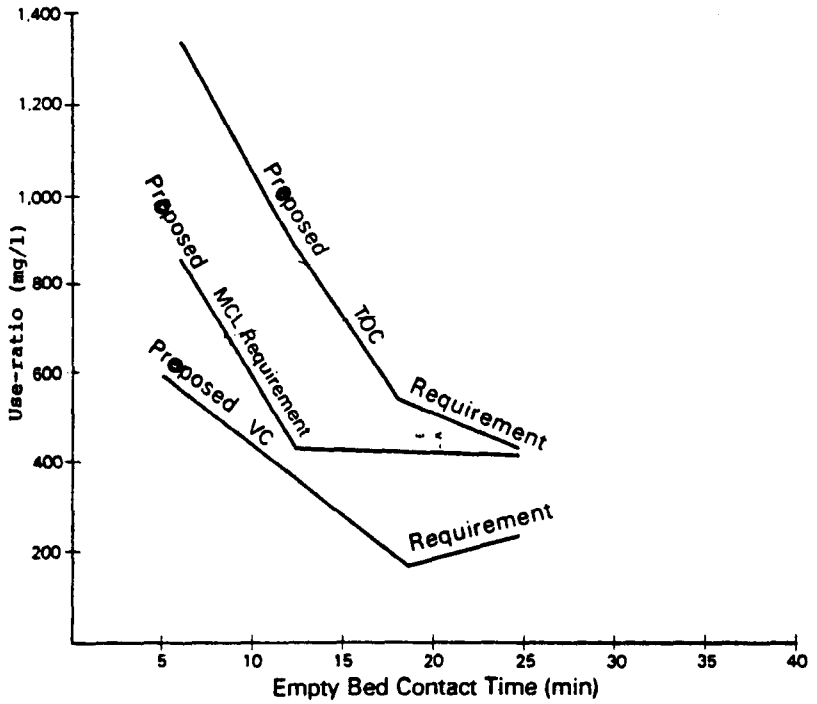

Figure 21. Use Ratio Versus Contact Time for Removal of Contaminants

If the adsorbent use ratio decreases with increasing empty bed contact time, then a more than proportional improvement in performance is gained by increasing the EBCT. Figure 21 shows some typical use ratios plotted vs. EBCT as obtained from field studies (7). The decrease in use ratio with increasing EBCT varies considerably among contaminants to be removed. At some point, however, the use ratio becomes constant, implying a point at which increasing the empty bed contact time no longer increases efficiency of removal.

One can calculate use ratio per million gallons, for example, by assuming an activated carbon use ratio as described above and converting to lbs/million gal. Assume a use ratio of 530 mg/l. The use ratio is converted as follows:

$$\text{Use ratio} = (530 \text{ mg/l}) \times (8.34 \text{ lbs/gal})$$

$$= 4{,}430 \text{ lbs/mil gal}$$

An equation relating EBCT and use ratio has been developed as follows:

$$TC = 73184.6\ C_T^{0.72} URTE^{0.79} \quad (r^2 = 0.99) \qquad (14)$$

where,

TC = total annual cost for GAC in $/yr for post-filter adsorbers

C_T = empty bed contact time in minutes

URTE = carbon use ratio in lbs/mil gal

Table 9 shows the relative elasticities between use ratio and contact time.

Table 9
Elasticities for Equation 14

∂Y =	∂X =	ln C_T	ln URTE
ln C_T		-	- 1.10
ln URTE		- 0.91	-

According to Table 9, for cost to remain constant if contact time increases by 10 percent, use ratio must decrease by 11 percent. From Figure 21, however, at some point use ratio reaches a constant.

Using equation 14 it is possible to find the optimal empty bed contact time as a function of the relationship between activated carbon use rate and contact time. For example, assume the following relationship between use ratio and contact time:

$$URTE = F(C_T) \tag{15}$$

Taking the partial of equation 14 with respect to C_T yields:

$$\frac{\partial TC}{\partial C_T} = 52693\ C_T^{-0.28}\ URTE^{0.79} + 57816\ C_T^{0.72}\ URTE^{-0.21}\ \frac{\partial URTE}{\partial C_T} \tag{16}$$

Setting equation 16 equal to zero results in the following relationship:

$$C_T = \frac{-0.91\ (URTE)}{\frac{\partial URTE}{\partial C_T}} \tag{17}$$

Substituting equation 15 into equation 17 yields:

$$C_T = \frac{0.91\ F(C_T)}{\frac{\partial F(C_T)}{\partial C_T}} \tag{18}$$

The solution to equation 18 (if there is one) will result in the minimum cost empty bed contact time. If no solution exists to equation 18, then the situation discussed earlier of the constant carbon use ratio exists and the shallowest possible bed will result in minimum cost.

OTHER ECONOMIC IMPACTS

There are other economic impacts that are related to the influence of operating variables on the cost of GAC. These impacts include general inflation, increased energy costs, etc.

INFLATION IMPACT

As shown in Table 1 for static economic conditions, sand replacement systems are slightly less expensive than are post-filter adsorption systems. Because post-filter adsorption is

less labor-intensive than sand replacement, inflation may make it less expensive some time in the future. To illustrate this effect, the cost for a 100 mgd (400,000 m^3) sand replacement system has been assumed as 10.1¢/1,000 gal (2.77 ¢/m^3).

A filter adsorber system of 100 mgd has been assumed as 11.7 ¢/1,000 gal (3.1 ¢/m^3) at year 0. Both systems have been allowed to increase at inflationary rates of 8, 11, and 15 percent over 20 years. The results of assuming the impact of 11 percent inflation on the two types of systems is shown in Figure 22. The figure shows that the sand replacement system becomes more expensive than the equivalent post-filter adsorption system after approximately 10 years. Total increase in cost caused by inflation in both systems is significant. This occurs because the capital expenditures for the systems are assumed fixed over the life of the investment, while operating costs were increased according to the assumed inflation rate.

To account for total expenditures, a "present value" analysis was made for the systems listed. Four discount rates (4, 6, 8, and 10 percent) and three inflation rates (8, 11, 15 percent) were used in the analysis. The results are summarized in Table 10. For the larger plants at the 11 and 15 percent inflation rates, for all discount rates, the post-filter adsorber has a lower present value, indicating that the post-filter adsorber is the least costly system.

ENERGY COSTS

From the earlier analysis, GAC operating costs are not highly sensitive to small changes in energy cost. Because the energy picture is so chaotic, however, energy use should be examined more intensively.

Tables 11 and 12 show the costs of energy use per lb of activated carbon, based on the assumptions in Table 1 for post-filter adsorption. Fuel and power costs range from 10 percent to 30 percent of total cost for reactivation. Energy cost is more nearly constant for contactors. The energy ratios given in both tables can be used to estimate the cost impacts resulting from drastic increases in energy cost.

COMBINATIONS OF UNIT PROCESSES

As all of the previous analysis emphasizes, the reactivation frequency has an important impact on the cost of GAC operation. GAC in combination with another unit process that helps lower reactivation frequency might result in a cheaper system. Figure 23 shows a hypothetical analysis in which ozone is assumed in combination with post-filter adsorption. If the system is initially at point P_1 (2 months) without ozone, then

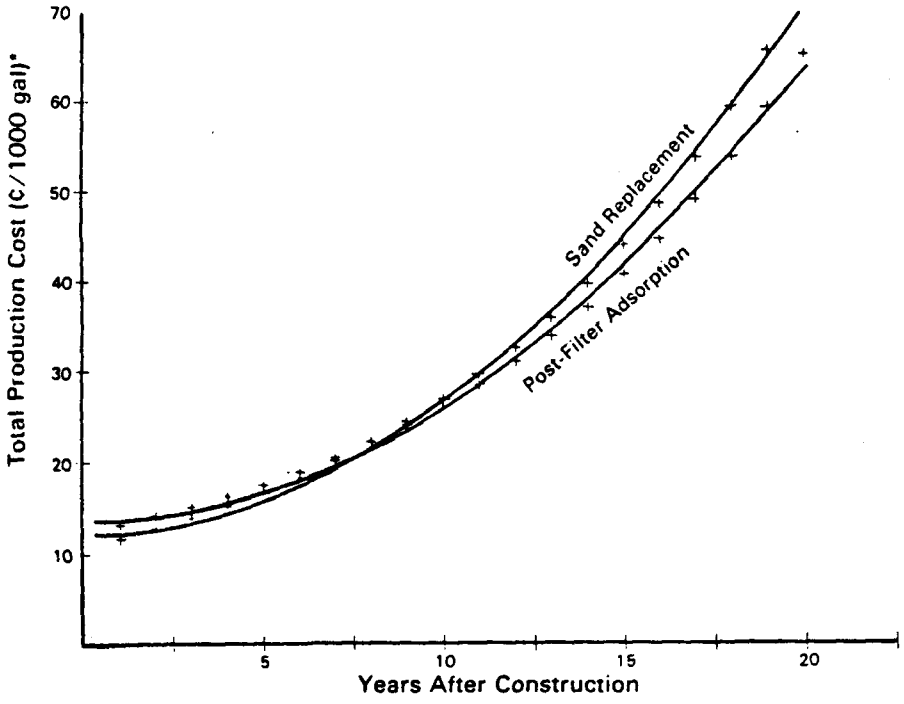

Figure 22. Effect of 11% Inflation on 100 mgd Sand Replacement and Post-Filter Adsorption Systems

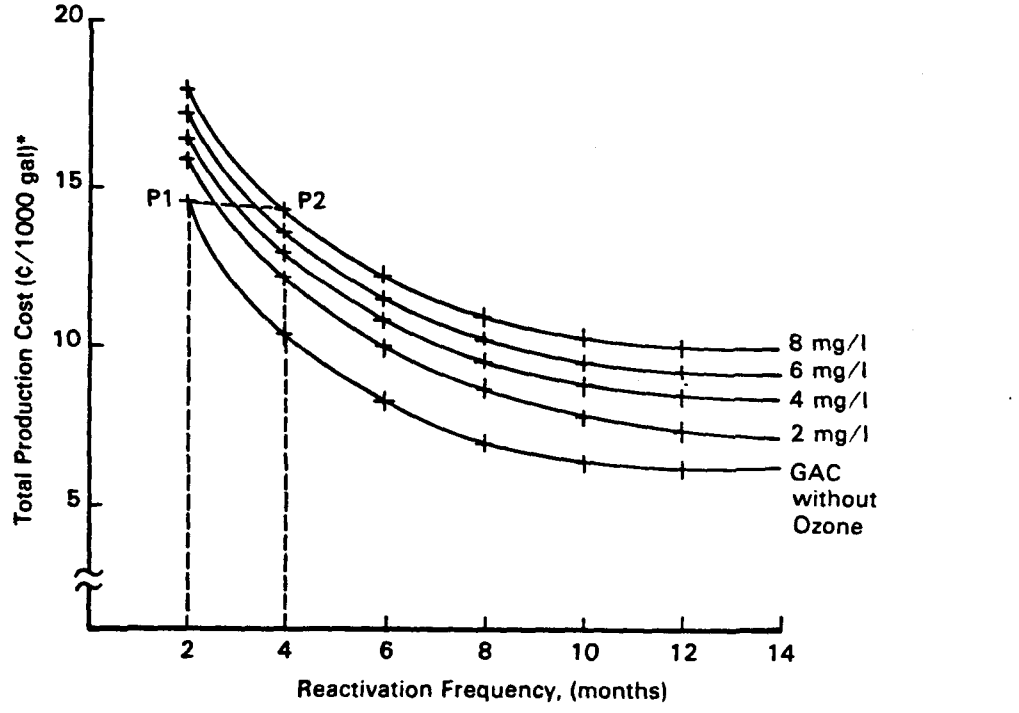

Figure 23. Cost of Ozone and GAC in Combination

***(To Convert fron ¢/1000 gal to ¢/m³, Multiply by 0.26)**

Table 10

Present Value Analysis

		Present Values			
		10 mgd		100 mgd	
Inflation rate (%)	Discount Rate (%)	Post-Filter Adsorption	Sand Replacement	Post Filter Adsorption	Sand Replacement
8	.04	482.84	456.75	305.96	302.99
	.06	397.67	374.18	251.18	246.85
	.08	333.06	311.74	209.71	204.52
	.10	283.38	263.88	177.88	172.17
11	.04	613.24	597.46	395.59	408.19
	.06	496.41	480.74	319.06	326.60
	.08	408.78	393.45	261.76	265.61
	.10	342.18	327.32	218.3	219.61
15	.04	885.16	890.91	582.52	627.65
	.06	699.94	700.39	458.97	490.78
	.08	562.84	559.84	367.75	390.05
	.10	460.37	454.88	299.55	315.01

Table 11

Energy Impact - Contactors*

Reactivation Rate (lbs/day)	System Cost ($/lb)	Energy Cost ($/lb)	Energy Ratio (kw hr/lb)
816.4	0.091	0.0045	0.15
3,673.8	0.062	0.0044	0.15
7,347.5	0.056	0.0043	0.14
73,266.7	0.042	0.0040	0.13
109,900.0	0.042	0.0039	0.13

Table 12

Energy Impact - Reactivation

Reactivation Rate (lbs/day)	System Cost ($/lb)	Energy Cost		Energy Ratio	
		Power ($/lb)	Fuel ($/lb)	Power (kw hr/lb)	Fuel (BTU x 10^5/lb)
816.4	0.352	0.028	0.034	0.92	0.19
3,673.8	0.180	0.011	0.026	0.36	0.15
7,347.5	0.141	0.007	0.025	0.23	0.14
73,266.7	0.076	0.002	0.019	0.06	0.11
109,900.0	0.070	0.001	0.018	0.05	0.10

*To convert from lbs/day to kg/day multiply by 0.4535. To convert from $/lb to $/kg multiply by 2.21. To convert from kw hr/lb to kw hr/kg multiply by 2.21. To convert from BTU x 10^5/lb to J/kg multiply by 2326.4.

the addition of ozone would have to increase the reactivation frequency to P_2 (4 months) to break even at an ozone dose of 8 mg/l. If, however, the system without ozone had a reactivation frequency of 6 months, no breakeven point exists to justify the addition of more than 4 mg/l ozone.

COST IMPACT ON INDIVIDUAL UTILITIES

The Safe Drinking Water Act, as conceived, intended that the direct costs of water treatment improvements be passed on to the consumer. This section will discuss some of the hypothetical impacts of GAC systems on the consumer. Cost impact analysis for 10 and 100 mgd systems (40,000 and 400,000 m^3/d) are shown in Tables 13 and 14.

Table 13 summarizes the costs that might be incurred when GAC is added to an existing system. Water bill increases are assumed based on a family of four consuming 117,000 gal of water per year. From the table, the costs of adding GAC to small systems are significant, but become more reasonable at larger plant sizes.

Table 14 shows the principal and total project cost (principal plus interest) required for both types of GAC systems at the 10 and 100 mgd levels.

SUMMARY AND CONCLUSIONS

In this paper, the sensitivity of GAC system costs to changes in certain operating variables has been examined. Several variables have been identified as important. These include choice of system configuration, loading rate and size of system, reactivation frequency, interest rate and life of system, local construction and operating costs, inflation, and carbon use rate. With the help of the equations and curves presented in this paper, these sensitivities can be studied.

For a given EBCT, fewer contactors of greater volume yield minimum cost. Based on activated carbon use rate, however, bigger is not better. If the activated carbon use rate decreases with EBCT, then larger volumes or greater EBCT's yield lower cost. When activated carbon use rate is held constant, however, deeper beds result in higher cost. The relationship between activated carbon use rate, activated carbon loss, and reactivation frequency must be studied carefully. Cheaper activated carbon could mean higher activated carbon losses and more frequent reactivation. Regional reactivation may result in lower costs particularly for small utilities. Inflationary effects may cause labor intensive sand filtration systems to be ultimately more expensive than capital intensive post-filter adsorption systems.

Table 13

Granular Activated Carbon Cost**

Treatment alternative	1-MGD plant: Unit Cost for GAC (c/1,000 gal)	1-MGD plant: Current* Cost (c/1,000 gal)	1-MGD plant: % Increase with GAC	100-MGD plant: Unit cost for GAC (c/1,000 gal)	100-MGD plant: Current Cost (c/1,000 gal)	100-MGD plant: % Increase with GAC
Sand replacement	44.3	121	37	10.1	59.0	17
Post-filter adsorber	51.5	121	43	12.3	59.0	21

*Inflated at 6% per year from 1974 to 1979 from figures shown in reference 9.

**To convert from c/1,000 gal to c/m^3 multiply by 0.26.

Table 14

Capital Costs for GAC

System	1-MGD Plant: Principal ($)	1-MGD Plant: Total project cost (principal & interest) ($)	100-MGD Plant: Principal ($)	100-MGD Plant: Total project cost (principal & interest) ($)
Sand replacement	640,000	1,270,000	4,900,000	8,700,000
Post-filter adsorber	737,000	1,500,000	12,400,00	24,000,000

This analysis emphasizes that although GAC systems are relatively complex, they can be designed to operate efficiently. The key to efficient operation is careful study and common sense which lead to an intelligent understanding of system design and operation.

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COST OF GRANULAR ACTIVATED CARBON TREATMENT IN FRANCE

F. Fiessinger

INTRODUCTION

To present cost data to an international audience is always difficult because costs depend upon the economic conditions particular to each country, as well as the accounting methods of the companies which must bear the costs. This is certainly true for amortization, and in this study we have, therefore, adopted a method that is relatively simple, if somewhat schematic in nature. We are particularly interested in capital and direct operating costs (reactivation costs, labor, power, etc.), and it is really their relative significance which we must establish: an order of importance based upon our finding in various countries and a comparison with the costs of other treatments. In the present study we shall examine the incremental costs related to the use of granular activated carbon (GAC) in addition to an existing treatment process.

All costs are given in U.S. dollars; the rate of exchange used is 1 U.S. $ = 4.50 FF.

COST OF GAC TREATMENT

Table 1 gives the characteristics of six plants in different regions of France which represent a significant, if not complete, range of GAC treatment in this country. We may make the following general observations:

- GAC is still used mainly to eliminate tastes and odors, and the life time of the carbon is generally longer than 1 year.
- The carbon used is generally of high quality and may be thermally reactivated.
- The carbon is reactivated by the manufacturers; plants for on-site reactivation do not as yet exist in France.

Table 1

Characteristics of Treatment Plants Using GAC

NAME OF THE PLANT	VIGNEUX	VIRY-CHATILLON	MORSANG	MOULLE	LAC MOURISCOT	ST. CHARLES
Area of supply	Paris area	Paris area	Paris area	Dunkerque (Ground water recharge)	Biarritz	Nancy
Water Resource	Seine river	Seine river	Seine river	Houlle river	Mouriscot lake	Moselle river
First year of GAC operation	1971	1973	1975	1973	1974	1975
Maximum production rate ($10^3 m^3$/day)	50	100	75	25	8	100
Total 1978 production 10^3 m^3	11400	17400	9500	4800	580	25500
Average 1979 daily production rate 10^3 m^3/day	33	50	27	25	17	72
Treatment Process	B.P. Prechlorination Coagulation-Flocculation Floc Blanket clarification GAC Filtration ClO_2 disinfection	B.P. Prechlorination Coagulation-Flocculation Floc Blanket clarificiation GAC Filtration ClO_2 disinfection	B.P. Prechlorination Coagulation-Flocculation Floc Blanket clarification Sand Filtration Ozonation GAC Filtration Cl_2 disinfection	B.P. Prechlorination Coagulation-Flocculation Floc Blanket clarification GAC Filtration	P.B. Prechlorination Coagulation-Flocculation Floc Blanket Clarification GAC Filtration Cl_2 disinfection	B.P. Prechlorination Coagulation-Flocculation Sedimentation GAC Filtration Ozonation
Contactors	10 filters : of $27m^2$ x 0.85m Total : 250 m^3 of GAC	15 filters : 9f. of $50m^2$ x 0.8m 6f. of $36m^2$ x 0.9m Total : 560 m^3 of GAC	4 filters : $60m^2$ x 1.5m Total : 360 m^3 of GAC	3 filters : $50m^2$ x 0.8m Total : 120 m3 of GAC	2 filters : $33m^2$ x 0.8m Total : 54 m^3 of GAC	22 filters of $60m^2$ x 0.8m Total : 1100 m^3 of GAC
Contact time at average production rate minutes	10	16	19	7	45	22
Type of GAC	Chemviron F 300 Chemviron F 500 Lurgi BS 12 Norit Row 0,8 S	Chemviron F 300 Norit Row 0,8 S	Chemviron F 400	Chemviron F 300 Norit Row 0,8 S	Chemviron F 300	Chemviron F 300 Pica NCY 103
Duty of GAC	Taste Removal	Taste Removal	COD Removal	COD Removal	Taste Removal	COD Removal
Possibility of additional PAC treatment	x		x			
Life time of each filter year	1.0	2.5	4	1.0	3	2.6
GAC treatment cost 1978 estimate - ct/m^3	0.79	0.50	1.20	0.85	0.60	0.65

- GAC is almost always used in the first stage of filtration. In this stage, carbon is fed with water which has been merely clarified, whereas in the second stage, carbon receives clarified water which has also been sand filtered. Investment is minimal and the cost of treatment is essentially that of reactivation.

- The cost of GAC treatment is quite low - generally less than $\$0.01/m^3$—even for those plants which are relatively small in size.

THE COST COMPONENTS

Let us now proceed from these general considerations to two specific examples: the plant at Vigneux-sur-Seine which represents the first GAC filtration treatment in France and the plant at Morsang-sur-Seine which, with its ozonation treatment preceding a second stage GAC filtration, constitutes what is presently considered the best treatment chain for surface water. In our comparison we have included cost estimates for a project to replace the first stage filtration (now used at Vigneux) by a second stage filtration.

CAPITAL COSTS

Initial Carbon Charge

The cost of carbon depends, of course, on its quality. As we have seen, most of the plants use high quality carbons whose prices in France are quite similar. Previous studies (1) indicate that non-reactivatable carbon generally gives poorer results; thus, it has been almost completely abandoned. Table 2 shows the prices charged in the Paris area by the two major carbon manufacturers.

TABLE 2

Price of Fresh Carbon for Morsang and Vigneux
(Delivered)

		Price in US$/kg	
	Bulk Density kg/m^3	1978	1979
CHEMVIRON F 300	420	1.60	1.71
CHEMVIRON F 400	400	1.74	1.86
NORIT ROW 0,8 S	360	1.99*	1.93*

*converted from the manufacturer's quoted prices of $\$716/m^3$ (1978) and $\$695/m^3$ (1979).

From this table we may make the following observations:

- Certain carbon manufacturers give prices by unit of weight although the contactors in water treatment plants are characterized by carbon volumes. It is much easier to work with a price per volume of carbon; the conversion of weight to volume is complicated by the variation in the apparent density of the carbon due to the extent of packing.

- Certain manufacturers attempt to widen their market by keeping their price increases to a minimum - or even lowering prices, as in the case of Norit at the present time. The French GAC market is highly competitive. The prices referred to here are those charged for small quantities. For larger supplies of several hundred m^3, with competitive bidding, the prices would be considerably lower.

The amount of carbon used depends directly upon the desired contact time. Our experience indicates that an optimum time is about 8 minutes for taste removal and 10 to 12 minutes for COD removal. Below these values, GAC's efficiency decreases sharply; above them it increases very slowly. Only a much longer contact time - higher than 30 minutes - would result in appreciably improved removal.

The problem, however, is how to calculate the contact time for a water plant which usually operates with a variable flow rate. At Morsang and Vigneux an 8 minute contact time was determined from the average flow during the peak month of June. Table 3 indicates the volumes of carbon and the corresponding costs for these two plants together with estimated figures for the project at Vigneux.

Contactors

It is preferable to speak of contactors rather than adsorbers, for in most cases, GAC's efficiency is more closely related to biological than adsorptive phenomena.

If we are considering only incremental costs, the use of activated carbon in the first stage - as is the case at Vigneux - does not represent such a cost. The contactors are composed of filters, required in any case, which use sand instead of carbon. The adaptations of backwashing sequences, the possible modifications of the filter, the installation of carbon transfer devices, even though crucial for the success of the treatment, represent investments which are negligible in the overall cost.

Table 3

Capital Costs for GAC Treatment at Morsang and Vigneux

	MORSANG II	VIGNEUX 1st Stage existing	VIGNEUX 2d Stage Project
FIRST YEAR OF GAC OPERATION	1975	1971	1979 ?
MAXIMUM PRODUCTION Rate 10^3 m3/hour	3.3	2.4	2.4
VOLUME OF CARBON m3	360	230	480
MINIMUM CONTACT Time - Minutes	6.5	5.8	12
COST OF CARBON 10^3 $	160	90	250
CHARACTERISTICS OF CONTACTORS	4 concrete rect.-gravity 60m^2 x 1.5m closed stainless steel equip.	10 concrete rectangular 27m^2 x 0.85m open Steel equip.	4 concrete cylindrical 6.2m diameter 31m^2 x 3.80m Stainless steel equipment
ADDITIONAL CAPITAL COST DUE TO CONTACTORS 10^3 $			
Civil work	180	-	650
Equipment	220	-	510
PUMPING CAPITAL COSTS 10^3 $	140	-	200
TOTAL CAPITAL COSTS 10^3 U.S. $	700	90	1 610

NOTE: The construction costs given here reflect price levels during the construction period corresponding approximately to the year in the first row of the Table.

In the case of Morsang, the second stage represents a more considerable investment. Table 3 indicates its importance. There we can also see the cost of the project for second-stage filtration at Vigneux. Prices are stated in 1971 dollars for Vigneux, 1975 dollars for Morsang and 1979 dollars for the Vigneux project.

Pumping

Here again, only the second stage of filtration requires additional pumping. Table 3 also indicates the cost of the pumping installation for Morsang and the Vigneux project.

Total Capital Cost

Table 3 shows that, in comparison with Morsang, the project for second stage filtration at Vigneux is relatively expensive. Since the second stage at Morsang was included in the original project, its marginal cost was small. The second stage at Vigneux would have to be added to an already existing plant, which would result in a considerably greater additional cost.

Because of the cost of materials in France, the use of concrete rather than steel, is preferred for works of this size. In order to keep the cost of contactors as low as possible, it is also advantageous to construct only a few filters, each designed cylindrically with a deep carbon bed and high filtration velocity even though this requires additional pumping expenditures. On the other hand, for operational considerations, particularly regeneration, it is preferable to have more filters. A good compromise appears to be four filters which will ensure a minimum contact time of 12 minutes at a maximum flow rate. Although the minimum acceptable contact time could probably be slightly reduced, the total cost would not change appreciably.

In summary, the construction of a second stage of filtration represents an important investment. The crucial question is whether the investment improves the quality of the water and/or whether it is compensated by a reduction in the regeneration cost.

OPERATING COSTS

Amortization

An interest rate of 9 percent per annum has been used throughout. This does not include an inflation allowance and might be considered rather low. As we have mentioned above, the calculation of amortization varies greatly from one water department to another, so that the costs of amortization are only approximate values. In any case, they are of minor importance.

The depreciation time was fixed at 20 years for all works, as an average figure. Amortization affects the contactors, pumping installations, and carbon, but the carbon amortization is arbitrary. One may consider that the carbon is renewed with each reactivation and does not suffer any depreciation. One may also consider that the carbon is degraded in the course of successive regenerations and after a certain time must be entirely renewed. Our experience at Vigneux, where certain filters have been reactivated up to seven times since they have been in use, has shown that the carbon remains efficient through successive regenerations. However, its physical characteristics are degraded and the carbon losses during washing, through the formation of fine particles, increase steadily. Thus, we feel that a depreciation time of 20 years represents a satisfactory compromise.

Table 4 shows the amortization figures for Morsang and Vigneux. The second stage at Morsang is, of course, quite costly.

TABLE 4

Operating Cost for GAC Treatment at Morsang and Vigneux
1978 Estimate in US$/100m^3

	MORSANG II	VIGNEUX 1st Stage Existing
Amortization (contactors + pumps + carbon) 9% over 20 years	0.73	0.08
CARBON REACTIVATION	0.30	0.60
LABOUR	0.04	0.05
POWER	0.04	-
MAINTAINANCE	0.01	-
BACKWASH (Air + Water + Power)	0.00	-
CARBON LOSSES	0.08	0.06
TOTAL TREATMENT COST US$/100 m^3	1.20	0.79

Reactivation

As can be seen in Table 4, the cost of reactivation is a significant portion of the operating costs. This reactivation cost depends, as we shall later see, on the quality of the untreated water and the quality objective for the treated water. The frequency of reactivation, and therefore its cost is considerably lower for a carbon in second-stage filtration than a carbon in first-stage filtration. At the present time, carbon is reactivated off-site by the manufacturers. The prices of reactivation for the principal carbons used are indicated in Table 5. If reactivation were carried out on-site, the saving would be roughly \$0.22/kg of carbon. The total amount of reactivated carbon in the neighboring plants of Morsang, Vigneux and Viry-Chatillon is now about 200 tons per year. Our current study of on-site reactivation indicates possible cost reductions for water treatment of approximately \$0.002/m^3 at Vigneux and \$0.0009/m^3 at Morsang. It would be even more attractive if the frequency of reactivation were to be increased. The frequency of reactivation is presently about once a year at Vigneux, where the quality of the untreated water is rather poor, and about once every four years at Morsang.

TABLE 5

GAC Reactivation Costs at Morsang and Vigneux
US\$/kg GAC

	1976	1977	1978	1979
CHEMVIRON F-300	0.511	0.613	0.664	0.677
CHEMVIRON F-400			0.744	0.744
NORIT ROW 0.8-S			0.711*	0.703*

Costs include transportation and "make-up" carbon.
*Based on costs of \$256/m^3 (1978) and \$253/m^3 (1979) and a bulk density of 360 kg/m^3.

Labor Costs

Labor costs are essentially the costs of handling the carbon before and after reactivation, and are therefore almost directly proportional to the frequency of reactivation. An eductor is used for the procedure, which is relatively rapid; the loading and unloading of a filter of 60 m^3 can be performed by three men in 8 hours.

At Morsang, additional labor is also needed for the backwashing of the second stage filters, but this is done only once every 3 to 4 weeks.

Power

Power is the energy required for pumping the water to the second stage of filtration. At Morsang there is an elevation of 2 3m for the entire flow. The energy expended is 5 watts per m^3/h raised 1 m. The cost of electricity is $0.045/kWh (1978).

Maintenance

Maintenance labor, materials, and supplies are included as 5 percent per annum of the equipment capital cost. Cost related to maintenance of carbon and structures appear negligible.

Backwash

The backwash process uses water and air to scour and wash the carbon from the second stage of filtration. As before, we have not shown any additional cost for the carbon in the first stage, since we assumed that the expenses of the first stage GAC filtration are no greater than those of sand filtration. Washing of the GAC filters at Morsang occurs every 3 to 4 weeks.

Carbon Losses

In addition to the depreciation of the carbon, which we considered above in our discussion of amortization, there must be compensation for the losses which occur during backwashing of the contactors. These losses, due mainly to attrition, vary from year to year and are related to the density, size, and hardness of the carbon. These characteristics may change significantly from one reactivation to another. The losses during the year 1978, were about 3 percent at Morsang and 5 percent at Vigneux. The carbon of Morsang is washed much less frequently than that of Vigneux but is less dense, finer and softer. Its effective size seems to decrease with time, but attrition during backwashing and particularly air scouring are not sufficient to explain this phenomenon. It is possible that a preliminary oxidation treatment (prechlorination at Vigneux plus ozone at Morsang) contributes to the degradation of the carbon. Some carbons are considerably degraded with time, while others of the same quality seem much more resistant.

The quantity of fine particles is a subject to which many have given much thought (2). We had originally required carbons from which fines had been sieved-out (e.g., Chemviron F 300 D), with an effective size of 0.85 mm, a uniformity co-

efficient of less than 1.7, and a maximum of 1.5 percent passing through a U.S. mesh 30 sieve (0.59 mm). However, the cost of such a carbon is 12 to 15 percent more than unclassified carbon and makes its use prohibitive. The physical characteristics of carbon are thus very important. The washing conditions (air and water or water alone, water velocity, time of washing, etc.) are equally important. The main point is that costs associated with carbon loss may vary greatly.

Control of Water Quality and GAC Efficiency

Correctly monitoring the efficiency of the carbon requires frequent analyses which are both complex and costly. For this reason, GAC treatment may entail an important additional cost. The simple methods used in our plants (measurment of taste threshold numbers, DOC, TOC, UV absorbance) have not created any appreciable supplementary costs, however, and thus do not appear in Table 4.

Total GAC Treatment Cost

We conclude that the overall cost of GAC treatment is quite reasonable - particularly at Vigneux. The selling price of water in the Paris region is roughly $\$0.50/m^3$ ($1.89 per thousand U.S. gallons). The cost of GAC treatment therefore represents approximately 1 to 2 percent of this price. If we consider only the total treatment cost, without distribution and other costs, the cost of GAC treatment is about 15 percent of the total at Morsang and less than 10 percent of the total at Vigneux.

DISCUSSION

Determination of the Reactivation Rate

The effectiveness of GAC progressively decreases with its use. This trend, both measured and schematically represented, is indicated on Figure 1 and 2 for taste removal, figure 3 for COD removal and Figure 4 for TOC removal. The central plateau undoubtedly corresponds to the development of biological activity within the carbon bed. These results are for the plant of Vigneux, but similar data presented in more detail elsewhere (4) were also found at the plant of Morsang.

After a period of time, however, the carbon no longer produces the desired results due to saturation and should be regenerated. This time depends upon several factors: the quality of the water to be treated, the quality criteria, and the quality objectives for the treated water.

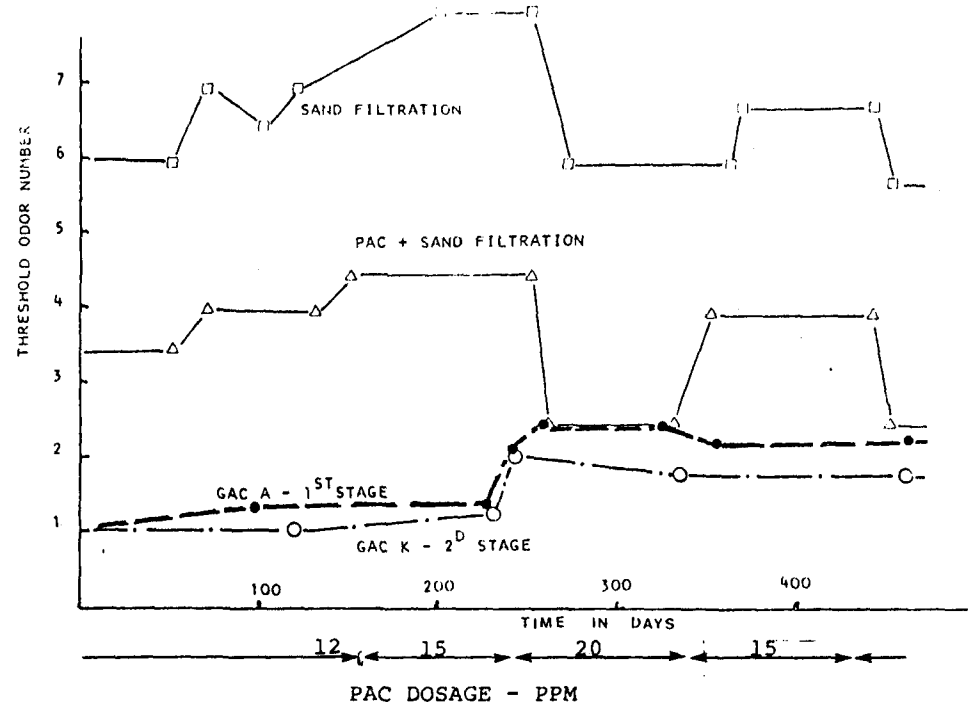


Figure 1. General Trend of Odor Thresholds with Various Activated Carbon Treatments in Vigneux-Sur-Seine

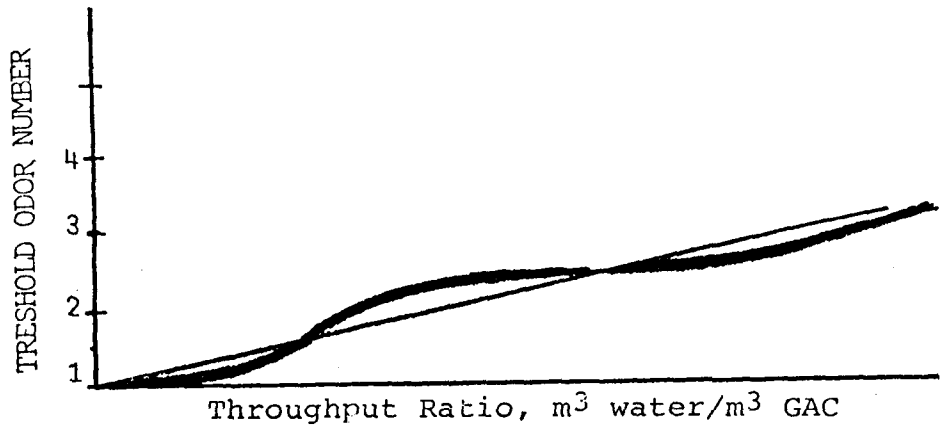


Figure 2. General Trend of Taste Thresholds of Water Produced by GAC Filtration

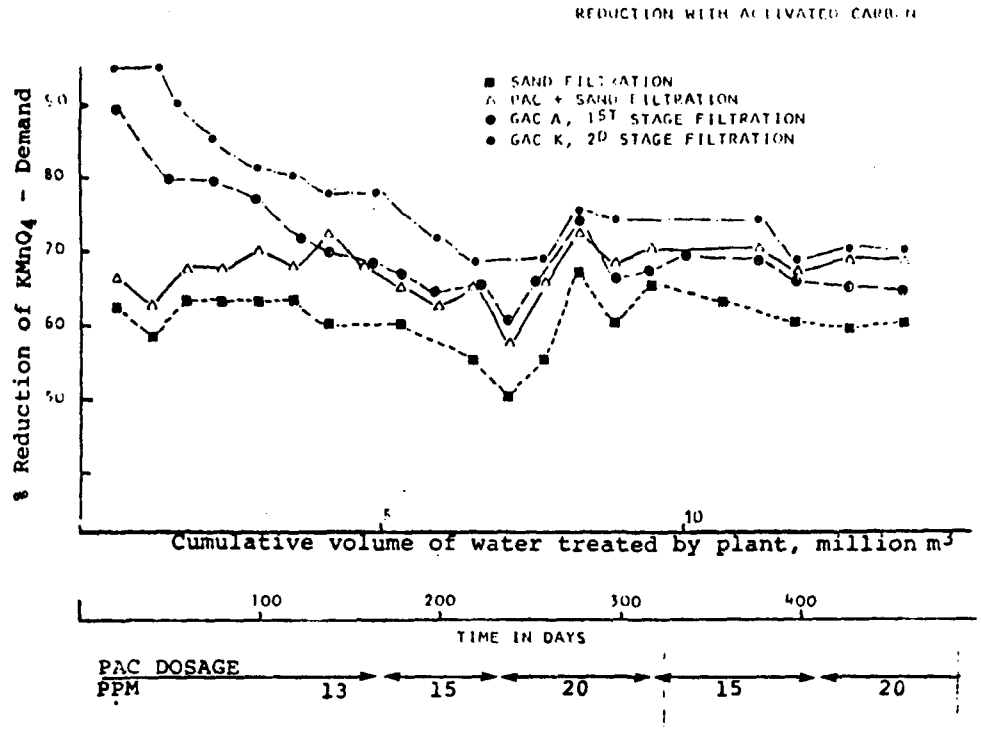


Figure 3. General Trend of COD ($KMnO_4$) Reduction with Activated Carbon Treatment in Vigneux-Sur-Seine

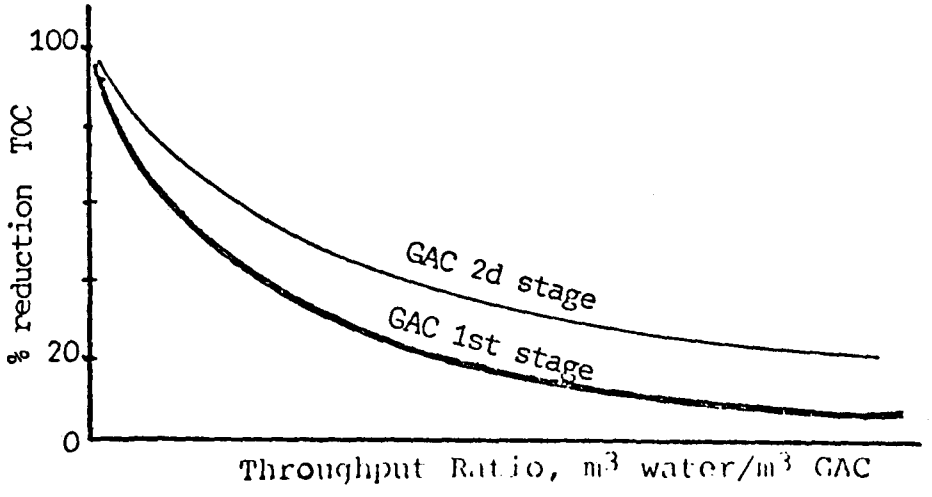


Figure 4. General Trend of TOC Removal Through GAC Filtration

Nature of the Water to be Treated--

The more polluted the water, the more rapidly the carbon will be saturated. This is not restricted to organic elements only. Certain inorganic compounds, such as manganese (at Morsang) or calcium carbonate, may also have an extremely negative effect on the carbon, particularly if they tend to precipitate. The presence of an oxidant such as ozone can improve the effectiveness of the carbon by promoting biodegradation.

Quality Criteria Used--

The plants we have mentioned use GAC to eliminate objectionable tastes in the water. Tastes can be easily reduced by activated carbon; the lifetime of the filters between two regenerations in such applications is generally several years. Other compounds, such as those represented by DOC and TOC, saturate the carbon more rapidly. For some organics such as the trihalomethanes (THM), the carbon must be reactivated quite frequently to ensure efficient removal; no more than 3 months can be allowed between regenerations to reduce at least 50 percent of the THM at Morsang.

Level of Quality Sought--

Along with the quality criteria, the quality objective is a determining factor for the frequency of reactivation. If a high level of quality is desired, the frequency of reactivation must increase.

Figure 1 shows the average odor threshold, as a function of time, for the Vigneux plant. During a single day, the efficiency of the carbon is highly variable, but over the period of a month or a year the trend of the average values is more gradual. We can therefore consider that the general trend is linear. In Figure 5, we see that in order to have an average odor threshold of 2.5, a second stage filter filled with GAC K must be reactivated approximately once a year. This conclusion depends, of course, on the quality of the Seine water, which varies from year to year. Simple criteria have therefore been established for the plant operators. The criterion used at Vigneux is the load of odor threshold numbers (Figure 6) eliminated by the filter, which must be kept smaller than 12,000,000. This load is equal to the average taste threshold number of the clarified water minus that of the water filtered through GAC times the number of cubic meters treated during the considered period. At Vigneux each filter contains 23 m^3 of carbon; thus the calculated maximum load is approximately 52,000 per m^3 of carbon. This figure depends, of course, on the nature of the carbon, as certain carbons are more efficient than others. It is, nevertheless, a very practical criterion, which is also used at other Seine water treatment plants, such as Viry-Chatillon.

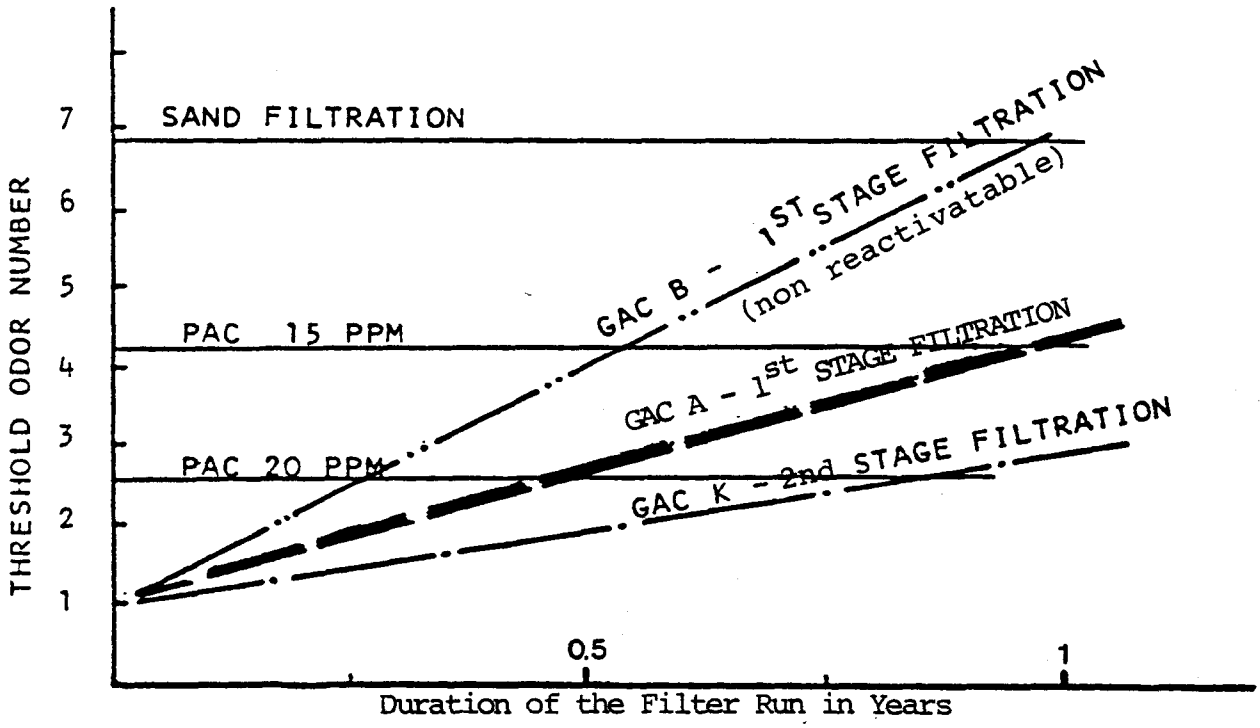


Figure 5. Average Odor Thresholds of Water Produced with Various Activated Carbon Treatments in Vigneux-Sur-Seine

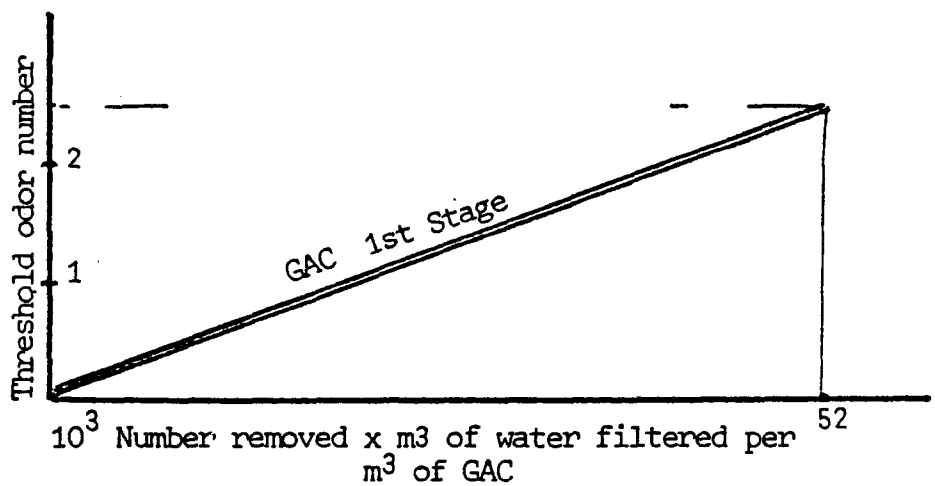


Figure 6. General Trend of Carbon Odor Number Removal in Vigneux

At Morsang, however, the criterion used at the present time is the elimination of at least 20 percent of the COD ($KMnO_4$) from the Seine water (Figure 7).

Our experience with GAC treatment of the water at Vigneux made possible cost predictions as presented in Figure 8 and Table 6.

TABLE 6
Carbon Treatment Cost* in Vigneux Versus Quality Level

% TOC Removal	10	20	40
GAC 1st Stage cost in $/m^3	0.003	0.008	0.0029
Gac 2nd Stage cost in $/m^3	0.014	0.015	0.021

1979 Predictions

GAC 1st Stage + PAC 10 ppm		0.011	0.026
THM - $CHCl_3$ g/l		30	15

*1978 Estimate
Costs in $ per m^3 wastewater treated

The Technology of GAC Treatment—

GAC technology also has a considerable influence on the frequency of reactivation. The most important technological aspects to be considered are the contact time, the thickness of the filter bed and the speed of filtration, each of which seems to have a relatively independent influence (3).

As mentioned earlier, contact times of 8 to 12 minutes appear optimum. It should also be noted that for a given contact time, better results are obtained with low filtration velocities. Tests presently being conducted at another plant in the Paris region have indicated that a very slow filtration velocity (0.5 m/h) through very thin carbon beds (10 to 15 cm) gives excellent results and delays the need for reactivation.

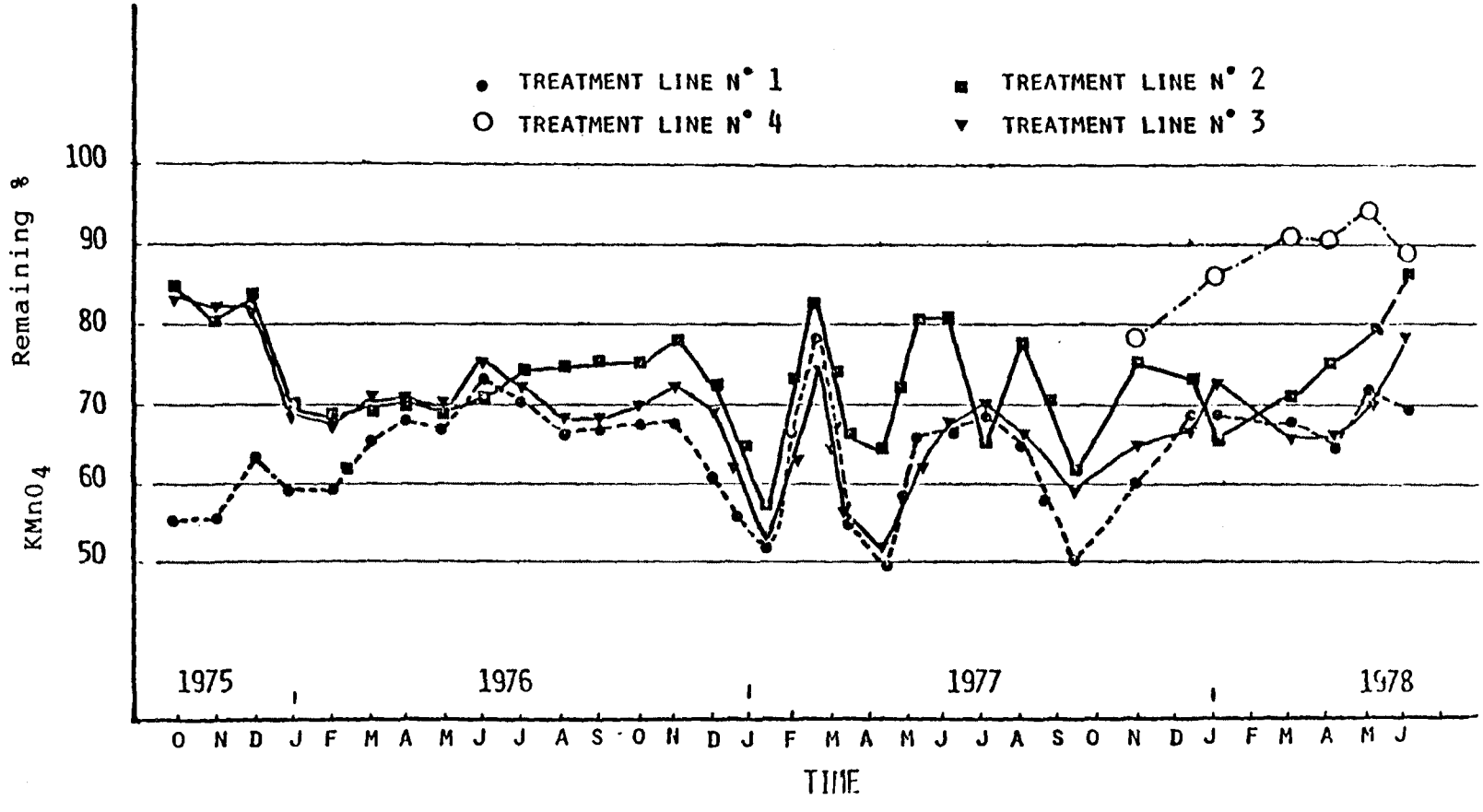


Figure 7. Trend of COD ($KMnO_4$) Removal By Different Treatment Lines at Morsang Sur Seine

It should nevertheless be kept in mind that from the investment standpoint, it is generally more economic to filter at high velocity through very deep carbon beds.

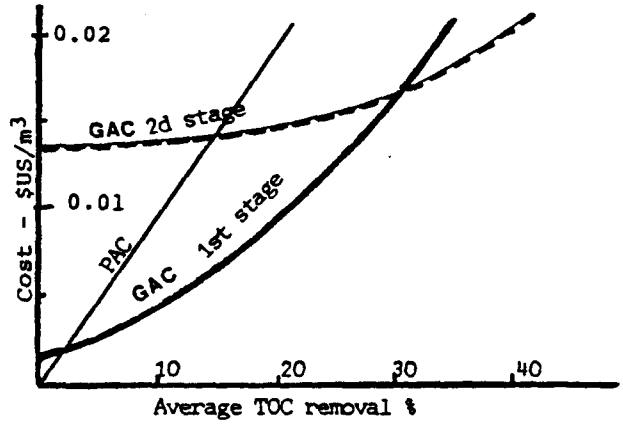
The constancy of the flow is also an important parameter. Most of the above-mentioned plants function with a highly variable flow rate. Such variations seem to have a particularly harmful effect if the carbon mainly functions biologically.

Stage of Filtration—

Another very important aspect is the position of the GAC in the overall treatment process. The carbon in the second stage of filtration is saturated less rapidly than the carbon in the first stage. Also, for a given quality objective, the use of carbon after ozone will delay the need for reactivation, especially if the carbon is in a second stage of filtration.

The economic advantage of these technologies is not obvious. The simplest solution is first stage filtration - as at Vigneux - which does not require any additional investment. However, in this case, the frequency of reactivation is greater. For the same contact time with the same water, our experience has shown that reactivation is required from 1.5 to 2 times more frequently in first stage versus second stage treatment. This is due, in particular, to the possibility of using finer carbon in the second stage. If second stage filtration is chosen, the investment required must be compensated by the savings on reactivation. However, the higher the quality objectives, the more advantageous it is to use a second stage filtration. Figure 8 illustrates this observation with the example of Vigneux. For commonly required quality levels, first-stage filtration is the best solution. If high quality water is sought, second-stage filtration is more economical. For intermediate quality objectives a combination of GAC with powdered activated carbon might be optimal.

Figure 8
Total Carbon Treatment Cost
1978 Estimate - Vigneux Plant



Combination of Powdered Activated Carbon with GAC

The use of PAC in addition to GAC gives highly interesting results. During use, GAC often desorbs organic matter. These desorptions are difficult to predict and are related to variations in the concentration of the organics in the influent water. Treatment with even a weak dose of PAC greatly reduces these variations. The PAC is introduced in a flocblanket clarifier. The contact time is quite important.

The dosage of the PAC may be adjusted depending on the quality of the influent water. The goal is to maintain an almost constant water quality introduced to the GAC. We are presently attempting this approach at Vigneux, and plan to use it at Morsang as well.

Treatment with PAC also results in a considerable improvement in the elimination of THM's, if only in reducing the chlorine contact time.

Table 6 lists predictions of costs versus efficiency for the various carbon treatments. For the existing quality objective (10 percent TOC removal), GAC in the first stage still constitutes the best solution. Economics are further improved if on-site reactivation is assumed. As the percentage of TOC desired to be removed increases to a point above 20 percent, GAC in the second stage becomes the optimum, as is the case if 40 percent TOC removal is required. However, Vigneux plant operators are not yet ready to spend more than $\$0.02/m^3$ for carbon treatment as would be required to achieve a TOC removal of 40 percent.

The level of THM's, mainly due to breakpoint prechlorination, remains reasonable. A very high frequency of reactivation would result in more effective control of THM's, but GAC treatment does not appear to be an economical solution for the reduction of such a pollutant.

CONCLUSION

When GAC treatment was introduced in France, an attempt was made in most plants to simplify its use in order to encourage its development. To this end, the following guidelines were applied:

- First stage filtration to minimize investment.
- Use of simple parameters with which the plant operators were already familiar.
- A relatively low frequency of reactivation.

- The use of reactivatable carbon whose physical characteristics are well adapted to filtration.

- The optimal use of existing equipment and careful adjustment of existing procedures without recourse to sophisticated technology.

The result has been a relatively modest cost and an almost universal recognition by French water suppliers of GAC's advantages.

GAC filtration is now accepted as the most reliable means to control organics in potable water. Based on this conviction, French water suppliers are now ready for gradual improvement in its application: better use of biology (BAC), development of second-stage filtration; use of GAC and PAC in combination; and introduction of on-site reactivation. However, GAC is probably not the only solution for the control of specific pollutants like THM's, and French water suppliers certainly would react unfavorably to it being considered as such.

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DISCUSSION

WEDNESDAY, MAY 2

MORNING SESSION

Q PROF. PAUL ROBERTS, Stanford University: I have some questions about the economics of carbon reactivation in waterworks practice. (1) Have the Europeans done a cost comparison to determine what would be the minimum size capacity, in tons per day, for a reactivation facility that would justify itself economically over the cost of fresh makeup carbon at a waterworks; (2) The reactivation facilities described, which are rather expensive, complicated units, are used less than 50 percent of the available hours in the year. Could they be used more or is it necessary to design excess capacity in case the carbon should be exhausted by some spill or other accident? Is there a criterion as to how much excess capacity is needed?

A PROF. DR. SONTHEIMER: The lowest amount of carbon reactivated should be in the range of 1-1/2 tons per day to make it economically feasible. This should be an average figure for the entire year. Sometimes you may have twice as much reactivation and sometimes the facility will be idle. It is not important if the plant is fully automated. The difference is in sizes of the furnaces, which is very important. There should be lower limits, especially for reactivation furnaces, or it stops being economically feasible.

MR. SCHALEKAMP: It would be best if a reactivation plant could operate regularly, then there would be little trouble. If the plant is on standby part of the time, there are problems with bringing it on line. Therefore, it shouldn't have too much excess capacity. I think that's important.

Q PROF. VERN SNOEYINK, University of Illinois: We've had different figures presented for losses. If I remember correctly, Mr. Schalekamp said 3-1/2 percent yesterday. Today we hear 10 to 15 percent. Dr. Klein mentioned that it should be possible to achieve what Mr. Schalekamp referred to yesterday. I wonder if the losses that have been discussed at the operating plants are primarily due to start-up problems or getting to know the systems. Do the people using the plants think maybe the 3, 4, or 5 percent is something that can be achieved only if the loadings are as low as achieved at Zurich?

A PROF. DR. SONTHEIMER: I would like to comment on this. I think we should keep something in mind when we speak about losses. The prime objective is high quality of the reactivated carbon. Moreover, if you save time between regenerations, in some cases, it may be enough of an advantage to compensate for some losses. The other point is that it's very difficult to collect exact data on losses. I think--and I believe my two colleagues will agree--that the only acceptable way is to regenerate the same carbon five, six, or ten times to accurately estimate total losses. Then the effects of backwashing, which removes small particles (all those less than .5 millimeters) and could make a difference, would be taken into account. Sometimes some plants don't regenerate frequently, so we have to be patient. We discussed this problem yesterday too, and we decided that we would have a special meeting with the people who measured losses in regeneration to determine the best ways to measure it. It's not an easy thing to do, but I wouldn't say this is so important. Some people try to reduce losses, but even for losses of 10 and 12 percent, it remains economical.

MR. SCHALEKAMP: I agree with Professor Sontheimer. I only can say that the loss we experienced in Zurich resulted from one regeneration. If you regenerate three times, there will be much more loss. I will say we have used carbon from another manufacturer and contracted with them to perform reactivation. When it came back, we put it into our filters and discovered we had a loss of 20 percent, because it was all powder and we had to get rid of it.

DR. KLEIN: As I tried to explain in my paper, the loss is dependent on the kind of the carbon and adsorbate. If the activity of the carbon is in the same range as that of the adsorbate, you have a loss. I think you can't avoid it, but if you have an adsorbate that is more reactive than the carbon itself, then you can get a minimum carbon loss.

Q FOSTER BURBA, Louisville, Kentucky: My first question is the factor for converting Deutsche marks to dollars; secondly, I would like to get an idea of the life of the furnace regeneration equipment.

A PROF. DR. SONTHEIMER: The conversion factor is 1.9 marks to one dollar; the life of the furnace, we don't know.

A MR. SCHALEKAMP: From experience in the gas works, I think it will be about 10 years, but every time it is taken out of operation, you will have to make minor repairs.

A DR. KLEIN: We have an oven used for the regeneration of carbon which has been working since 1964; that means about 15 years.

Q MR. BURBA: I have one other question. Has there been any investigation of the possible toxic chemicals formed during the regeneration process which would be retained on the GAC and perhaps leached into the water after the GAC is regenerated and put back into service?

A PROF. DR. SONTHEIMER: We did numerous studies on this problem because certain compounds under certain temperature conditions can form toxic compounds. That is the reason why we say you must exceed a minimum temperature. We are very sure that if high enough temperatures are maintained, no toxic compounds will be formed because they and all other compounds are burned. We found, first, that if we have too low a temperature, organic compounds will remain on the carbon. We control the minimum temperature as well as other aspects of carbon regeneration. We are very sure that all the problems which may arise don't arise in this plant.

Q MR. D. J. OSBORNE: Is the particle size reduction after regeneration due to the mechanical abrasion of the granular activated carbon and is this increased due to embrittlement by the quench after regeneration? Have you done any work with slow cooling in an oxygen-free environment to reduce this?

A PROF. DR. SONTHEIMER: We didn't do this work and we are not sure exactly where reduction of grain size occurs. I doubt that the most important step is the cooling, and for this reason we didn't study it at all. We also have to get more experience. Working with such a plant, we found that the largest reduction in size occurs the first time, but then there is no further change for a very long time. You have to observe it four, five, six, seven times, before significant conclusions can be made. We have not done any studies because we didn't see any need.

A DR. KLEIN: We have regenerated active carbon in a plant 25 times. The distribution of particle size did not differ very much from that of the first time. The main reductions come in backwashing and hydraulic transportation, not by regeneration.

Q MR. PEARSON: A question was raised earlier about the amount of time that the Düsseldorf reactivation plant was not in service. I have spoken with Professor Sontheimer about the fact that it was originally designed when the pollution in the Rhine was very high. Because of the improvement in the waste discharges from one of the huge industrial complexes—the BASF plant upstream—the TOC and organics loading has been greatly reduced. This is one of the reasons that the plant doesn't operate as much

as it originally was designed to. Would you care to comment on that for the benefit of the audience, Professor Sontheimer?

A PROF. DR. SONTHEIMER: I would be very pleased to because I think all of us working in the drinking water field have to fight against pollution. In Germany, we have an association of waterworks along the Rhine river to fight against the pollution of the Rhine. Mr. Schalekamp is the President. We have achieved some improvements in the quality of the Rhine River water. Thanks to this improvement in raw water quality at Düsseldorf, instead of three furnaces, only two are now needed. There is some safety factor in this too, instead of 3 months we now range from 5 to 6 months between regenerations. However, I don't believe that we will progress with our industrial society to levels of water quality where activated carbon is no longer needed. We always will need it as a safety factor.

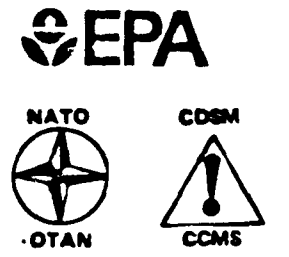
Q WALTER McCUSKY, U.S. Army Construction Engineering Research Lab: The first question is for Dr. Klein. Did I understand your graphs correctly, that you get selective chemical reaction in the regeneration atmosphere of the carbonized organics up to a certain point and at that point you begin to get attack on the carbon matrix? If so, how do you tell where that point is so that you can get the carbon out of the furnace in time?

DR. KLEIN: We first investigated on a small-scale plant in the lab to find the optimum conditions for the temperature and the residence time. Then we applied these conditions in a large-scale plant. The residence time distribution in the full-scale furnace is important. Particles which are retained too long can be destroyed.

MAC McGINNIS, Shirco, Inc.: We have observed a consistent increase in the ash content of the regenerated carbon, which is indicative of deposition of some sort of inorganic material on the carbon. Alum and lime are used in this plant and one would suspect that they may be sources of the ash increase: a logical conclusion is that that may preclude complete restoration of virgin properties.

Q MILLER, Cincinnati: Dr. Love, I have a plea for help. In the furnaces that you're seeing, it sounds as though some of the problem is determining the points of loss or attrition. It would seem as though it is in the transportation system in the furnace itself. If they're doing this in Germany, or in any of your projects, I think it would be helpful if we all know about this.

A DR. LOVE: I think Professor Sontheimer addressed at least part of that this morning; he felt the losses in the furnance were very low, 1 to 2 percent.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NEW DEVELOPMENTS IN ADSORPTION TECHNIQUES

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GENERAL CONSIDERATIONS IN ASSESSING THE BENEFICIAL ASPECTS OF MICROBIAL ACTIVITY ON GRANULAR ACTIVATED CARBON

Francis A. DiGiano

INTRODUCTION

The term "biological activated carbon" has found its way into the U.S. technical literature in the last year as a result of reports by Miller and Rice (1) and by Rice, et al. (2) on European drinking water practice. Professor Sontheimer's research group (3) at Karlsruhe University was the first to conduct practical tests of the beneficial aspects of microbial activity on granular activated carbon (GAC) in pilot plant tests at Bremen, Federal Republic of Germany from 1970 to 1974. They proposed that through microbial degradation of organics, the service time of a GAC bed could be greatly extended. More recently, research groups led by Professors Benedek (4), Tien (5), and Weber (6) have focused on formulating and verifying conceptual mathematic models to describe the interaction between biodegradation and adsorption on GAC. The intent of this paper is to discuss the present status of microbial activity on GAC as a method of water treatment and to point to further research needs.

BACTERIAL ATTACHMENT

Attachment of bacteria (and protozoa) to the external surface of GAC has been shown clearly by electron micrographs (7) but the mechanisms responsible have not been investigated as yet. Mechanisms for surface attachment in general have been recently discussed by Marshall (8). Apparently, attachment can be either reversible, with desorption produced by the shearing action of fluid mixing or by mobility of sorbed bacteria, or it can be irreversible, involving adsorption of extracellular materials (9).

Irreversible attachment may require time for preparation of the surface. This was referred to as "seasoning time" by Pipes (10), in investigation of phenol biodegradation in a sand filter; about 6 days were required. In pilot plant studies of water treatment by GAC, van der Kooij (11) noted that 20 to 30 days were needed before the maximum level of 10^8 colonies per gram was reached. This could imply either that extracellular materials were adsorbing or that a build-up of sorbed organics

was necessary before microbial activity could increase; in the latter case, a form of bioregeneration must be assumed. The evidence is insufficient to conclude which of these possibilities was in fact the case.

An attempt has also been made to quantify the adsorption of a mixed population of bacteria on GAC in a batch experiment similar to that used to measure adsorption equilibrium (12). While an adsorption "isotherm" was obtained, its meaning seems lost because "equilibrium" was not reached; i.e., bacterial death and desorption continued to occur without regard for solid-liquid phase equilibrium.

The question also remains as to whether or not GAC provides a more favorable environment for attachment than sand or non-activated carbon. This uncertainty is shown quite clearly by comparing surface bacterial counts for these three media in Figure 1. In this research, van der Kooij (11) claimed that any advantage shown by GAC was accounted for by its larger external surface area.

HIGHLIGHTS OF BREMEN STUDY

The Bremen pilot plant study is probably the longest observation of GAC bed performance without regeneration (3-1/2 years). Since results of this study have been published only in German (3), it is worthwhile to present highlights here. At the outset, it is important to recognize that only practical measures of organics were used, such as potassium permanganate demand ($KMnO_4$), total organic carbon (TOC), and UV absorbance. Thus, it is impossible to cite which specific organics, or even which broad groups of organics, were biodegraded. Unfortunately, this deficiency is common to all pilot plant studies of GAC in which microbial activity is of interest. Nevertheless, the Bremen study provides insight into overall efficiency of the process.

Removal of $KMnO_4$ in a pilot plant GAC bed is compared with that in the full-scale slow sand filter in Figure 2. As expected, the performance of the GAC bed was superior during the first 5 months because of adsorption. However, in the remaining months, both systems produced the same removal, suggesting that microbial activity was responsible. Although it is difficult to state the exact contact time in each system, that of the slow sand filter is on the order of several hours, while that of the GAC bed is between 15 and 30 minutes. Based on this rough comparison, GAC seemed to provide more efficient biodegradation.

As shown in Figure 3, oxygen consumption was much higher in summer than in winter months; yet nitrification, which accounts for significant oxygen consumption, was nearly absent in summer but in evidence in winter. The fact that oxygen consumption remained high in summer was explained by not only more active

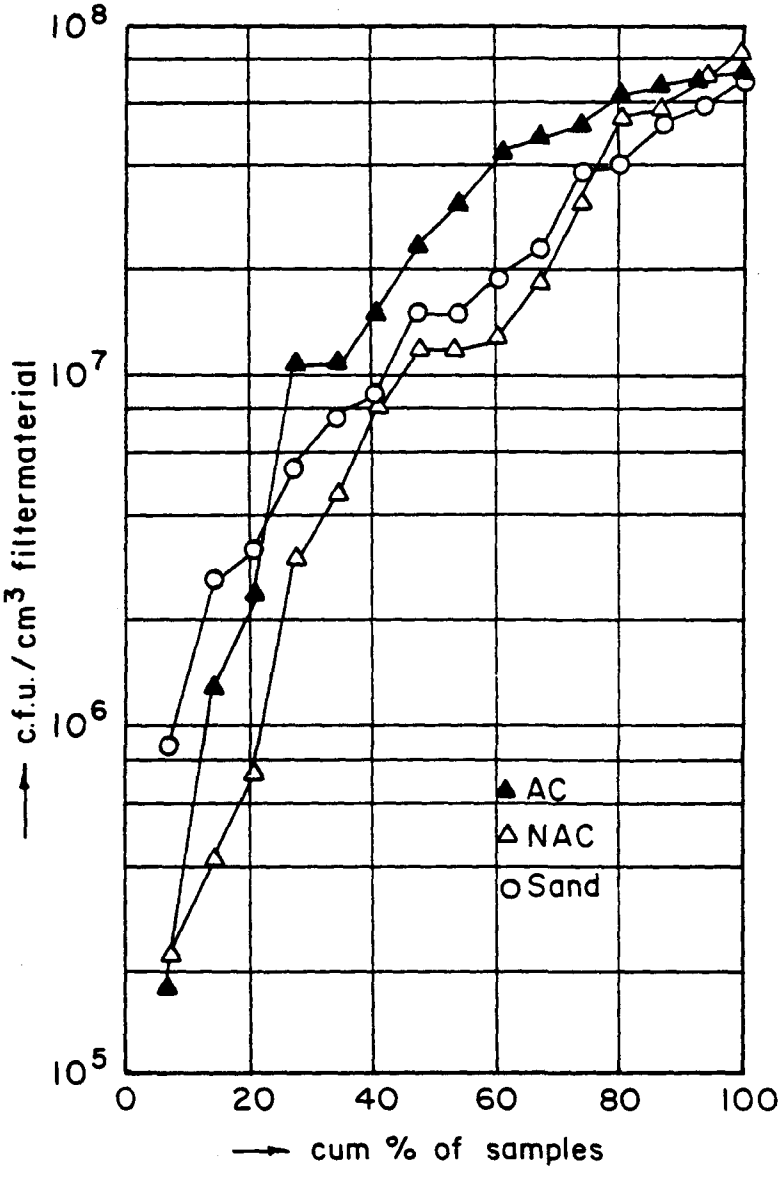

Figure 1. Comparison of adsorption of colony forming units (c.f.u.) on activated carbon (AC), non-activated carbon (NAC) and sand in filter columns (diameter of 6 cm) operated for one year. Filter columns were supplied with nonchlorinated tap water having an organic carbon concentration of 3 mg/l. Incubation of plates used for counting c.f.u. was at 25°C for 10 days. From van der Kooij. (11)

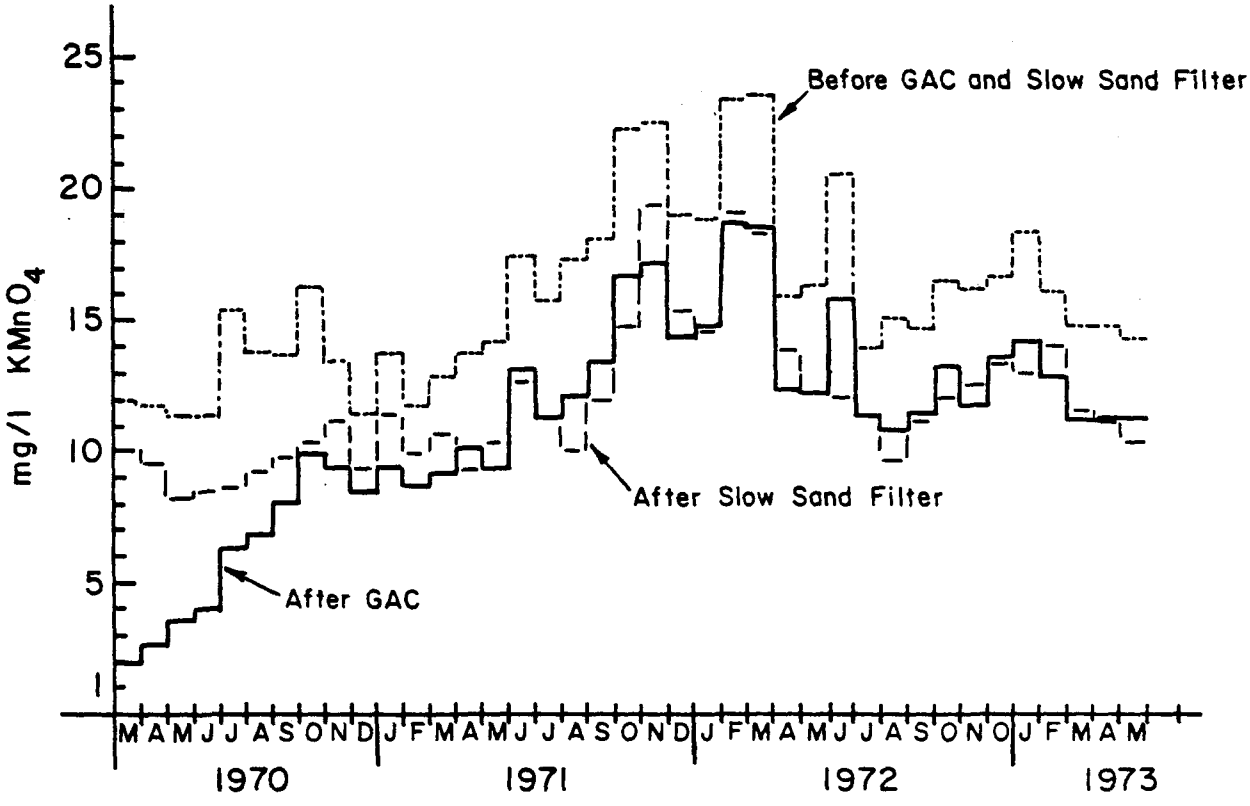

Figure 2. Comparison of removal of $KMnO_4$ demand by slow sand filters operating at Bremen and by pilot plant scale GAC beds (diameter of 14 cm and depth of 3 m). Influent to both the slow sand filter and GAC beds is product water of full-scale rapid sand filters. Contact time of GAC beds is between 15 and 30 minutes. From Eberhardt, et al. (3)

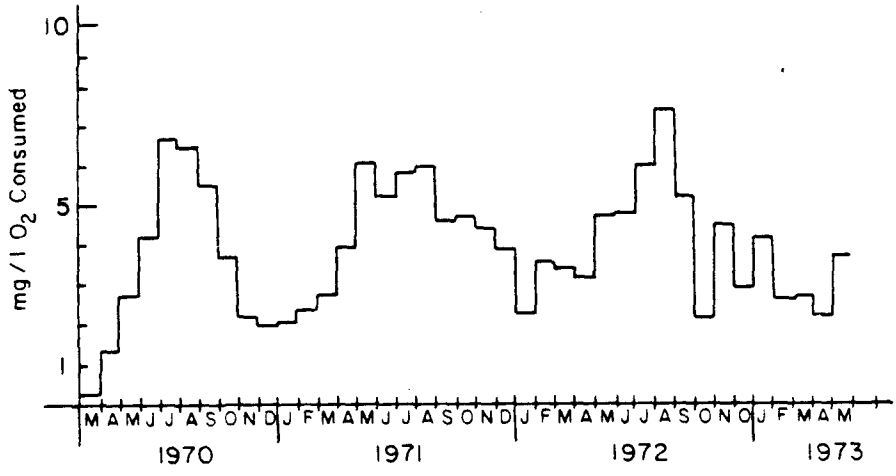

Figure 3. Oxygen consumed (uptake) during passage through pilot plant-scale GAC beds at Bremen. From Eberhardt, et al. (3)

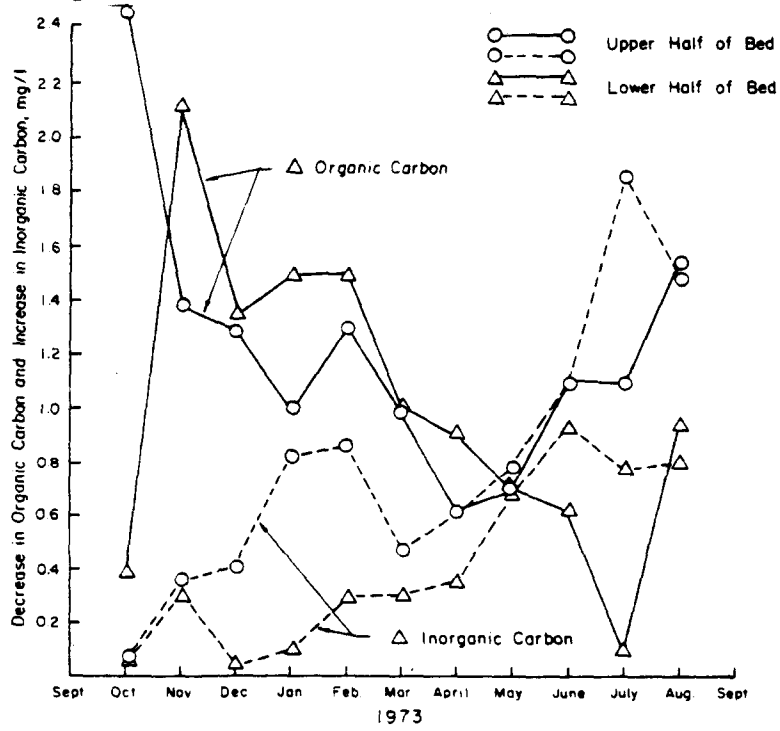

Figure 4. Comparison of decrease in organic carbon with increase in inorganic carbon in the upper and lower halves of pilot plant-scale GAC beds at Bremen. Carbon type is LSS with particle diameter of 0.5-1 mm. Total bed depth is 6 m and total contact time is about 36 minutes (assuming velocity of 10 m/hr. Data was derived from Table 21 of Eberhardt, et. al.[3]

biodegradation of organics at higher temperatures, but also by bioregeneration of adsorbed organics. In fact, inorganic carbon production (as measured by carbon dioxide) was much greater in summer than in winter, thereby supporting the bioregeneration concept.

The interplay between adsorption and biodegradation is clearly seen in Figure 4. Here, the reduction in organic carbon and the production of inorganic carbon are shown for the upper one-half and lower one-half of a GAC contact system at the Bremen pilot plant. Organic carbon removal decreased in the upper half as adsorption capacity became exhausted. However, microbial activity then began to predominate, as indicated by increased production of inorganic carbon. Bioregeneration was suggested in one summer month when the increment in inorganic carbon exceeded the decrease in organic carbon. Both adsorption and biodegradation processes in the lower half of the contactor lagged that of the upper half. This lag is understandable from adsorption principles; i.e., adorption capacity must first be exhausted in the upper half before substrate becomes available for microbial growth in the lower half of the bed.

The extent of bioregeneration was also examined by recycling water through a GAC bed. In two months of testing, a steady state production of carbon dioxide was reached which could be expressed as a bioregeneration rate of 57 g carbon per m^3 of GAC per day. Given the typical sorptive capacity of GAC, it was estimated that complete in situ bio-regeneration could be achieved in 6 months.

Another indirect indication of bioregeneration in the pilot plant operation was obtained from dioxane and dimethylformamide extractions of sorbed organics. The total amount of organic carbon extracted was stated to be far less than that adsorbed by GAC, based upon measurements of organic carbon in the feed and product streams of the GAC bed. It was concluded that sorbed organics were being biodegraded; however, the accuracy of the extraction procedures and the overall mass balance on sorbed organics was not discussed.

Based upon all the pilot plant testing at Bremen, it was concluded that a steady state removal of about 2 mg/l TOC could be obtained in a GAC contact time of 30 minutes. This is equivalent to a biodegradation rate of 4 g TOC per m^3 GAC per hour. However, it must be noted that this rate was only approached when a very highly activated carbon (LS-supra) was used; other carbon types gave values on the order of 2 g TOC per m^3 GAC per hour which means that in a contact time of 30 mintues, only 1 mg/l TOC can be removed. Hence, by comparison to adsorption, the process of microbial degradation on GAC is relatively inefficient. Nevertheless, attainment of a steady-state removal offers a unique advantage over adsorption. The important question left

unanswered by this study is: which specific organics can be removed during steady-state operation?

POSSIBLE EXPLANATIONS FOR ENHANCED MICROBIAL ACTIVITY

Whether or not GAC supports a higher rate of biodegradation than sand or non-activated carbon has not been proven in a rigorous fashion. However, in their study, Ying and Weber (6) proposed three possible explanations for advantages offered by GAC: enrichment of oxygen by sorption; enrichment of substrate in the biofilm; and extended adsorption due to bioregeneration and development of bioforms which can degrade less biodegradable, but adsorbable, organics.

Although as much as 19 mg oxygen per g GAC can be adsorbed (13), its availability to the biofilm is questionable if irreversible chemi-sorption occurs; this form of adsorption is supported by a well established body of literature (14). Conceivably, chemisorption of oxygen could still be important if it provides a driving force for transport of oxygen across the biofilm, in which case aerobic biodegradation can be assured. However, this seems unimportant in water treatment applications of GAC where oxygen concentration is high enough in the bulk solution phase and biofilm thickness is not large.

With respect to the second explanation offered, substrate enrichment in the biofilm seems likely. This may depend, however, on the substrate concentration in the bulk solution phase and on the ability of substrates to adsorb to the biofilm layer itself.

The third explanation, that of bio-regeneration, is probably the most controversial. Because microorganisms have a diameter of about 1 μm, they are too large to enter the micropores which have diameters of 1 nm to 100 nm. However, extracellular enzymes would be able to reach substrate otherwise considered inaccessible; it has also been shown that these enzymes can biodegrade high molecular weight organics (15). Proof of their importance has been offered in studies of attachment of film-forming marine bacteria to surfaces; 23 extracellular and intracellular enzymes were found (16).

There is also evidence which argues against bio-regeneration. For example, in pilot plant studies at the Morsang water works in France, Benedek (4) withdrew carbon particles from a microbially active GAC bed and attempted to adsorb more organics. The fact that no further adsorption was possible argued against bioregeneration. In another pilot plant study, van der Kooij (11) reported that the majority of microorganisms isolated from a GAC bed were able to grow on simple, non-adsorbing substrates but not on adsorbable aromatic compounds. However, the data offered to support this argument were not conclusive.

Thus, aside from evidence provided by the Bremen study and highlighted herein, there is a lack of data, either from laboratory or pilot plant studies, to support or refute the hypothesis of bioregeneration. If bio-regeneration is unimportant, then extended service time of GAC beds can only be explained by removal of biodegradable, weakly adsorbable organics. Should this be the case, then other organics, perhaps of more health concern, will escape the bed during extended operation.

EFFECT OF PRE-OZONATION

In some discussions of the so-called biological activated carbon (BAC) process, pre-ozonation has been proposed as a prerequisite for enhanced microbial activity on GAC (1,3). The crux of the argument is that organics are made more biodegradable by ozonation. However, there is little direct evidence to support this contention, and in fact, a study showing the positive effects of pre-ozonation in wastewater treatment at the Cleveland Westerly plant drew open criticism in the literature (17, 18, 19). In two other pilot plant studies of wastewater pre-ozonation at Water Factory 21 and Lake Tahoe, some improvement in GAC performance was measured, but it could not be traced to enhanced biodegradation (20). At the Morsang water works, pilot plant operation of pre- and post-ozonation produced almost equivalent water quality (4). Only a small increase in oxygen uptake and organic carbon removal was noted through GAC in the pre-ozonation system. In this case, however, it was reasoned that pre-chlorination probably produced organics which were less biodegradable even when ozonation was used. On the positive side, extensive pilot and full-scale testing of pre-ozonation at the Mülheim water works gave substantial improvement in final water quality (21). However, whether or not this involved enhanced microbial activity needs further discussion.

The Bremen pilot plant study (3) preceded that at Mülheim (21) and offers an interesting insight into the effect of ozone dosage on organic removals in the ozone contactor and in the GAC bed. Table 1 shows these removals and that achieved through parallel full-scale operation of slow sand filters without pre-ozonation. By itself, GAC contact did not produce as much removal as slow sand filtration. However, when taken together with the ozonation step, total removal exceeded that of slow sand filtration, except at the lowest ozone dosage of 2.3 mg/l. This suggests that when evaluating the effect of ozonation, both oxidation and adsorption steps should be considered separately. Although not directly proven, it appeared that increasing the GAC contact time increased organic removal by microbial activity. For comparison, it should be noted that organic carbon removal by GAC with pre-ozonation was estimated (by means of a correlation of UV absorbance with TOC) as 1.9 mg/l; this is not significantly greater than that found in the Bremen studies without ozonation.

Table 1. Summary of Results of Pre-ozonation in Pilot Plant Studies at Bremen

Ozone Dosage mg/l	Period of Testing weeks	Δ $KMnO_4$ Demand by Ozonation mg/l	Δ $KMnO_4$ Demand by GAC mg/l	GAC Contact Time min	Δ $KMnO_4$ Demand by Slow Sand Filtration without Pre-ozonation mg/l
2.3	6	-1.7	-0.4	14	-3.5
8.5-10	3	-3.6	-1.7	15	-3.8
5.8	4	-3.2	-2.3	17	-3.6
4.3	9	-2.5	-2.2	30	-3.3
4.8	4	-2.5	-2.9	30	-1.9

NOTE: Table 1 is a summary of results originally presented in Tables 6, 7, 8, 9, and 10 of reference 3. The pilot plant process scheme consisted of ozonation and GAC contact. Slow sand filters in the full-scale plant were operated as controls in parallel with the ozonation-GAC pilot plants. Influent to both the pilot and full-scale units was from the full-scale rapid sand filter.

Table 2. Performance of Pilot Plant GAC Beds at Mülheim with Pre-ozonation

Activated Carbon	Δ DOC mg/l	Δ Inorganic Carbon mg/l	Δ NH_4-N mg/l	Δ O2 mg/l
LSS 2.5 m	-0.92	+0.83	-1.31	-6.32
LSS 5.0 m	-1.69	+0.96	-1.34	-6.67

Source: Reference 21

NOTE: LSS is a carbon manufactured by the Lurgi Company. Values of Δ refer to changes in the first 2.5 m and in the total depth of 5 m, respectively. Data are mean values for a 6-month operation after a 3-month starting period. Contact time in each bed segment is 15 minutes.

Much lower ozone dosages were tried at the Mülheim water works (about 2 mg/l) and performance improved. However, it is important to recognize that the treatment process change at Mülheim included elimination of pre-chlorination. In a parallel study of pre-ozonation with and without pre-chlorination, extended organic removal on GAC occurred only in the latter process stream. This implies that chlorination produces less biodegradable organics or otherwise inhibits microbial activity. Another important observation was the noticeable improvement in organic removal which was brought about by ozone addition prior to flocculation. This no doubt contributed to extended GAC service time.

The positive effect of ozonation on flocculation, together with elimination of a negative effect on GAC performance (i.e., the elimination of pre-chlorination) may leave unanswered the question of whether or not pre-ozonation enhances microbial activity, per se. If the removal of organic carbon through GAC contact is compared in the Mülheim (Table 2) and Bremen studies (Figure 4), the latter obtained without pre-ozonation, it is difficult to conclude that pre-ozonation actually improved biodegradability. Table 2 shows that most of the microbial activity was found in the upper 2.5 m after a contact time of 15 minutes; the amount of inorganic carbon produced is similar to that shown in Figure 4 at Bremen. As is also evident from Table 2, nitrification is a very important process at Mülheim. From stoichiometry, 4.6 mg of oxygen are required to oxidize 1 mg of ammonia nitrogen to nitrate. Accordingly, nearly all of the oxygen depletion shown in Table 2 can be accounted for by nitrification; in fact, some production of carbon dioxide must also be attributed to this process. Hence, any conclusions regarding the extent of carbonaceous bio-oxidation and bio-regeneration should be made cautiously.

Pre-ozonation was shown to improve the removal of precursors to trihalomethane formation, as measured by the trihalomethane formation in pilot plant studies conducted by the U.S. EPA in Cincinnati, Ohio (22). The effect of ozone was to oxidize these precursors, which are most likely of humic origin: the resulting products were either more readily adsorbed or biodegraded on GAC. An additional indicator of improved performance was better removal of TOC. These results were obtained with an ozone dose of 1 mg/l and a GAC contact time of 9 minutes. While effluent TOC concentrations increased steadily in both the ozonated and non-ozonated systems, complete breakthrough was not reached in either system during 10 months of operation. Thus, microbial degradation was probably occurring in both systems. However, pre-ozonation gave better performance.

The potential detrimental effect of ozonation on adsorbability of organics must also be considered. Figures 5 and 6 are taken from two independent studies that showed this effect

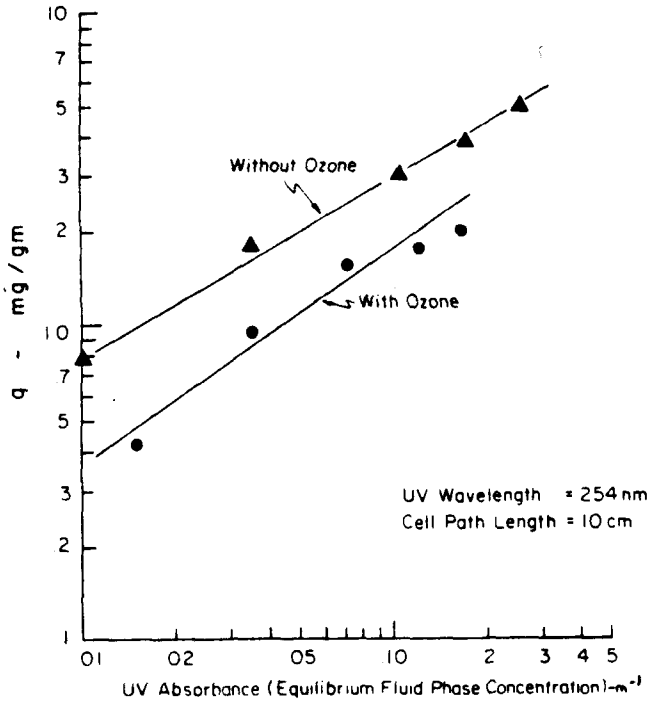

Figure 5. Effect of ozonation on equilibrium adsorption of organics as measured by UV absorbance. Data taken during pilot plant-scale operation of GAC beds at the Morsang Water Works in France. From Benedek (4).

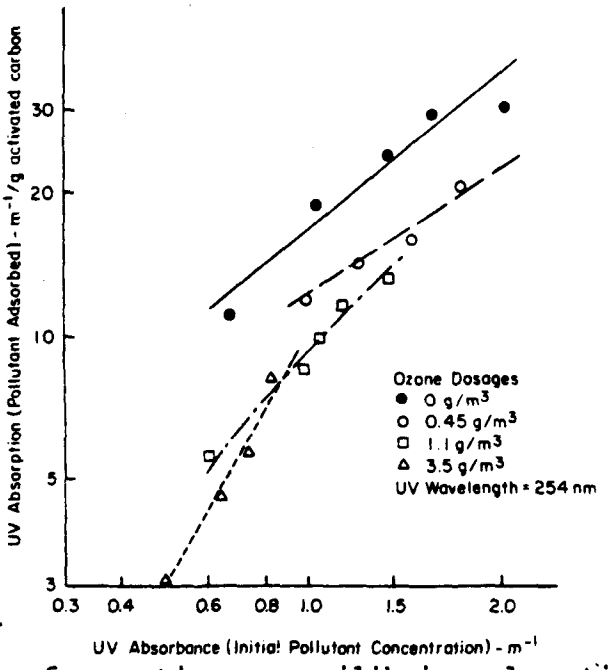

Figure 6. Effect of ozonation on equilibrium adsorption of organics as measured by UV absorbance. Abscissa values represent initial rather than equilibrium concentrations of UV absorbing organics. Absorbance values are calculated for an equivalent cell path length of 1 meter. Data taken in laboratory test with pre-filtered Lake of Constance water. From Kühn, et al. (23)

at dosages as low as 0.45 mg/l (4,23). Decreased adsorbability may reasonably be expected because ozone tends to give more polar organics such as carboxylic acids, catechols, and aldehydes that are characteristically more weakly adsorbed. Any potential, though as yet unproven, increase in biodegradability must, therefore, be weighed against decreased adsorbability. Benedek (4) accounted for both effects in predicting the performance of GAC adsorbers at Morsang. Because this study revealed little increase in biodegradability, the mathematical model predicted that ozonation would only be beneficial if extremely long service times could be used (on the order of 2 years) such that full advantage was taken of microbial activity; otherwise, the decrease in adsorbability was the overwhelming effect.

PREDICTING THE INTERACTION BETWEEN BIODEGRADATION AND ADSORPTION

The objective of developing a predictive, mathematical model which accounts for microbial activity on GAC, is ultimately to provide a more sound basis for design and operation of GAC beds. Clearly, the classical pattern of organic carbon breakthrough caused by exhaustion of sorption capacity will be altered by microbial degradation of organics. Simplifications are needed in the mathematical representation of the adsorption process (e.g., competitive adsorption is often ignored) in order to provide a more useable tool. Simplifications will be even more important when attempting to "overlay" the effects of microbial activity.

Available models use the simple, and perhaps unrealistic, assumption that all organics in a complex mixture are biodegradable. Figure 7 shows the resulting general shapes of concentration gradients in the outer biofilm, the internal pores, and the sorbed phase of a carbon particle. At time t_1, the biofilm has not developed and therefore adsorption predominates. Growth of the biofilm depends upon microbial kinetics in response only to the substrate available external to the carbon particle. At a later time, t_2, biodegradation in the biofilm accounts for most of the substrate removal and the adsorption capacity becomes dependent on the concentration at the innermost boundary of the biofilm, C_i, rather than upon the external concentration, C_c.

Important characteristics for three available mathematic models (4,5,6) all of which consider organics to be biodegradable and adsorbable, are presented in Table 3. These models differ in description of microbial kinetics, mass transfer, and adsorption equilibria. However, all yield the same general pattern of organic component concentration leaving the GAC bed with service time. Unfortunately, very few comparisons are available between predictions and experimental data. Of particular concern is the lack of verification for organics which are strongly adsorbed and also biodegradable. This may be because such organics are not easily found. If such compounds are rare, then the interaction between adsorption and biodegradation may be less important than the

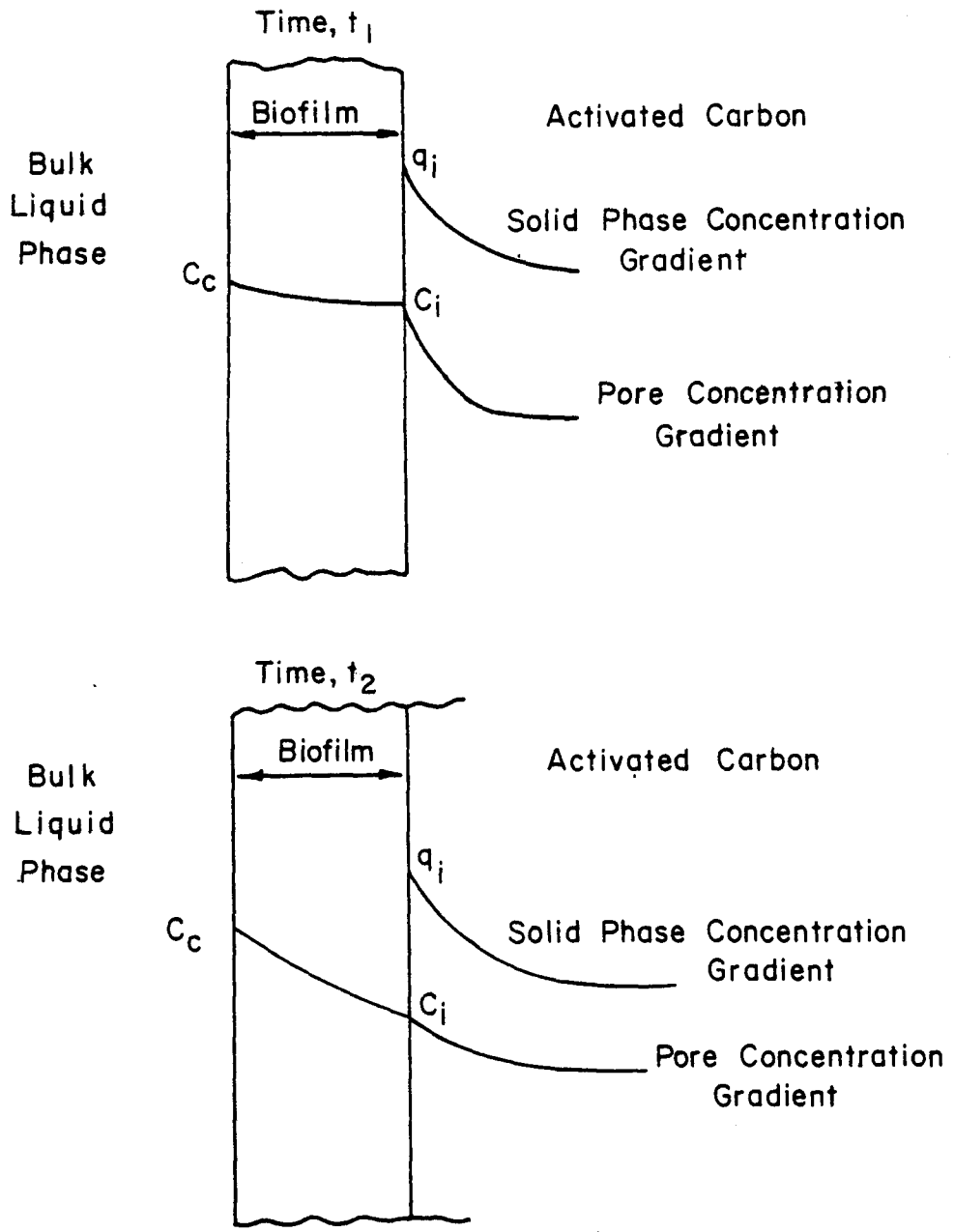

Figure 7. Hypothetical concentration gradients existing in biofilm and solid phase media when biodegradation and adsorption occur simultaneously. At time t_1, the biofilm is not well developed and adsorption predominates. At time t_2, the biofilm is developed and biodegradation predominates.

Table 3. Characteristics of Three Available Mathematical Models Describing the Interaction Between Biodegradation and Adsorption

	Benedek (4)	Tien (5)	Ying & Weber (6)
Biofilm Thickness	Fixed	Variable	Variable
Biofilm Kinetics	Zero-order	First-order[a]	Non-Linear, Monod
Mass Transfer			
External Film	Yes	No	Yes
Diffusion through Biofilm	Yes, Pseudo Steady State	Yes, Pseudo Steady State	No
Internal Diffusion	Linear Driving Force[b]	Linear Driving Force[b]	Surface Diffusion[c]
Adsorption Equilibrium Model	Freundlich[d]	Linear	Freundlich
Reactor Description	Plug Flow, Stationary Bed	Plug Flow, Variable Bed Depth[e]	Plug Flow-Stationary & Completely Mixed Bed[f] Dispersive Flow-Stationary & Completely Mixed Bed[f]
Verification of Model	Pilot Plant TOC	None Available	Laboratory Scale-Glucose & Sucrose[g]

NOTES:

a. Non-linear Monod kinetics approximated by linear function.
b. Gleukhauf's linear diffusional driving force model.
c. Complete profile of solid phase concentration developed by finite difference technique.
d. Earlier model by Benedek considered production of adsorbable, non-biodegradable organics by microbial activity as a species competing for adsorption sites but no details were given.[24]
e. Bed depth increases as a result of expansion of bed by growth of biofilm.
f. Two different reactor models were developed.
g. Verification for laboratory data on strongly adsorbable, weakly biodegradable organics (toluene sulfonate and potassium biphthalate) was not given.

uncoupled removal of biodegradable organics by the biofilm and non-biodegradable organics by adsorption at internal sites. Such a conclusion, however, is premature.

The nature of mathematical predictions is best illustrated by the results given by Ying and Weber (6) for the two extreme cases of strongly and weakly adsorbed organics. Figure 8 shows the importance of adsorption in the initial stage of operation and microbial activity in the later stage. The level of steady-state removal of organics depends upon the assumed microbial kinetics, as seen in Figure 9. Unfortunately, there is a paucity of information on the GAC system in this regard. In fact, the initial concentration of attached biomass is also unknown and this parameter greatly influences the shape of the breakthrough curve.

Two alternative models, which would be more complex but perhaps more realistic, are proposed here. In one model, two categories of organics—biodegradable and non-biodegradable—are considered. As an added complication, the second model would include the availability of substrate from internal sorption sites as well as from the external, bulk solution; in this case, the effect of bioregeneration is accounted for. Tien (5) has indicated research progress on the first of these models, but specifics are unavailable. An earlier model by Peel and Benedek (24) also considered the production of non-biodegradables by bacterial action and these were then assumed to adsorb in competition with biodegradable organics; however, details were not provided and later work (4) considered all organics as biodegradable. In both models, gradients may be very complex and even reverse in direction as service time increases. This may be caused by competitive adsorption between the biodegradable and non-biodegradable fractions and by intermittent decreases in sorptive loading as a result of bioregeneration.

CONCLUSIONS

The development of microbial activity on GAC is a natural consequence of treating water containing biodegradable organics. This effect has been observed in pilot and full-scale studies in Europe, where limited data are available concerning the overall rate of biodegradation and the contact time required. However, many questions remain unanswered. Among these are: Which organics are removed by microbial activity? How can bacterial attachment be optimized? How important is bio-regeneration of sorption sites as compared with biodegradation of externally available substrate? Does pre-ozonation increase the biodegradability of organics or does it simply improve the treatment process prior to GAC? Can mathematical models account for the interaction between microbial activity and adsorption in a realistic, yet practical manner?

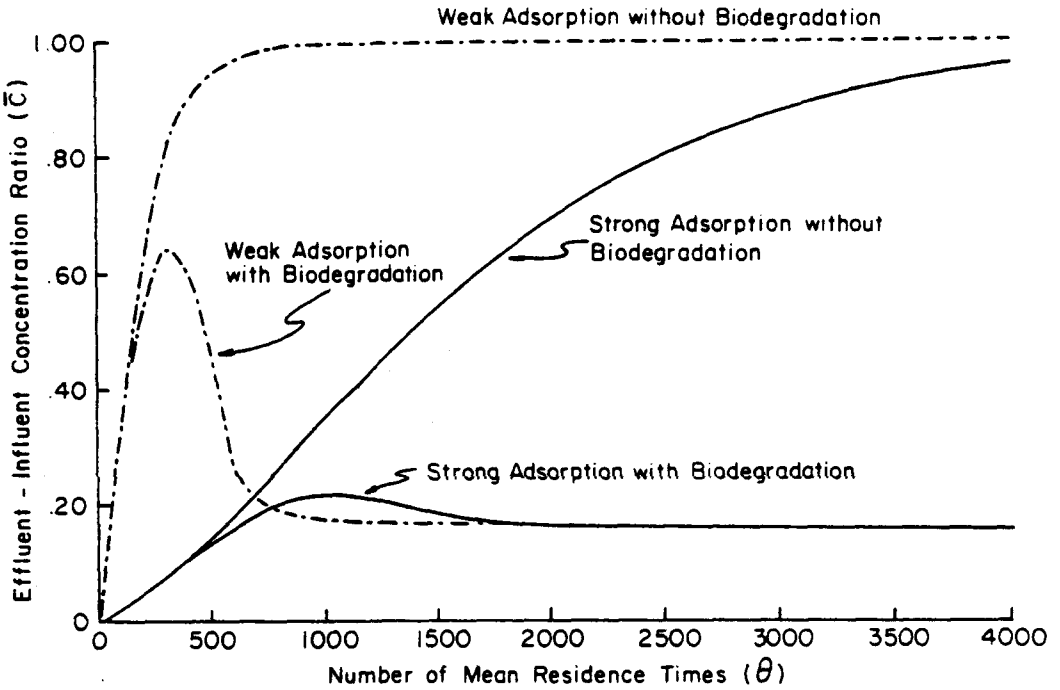

Figure 8. Predicted effluent concentration as a function of service time with the GAC bed behaving as a stationary phase and with plug flow in the liquied phase. The effect of biodegradation on removal of both weakly and strongly adsorbable organics is shown. From Ying and Weber (6).

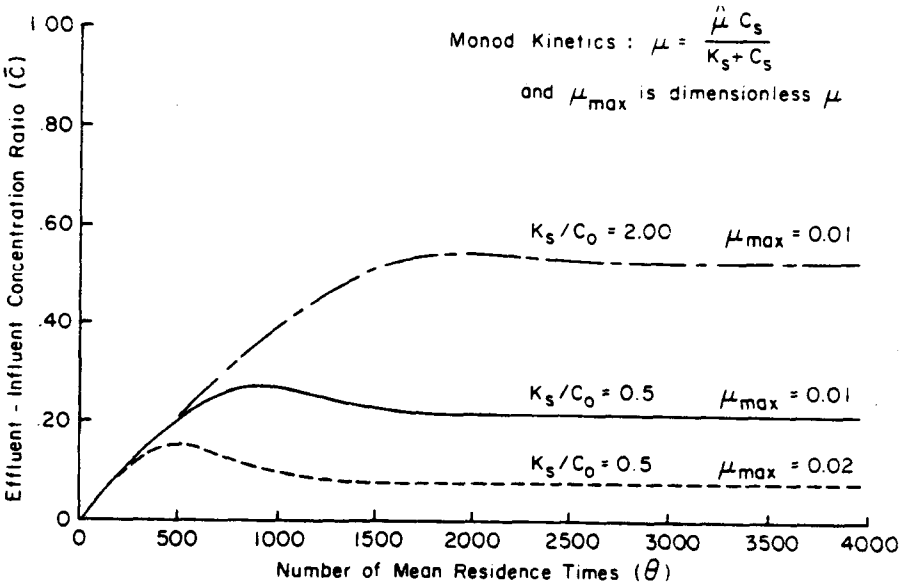

Figure 9. Predicted effluent concentration as a function of service time with the GAC bed behaving as a stationary phase and with dispersive flow in the liquid phase. The effect of bacterial growth kinetics on removal of a strongly adsorbed organic is shown. Decreasing the half-saturation constant, K_S, or increasing the maximum specific growth rate constant, μ_{max}, decreases the steady-state effluent concentration. From Ying and Weber (6).

This paper has intentionally avoided the issue of whether or not microbial activity on GAC can facilitate meeting the proposed new U.S. EPA regulations (Federal Register of February 9, 1978) regarding control of trace organics. It would be speculative to address that question, because not much is known about the biodegradability of chlorinated organics in extremely low concentrations. One possible mode by which microbial activity could extend GAC service time is by removing otherwise adsorbable organics, thereby lessening the competition for adsorption sites and enhancing the removal of those less biodegradable organics. However, the range of adsorbability and biodegradability of organics present in drinking water sources first must be investigated more carefully.

The general tenor of this paper has been to raise more questions than are answerable at present. Clearly, before design recommendations can be made, far more research under controlled conditions must accompany pilot and full-scale tests in order to achieve a better understanding of the influence of microbial activity on GAC performance.

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CONSIDERATIONS IN THE SEQUENCING OF CHEMICAL OXIDATION AND ACTIVATED CARBON ADSORPTION

A. Benedek

INTRODUCTION

Chemical oxidation and adsorption are the two primary methods of organic removal in current water treatment practice. More specifically, in many newer plants, the flow scheme incorporates an ozonation step followed by a granular activated carbon adsorption step. It is difficult to predict, on a theoretical basis, whether the combination of ozonation followed by activated carbon adsorption is indeed the optimum way of combining these two methods.

The advantages and disadvantages of ozonation prior to activated carbon contacting have been recently reviewed by Benedek (1979). He listed the advantages of pre-ozonation as: precipitation and subsequent removal by filtration of reduced iron and manganese ions when present, and increased organic removal and activated carbon run length due to the increased biodegradability of ozonated organics (assuming that biodegradable organics are removed by biodegradation and not adsorption in granular activated carbon contactors).

The disadvantages of pre-ozonation are as follows: lower adsorptivity on activated carbon of ozonated molecules; loss of adsorptive capacity due to the effect of residual ozone on activated carbon surface; and potential problems with bacterial slugs in the activated carbon contactor effluent due to the bacterial growth promoted by pre-ozonation.

The combination of granular activated carbon treatment followed by ozonation would eliminate all of the above noted disadvantages of pre-ozonation and, furthermore, would ensure disinfection of the activated carbon effluent. On the other hand, it would not aid biological activity in the contactor and may precipitate inorganic hydroxides at a stage in the process where no further filtration is likely to occur.

In the case of groundwater or bank-filtered water, the precipitation of iron and manganese is an important requirement in the treatment. Thus, in the Federal Republic of Germany, where

bank filtration is a common method of pretreatment, the combination of ozonation followed by activated carbon adsorption is the accepted treatment combination. In France, on the other hand, surface waters are commonly pretreated by coagulation and sedimentation similar to the common North American practice. In such cases, the choice between pre-ozonation and post-ozonation is much more complex. furthermore, pretreatment requirements such as prechlorination also become important variables

THE WATER TREATMENT PLANT AT MORSANG-SUR-SEINE, FRANCE

Motivation for Pilot Studies

In recognition of the above factors, the operators of the Morsang-sur-Seine, France, water treatment plant, the Societe Lyonnaise des Eaux et de L'Éclairage (SLEE), in conjunction with the designers of the plant (the Degrémont Company), decided to undertake long term studies on the optimum combination of ozonation and activated carbon adsorption. As shown in Figure 1, four parallel treatment sequences are operated at this plant. These four processes are chosen in such a way that they enable an evaluation of the relative cost of powdered versus granular carbon, the relative merits of pre-ozonation versus post-ozonation, and the effect of prechlorination.

The first three sequences are full scale operations and have been operated in the indicated mode over the last three years. The fourth sequence has been started up in late 1977 and, therefore, has only little over one year of operational data at the time of writing.

An initial summary of operating results has been presented by Richard and Fiessinger (1977). Subsequently, the author spent some time in France working with Messrs. Richard and Fiessinger on a mechanistic study of activated carbon contactor behavior of treatment sequences 2 and 3. The results of this work are described in detail by Benedek (1979). This paper serves to review previous work, update the earlier data with more recent results (particularly in connection with the fourth treatment sequence), and to recommend, on the basis of the Morsang results, the optimum combination of ozone and activated carbon contacting.

Description of Full-scale Treatment Plant

The Morsang plant draws its water from the Seine, about 30 km upstream (south) of Paris. At this point, the Seine is still free of most of the pollutants generated by human activities in and around Paris.

The plant is constructed in an aesthetically pleasing tri-pointed star (or winged) pattern (See Figure 2). The first "wing" of the plant was constructed in 1970 and has always been

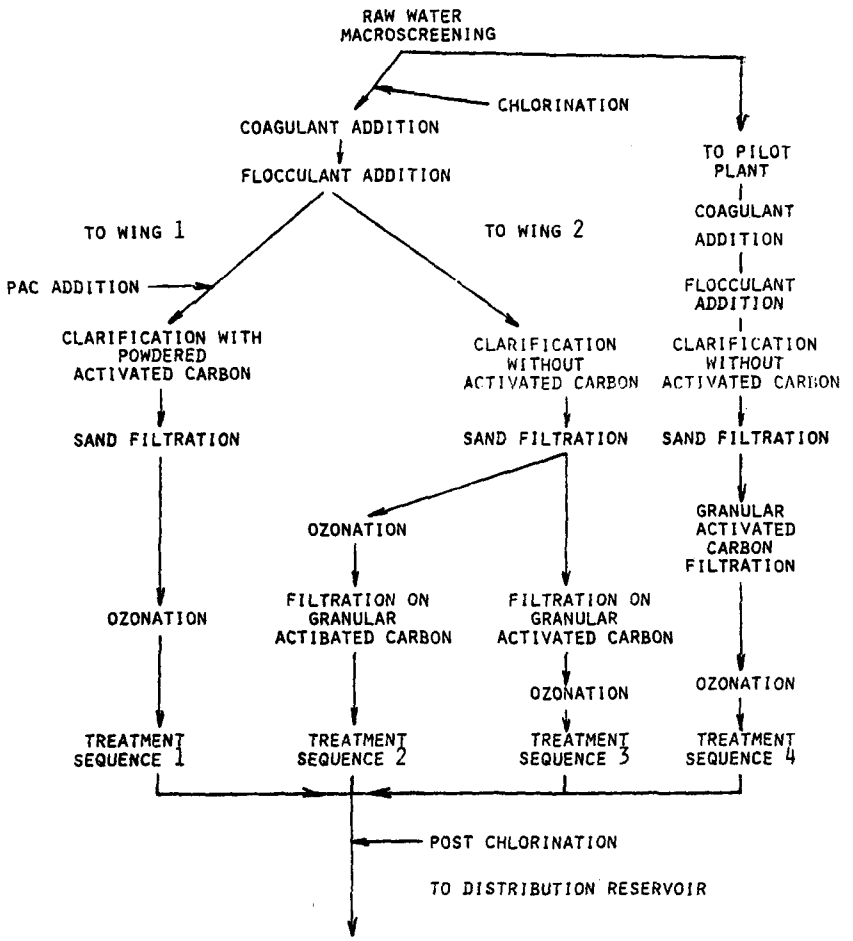

Figure 1. Treatment Schematics of the Morsang Water Treatment Plant

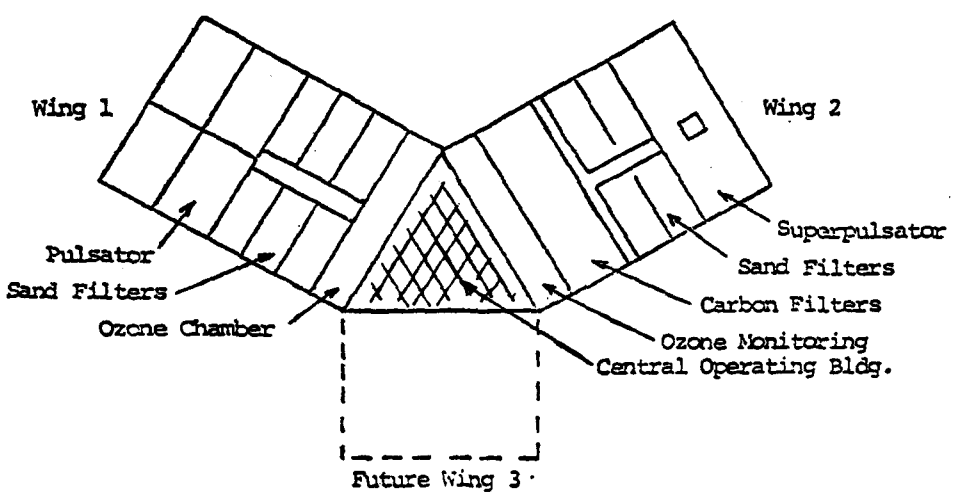

Figure 2. The Three-Pointed Star Layout of the Morsang-sur-Seine Plant

operated according to process sequence 1 in Figure 1. The second wing went on stream in October 1975. Initially, the entire wing was operated in process sequence 2 mode (see Figure 1); however, 6 months later, half of the wing was switched to process sequence 3. As already indicated, sequence 4 was started up in the fall of 1977. The various sequences are designed primarily to determine the optimum treatment sequence for the future wing 3, as well as a second future three-pointed star.

Wings 1 and 2 process an average of 40,000 m^3/d of water each. Thus, approximately 20,000 m^3/d of water is treated by processing sequence 2 and 20,000 m^3/d is treated by processing sequence 3. Processing sequence 4 treats only 5.2 m^3/d of water in separate pilot scale equipment.

The average chemical dosages at the plant during the past year are summarized in Table 1.

Table 1
Chemical Dosage at the Morsang Plant

Chemical	Use	Dose
Chlorine	Prechlorination	2.0 mg/l as Cl_2
Alum	Coagulation (with alum)	40 to 80 mg/l as $Al_2(SO_4)_3 18H_2O$
Activated Silica	Flocculant	2 mg/l as SiO_2
Powdered Activated Carbon (PAC)	Adsorbent	7 mg/l
Ozone	Chemical oxidation	to a residual of 0.4 mg/l (typically the applied dosage is 1.2 mg/l).

The ozone is provided by the 6.6 kg/h electric discharge units (Degrémont Company). A contact time of 10 minutes is provided for ozonation.

Full scale activated carbon contacting is accomplished in Degrémont Model T Aquazur filters. These filters are specially modified to allow air/water backwash of the 1.3 m deep layer of granular activated carbon (GAC). The 34 tons of activated carbon placed in each filter is type F400 (Chemviron Ltd., Brussels,

Belgium). The average superficial contact time in these filters is 16 minutes at a feed velocity of 5 m/h.

The pilot scale activated carbon contactor contains 26.8 kg of F400 activated carbon. The pilot plant operating conditions are similar to those of the full-scale contactors (superficial contact time of 17 minutes at a feed velocity of 4.5 m/h).

DATA COLLECTION AND ANALYSIS

Water samples have been collected on a monthly basis since 1975, after each contacting mode. On each of these samples, water quality analyses have been done in the laboratories of the Degrémont Company, Rueil, France, and/or in the laboratories of SLEE at Le Pecq, France. Activated carbon samples were usually removed from the filters by direct insertion of a cup sampler. Four separate analyses were used to determine the organic level, namely ultraviolet absorbance, chemical oxygen demand (COD), total organic carbon (TOC), and threshold odor number (TON). Ultraviolet adsorbance was determined at 253.7 nm wavelength in a 10 cm cell using a Beckman Acta III spectrophotometer. COD was measured by $KMnO_4$ titration in acidic medium, and TOC was measured by a TOCSIN analyzer (manufactured by Phase Separation Ltd., United Kingdom). TON was determined by successive dilutions of the original sample until taste of any kind disappeared. The required number of times the original sample is diluted is then expressed as the TON. Additional experimental details are available in the articles by Richard and Fiessinger (1977), and Benedek (1979).

ORGANIC REMOVAL RESULTS

Table 2 details the overall organic removal observed at this plant during the first 9 months of operation of the four parallel treatment sequences. As shown in Table 2, all four treatment sequences produced a high caliber water, low in taste and organic content as well as trihalomethanes. Treatment sequences 2 and 4, using pre-ozonation, produced the highest odor and collective organics parameter removal, with sequence 3 very close behind. The poorest quality water is produced by sequence 1 using PAC instead of GAC. The greatest overall organic removal was observed in sequence 4. The removal here, however, cannot be directly compared to other processes because the granular activated carbon in process sequences 2 and 3 has served over 2 years longer than the GAC in sequence 4. In terms of trihalomethanes, sequence 4, without prechlorination, produced the lowest level, as expected. The other three sequences averaged 27 $\pm$ 4 µg/l of trihalomethanes.

The removal of organics by the different processing steps in the four treatment sequences is summarized in Tables 3 and 4 for COD and TON, respectively. As shown in Table 3, the bulk of

Table 2. A Comparison of the Organic Removal Effectiveness of the Four Treatment Sequences

Parameter	Units	Raw Water	Sequences 1	2	3	4
TOC[a]	mg/l	3.0	1.32	1.12	1.15	0.95
Absorbance[b]	-	0.953	0.198	0.142	0.174	0.03
COD_{KMnO_4}	mg/l	3.80	1.6	1.23	1.26	0.68
TON[c]	-	12	2	ND[e]	1.5	ND[e]
Trihalomethanes[d]	µg/l	0.8	26	31	24	1

[a]TOC is total organic carbon

[b]Absorbance is ultraviolet absorbance determined at 253.7 nm wavelength in a 10 cm long cell.

[c]TON is threshold odor number

[d]Trihalomethanes is essentially the chloroform level in this plant.

[e]ND means not detected, i.e., in the case of TON, ND implies a lack of odour in the undiluted sample.

the organic substances are removed in the processing steps intended primarily for turbidity removal--coagulation, clarification, and sand filtration--and prechlorination (in sequences 1 to 3). Interestingly, the greatest COD removal during the turbidity removal steps occurs in sequence 4, possibly due to the fact that lack of prechlorination allowed some biological degradation to proceed during the process steps. Ozone appears to remove very little COD at the low applied dosages of this study. Granular activated carbon contacting also removes relatively little COD with the exception of sequence 4 where, as discussed earlier, the carbon has had a low service time.

In the case of odor removal (Table 4), once again the first four, primarily turbidity removal steps, are credited with eliminating the bulk of the odor in sequences 1 to 3. In sequence 4, the lack of prechlorination means that only 50 percent of the odor was eliminated by the first three steps. On the other hand, in sequence 4 ozonation more than makes up for the odor removed by break point chlorination in the other processing steps. Activated carbon plays an important role in taste removal as in

Table 3. Removal of COD_{KMnO_4} in mg/l Across Various Types of Process Steps in the Different Treatment Sequences

Process	Treatment Sequence			
	1	2	3	4
Coagulation, Clarification plus Sand Filtration	1.6*	1.44	1.43	2.0
Ozonation	-0.1	0.13	0.21	0.0
Carbon Adsorption	-	0.33	0.23	1.12

*Includes the effect of powdered carbon adsorption as well

Table 4. Reduction of Threshold Odor Number Across Various Types of Process Steps in the Different Treatment Sequences

Process	Treatment Sequence			
	1	2	3	4
Coagulation, Clarification plus Sand Filtration	9*†	8.5†	8.5†	6
Ozonation	1	0.5	-1.5	4
Carbon Adsorption	-	$\geq$3.	$\geq$3.5	$\geq$2

*Includes the effect of powdered carbon adsorption as well as prechlorination.

†Includes the effect of prechlorination

every case, after GAC contacting, the water became tasteless. Interestingly, ozone reintroduced some taste to the water in sequence 3.

On the whole, the above data indicate that sequences 2 and 4, employing pre-ozonation, seem to produce the best treated water quality, especially when odor removal is of key importance to consumer acceptance (as is the case for this particular plant).

ORGANIC REMOVAL MECHANISMS DURING CARBON CONTACTING

The mechanism of organic removal during carbon adsorption has been examined in detail by Benedek (1979) for this plant. The cumulative removal curves for the granular carbon contactors of sequences 2 and 3 are plotted in Figure 3. The slope of such cumulative plots is equal to the percent removal attained in the contactor. According to this figure, the pre-ozonated carbon contactor of sequence 2 removes slightly more than the post-ozonated carbon contactor of sequence 3.

As indicated in the introduction, ozonation is expected to decrease adsorptivity. This is clearly illustrated in Figure 4, where the isotherms of ozonated and non-ozonated water samples are compared. Thus, it can be hypothesized that biological, as well as adsorptive mechanisms, must be involved in the removal of organics in these contactors. A small program was subsequently undertaken to examine bacterial activity in the contactors. Figure 5 shows that high levels of viable cells were present in both contactors; however, the contactor treating ozonated water harbored nearly ten times as many bacteria. Interestingly, the highest bacterial levels were found near the surface of the contactors in spite of the fact that some residual bactericide (chlorine or ozone) may be present in the feed. This was explained in a recent review article by Benedek (1978) in terms of bacterial habitats having been established within the activated carbon macropores, wherein the bacteria were expected to be protected from chemical bactericides of an oxidizing nature.

Additional research described by Benedek (1979) indicates that bacterial respiration rates further confirm the viable cell bacterial distributions data of Figure 5. Thus, significantly higher oxygen uptake rates were observed in the preozonated contactor and the oxygen uptake rates generally declined with depth. On the basis of the data in Figures 3 to 5, bacterial oxidation is the most likely explanation for the operating results during the final straight line region of the results reported in Figure 3.

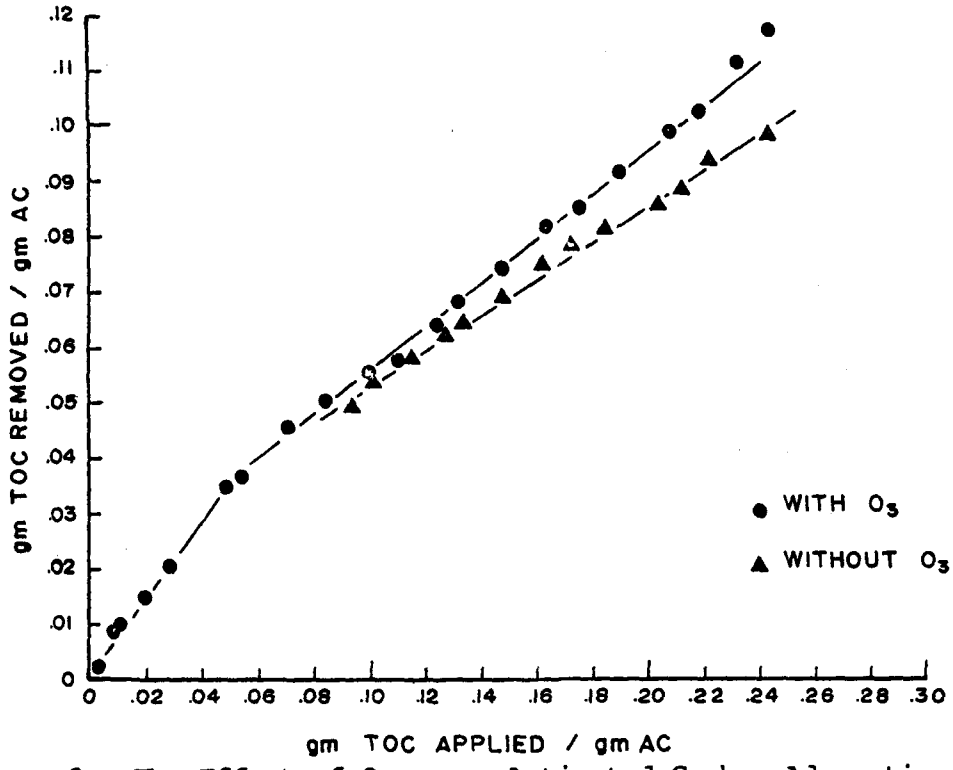

Figure 3. The Effect of Ozone on Activated Carbon Adsorption at Morsang-sur-Seine, France. (From Benedek, 1979.)

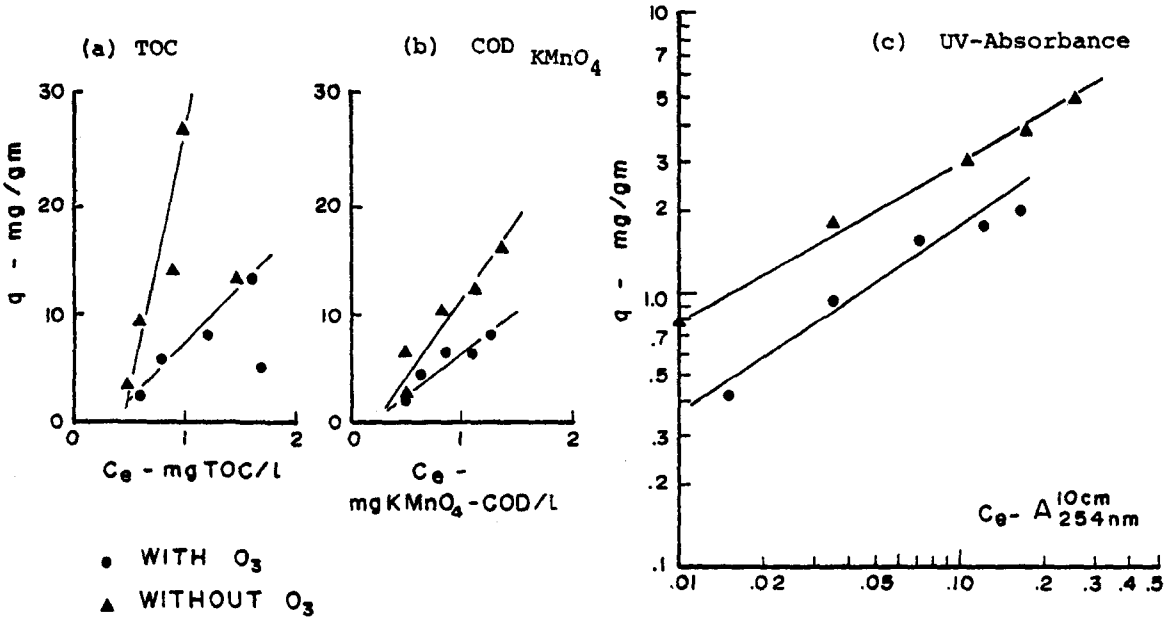

Figure 4. Morsang Isotherms in Terms of a) TOC, b) COD-$KMnO_4$ and c) UV Absorbance. (Q-Carbon Equilibrium Loading; C_E-Equilibrium Liquid Concentrations) (From Benedek, 1979).

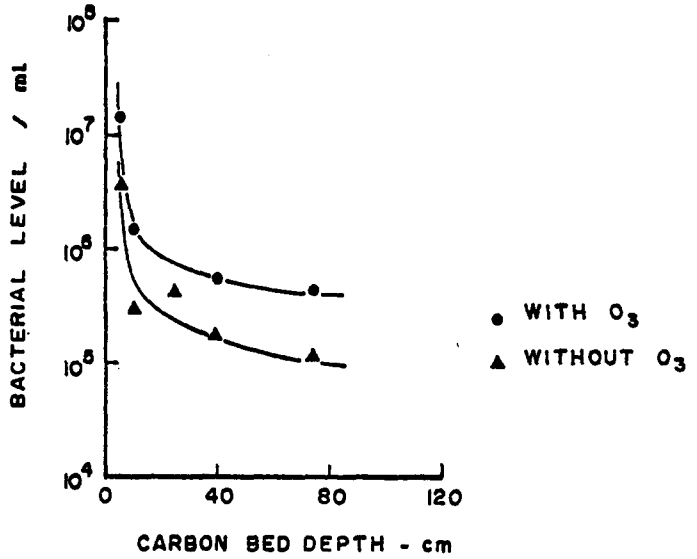

Figure 5. The Effect of Ozone on Bacterial Distributions in Activated Carbon Contactors Treating Prechlorinated, Coagulated, Settled and Prefiltered Seine Water. (From Benedek, 1979).

MATHEMATICAL MODELLING OF BIOLOGICALLY ACTIVE CARBON CONTACTORS

A biologically active carbon contactor can be modelled through the use of a differential mass balance in the column, whereby

$$v_s \frac{\partial c}{\partial z} - R_f\left(\frac{6}{d_p}\right)(1-\varepsilon) = (\varepsilon)\frac{\partial c}{\partial t} + \rho_o \frac{\partial \bar{q}}{\partial t} \qquad (1)$$

where R_f = biological reaction rate per unit surface area of the carbon particle

d_p = carbon particle diameter

ρ_o = mass of carbon per unit volume

$1-\varepsilon$ = volume fraction of carbon in contactor

v_s = superficial velocity

c = organic substrate concentration

z = contactor bed depth

$\bar{q}$ = average weight of substrate per weight of GAC in the carbon particle

The above mass balance is only applicable to thin biological films. In the case of water treatment plant contactors, the films are extremely thin, and the carbon surface is believed to

be only partially covered (Klotz, et al.). Thus, the effect of film thickness in changing particle size is neglected in equation 1 and the reaction rate is based purely on the external surface area of the carbon particles.

To solve the contactor mass balance, as outlined by Maqsood and Benedek (1977), additional equations, such as equilibrium and mass transfer kinetic expressions, are needed. The major experimental model inputs are: adsorption isotherm(s), batch adsorption kinetic data, and biological reaction rate (R_f).

For Morsang, the collection and evaluation of the input data was discussed by Benedek (1979). The value of R_f at Morsang, as obtained from the constant slope region of Figure 3, was evaluated to be 6.5×10^{-8} g TOC removed$\cdot$cm$^{-2}\cdot$hr^{-1} for non-ozonated water, versus 7.6×10^{-8} g TOC$\cdot$cm$^{-2}\cdot$hr^{-1} for ozonated water. The relative magnitude of this biological rate, as compared to other types of water, is revealed by an examination of Table 5. In general, the rates at Morsang are similar to other potable water treatment data, and water treatment contactor rates are generally well below the rates obtained with the more concentrated and degradable organics found in wastewater.

The operation of the non-ozonated (sequence 2) contactor can now be compared to that of the pre-ozonated contactor (sequence 3) through the model. As shown in Figure 6, the contactor without pre-ozonation initially removes a greater fraction of the applied organics. This greater removal primarily occurs in the range of 0.02 to 0.05 g applied TOC/g GAC, where adsorption continues to occur in the contactor without preozonation. Subsequently, however, the ozonated contactor removes slightly more of the organics by biological action and the pre-ozonated contactor appears superior. Figure 6 points out that post-ozonation is favored at high carbon usage or short regeneration time systems. Pre-ozonation is, of course, favored in systems with long carbon regeneration times. Up to now, most of our contactors were regenerated at periods greater than two years. Thus, pre-ozonation appears to be favored from an organic standpoint in such systems. On the other hand, post-ozonation may be best for the near complete synthetic organic compound removal that may be required for health protection, as in such cases, regeneration frequencies may turn out to be as low as once per month.

CONCLUSIONS

The following conclusions can be drawn from this study:

(i) Pre-ozonation of GAC contactors is favored for odor removal, especially when prechlorination is not practiced.

Table 5. Observed Biological Reaction Rates, Expressed on the Basis of External Activated Carbon Surface Area (From Benedek, 1978)

Type of Water	Presence of Oxygen	Specific Reaction Rate $\frac{g\ TOC}{cm^2 \cdot hr}$
Chemically clarified and filtered domestic wastewater	Anoxic	2×10^{-6} at 25°C 1×10^{-6} at 5 °C
Chemically clarified and filtered domestic wastewater	Anoxic	2×10^{-6}
Chemically clarified domestic wastewater with nitrate addition	Anoxic	3×10^{-6}
Chlorinated, chemically clarified and sand filtered Seine water (at Morsang)	Aerobic	7×10^{-8}
Chlorinated, chemically clarified, sand filtered and ozonated Seine water (at Morsang)	Aerobic	8×10^{-8}
Chemically clarified, sand filtered and ozonated Rhine water	Aerobic	$3\text{-}10 \times 10^{-8}$
Synthetic phenol solution	Aerobic	2×10^{-4}
Synthetic phenol solution	Anoxic	5×10^{-5}

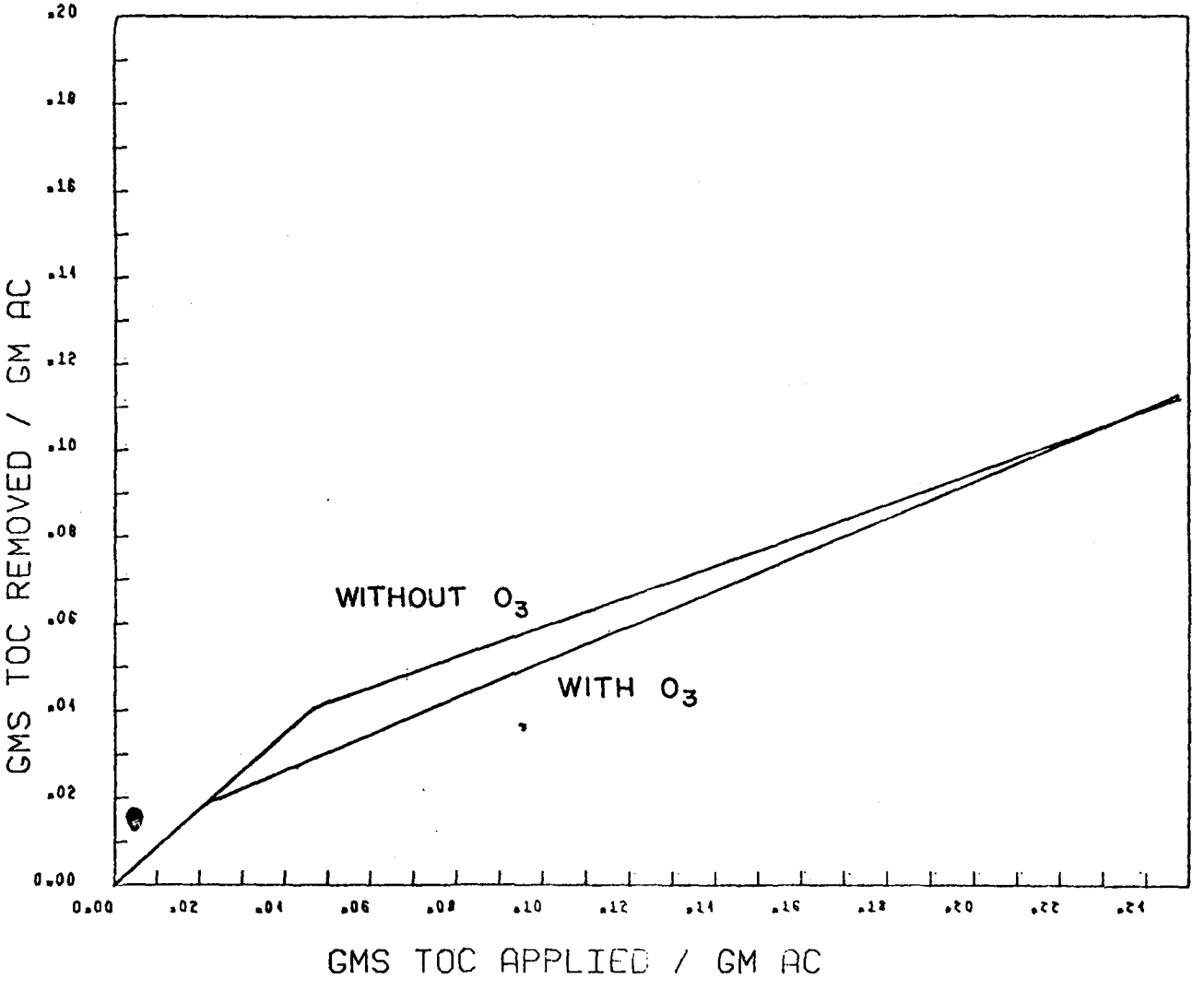

Figure 6. A Comparison of Ozonated and Non-Ozonated Adsorbers with Biological Activity (Ozonated R_f = 7.6 x 10^{-8}, Non-Ozonated 6.5 x 10^{-8} g TOC/cm^2 hr.) (From Benedek, 1979)

(ii) In terms of organic removal, pre-ozonation is favored at low carbon regeneration frequency, but at high frequencies, post-ozonation is probably favored.

It also appears that prechlorination tends to reduce overall organic removal; however, this conclusion will require further long-term pilot studies for substantiation.

ACKNOWLEDGEMENTS

Many people have been instrumental in making this paper possible. Mr. Richard of Degrémont and Mt. Fiessinger of SLEE gave encouragement and advice. In addition, at Degrémont, Messrs. Brener, Conan and Le Baron; at SLEE, Mmes. Rizet and Dalga; and at McMaster, Messrs. Bancsi and Peel helped to carry out different aspects in the study. Financial support for the author's European stay came from McMaster University and the Department of Health and Welfare, Government of Canada.

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QUESTIONS AND ANSWERS

(after Dr. Benedek)

DR. RIP RICE: I would like to comment on the detrimental effects of ozonation on the adsorption of the total organics, measured as DOC. First, one should say that ozone will decrease adsorbability of those organics which it does oxidize; but for those that it does not oxidize, such as some of the halogenated compounds, it does not decrease adsorbability. Secondly, there are some data from the full scale plant operation at Düsseldorf showing that both adsorption and biological degradation occur simultaneously.

Q PROF. WALTER MAIER, University of Minnesota: Please comment on the temperature in the columns that you have examined.

A PROF. ANDREW BENEDEK: We didn't make an attempt to study temperature in this particular case, but we had an earlier paper which was published in JWPCF about 2 years ago. The purpose of that particular paper was to look at the effect of temperature: we found that decreasing temperature increases adsorptivity but decreases biological degradation. Initially, the adsorptivity was important. Subsequently, since biological degradation became the key mechanism, the separation and slope corresponded to what you would expect from biokinetics.

Q MR. MAIER: I am curious whether or not you would look at temperature in your modeling. Obviously, in filter operations, temperature had been used to establish the weight limitations that accrued from diffusion limitations as opposed to the biological, because the effect of temperature is greater on the biological system. I just wondered whether the same analogy could be applied here.

A PROF. BENEDEK: The model has every physical property and the biokinetic coefficient, as well as temperature, modulated.

Q PROF. DR. SONTHEIMER: A very silly question, maybe. I want to ask Dr. Benedek if he really knows enough about BAC to make modeling worthwhile?

A PROF. BENEDEK: I don't know how to answer that. The problem is that we know so much about it. We are trying to come to grips with it, but I have no illusions of understanding it fully. I know how to describe it mathematically, and we're making improvements in our description.

Q PROF. MICHAEL SEMMENS, University of Minnesota: I had a question concerning the length of time it takes to establish the biological community on the activated carbon. If you put a freshly reactivated granular carbon into a filter and put it in service, what length of time might you expect before the biological activity reaches its peak?

A PROF. BENEDEK: That's a very good question. I didn't have time to show data on the bacteria that build up in the carbon column as a function of time. There have been data published by us and various people in Europe, which indicates that this is very rapid. From our data in France, when you put a fresh new generative carbon contactor in service virtually all the bacteria initially adsorb. It is then strictly a function of the amount of bacteria in the feed and the final equilibrium that you have, adsorptive equilibrium if you like, between the feed and what's on the carbon.

Q PROF. FRANCIS DiGIANO: May I just add a little bit to that. I think probably just as important, Mike, is what are those bacteria doing? I mean, they may be there as Dr. Benedek mentioned; they're adsorbed from the feed stream, but if the substrate isn't available in sufficient amounts, how effective are they in the system?

A PROF. BENEDEK: Fran, I agree wholeheartedly. I would add that it is difficult to know when biodegradation becomes important if you have adsorption and biodegradation going on simultaneously. It's hard to separate the two.

HUMIC ACID REMOVAL WITH MACRORETICULAR ION EXCHANGE RESINS AT HANNOVER

Walter Kölle

THE FUHRBERG WATERWORKS PLANT

The Fuhrberg waterworks plant of the Hannover waterworks covers about 30 percent of the drinking water supply for the city of Hannover, corresponding to an annual output of about 18 million cubic meters. At Fuhrberg, a high-color groundwater is used which contains many high-molecular-weight components, especially humic acids. The conventional treatment methodology used to handle this water quality problem was: aeration, flocculation (precipitation of iron and of calcium carbonate by adding calcium hydroxide and activated silica), potassium permanganate addition, and filtration. Chlorination was carried out at the flocculators to support flocculation, at the filters to keep them sterile and at a proper pH, and at the clearwell to eliminate ammonia by exceeding the breakpoint. The total chlorine dosage amounted to about 19 mg/l. Typical quality criteria of the raw and finished water are summarized in Table 1.

The disadvantages of the finished water include a high concentration of dissolved organic carbon, 6 mg/l, and the simultaneous presence of 10 mg/l of oxygen. This enabled a rapid aerobic bacterial growth which was characterized by a doubling time of the bacterial counts during the logarithmic growth phase of 5 hours (temperature = 10°C). Dealing with this problem is difficult because organic carbon causes a substantial chlorine demand.

Keeping the finished water sterile during distribution was difficult and resembled a running match between chlorine consumption and bacterial growth on the one hand, and control measures like flushing or subsequent chlorination in the distribution system on the other hand (1). In addition, the total organic chlorine and haloforms resulting in the finished water were a hygienic disadvantage which could not be tolerated (2,3,4). The haloforms formed during treatment consisted mainly of chloroform.

Attempts to reduce the humic acid content by conventional, economically acceptable processes (e.g., additional flocculation) were unsuccessful. Only the use of a strong basic macroreticular

ion exchange resin offered a solution to the problem (5-8). Extensive tests were carried out with Lewatit MP 500 A (Bayer Chemical Co.), which has been used in the full scale operation of the plant since July 1978.

Table 1. Analytical Characterization of the Conventional Water Treatment at the Fuhrberg Water Works Plant

	Raw Water	Finished Water
Odor	H_2S	not detect.
Oxygen (mg/l)	not detect.	10
Iron (mg/l)	15	<0.05
Manganese (mg/l)	1.1	<0.02
Ammonia (mg/l)	1.1	<0.05
Sulfate (mg/l)	130	130
Chloride (mg/l)	45	64
Dissolved org. carbon, DOC (mg/l)	9	6
Chemical oxygen demand, COD (mg/l)	27	17
Total organic chlorine, TOCl (µg/l)	not detect.	400
Total haloforms (µg/l)	not detect.	69

THE EFFECT OF RESIN TREATMENT

Strong base anion exchange resins for humic acid removal are generally used in their chloride form and are regenerated with a solution containing 10 percent sodium chloride and 2 percent sodium hydroxide. The resin is able to remove about 85 percent of the humic acids from the Fuhrberg drinking water. However, according to the normal behavior of anion exchangers in the chloride form, chloride exchanges for sulfate. The rate at which the exchanger transforms into the sulfate form depends on the sulfate content of the drinking water to be treated. In the case of the Fuhrberg drinking water, this transformation is finished after a throughput of about 300 bed volumes. After that, the mean humic acid removal is scarcely better than about 50 percent, but this efficiency decreases only slightly during the remaining operation cycle. After a throughput of about 5,000 bed volumes, regeneration of the resin is necessary. At this point, the resin is loaded with humic acids to the extent of 15 g of DOC per liter of resin. The behavior of the resin is evident from Figures 1 and 2.

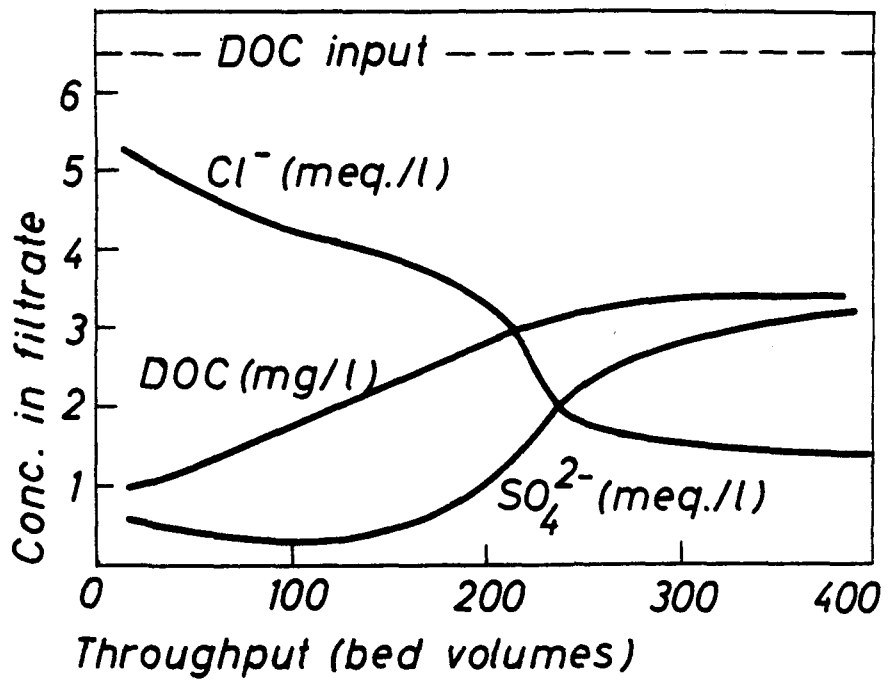

Figure 1. Changes of Chloride, Sulfate and DOC in the Filtrate of the Resin, Immediately after a new Cycle has Started (preceding regeneration with unused regeneration solution)

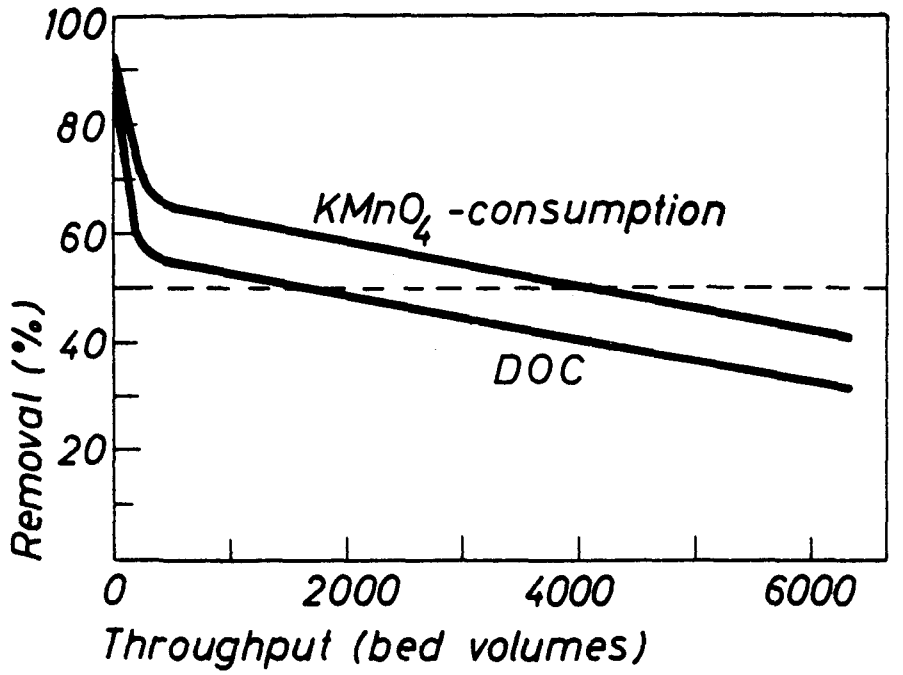

Figure 2. Decrease of the Humic Acid Removal (as DOC and as $KMnO_4$-consumption) during an Operation Cycle. Throughput: 54 bed volumes per hour

Numerous tests indicated that the resin's efficiency for humic acid removal is almost independent of the filtration rate. This held true for filtration rates up to about 60 bed volumes per hour or 70 meters per hour.

Laboratory tests indicated that the following improvements of the water quality could be expected:

1. Decrease of organic carbon and organic chloride.

2. Increase of the bacterial doubling time from 5 to about 12 hours.

3. Decrease of the consumption of free chlorine, approximately proportional to the decrease of organic carbon and strongly dependent on the decrease of chemical oxygen demand.

THE RESIN TREATMENT PLANT

The results obtained in extensive tests at a pilot plant and in the laboratory were the basis for constructing an additional treatment unit in the full scale range at the Fuhrberg waterworks. This project is sponsored by the German government. The design data of the plant are: 4 filters with 12.5 m^3 resin, each; throughput 625 m^3/h each, equivalent to 50 bed volumes per hour; operation cycle 62,500 m^3, corresponding to 4 days. The total throughput amounts to 2,500 m^3/h, which is 60 percent of the total design throughput of the Fuhrberg waterworks. Thus, during peak water demand situations, the surplus of water beyond design capacity by-passes the resin filters.

Strong base anion exchange resins may detach trimethylamine from the production process into the water. This compound is hygienically dubious because of the nitrosamine problem. Gas chromatographic analyses showed that the previously unused resin is leached according to an exact exponential law with a "half-life" of the trimethylamine concentration of a few hours, depending on the operating conditions. This behavior of the resin could be verified down to the detection limit of the analytical method, which was 0.5 µg/l. After reaching this level, trimethylamine remained below the detection limit at all operation conditions and is, consequently, no problem at all.

REGENERATION OF THE RESIN

The regeneration of the resin is carried out with 2 bed volumes of a solution containing 10 percent sodium chloride and 2 percent sodium hydroxide. The used solution is adjusted in its content of sodium chloride and hydroxide and reused seven times. The DOC of the solution increases to about 25 g/l during

reuse. Naturally, sulfate is also enriched in the solution, reaching approximately the same level as the chloride concentration. Then the solution has to be discharged. It is interesting that the sulfate enrichment in the regeneration solution affects the behavior of the resin immediately after starting a new operating cycle according to Figure 1. The efficiency during the main period of a cycle seems to be quite independent from the sulfate content.

The relation between the volume of treated drinking water and the volume of spent regeneration solution is 20,000: 1. Thus, the volume of the solution is small enough to be transported by truck for disposal. Resin treatment clearly has less environmental impact than conventional treatment, even if the solution is discharged into the sewage plant; the chloride impact originating from resin regeneration is less than 25 percent of the impact caused by the excessive chlorination that was previously necessary. In regard to the environmental burden of humic acids, the only change occurs with the route by which they reach the sewage plant.

ADDITIONAL MEASURES AT THE FUHRBERG WATERWORKS

Special attention was directed to reducing the formation of haloforms. The first step of chlorine-saving was the replacement of activated silica as a flocculation aid by a polyacrylamide polymer. This guarantees excellent flocculation without the additional need of chlorination. As a consequence, the filters could also be operated chlorine-free. For pH-adjustment (originally an effect of chlorination) sulfuric acid had to be introduced. Under these conditions, biological nitrification of ammonia could start, although very slowly. Thus, an additional portion of chlorine could be saved. In addition, the chlorine content of the finished drinking water could be reduced because of the treatment effect of the ion exchange unit. Every step of lowering the chlorine dosage decreased the formation of haloforms. Table 2 illustrates how the haloform concentration was influenced by the changes in chlorination.

Table 2 shows that the haloform problem no longer exists for the Fuhrberg water, provided that the dosage of combined chlorine can be maintained without resulting bacterial difficulties.

PRACTICAL EXPERIENCES

The installation of the new treatment plant was carried out as a research program because the effects to be realized in practice cannot be anticipated by laboratory tests in a reliable way. The interdependence among chlorination, organic substances, bacterial growth, manganese precipitation, and corrosion phenomena within real distribution systems is extremely complicated.

Indeed, extensive research was carried out in this context for corrosion phenomena in the old portions of the Hannover distribution system (9,10). In the case of the Fuhrberg water, no significant effect of the humic acid removal on corrosion processes has been observed. Apart from the remaining questions to be answered by long term observation, the experiences with the macroreticular resin treatment so far are quite positive.

Table 2. Haloform Formation as a Function of Chlorination in the Fuhrberg Waterworks Plant

Date	Changes in Chlorination	Haloforms (µg/l)
Aug. 76	Conventional operation; chlorination of four flocculators; finished water: 0.45 mg/l free chlorine; finished water quality as in Table 1.	69
Feb. 78	Half of the flocculators and half of the filters chlorine-free; finished water: 0.45 mg/l free chlorine	55
Nov. 9, 78	All flocculators and filters chlorine-free; resin treatment; finished water: 0.45 mg/l free chlorine	36
Nov. 23, 78	Reduction of chlorine dosage; finished water: 0.25 mg/l free chlorine	20
Feb. 5, 79	No longer breakpoint chlorination; finished water: 0.30 mg/l combined chlorine	0.4

ACKNOWLEDGEMENT

The program is sponsored by the Bundesministerium für Forschung und Technologie; the Hannover waterworks are grateful for their support. In addition, the author wishes to thank Dr. Richard Heck and Prof. Dr. Heinrich Sontheimer for their intensive support and Dr. Ludwig Stieglitz for carrying out the trimethylamine analyses. Last but not least, the author thanks his many colleagues of the Hannover waterworks who are cooperating in this program.

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INVESTIGATIONS CONCERNING THE MICROBIOLOGY OF GAC-FILTRATION FOR DRINKING WATER TREATMENT

P. Werner, M. Klotz, and R. Schweisfurth

INTRODUCTION

In granular activated carbon (GAC) treatment of drinking water, populations of microorganisms always develop on the filter granules and are found in the filtrate. Prior to the investigations reported here, understanding of microbiological activity during activated carbon treatment was very limited. This was because microbiological investigations in this field were carried out by the waterworks using standard methods for water examination, which can describe neither quantitatively nor qualitively, the populations of microorganisms present (1).

The studies described here concerning the microbiological activity on activated carbon used for drinking water treatment were carried out for the most part at a water treatment plant on the Rhine River. The water is taken from the river, aerated, settled, chlorinated, and flocculated. The water then follows rapid filtration through sand and activated carbon before it is infiltrated into the ground. Using German Standard Methods for the determination of colony counts, the water of the effluent of the GAC-filters usually satisfies the drinking water quality requirement.

QUANTITATIVE DETERMINATION OF THE POPULATION OF MICROORGANISMS

The determination of the number of bacteria in the water of the activated carbon filters can be conducted using media either rich or poor in nutrients. The only important condition for high colony counts is the incubation of the samples for 7 days at a temperature of 27°C (1). Ford observed that an incubation period of 3 days was not sufficient; he therefore suggested to extend it to 7 days (2).

Figure 1 shows mean values of colony counts of some characteristic stages in this waterwork. The colony counts of raw water (approximately 2 x 10^5/ml) are almost completely eliminated by chemical pretreatment (high chlorination and flocculation) before the GAC-filter. Without high chlorination, the colony counts in the water at this sampling point decrease only to 10^3/ml. In the activated carbon filters, there is an increase of bacteria to values of about 5 x 10^4/ml water in the filtrate. In contrast, the values generally are below 100/ml using the method, normally applied, for the determination of colony counts (German Standard Method: 2 days incubation at a temperature of 22°C).

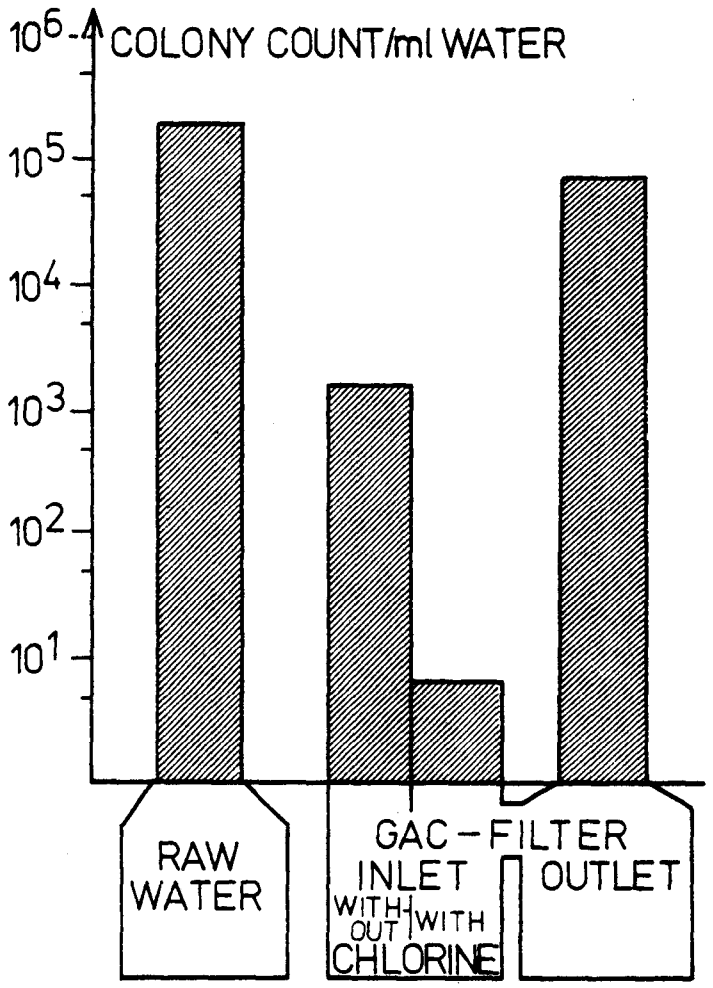

Figure 1. Colony Counts at Different Stages of Treatment (SPC-Agar, 7 Days Incubation at 27°C)

On the activated carbon, one can find about 10^8 bacteria per g wet weight. These colony counts can be obtained only by the special method mentioned above; no standard method is available for this application. Applying this special method, one can get 20 percent of the living cell number and about 5 percent of the total cell number, including all dead and living bacteria in the water of the activated carbon filters (Figure 2).

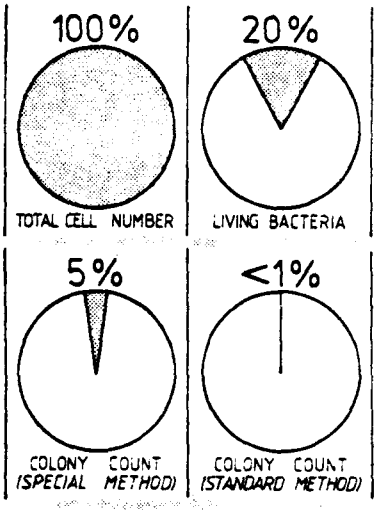

Figure 2. Percentage Colony Counts in Effluent from GAC Filter by Different Methods

Freshly filled activated carbon filters will reach the mentioned high colony counts within a short time (Figure 3). The speed at which the populations of microorganisms develop depends on the temperature. The higher the temperature, the earlier the maximum colony counts are achieved. The fresh filter material, which is initially sterile, is fed into the empty vessel with water from the effluent of the activated carbon filters; therefore, the GAC is contaminated by already adapted microorganisms. This is the reason why there is no lag phase at the beginning of the curves in Figure 3. The filter velocities also have an influence on the speed of the development of populations of microorganisms in the GAC filters. The slope of the curves in the initial phase decreases with increasing velocity. Moreover, it can be seen in Figure 3 that the largest increase of colony counts takes place in the upper part of the carbon column; therefore, the elongation of the GAC filters (e.g., by connecting two filters in series) causes no further increase of colony counts.

After the initial phase, the colony counts remain at a level of about 5×10^4/ml water if no manipulation takes place in the pretreatment of the raw water.

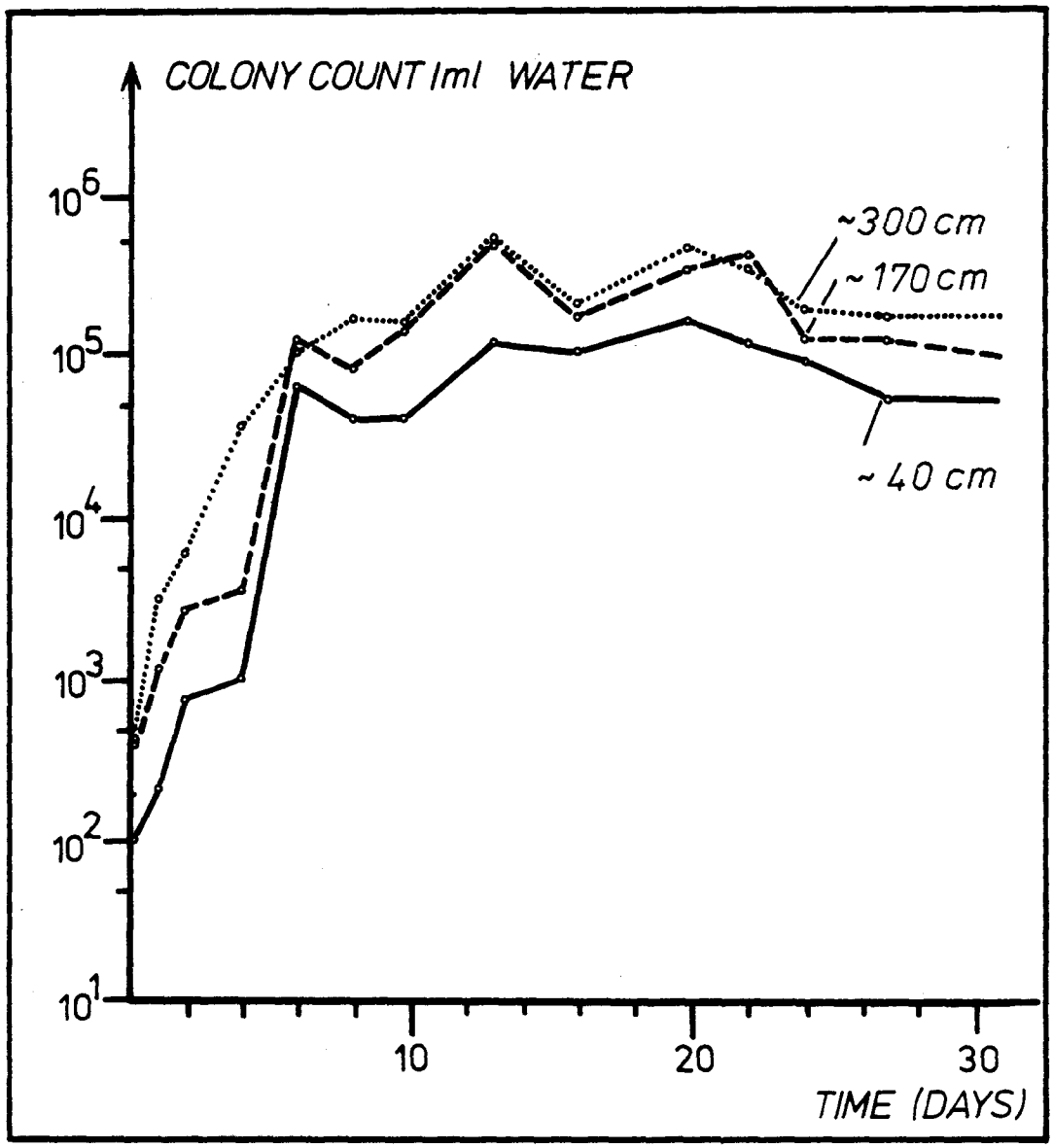

Figure 3. Colony Counts as a Function of GAC Service Time and Bed Depth

(SPC-Agar, 7 Days Incubation @ 27°C)

Investigations show that the magnitudes of colony counts discussed above depend on the pretreatment of the water. If the mass and degradability of the organic substances in the raw water decrease because of enhancement of the biological activity occurring in the pretreatment step, colony counts in the effluent of the GAC filters decrease. In another water treatment plant where slow-sand filtration of the raw water takes place before activated carbon filtration, extremely low colony counts of the water of the GAC filter effluents were found (3). The success of slow-sand filtration can be explained in terms of degradation of organic substrate that otherwise would support biological activity during activated carbon treatment.

The observed maintenance of constant colony counts in an activated carbon filter suggests the analogy to a chemostat. A chemostat is a well-mixed vessel into which nutrient broth flows at a constant rate. The quantity of inflowing nutrient broth is responsible for the density of the suspension of bacteria leaving the vessel. If the quantity of nutrient broth is constant, the density of suspension of bacteria is also constant. However, the nutrient concentration in an activated carbon filter is not constant, because of the changing quality of the raw water, but the organic substances are adsorbed by and desorbed from the activated carbon in the steady state and can therefore be utilized by the bacteria.

This interplay of adsorption and desorption results in a relatively constant concentration of nutrients in the water of GAC filters; hence, an activated carbon filter can be compared, in a crude sense, with a chemostat.

Figure 4 is a typical picture of loaded activated carbon from the waterwork. In order to investigate the distribution of

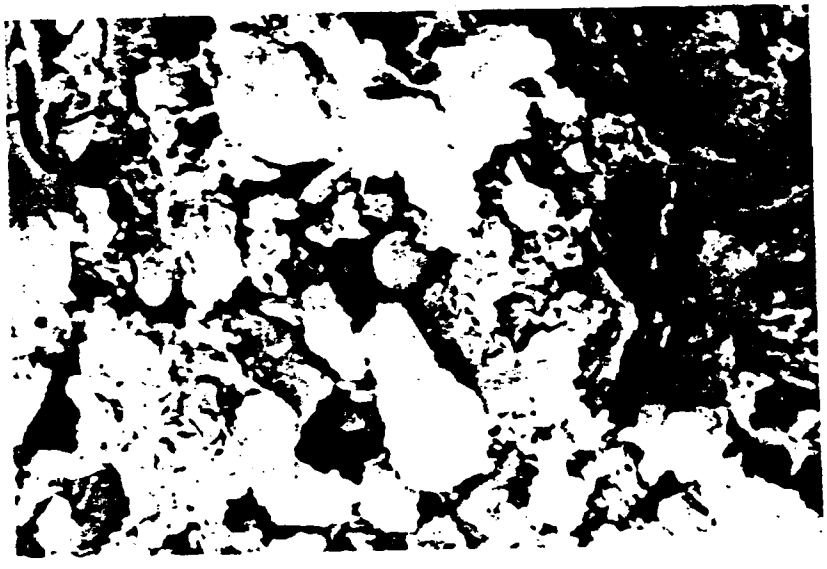

Figure 4. Bacteria on Activated Carbon

microorganisms on the carbon granules, electron-scan microscopy can be used after special treatment of the GAC (4,5). Only single bacteria could be found on the coal; the area available for bacteria (carbon surface including that of pores of diameter > 1 μm) is only partially covered (less than 1 percent). Electron-scan microscopic investigations of GAC from other waterworks confirm this result.

QUALITATIVE DETERMINATION OF THE POPULATION OF MICROORGANISMS

As described earlier (Figure 1), the bacterial content of the raw water and the GAC effluent is nearly the same. Between these two treatment steps there is high chlorination which kills almost all bacteria. Studies to characterize the two populations of microorganisms from the raw water and from the GAC effluent were carried out by methods of numerical taxonomy to find qualitative differences between them. For this purpose a large number of bacteria strains were collected from both sampling points to determine, in as many as possible, their morphological and biochemical properties. With the characterization of these properties, it was possible to determine the genera of the bacteria. The properties of the various strains were compared statistically; strains with a high degree of similarity were grouped into clusters. The expression "population" is defined as the sum of all bacteria in a certain biotope.

It has been found that the bacterial population of the raw water is more diversified than that of the filter effluent. This can be seen not only in the number of different species of microorganisms, but also in the biochemical activities of the various strains of bacteria. The cluster analysis shows that the clusters formed by the strains of the filter effluent are more similar than those of the raw water (Figure 5). The fraction of bacterial strains belonging to the genus Pseudonomas increases from 55 percent in the raw water to 80 percent in the filter effluent. It is obvious that, although both populations express themselves in nearly equal colony counts, the population of microorganisms found in the water of the GAC filters is substantially different from that of the raw water.

Furthermore, the results of the numeric taxonomical studies showed that bacteria of different genera may indeed have similar biochemical properties; consequently the classification of the bacteria gives no reliable indication of the behavior in the biotope.

The qualitative microbial tests were completed by the determination of the microorganisms most common in the water of the GAC filters at the waterworks. In Table 1 the species of bacteria are shown: 26 species of bacteria out of 11 genera were found; 9 species belong to the genus Pseudomonas and 6

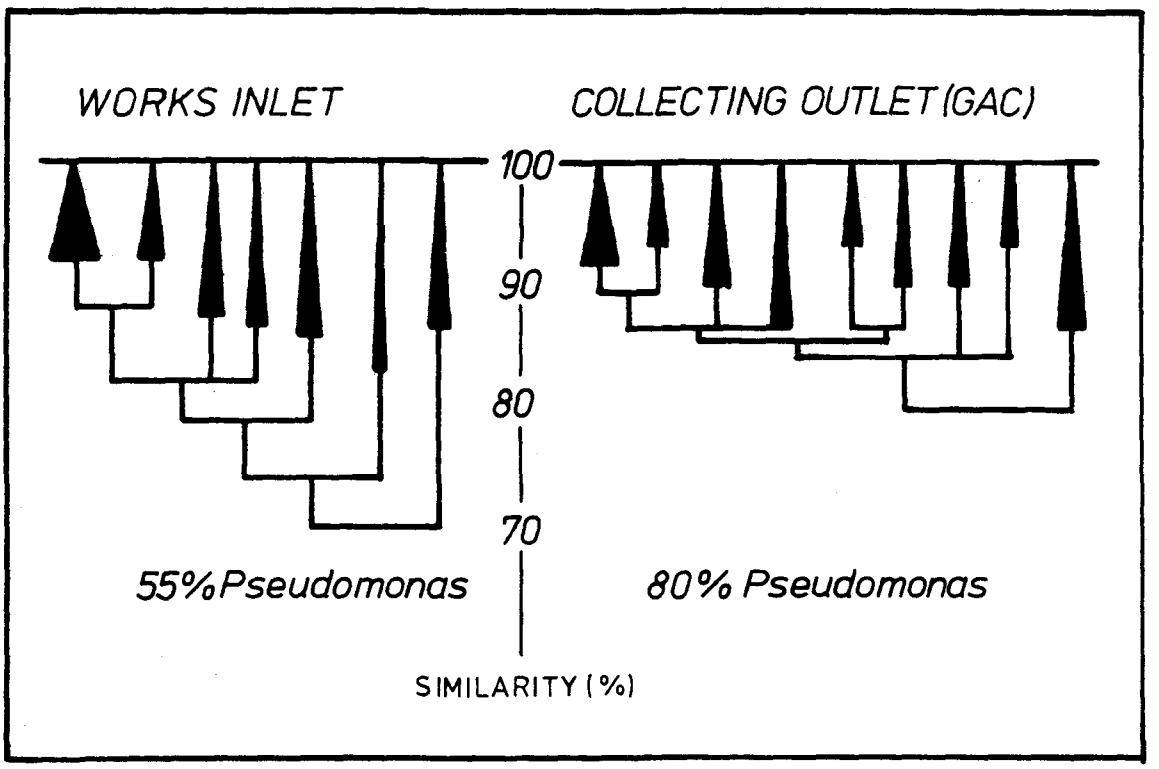

Figure 5. Similarity of Bacterial Clusters in Raw versus Treated Water

Note: Clusters are described as triangles whose baseline is proportional to the number of strains per cluster. The baseline of each cluster is situated on the level of the average similarity of all strains forming the cluster. The connecting lines between the clusters describe the similarity among each other.

Table 1

Bacteria in the Effluent From Activated Carbon Filters of the Rhine Waterworks

Pseudomonas alcaligenes	Chromobacterium violaceum
Pseudomonas cepacia	Neisseria sicca
Pseudomonas facilis	Acinetobacter calcoaceticum
Pseudomonas fluorescens	Micrococcus Tuteus
Pseudomonas lemoignei	Staphylococcus saprophyticus
Pseudomonas mendocina	Bacillus cereus
Pseudomonas ruhlandii	Bacillus circulans
Pseudomonas stutzeri	Bacillus licheniformis
Pseudomonas spec.	Bacillus megaterium
Gluconobacter oxidans	Bacillus pumulis
Azomonas agilis	Bacillus thuringensis
Azomonas insignis	Corynebacterium spec.
Azomonas macrocytogenes	Micromonospora spec.

species to the genus Bacillus. All 3 known species of the genus Azomonas were detected. No human-pathogenic bacteria could be found in the water of the GAC filters of this waterwork. In none of six investigated German waterworks were bacteria of the family Enterobacteriaceae detected, nor did other authors find a proliferation of bacteria of this family in GAC filters (6,7).

Investigations to enumerate and to determine microorganisms in activated carbon filters were carried out in 1978 by McKeon and McElhaney (8).

If biological activated carbon filters (BAC) are to be used for drinking water treatment in the future, the question will arise as to the hygienic significance of bacteria and in particular as to their toxins in the filter. Endotoxins (lipopolysaccharides) are produced by Enterobacteria; the endotoxins are located in the cell wall and are released during the (auto) lysis of these bacteria. In the GAC-filters no Enterobacteria could be found. On the other hand, no information is available concerning other Gram-negative bacteria, which also produce endotoxins. Moreover, it is uncertain whether the endotoxin released by the decaying bacteria remains on the activated carbon. Furthermore, it is generally accepted that the oral use of endotoxins is absolutely harmless, at least for the healthy person, as these substances do not penetrate the intestinal walls (9).

Yeasts and filamentous fungi were found only occasionally, and seem to be of less quantitative and qualitative importance for drinking water treatment (Table 2). None of these detected microorganisms is human-pathogenic.

Table 2

Yeast and Filamentous Fungi in the Effluent From Activated Carbon Filters of the Rhine Waterworks

Phialophora hoffmannii	Cryptococcus uniguttulatus
Phialophora mutabilis	Candida guilliermondii
Taphrina spec.	Hansenula anomala
Rhodotorula minuta	

INTERACTION BETWEEN BACTERIA AND ACTIVATED CARBON

Activated carbon adsorbs organic substances that can be used by bacteria as a substrate and it also adsorbs bacteria. This result was found in batch tests and the adsorption of bacteria by GAC agrees with the Freundlich isotherm (Figure 6).

With increasing ion concentration (phosphate buffer pH 7.2), the bacterial loading on the carbon increases. No dependence on temperature was noted in the range of 5 to 37°C and on the pH-value in the range of 5 to 8. Dead bacteria are slightly better adsorbed than living bacteria.

Bacteria and nutrient molecules are of different size; therefore, bacteria and nutrient molecules are separated, selectively, due to the pore structure of the activated carbon.

Figure 7 shows the influence of activated carbon on the metabolic rate of bacteria. In this case phenol was the substrate. Phenol is highly adsorbable and at low concentrations easily degradable, but in higher concentrations it is toxic to bacteria. Using 0.3 g/l phenol as a substrate, activated carbon has a negative influence on the bacterial utilization of phenol; this means that carbon hinders the metabolism. Using 2.5 g/l phenol, there is no decomposition in the absence of activated carbon because of the toxicity at this concentration. However, in the presence of activated carbon the following is observed: the carbon adsorbs phenol and renders it harmless for the bacteria; in the steady state, phenol desorbs in non-toxic concentrations and bacteria can utilize this substance as a substrate. Hence, GAC shows a positive influence on the metabolization of phenol by bacteria. One can imagine a similar effect in a GAC filter for drinking water treatment. Moreover, GAC increases the retention period of slowly degradable substances, thereby providing more time for their decomposition by bacteria.

Furthermore, GAC may accumulate organic substances present in small concentrations in the water and thereby make bacterial decomposition possible. The biodegradation depends on the

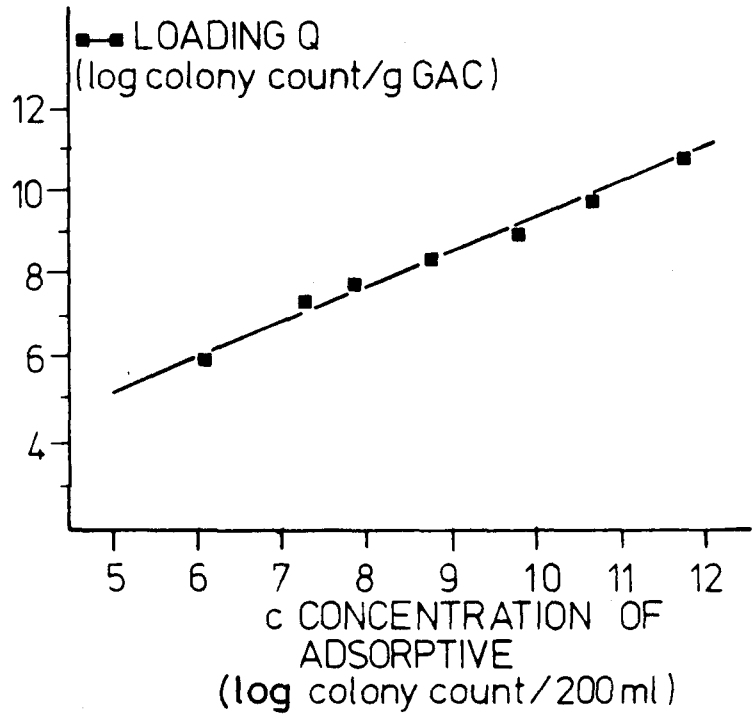

Figure 6. Adsorption Isotherm of Bacterial Loading on Activated Carbon

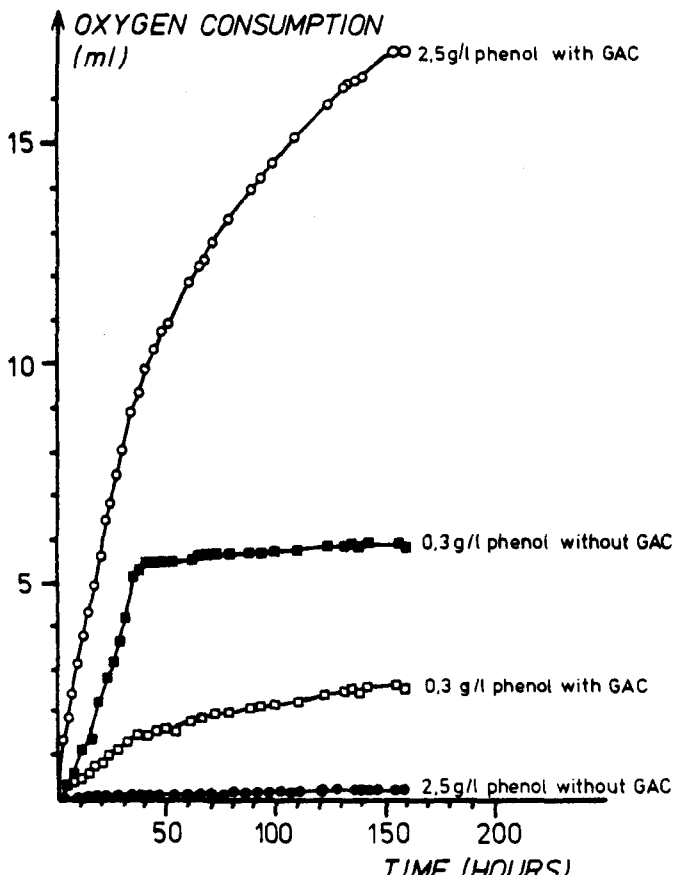

Figure 7. Influence of Activated Carbon on the Metabolic Rate of Bacteria

steady state concentration of substances in the liquid phase. The substrate is released from the GAC into the liquid phase by diffusion. Diffusion is a time-dependent step and therefore has a decisive influence on the rate of decomposition of the substrate. This is one reason why faster decomposition occurs if the diameter of the granules decreases. The other reason is the increasing specific surface area with decreasing diameter which affords more opportunity for bacterial attachment.

Using pumice stone as granulated material, the same substrate enhancement of the metabolic rate is observed because there is no separation between bacteria and substrate caused by the structure of pumice stone. In this case, bacteria, substrate, and enzymes accumulate on the exterior surface. Investigations showed a positive correlation between available surface and rate of decomposition; this means that the size of the granules is a decisive factor. But if phenol is used in high concentrations there is no protection from its toxicity (as there is in the presence of activated carbon) and the microorganisms will be destroyed.

The pH-value influences not only the adsorptive properties of activated carbon but also the metabolic rate. Using various buffered pH-values, in a range of 5.8 to 7.8, there is no noticeable influence on the metabolism in the presence or absence of activated carbon.

ACTIVITY OF THE BACTERIA IN THE GAC FILTER

Through their metabolization of organic substrate, microorganisms in a GAC-filter provide a valuable contribution to drinking water treatment. The question of the extent to which the microorganisms are responsible for the transformation of organic substances or their removal during GAC treatment was addressed by comparing a sterile and a non-sterile pilot plant. The raw water of the pilot plant was highly chlorinated and the efficiency of the GAC during these investigations was still very high. Under these conditions the contribution of the microorganisms to the decrease of organics during filtration is small (approximately 5 percent), as measured by UV-absorption, DOC and $KMnO_4$-consumption (4,5). On the other hand, the contribution of the microorganisms to the decrease of easily degradable organics is high (70 percent). BOD investigations demonstrated this. This observation is of special importance because it implies that the regrowth of bacteria which usually occurs in the distribution system, now occurs in the waterwork itself and can be better controlled.

It has been concluded from the comparison between a sterile and a non-sterile pilot plant that the contribution of the microorganisms to oxygen consumption and carbon dioxide production during filter passage is substantial, approximately 60 percent

for both parameters. The remaining 40 percent is caused by abiotic processes on the activated carbon. Observations indicated that microorganisms increase the efficiency of activated carbon filtration and prolong the running time for GAC by continuous regeneration. Other authors (10) previously have reported evidence of continuous regeneration of loaded activated carbon by biological processes, but these demonstrations have been limited to the field of sewage treatment.

CONCLUSIONS

Some years ago, drinking water treatment with sterile GAC filters (11) was tried with little success. On the other hand, the activity of bacteria in slow-sand filtration has been used for almost a century. Why should we not use the activity of microorganisms in activated carbon filters? Bacteria must be tolerated because there are no means or methods which are successful or applicable for the sterile operation of large GAC-filters.

Sporadically, people try to enhance the activity of bacteria in GAC filters by replacing breakpoint chlorination by ozonation (12). As a rule, breakpoint chlorination changes the organic substances in water to substances difficult to degrade while ozonation has the opposite effect.

It might be proposed to replace activated carbon by another porous but not activated material, which might be less expensive and equally effective. This material could serve, as well as activated carbon, as an attachment surface for the microorganisms. Nevertheless, it must be pointed out that the superiority of adsorption and especially the combination of adsorption and microbial processes has considerable advantages. On the one hand, bacteria metabolize the easily degradable organics which as a rule are difficult to adsorb; on the other hand, the slowly degradable substances are easily adsorbed by activated carbon. Moreover, there is a buffering effect and protection of the system by activated carbon if the water contains toxic substances. These substances will be adsorbed by activated carbon and thus will be separated from the microorganisms, thereby not destroying the population.

These are the reasons why we should not combat bacteria in activated carbon filters in the future as has been done in the past. On the contrary, we should make use of the activity of microorganisms for drinking water treatment in activated carbon filters.

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QUESTIONS AND ANSWERS

(after Dr. Werner)

Q UNIDENTIFIED QUESTIONER: It seems that on every GAC filter, there is biological activity. Calling something biological activated carbon is really calling something GAC, as we now refer to it. That's what you defined for us?

A DR. WERNER: We found that in every GAC filter examined, bacteria could be found everywhere. There was no sterile activated carbon filter. I think it's impossible to devise a method to maintain large activated carbon filters in a sterile condition. For small carbon filters in the laboratory you can use membrane filtration, but it's not practical for large filters. Contamination is everywhere.

Q BILL BATCHELOR, Texas A&M University: I was interested in your technique on how you measured total bacterial counts and living bacterial counts. Could you elaborate a little bit on that?

A DR. WERNER: Total bacterial counts were found by accumulation and staining on membrane filters. They were counted on the microscope. The living bacteria have active electron transport systems and dead bacteria don't. We used a stock that is colorless when oxidized; when it is reduced, it is colored red.

Q MR. BATCHELOR: Formalin?

A DR. WERNER: Yes.

USE OF POWDERED ACTIVATED CARBON TO REDUCE ORGANIC CONTAMINANT LEVELS

J.E. Singley, B.A. Beaudet,
A.L. Ervin, and W.C. Zegel

INTRODUCTION

In September, 1977, the City of North Miami Beach, Florida, received numerous taste and odor complaints regarding their drinking water. The problem was tracked to the East Drive Well Field. Analysis of the treated water from this field by a local laboratory showed the presence of pesticides at levels much above the Primary Drinking Water Regulations. The city immediately discontinued use of the well field and sought confirmatory analyses of the water. Subsequent analyses by other private and public laboratories showed the report to be false. However, 40 synthetic organic compounds were found in both the raw and treated well water.

These compounds could account for the taste and odor complaints. Many of them also exceeded the Maximum Contaminant Levels (MCL) proposed by the EPA based on the report, "Drinking Water and Health" (National Academy of Sciences, 1977) and published in the Federal Register, February 9, 1978. These limitations are, in summary form:

- The total trihalomethane (TTHM) content in the distribution water supply will not exceed 100 micrograms per liter (ug/l) for supplies serving populations greater than 75,000
- The concentration of volatile halogenated organic compounds (other than trihalomethanes) in the effluent shall not exceed 0.5 µg/l.
- The removal of influent total organic carbon (TOC) with fresh activated carbon shall be at least 50 percent.
- The effluent TOC may not exceed the value obtained from fresh activated carbon by more than 0.5 mg/l.

In addition, suspected carcinogens such as vinyl chloride should be reduced to concentrations that consider the toxic effects and the economics of treatment. The organics in the finished water that exceeded these limits are presented in Table 1.

Table 1

Organic Analysis of Finished Water
(which exceed EPA proposed MCL's)

Compound	Sample	Concentration (µg/l) 1	2	3	4	5
Vinyl Chloride		3.3	2.1	2.2	4.0	---
Vinylidene Chloride		1.7	1.7	1.1	---	1.7
Trans-1,2 dichloroethene		11.7	2.9	3.0	3.3	4.2
1,1 dichloroethene		5.0	5.3	5.0	4.4	5.0
1,1,1 trichloroethane		16.7	---	15	15	17
Trichloroethylene		---	---	1.9	2.4	3.2
Bromodichloromethane		21.7	1.5	1.5	0.9	1.3
Dibromochloromethane		6.7	4.4	5.9	---	3.3
Chlorobenzene		0.8	0.8	0.9	0.9	0.9
TTHM's		---	115	---	---	---

Although granular activated carbon was considered to be the best broad spectrum solution to the problem, the appropriate studies for the development of design criteria would have taken from 6 to 12 months to complete, and the city had no reasonable alternatives for a water supply. Thus, a short term solution was needed to allow use of the well field while granular activated carbon studies were undertaken. Environmental Science and Engineering Inc. developed such a short-term solution in the form of a powdered activated carbon system. The powdered activated carbon could be mixed with the raw water, then the carbon could be removed in the treatment plant; thus little additional equipment would be needed to treat the water. Since the general applicability of activated carbon to this problem has been established by EPA, a plant test of powdered activated carbon was designed and conducted.

DESCRIPTION OF THE TREATMENT PLANT

The water from the East Drive Well Field is processed in the Sunny Isles Water Treatment Plant. This is a conventional lime softening plant with a nominal capacity of 12.8 mgd (See Figure 1). The raw water is pre-chlorinated and then distributed to three Hydrotreaters where calcium hardness removal is accomplished by reaction with pebble lime. One of the Hydrotreaters is rated at 9.0 mgd, while the other two are rated at 1.9 mgd each. Pebble lime is fed to a single slaker, converted to hydrated lime slurry, mixed with return sludge, and pumped to a splitter box. The splitter box distributes lime to all three of the Hydrotreaters at the center drum of each unit. Anionic polymer (Nalco 8173) is blended with the raw water to assist settling in each Hydrotreater unit. The water is then recarbonated and distributed through nine high-rate filters prior to final chlorination and distribution.

Recarbonation is accomplished through three submerged, gas-burning recarbonation units. Further water stabilization is achieved by the addition of polyphosphate (Nalco 918) to each recarbonation unit.

Six of the filters are single media, containing anthracite, and are rated at 7.2 m/h (3.0 gpm per square foot). The other three are dual media containing both sand and anthracite and are rated at 12 m/h (5.0 gpm per square foot). Each has a filter surface area of 26 m^2 (280 square feet), giving a capacity of 0.053 m^3/s (1.2 mgd) each for filters 1-6, and 0.088 m^3/s (2.0 mgd) for filters 7-9.

PLANT TEST PROCEDURE

In performing the plant test, the system requiring the minimum time and additional equipment as well as minimum disruption to the operation of the treatment plant, was to introduce a slurry of the powdered activated carbon into the raw water at the well field. This would also maximize the contact time between the raw water and the activated carbon as it flows through a 0.61 m (24 inch) diameter, 0.5 km (16,500 foot) long line. Experience has indicated a minimum velocity of 1.5 m/s (5 feet per second) for maintaining a suspension of the carbon in water. This corresponds to a flow of 0.4 m^3/s (9 mgd), below normal flow rates. The contact time would be 30 to 40 minutes at normal flows. The injection point was selected to be as close to the wells as possible and convenient to the apparatus for producing the slurry.

The powdered activated carbon (PAC) mixing and feed equipment was set up in the space around an existing emergency generator. The apparatus is shown in Figure 2. The system was designed to meet a wide range of PAC feed doses for test

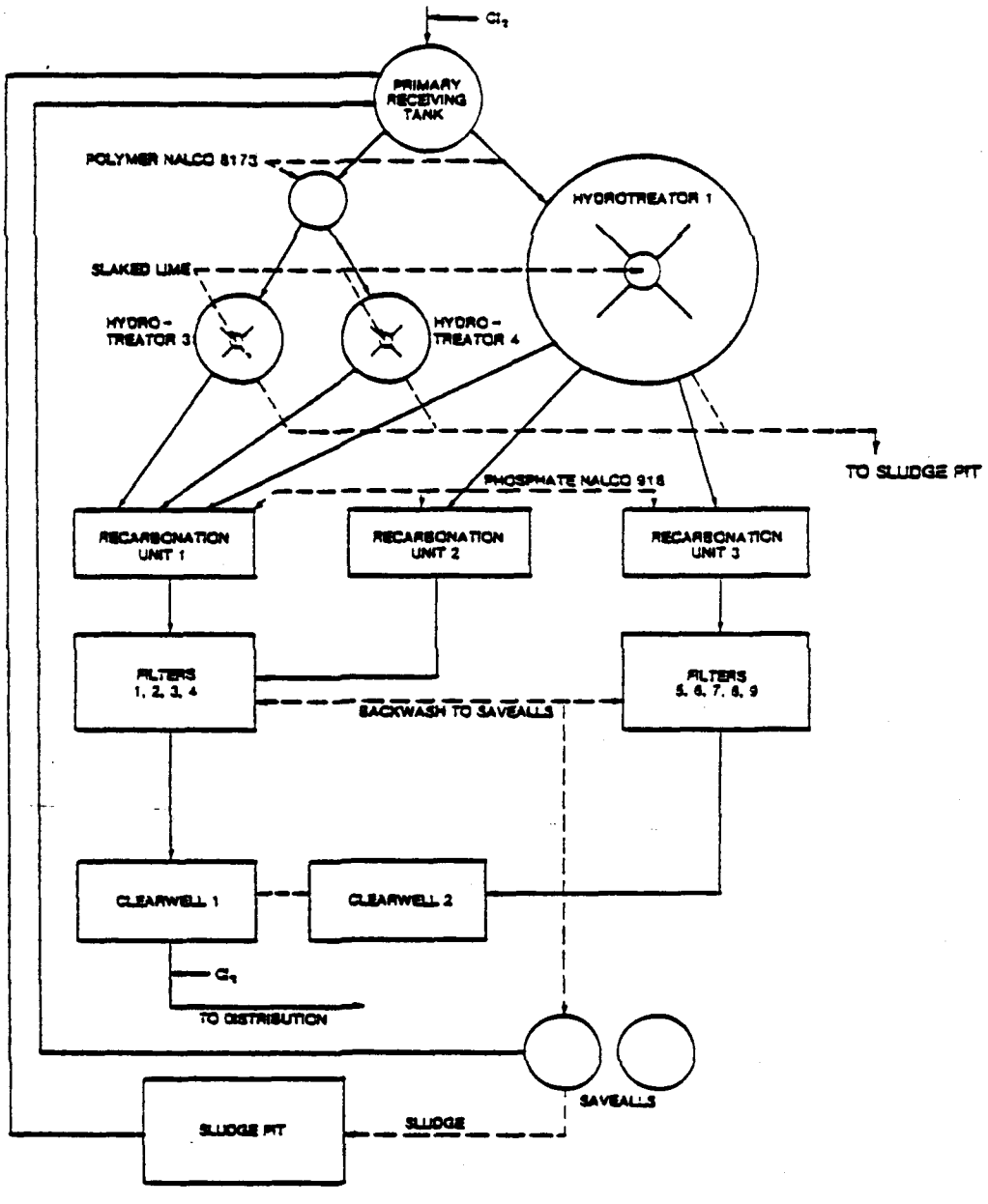


Figure 1. Sunny Isles Water Treatment Plant Schematic

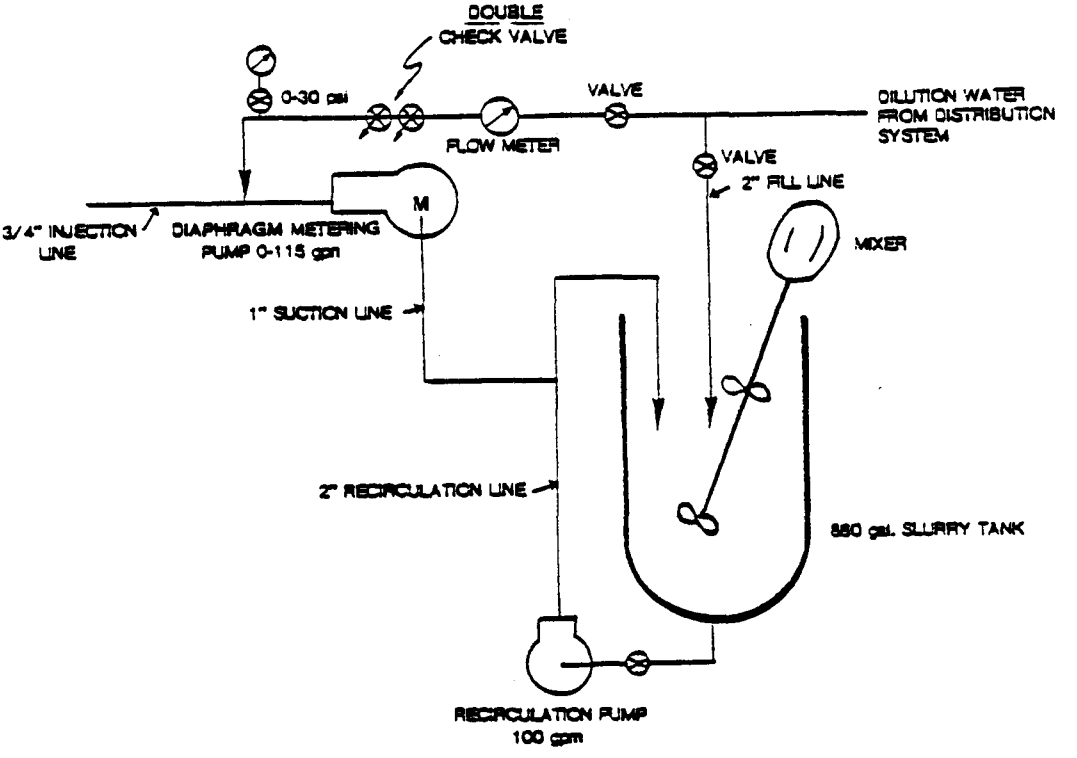


Figure 2. Process Schematic of the East Drive Well Field PAC Feed Site

purposes. A smiliar backup system was provided to insure continued utilization of the East Drive Well Field. PAC was added to a 3.3 m^3 (880 gallon) slurry tank to a design slurry mixture of 132 pounds carbon per m^3 (1.1 pounds per gallon). The tank was agitated by a dual-prop mixer that extended to two-thirds of the tank depth, and by a 100 gpm recirculation pump which drew slurry from the bottom of the tank and recirculated it to the top of the tank. The slurry was delivered to the injection line by a Wallace and Tiernan (Model 44-115) metering pump which was adjustable through a range of 0 to 0.43 m^3/h (0 to 115 gph). The suction of this metering pump was drawn from the discharge of the recirculation pump to provide a constant suction head. In the 19 mm (3/4-inch) injection line, the slurry was diluted with treated water. The injection point was through five 63 mm (1/4-inch) holes located at the center of well header and directed against the flow of raw water.

The PAC used in the test was ICI Hydrodarco-B, a lignite-base carbon exhibiting a preponderance of mid-range 5 to 500 nm pores as compared to micropores (less than 5 nm).

During the plant test, three levels of carbon dose were tested together with a control run. In addition, the recarbonation units were fed air and were not burning gas. The chlorination point was changed from the raw water receiving tank to the recarbonation unit during a portion of the tests. The average daily raw water flow to the plant was 10.4 mgd during the test period. This corresponds to a theoretical 47 minute contact time between the raw water and the carbon in the transmission line, and a 71 to 79 minute retention time in the Hydrotreaters. Hence, true contact time in these units is judged to be below 70 minutes. This corresponds to almost 2 hours total contact time. Each test run lasted for 24 hours.

Raw water samples were collected for analysis of volatile and non-volatile organic compounds. Dual samples for the non-volatile organic analysis were collected over a 12-hour period in XAD-4 resin cartridges. Flow rates through the resin cartridges were checked prior to, during, and at the completion of the sample run. Raw water samples were collected daily and the dual sample was reported as a single, average, daily result.

Samples for volatile organic analyses were taken in organically clean VOA bottles at the initiation of a resin cartridge run and at the termination of a cartridge run. The dual volatile sample was reported as a single, average, daily result.

The finished water samples were taken from a transfer pump on the discharge side of the clearwell at 1030 hours each day and terminated at 2200 hours each night. This provided a

sufficient lag time for PAC dose changes to stabilize through the raw water line and in the process equipment of the plant. These samples were collected in the same manner as the raw water samples.

Two TTHM samples were collected in VOA bottles at the plant clearwell. One TTHM sample was collected as an instantaneous sample and the second, as a 3-day formation potential sample. Immediately after the instantaneous sample was collected, sodium thiosulfate was added to prevent further reaction with chlorine. The 3-day formation potential samples were allowed to stand for 72 hours before dechlorination.

RESULTS OF THE PLANT TESTS

The plant tests were conducted in July 1978 over a 10-day period. Table 2 summarizes the test conditions for each day of the test. No PAC was added the first day. The PAC feed was

Table 2

Total Organic Carbon for Various Doses of Powdered Activated Carbon

PAC Dose (mg/l)	Chlorination Point*	Raw Water TOC (mg/l)	Finished Water TOC (mg/l)	Percent Reduction
0	R	(15.2)**	13.0	14.5
7.9	R	10.9	7.1	34.9
7.9	R	13.7	9.0	34.3
14.3	R	12.7	11.2	11.8
14.3	R	16.5	10.2	38.2
26.6	R	12.8	9.1	28.9
26.6	R	(14.5)	11.0	24.1
7.1	C	(16.0)	3.6	77.5
7.1	C	9.2	5.2	43.5

*R = Raw Water, C = Recarbonation Unit (also have post-chlorination in both cases)

**( ) = interpolated data based on measured non-volatile organics

started on the second day and an average concentration of 14.3 mg/l maintained for 2 days. The level was then increased to an average of 26.6 mg/l for two days. After a 1 day purge of the system, the carbon feed was restarted to maintain an average of 7.9 mg/l for the next 2 days, and 7.1 mg/l for the following 2 days. The chlorination point was changed from the raw water intake to the recarbonation units for these two days to determine whether the chlorine was inhibiting the adsorption of the organics.

TRIHALOMETHANES

The total trihalomethane (TTHM) data show no definite trend with increasing dose of PAC (see Figure 3). Apparently variations in the levels of precursor organics in the raw water occurred which masked the effects of PAC. In an effort to normalize these data, the isomers of dichloroethene and 1,1,1 trichloroethane were used as internal standards. These were selected because they represent chemicals that are present in the raw water at relatively high levels, and may be indicators of the level of synthetic organics in the raw water. Normalizing the TTHM data to the base data (zero carbon dose), yields Figure 4. This indicates that PAC may have a minor effect on reducing TTHM, and was successful in keeping the levels below 100 µg/l for all but one of the test days.

The TTHM levels tend to increase in the finished water with time due to slow reaction of precursors with residual chlorine. Data were also gathered on 3-day terminal TTHM. A comparison of the 3-day terminal TTHM levels with PAC dose shows a definite decrease with dose (see Figure 5).

These results indicate that PAC is not very effective in reducing TTHM, but does remove the precursors which will slowly react with residual chlorine to produce TTHM in the distribution system.

VOLATILE HALOGENATED ORGANICS

Nine volatile halogenated organics were detected in the finished water at levels exceeding 0.5 µg/l during the test period. These are the trihalomethane group, the dichloroethene group, chlorinated ethanes group and chlorobenzene. We have already examined the trihalomethanes, which contained chloroform, bromodichloromethane and dibromochloromethane in our test runs. The dichloroethene group contains cis-and trans-1,2 dichloroethene, and vinylidene chloride, with the cis isomer predominating. The variation in concentrations for this group with PAC dose is shown in Figure 6. This figure shows no clear trend, although some reduction with dose is possible. Normalization of the data, as was done for the total halogenated

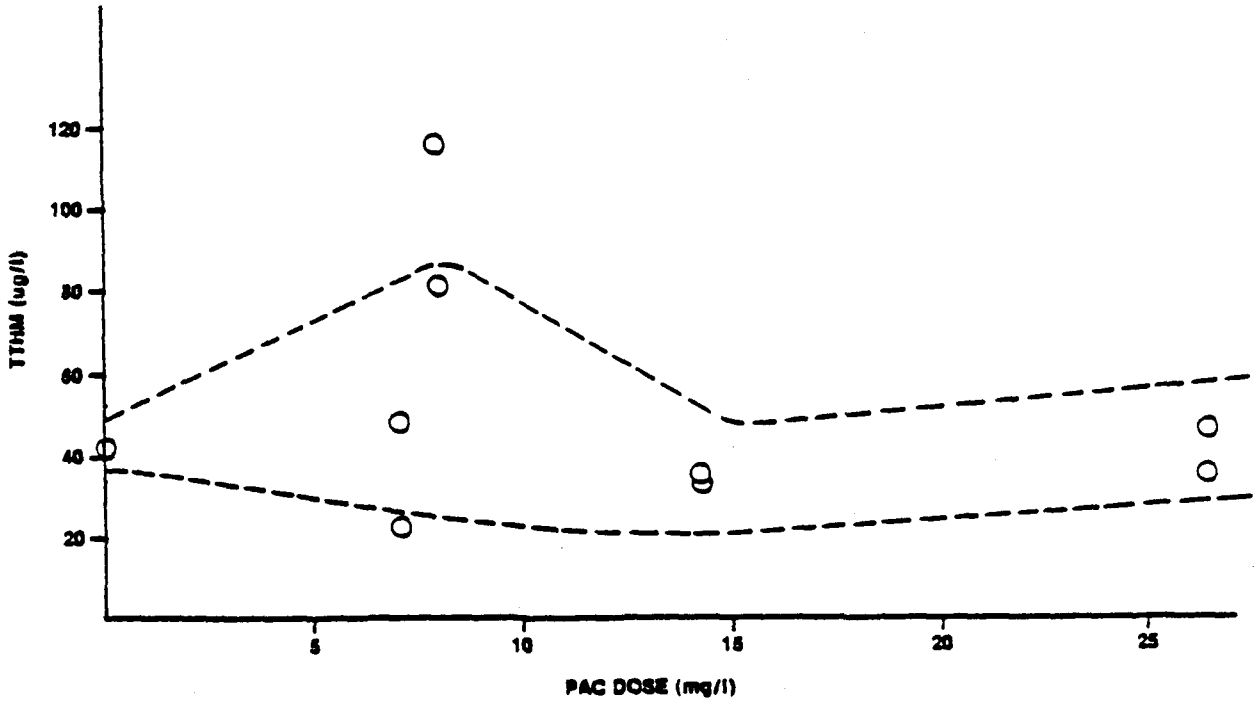


Figure 3. Total Trihalomethane Levels in the Finished Water at Different Doses of Powdered Activated Carbon During the Plant Test

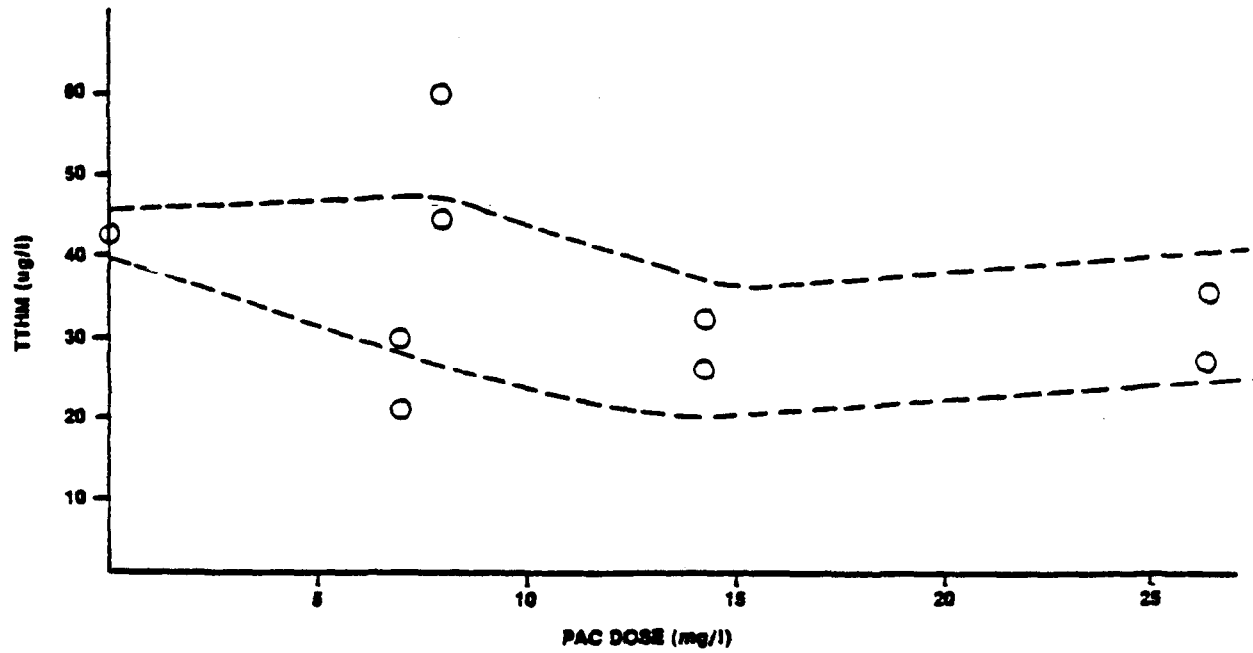


Figure 4. Total Trihalomethane Levels in Finished Water Normalized by Possible Indicator Species at Different Doses of Powdered Activated Carbon During the Plant Test

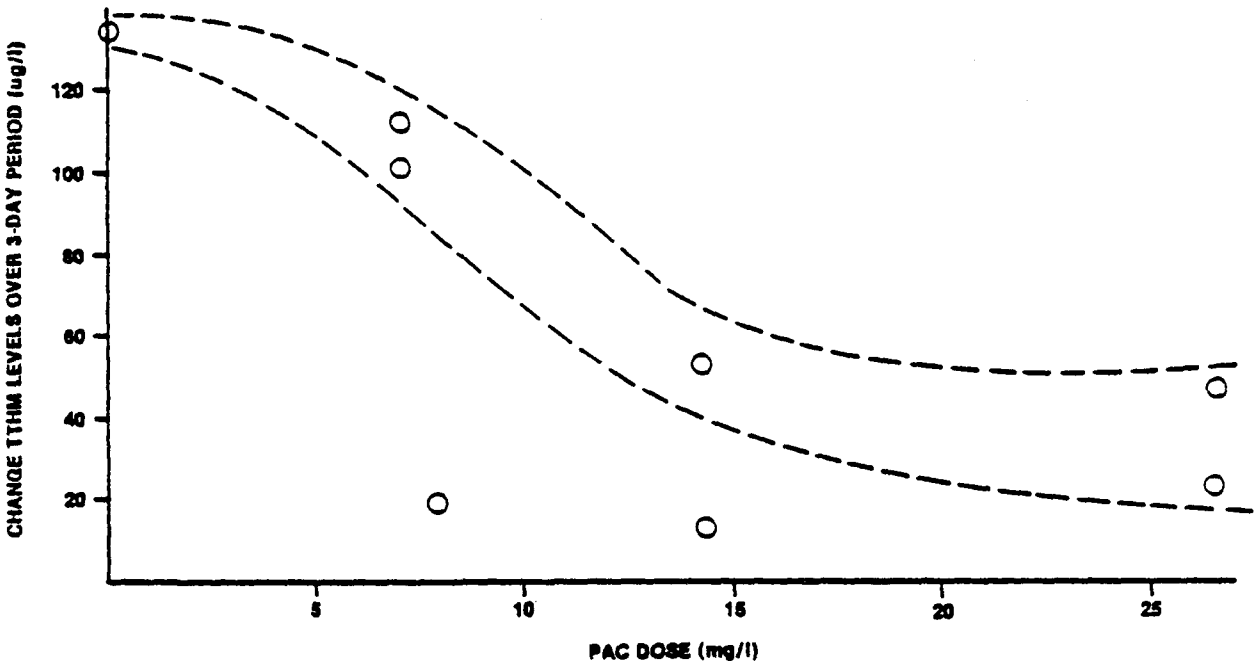


Figure 5. Three Day Total Trihalomethane Formation Potential in the Finished Water at Different Doses of Powdered Activated Carbon During the Plant Test

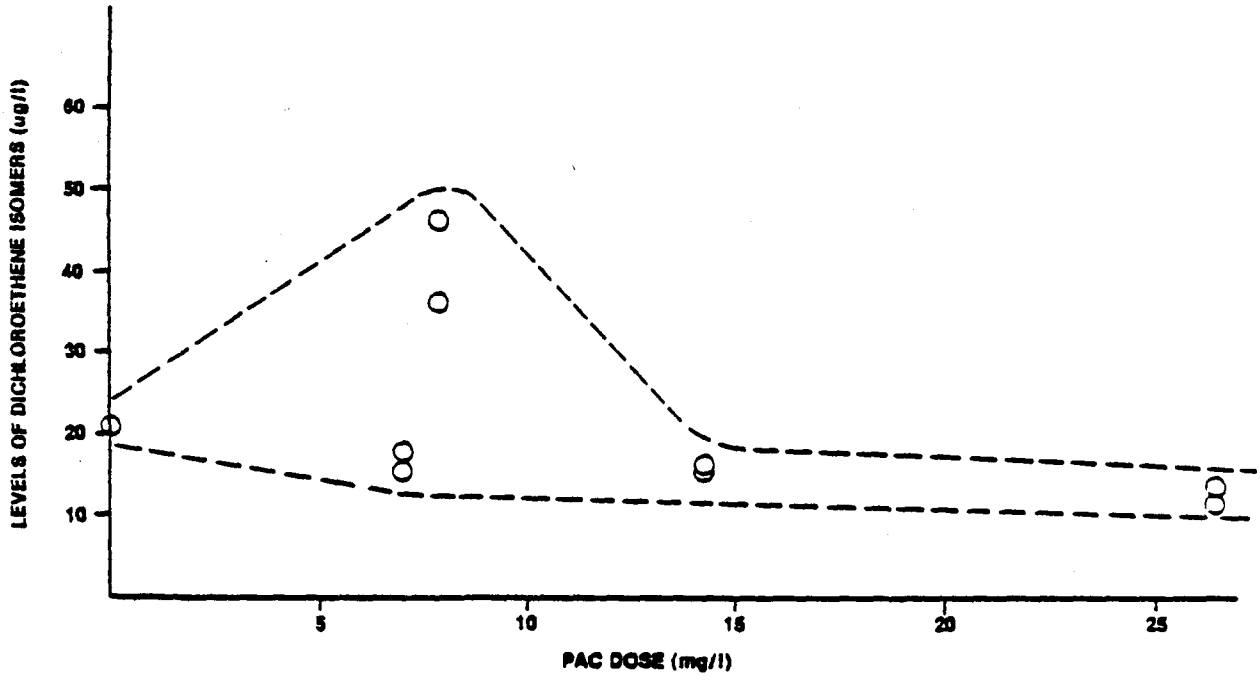


Figure 6. Levels of Dichloroethene Isomers in Finished Water at Various Doses of PAC for the Plant Test

methane, yields the results shown in Figure 7. This indicates some reduction with increasing dose of carbon.

The chlorinated ethanes group consists of 1,1 dichloroethane, and 1,1,1 trihalomethane, with the latter predominating. It also shows little trend in levels with increasing dose of PAC, and after normalization it indicates a slight decrease may occur with the addition of PAC (See Figures 8 and 9).

Chlorobenzene was present at low levels (0.5 µg/l) in the control run, and showed good removal by the addition of PAC. It was reduced to 0.1 µg/l or less by all dosages, except for one day in which there appeared to be higher than normal organics in the raw water (Figure 10).

Non-Volatile Synthetic Organics Compounds

Non-Volatile Synthetic Organics (NVSOC) are of high molecular weights such that special precautions need not be taken in their sampling or analysis to prevent their loss by exposure to the atmosphere. The response of NVSOC to the addition of PAC in the plant was immediate and obvious as shown in Figure 11. They are most effectively removed by the addition of even the lowest levels of PAC tested.

Total Organic Carbon

The total organic carbon (TOC) data obtained are fragmentary and no definite conclusions can be drawn except that TOC is reduced in all cases. The available TOC data show a close correlation with the total of the measured non-volatile organics. Using this relationship to fill in missing data yields the results shown in Table 2.

It is apparent from this Table and Figure 12 that the PAC reduces the TOC. However, the most dramatic reduction in TOC occurs when the chlorination point is changed and carbon is added.

CONCLUSIONS

- PAC was most effective in removing organics with low volatilities at all doses tested. Some reduction in volatile halogenated organics was observed, particularly for the halogenated organics of relatively higher molecular weight and lower volatility. It is suspected that the high percentage distribution of pores larger than 5 nm in the test carbon, may limit the effectiveness of removal for low molecular weight, highly volatile species. It is hoped that future tests of carbons which include a greater percentage of

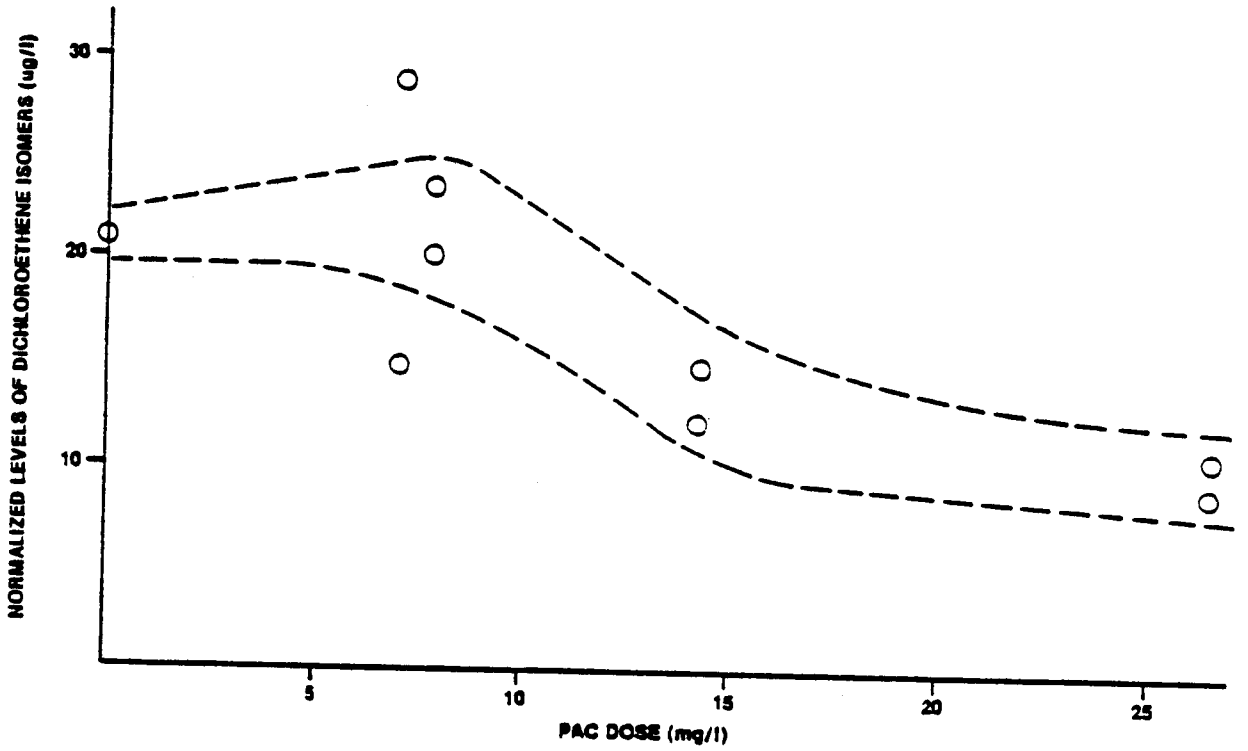


Figure 7. Levels of Dichloroethene Isomers in Finished Water (Normalized) at Various Doses of PAC for the Plant Test

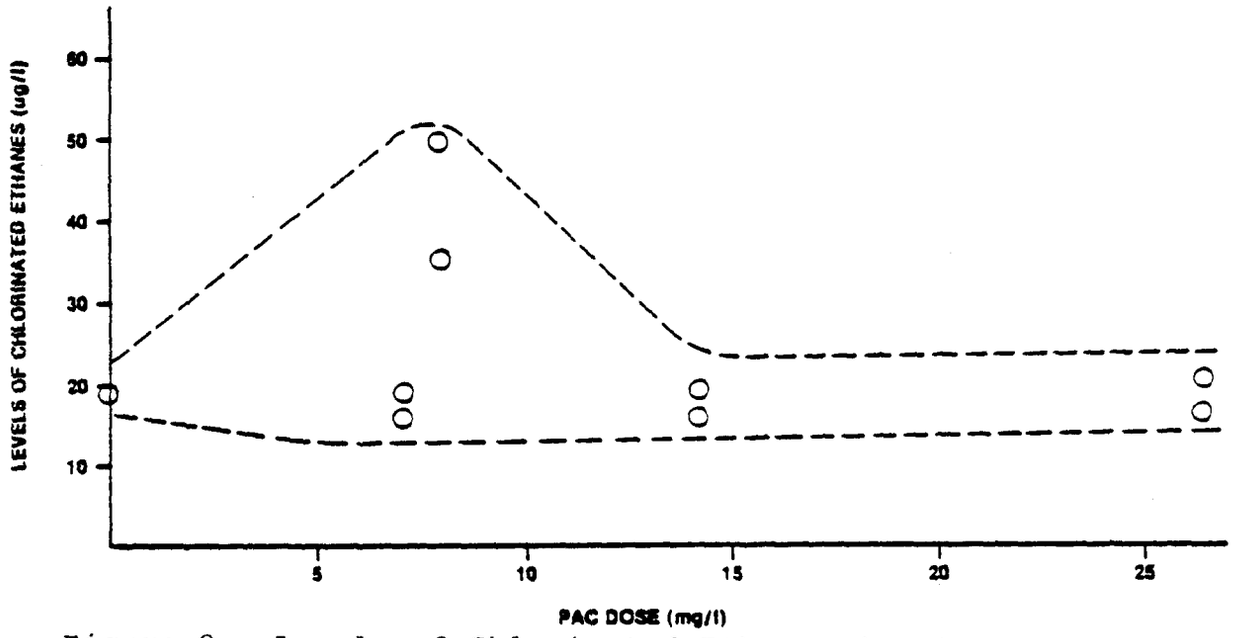


Figure 8. Levels of Chlorinated Ethanes in Finished Water at Various Doses of PAC for Plant Test

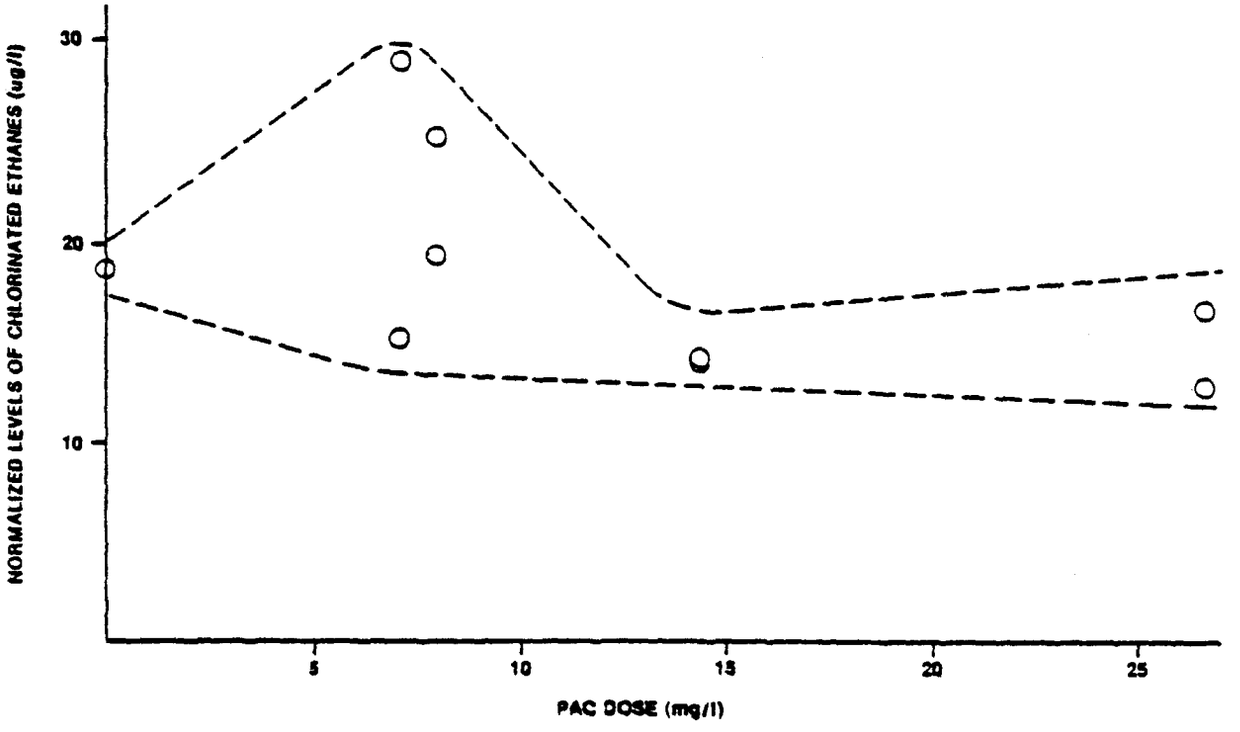


Figure 9. Levels of Chlorinated Ethanes in Finished Water Normalized by Raw Water Indicator Species at Various Doses of PAC for the Plant Test

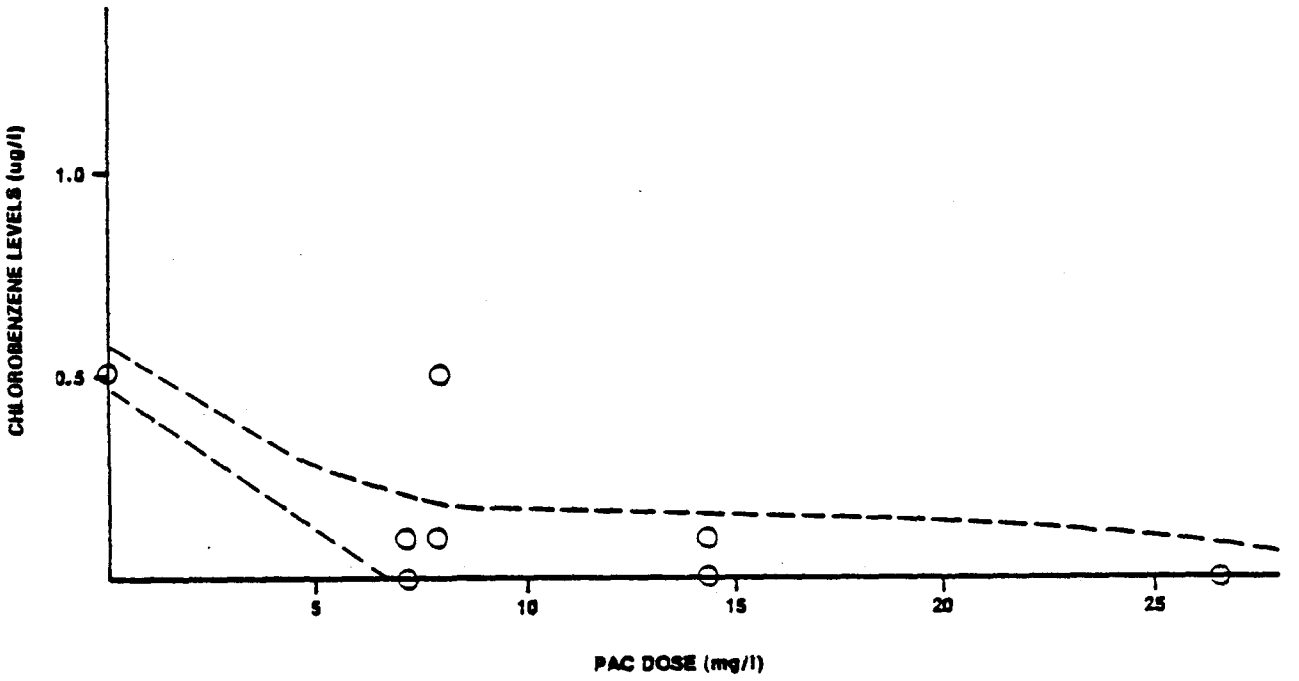


Figure 10. Levels of Chlorobenzene in Finished Water At Various Doses of PAC for Plant Test

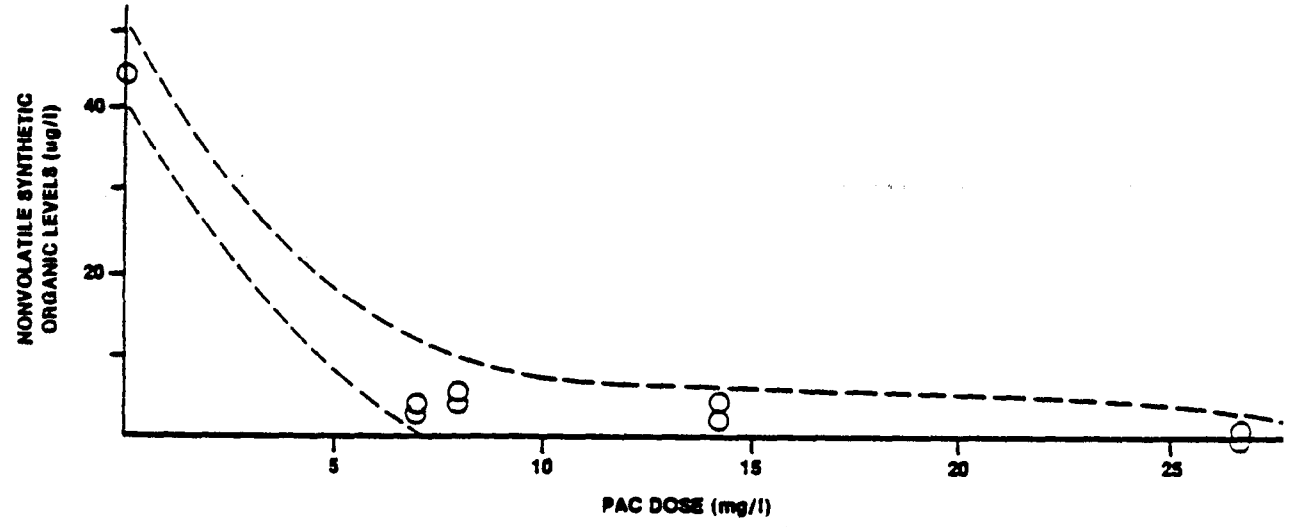


Figure 11. Levels of Non-Volatile Synthetic Organic Compounds with Various Doses of Powdered Activated Carbon During the Plant Test

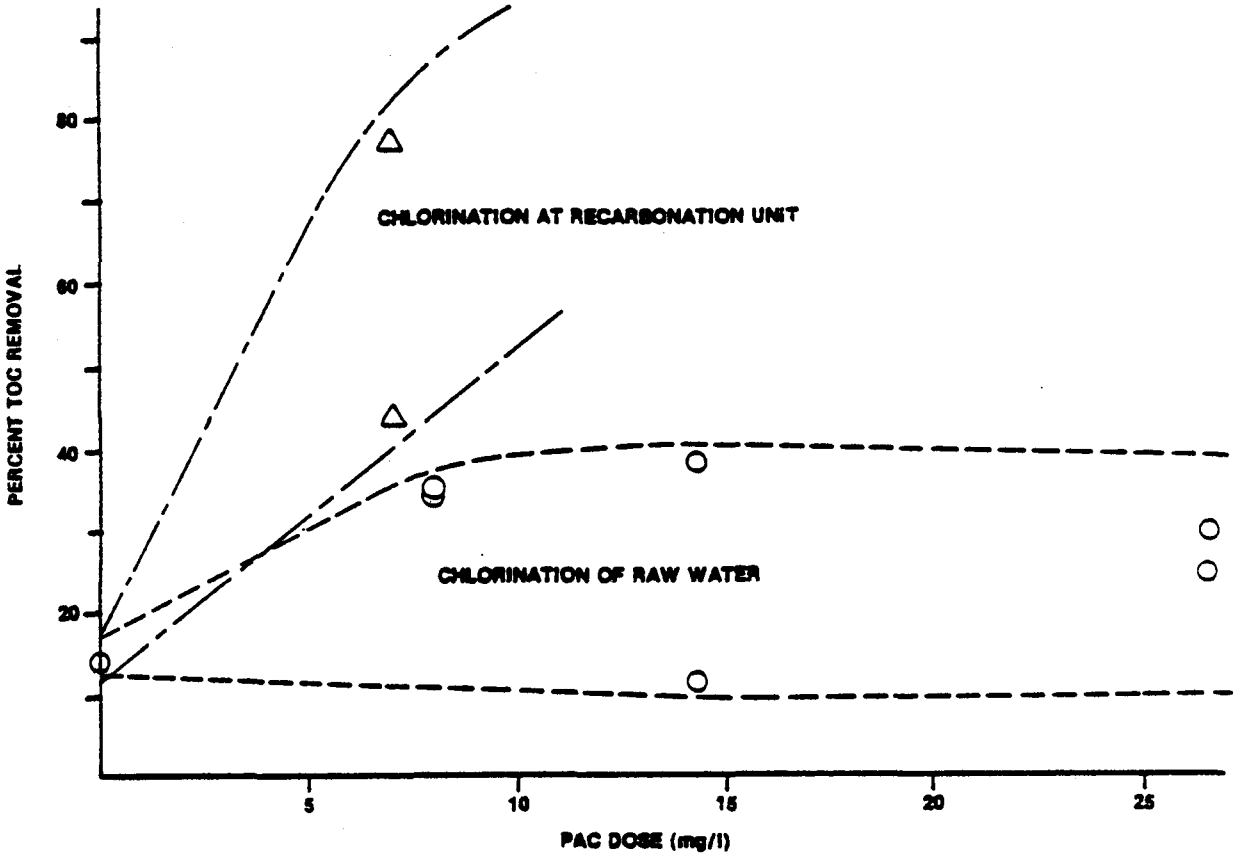


Figure 12. Percent Reduction in Total Organic Carbon with Various Doses of PAC and with a Change in the Point of Chlorination

micropores, will demonstrate more effective removal of these compounds.

- PAC was quite effective in controlling the TTHM that would be formed by "slow" reactions occurring in the distribution system, presumably by removal of the precursors. This conclusion coupled with the conclusion above demonstrates that the precursors participating in the "slow" reactions are low volatility organics.

- Changing the chlorination point from the raw water feed to the recarbonation units improved the effectiveness of the PAC in removing TOC, presumably by eliminating competition by chlorine for adsorption sites. Forty to fifty percent removal of TOC would be expected with PAC using this chlorination point. This removal of TOC is probably due to the removal of the low volatility component of the synthetic organics present.

- PAC slightly reduced instantaneous TTHM levels and the levels of volatile organics, but was not particularly effective in controlling these levels irrespective of the location of the chlorination point.

APPENDIX
(All levels µg/l unless otherwise noted)

Sampling Day / Site	Background		Day 1		Day 2		Day 3		Day 4		Day 5		Day 6		Day 7		Day 8	
	Raw	Finished	Raw	Finished	Raw	Finished	Raw	Finished	Raw	Finished	Raw	Finished	Raw	Finished	Raw	Finished	Raw	Finished
Vinyl Chloride	A*	A	A	A	A	A	A	A	A	A	A	T	A	T	A	A	A	A
Vinylidene Chloride	1.1	1.2	1.1	0.5	1.4	0.8	1.2	0.9	1.2	0.8	2.2	3.	1.8	2.7	1.4	1.8	1.6	1.3
Trans 1,2 Dichloroethene	2.5	4.8	2.8	3.7	3.1	3.0	2.9	2.4	3.3	1.8	4.6	8.3	5.0	6.8	1.3	3.2	2.7	2.5
1,1 Dichloroethane	3.7	4.2	3.3	3.6	3.5	3.8	3.1	4.1	3.4	3.6	4.8	9.0	6.0	7.1	2.2	3.8	2.7	3.4
Cis 1,2 Dichloroethene	6.6	14.9	6.2	12.5	7.8	12.1	7.2	11.0	7.3	9.4	11.4	34.6	11.9	26.9	2.9	13.2	6.1	11.5
Chloroform	1.2	33.3	7.0	27.1	1.0	25.7	0.7	35.6	2.1	26.7	1.1	85.5	1.6	60.5	0.2	35.0	0.3	16.2
1,1,1 Trichloroethane	4.4	14.5	6.0	12.1	6.7	14.5	7.6	17.1	7.3	13.1	10.5	40.7	7.8	27.9	3.6	14.6	4.7	12.4
1,2 Dichloroethane	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Carbon Tetrachloride	A	T	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Trichloroethylene	T†	T	T	T	T	T	T	T	T	T	0.6	0.9	0.8	T	T	T	T	T
Bromodichloromethane	A	7.0	A	6.8	0	6.1	A	7.8	A	7.0	A	26.2	A	17.2	A	8.4	A	3.3
Dibromochloromethane	A	1.8	A	2.0	0	1.8	A	2.0	A	1.7	A	4.3	A	2.6	A	3.9	A	1.7
Chlorobenzene	0.2	0.5	0.1	0.1	0.3	T	0.3	T	0.3	A	0.5	0.5	0.5	0.1	0.3	0.1	0.3	T
Bromoform	A	A	A	A	A	A	A	T	A	A	A	A	A	A	A	A	A	A
Ethyl Benzene	A	0.2	A	A	A	A	A	A	0.6	A	A	0.1	A	A	A	A	A	A
Toluene	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.8	0.2	0.2	0.5	0.5	0.6	0.1	0.1	0.1	0.2
Xylene	0.01	0.04	0.01	A	0.01	A	0.01	A	0.01	A	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
Diethyldisulfide	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Tetrachloroethene	0.2	0.2	0.2	T	0.2	A	0.2	T	0.2	A	0.4	0.4	0.4	0.1	0.1	T	0.2	A
Methyl Styrene and/or Indane	0.02	T	0.02	A	0.02	A	0.02	A	0.02	A	0.01	A	0.02	A	0.01	T	0.02	T
Methyl Indane	0.02	T	0.02	A	0.02	A	0.02	A	0.02	A	0.01	A	0.02	A	0.02	A	0.02	A
Naphthalene	0.01	0.01	0.002	A	0.003	A	0.003	A	0.003	A	A	A	0.01	T	0.004	T	0.01	T
Methyl Napthalene	T	T	T	A	T	A	T	A	T	A	T	A	T	A	T	A	T	A
C_2 Alkyl Napthalene	0.05	0.01	0.03	A	0.03	A	0.03	A	0.03	A	0.02	A	0.03	A	0.03	A	0.04	A
Acenapthene	0.4	0.09	0.33	T	0.39	T	0.38	A	0.39	A	0.26	0.01	0.5	T	0.46	T	0.51	T
Dibenzofuran	0.07	0.03	0.06	A	0.08	A	0.07	A	0.08	A	0.05	A	0.07	A	0.09	T	0.1	T
Octyl Phenol	0.29	A	0.2	A	0.23	A	0.2	A	0.23	A	0.14	A	0.03	A	0.27	A	0.28	T
2,6 Ditertbutyl-p-cresol	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Fluorene	0.24	0.09	0.17	A	0.37	A	0.24	A	0.24	A	0.14	0.004	0.26	T	0.12	T	0.28	T
Dibenzothiophene	0.02	0.01	0.02	A	0.02	A	0.02	A	0.02	A	0.01	A	0.02	A	0.02	A	0.02	A
Phenanthrene and anthracene	0.02	0.01	0.01	A	0.01	A	0.01	A	0.01	A	0.01	A	0.01	A	0.18	A	0.003	A
Methylene Phenanthracene	0.02	T	0.01	A	0.01	A	0.01	A	0.01	A	0.02	A	0.01	A	0.03	A	0.03	A
Fluoranthene	0.06	0.02	0.05	A	0.07	A	0.07	A	0.06	A	0.04	A	0.08	A	0.07	T	0.08	T
Pyrene	0.02	0.01	0.02	A	0.02	A	0.02	A	0.02	A	0.03	A	0.02	A	0.04	A	0.05	A
Diphenylamine	A	A	A	A	A	A	A	A	A	A	A	*A	A	A	A	A	A	A
C_3 Alkyl Benzene	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
C_4 Alkyl Benzene	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Chlorotoluene	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Tetrachloroethane	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Phthalates	0.04	0.03	0.03	0.04	0.02	0.02	0.02	0.01	0.06	T	0.01	0.01	0.03	0.04	0.02	0.03	0.03	0.02
Dichlorobenzene	0.14	0.12	0.11	A	0.14	A	0.12	A	0.14	A	0.09	0.03	0.22	T	0.15	0.01	0.21	0.01
Methylbenzofuran	0.02	A	0.01	A	0.02	A	0.02	A	0.02	A	0.01	A	0.02	A	0.02	A	0.02	A
Ethyl Styrene and Indane	0.01	0.01	T	A	0.01	A	0.01	A	0.01	A	0.02	T	0.01	A	0.02	T	0.02	T
TTHM inst	1.2	42.1	1.0	35.9	1.0	33.6	0.7	45.4	2.1	35.4	1.1	116.0	1.6	80.3	0.2	47.3	0.3	21.2
TTHM 3d	-	176.0	-	48.0	-	86.0	-	93.0	-	59.0	-	135.0	-	33.0	-	149.0	-	133.0
TOC (ug/l)	-	13.0	12.7	11.2	16.5	10.2	12.8	9.1	-	11.0	10.9	7.1	13.7	9.0	-	3.6	9.2	5.2

* A indicates absent
† T indicates trace

REMOVAL OF ORGANIC CONTAMINANTS FROM DRINKING WATER USING TECHNIQUES OTHER THAN GRANULAR ACTIVATED CARBON ALONE— A PROGRESS REPORT

James M. Symons, J. Keith Carswell,
Jack DeMarco, and O. Thomas Love, Jr.

INTRODUCTION

In the proposed Regulation (1) for the control of organic contaminants in drinking water published in the Federal Register, February 9, 1978, the use of granular activated carbon adsorption was proposed for water utilities serving more than 75,000 whose raw water source was vulnerable to organic contamination. In this proposed Regulation, the U.S. Environmental Protection Agency (U.S. EPA) included the use of granular activated carbon (GAC) adsorption because it was the best broad-spectrum organic removal unit process available at the time. In an effort to continue to expand the knowledge related to this drinking water unit process, the Drinking Water Research Division (DWRD) of the U.S. EPA has maintained an active research program on the subject of granular activated carbon adsorption. In addition to this research, the DWRD has also been performing research on other organic removal unit processes. These are: synthetic resin adsorbents; aeration; oxidants plus adsorbents; coagulation and clarification; powdered activated carbon; and reverse osmosis.

The purpose of this paper is to report on the progress to date (May, 1979) on the first three of these unit processes. The last three unit processes have not yet been studied extensively and will be reported on in a future paper(s). The studies on the unit processes of synthetic resin adsorbents and aeration have been carried out mainly on contaminated groundwaters, while the studies on the use of oxidants plus adsorbents have been made on both contaminated surface and groundwaters.

GROUNDWATER CONTAMINATION

In the past groundwater was thought in general to be largely free from organic contamination. However, recent surveys in New Hampshire, Connecticut, New York, and New Jersey have revealed that many groundwaters in this part of the United States are contaminated with various organic chemicals. Future surveys will reveal whether or not this problem is widespread throughout the remainder of the United States. Potential sources of groundwater

contamination are: pump lubricants (minor); industrial discharges; individual households; and groundwater recharge. The possibility of groundwater pump lubricants contributing major organic contamination to water has been discounted through calculations of contaminant potential. This leaves contamination from industrial discharges (either through spreading on the land or the improper disposal of industrial wastes in dump sites), the use of solvent septic tank cleaners and similar products in individual households, and the use of treated waste for groundwater recharge as the major threats to groundwater quality.

The groundwater protection research program of the U.S. Environmental Protection Agency located in Ada, Oklahoma, prepared a list of organic contaminants they judge troublesome in groundwaters (Table 1). The surveys mentioned above have confirmed the presence of four of the 12 compounds on the list and have added three more. Several of these compounds have appeared in more than one location and frequently are found in water whose total organic carbon (TOC) concentration is relatively low. Many of these organic chemicals have proven adverse health effects, making their removal important.

Table 1. Problem Groundwater Contaminants Suggested by Groundwater Research Program

Listed by USEPA Groundwater Protection Research Program	
Chloroform	Toluene
1,2-Dichloroethylene*	Xylenes
Tetrachloroethylene*	Chlorobenzene
Trichloroethylene*	Dichlorobenzene
1,1,2-Trichloroethane	Phthalates
Benzene	Methyl Chloroform*

Additional Compounds Found in Surveys

1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethylene

*Identified in Specific Locations

SYNTHETIC RESIN ADSORBENTS

Ambersorb XE-340*

Adsorption

Recently, the Rohm and Haas Company has developed a synthetic resin adsorbent reported to be highly active for the adsorption of low molecular weight chlorinated organic compounds. The performance of this material, called Ambersorb XE-340, has been investigated in six locations on a total of 10 different organic contaminants. Table 2 presents the performance of this resin for removing the ten different halogenated pollutants under the various operating conditions described. In many cases 10 percent of the influent concentration of the compounds had not yet appeared in the effluents at the time of preparing this paper. In other cases the service time at which 10 percent breakthrough occurred is shown. Although these data show that often adsorption of these ten organic substances was excellent (Summary Tables 3 and 4), removal was better in waters with lower TOC concentrations (Table 3) than those with higher concentrations of TOC and other contaminants (Table 4). In all of the locations in Table 4 the water was chlorinated and contained high concentrations of trihalomethanes. The poorer performance of XE-340 under these conditions shows the influence of competitive adsorption.

Figure 1 compares the ability of XE-340 to remove trihalomethane precursors as measured by trihalomethane formation potential (THMFP) in both raw and finished waters. The upper portion of Figure 1 shows that XE-340 is partially effective for removal of THMFP from raw water, but the lower portion of Figure 1 shows that when treating water that had been pretreated by softening, the resin could no longer remove any precursor material. This implies that the type of precursor that is adsorbable on XE-340 is also amenable to removal by coagulation and sedimentation, and the type of precursor that remains following lime softening is not adsorbable on XE-340.

Desorption

Studies were also performed to determine whether or not XE-340 would permit the desorption of previously adsorbed material if the influent concentration were lowered, similar to the situation experienced when using granular activated carbon as the adsorbent. To investigate this possibility, a column of XE-340 that had been loaded with a particular organic contaminant was placed in series following a fresh bed of resin. In this way, the influent concentration to the previously loaded column was now drastically reduced because of adsorption on the first column

*Mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency.

Table 2. Removal of Halogenated Pollutants by XE-340

COMPOUND	SITE	CONCENTRATION µg/L	LOADING gpm/ft^3	EBCT min	BED VOLUMES	TIME IN SERVICE DAYS	ORGANIC CARBON mg/L
Tetrachloroethylene	A	<1-4	0.8	9	20,160	≥126†	0.5
	B	<1-17	0.9	8.5	58,108	≥343†	-
	C	60-205	1.5	5	42,048	≥146†	0.5
	E	597-2500	0.9	8.5	17,788	105*	2-4
1,1-Dichloroethylene	C	41-74	1.5	5	42,048	≥146†	0.5
1,1-Dichloroethane	B	<1-9	0.9	8.5	58,108	≥343†	-
	C	3-7	1.5	5	42,048	≥146†	0.5
1,1,1-Trichloroethane (Methyl Chloroform)	A	<1-2	0.8	9	20,160	≥126†	0.5
	B	11-214	0.9	8.5	58,108	≥343†	-
	C	172-286	1.5	5	42,048	≥146†	0.5
cis-1,2-Dichloro-ethylene	A	3-9	0.8	9	20,160	≥126†	0.5
	B	<1-4	0.9	8.5	58,108	≥343†	-
	D	5-28	1.2	6.2	4,646	20	6.1
1,2-Dichloroethane	C	1-2	1.5	5	42,048	≥146†	0.5
Trichloroethylene	A	120-276	0.8	9	20,160	≥126†	0.5
	B	<1-10	0.9	8.5	58,108	≥343†	-
	C	1-2	1.5	5	42,048	≥146†	0.5

Table 2. Removal of Halogenated Pollutants by XE-340 (continued)

COMPOUND	SITE	CONCENTRATION µg/L	LOADING gpm/ft^3	EBCT min	BED VOLUMES	TIME IN SERVICE DAYS	ORGANIC CARBON mg/L
Carbon Tetrachloride	X	NF-87	0.75	10	15,120	105*	1.5-2.0
	X	NF-87	1.5	5	7,560	52*	1.5-2.0
Bromodichloromethane	D	27-56	1.2	6.2	11,615	50*	6.1
	X	14-39	0.9	10	14,688	102*	1-2
	X	26-39	1.5	5	12,097	42*	1-2
Chloroform	D	55-140	1.2	6.2	5,342	23*	6.1
	X	39-95	0.9	10	11,088	77*	1-2
	X	64-95	1.5	5	6,048	21*	1-2

†Effluent concentration did not reach 10% of influent value within the number of days shown, which corresponds to the run length for which data were available when this paper was written.

*Time at which effluent concentration reached 10% of influent value.

Table 3. Summary of Performance of XE-340
(< 1 mg/l TOC in water)
Two Locations

Compound	EBCT Min.	Maximum Conc. Range	Time in Service to 10% Leakage
		µg/l	Days
Tetrachloroethylene	5	60-205	> 146**
1, 1-Dichloroethylene	5	41-74	> 146**
1, 1-Dichloroethane	5	3-7	> 146**
Methyl Chloroform	5	172-286	> 146**
cis-1,2-Dichloroethylene	9	3-9	> 126*
1,2-Dichloroethane	5	1-2	> 146**
Trichloroethylene	9	120-276	> 126*

*No breakthrough at end of test.
**Test still continuing. These data collected at the time the paper was prepared (May, 1979).

Table 4. Summary of Performance of XE-340
(>1 mg/l TOC in water)
Trihalomethanes Present at three locations

Compound	EBCT Min.	Maximum Conc. Range	Time in Service to 10% Leakage
		µg/l	Days
Tetrachloroethylene	8.5	597-2500	105
cis-1,2-Dichloroethylene	6.2	5-28	20
Carbon Tetrachloride	5	NF-87	52
Chloroform	5	64-95	21
Bromodichloromethane	5	26-39	42

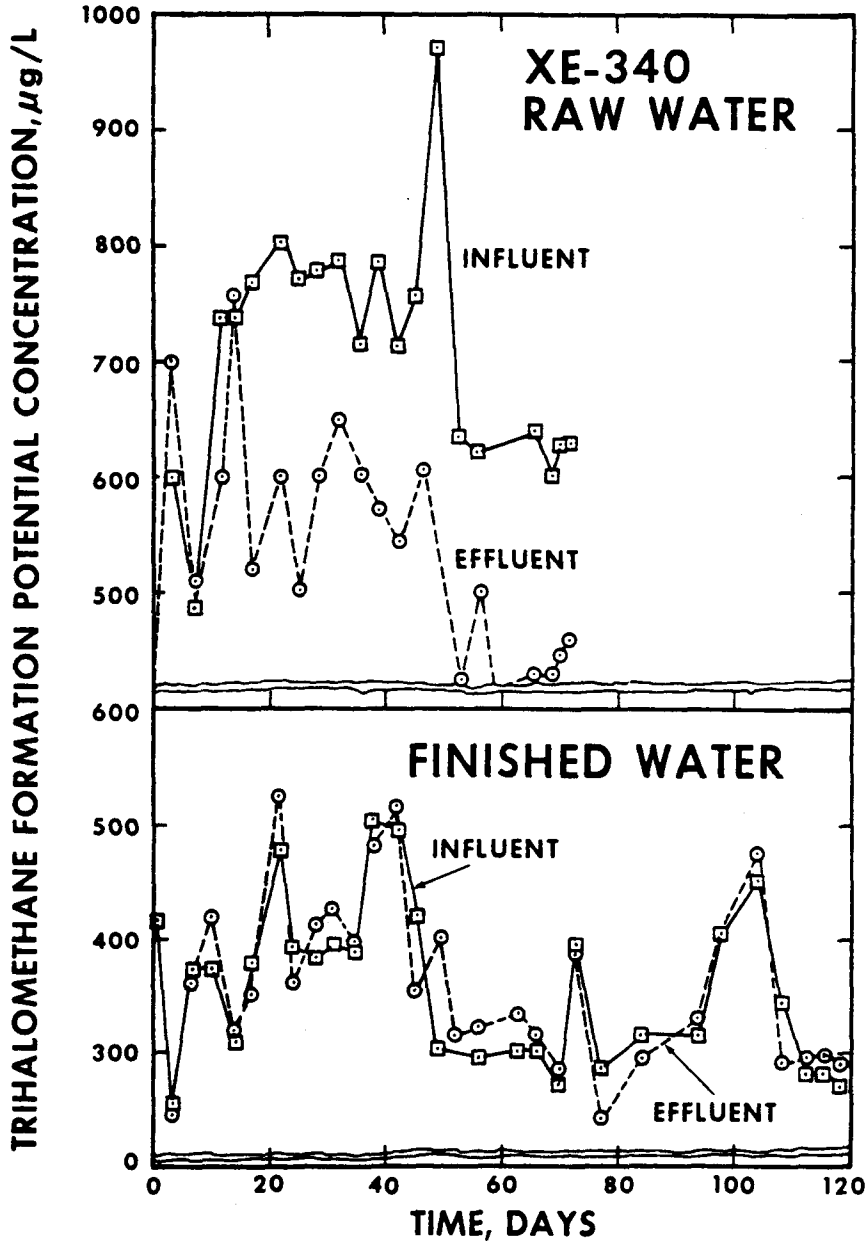


Figure 1. Removal of Trihalomethane Precursors by XE-340

in series. Figures 2 and 3 show that for chloroform and cis-1,2-dichloroethylene, desorption did occur. Another attempt was made to evaluate this phenomenon under different circumstances. In this case, a sudden increase in carbon tetrachloride concentration appeared in the water being treated with XE-340 resin. Shortly after the appearance of this high concentration of carbon tetrachloride, its concentration again fell to near zero. Figure 4 shows the adsorption pattern for carbon tetrachloride and a slight, but steady desorption following the disappearance of the carbon tetrachloride from the influent.

Regeneration

Another reported advantage of Ambersorb XE-340 is its ability to be regenerated with steam. This was investigated at one of the DWRD research project sites where chlorinated surface water was being treated. With respect to chloroform removal, steaming the XE-340 partially restored its ability to adsorb chloroform, but breakthrough times were shortened. The possibility of regenerating XE-340 with steam will be further investigated at another location starting in the summer of 1979.

Amberlite IRA-904

Another synthetic resin adsorbent manufactured by Rohm and Haas Company is IRA-904. This material, a strong-base anion exchange resin, is used as an organic scavenger in some industrial processes. Its ability to remove general organic contaminants as measured by the parameter TOC was compared to XE-340. Figure 5 shows that XE-340 had almost no capacity for removing general organic compounds as measured by TOC, while IRA-904 removed approximately one-third of the TOC from the influent. On the other hand, Figure 6 shows that for the organic compound cis-1,2-dichloroethylene, XE-340 showed nearly complete removal throughout the test while IRA-904 removed little, if any, of this organic compound. Finally, Figure 7 shows that for trihalomethane precursor material in raw water, as measured by THMFP, IRA-904 was initially quite effective, but, similar to XE-340, IRA-904 was unable to remove any precursor material from water that had been pretreated by lime softening. The left hand side of Figure 7 also shows that an unadsorbable fraction of precursor material existed in the raw water, as the initial adsorber effluent concentration for THMFP was the same even when the bed depth was doubled from 2.5 ft (75 cm) to 5 ft (150 cm), 9 and 18 minute Empty Bed Contact Time, respectively. Therefore, although synthetic resins are capable of removing organic contaminants from water, different products have different adsorption characteristics; some are likely to be very pH dependent.

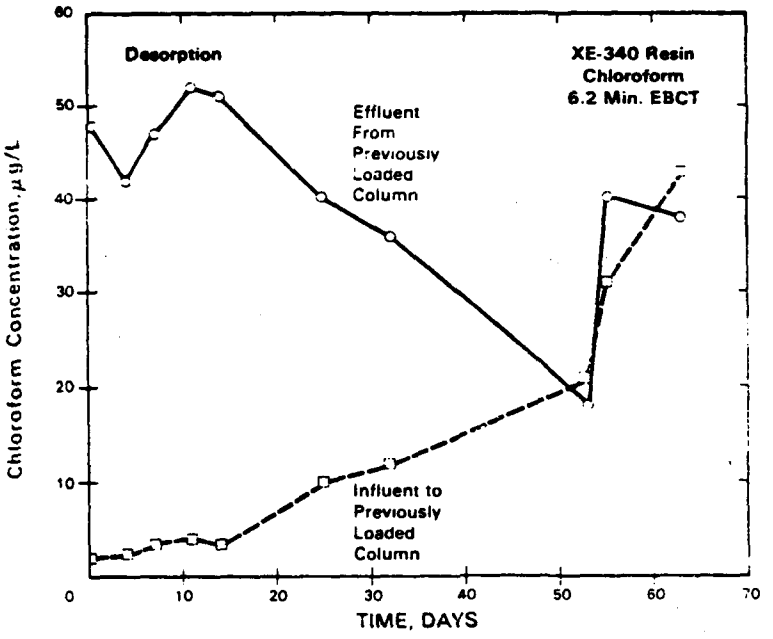


Figure 2. Desorption of Chloroform From XE-340

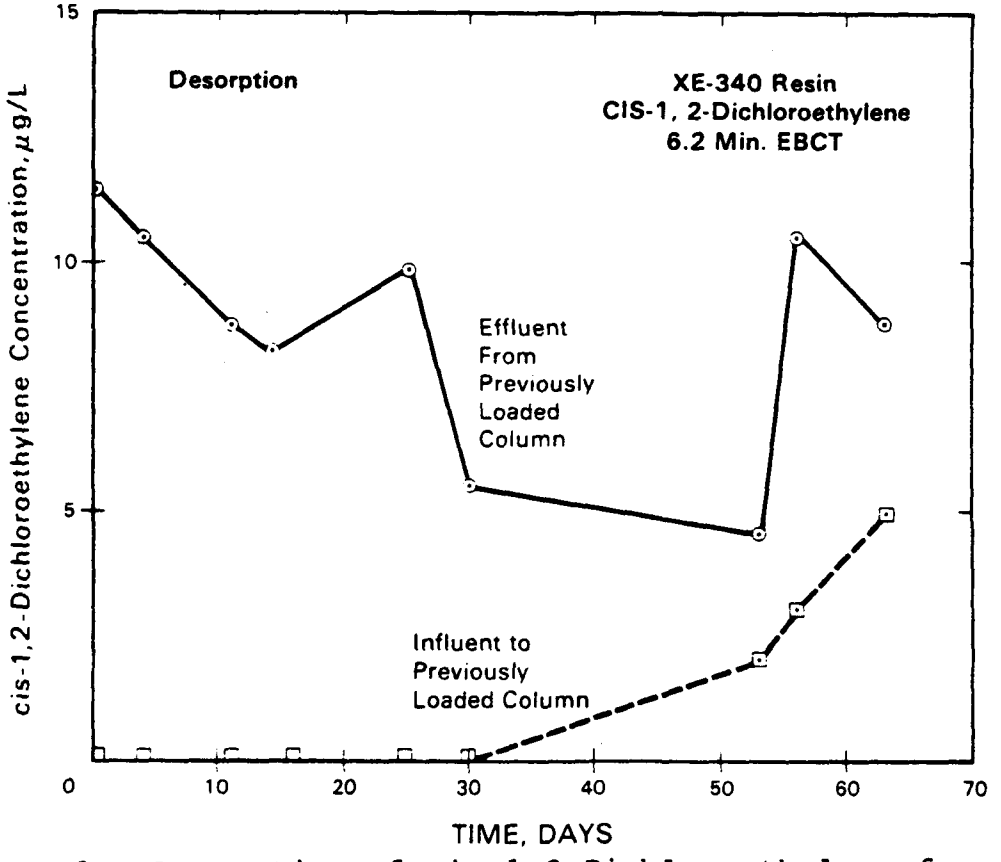


Figure 3. Desorption of cis-1,2-Dichloroethylene from XE-340

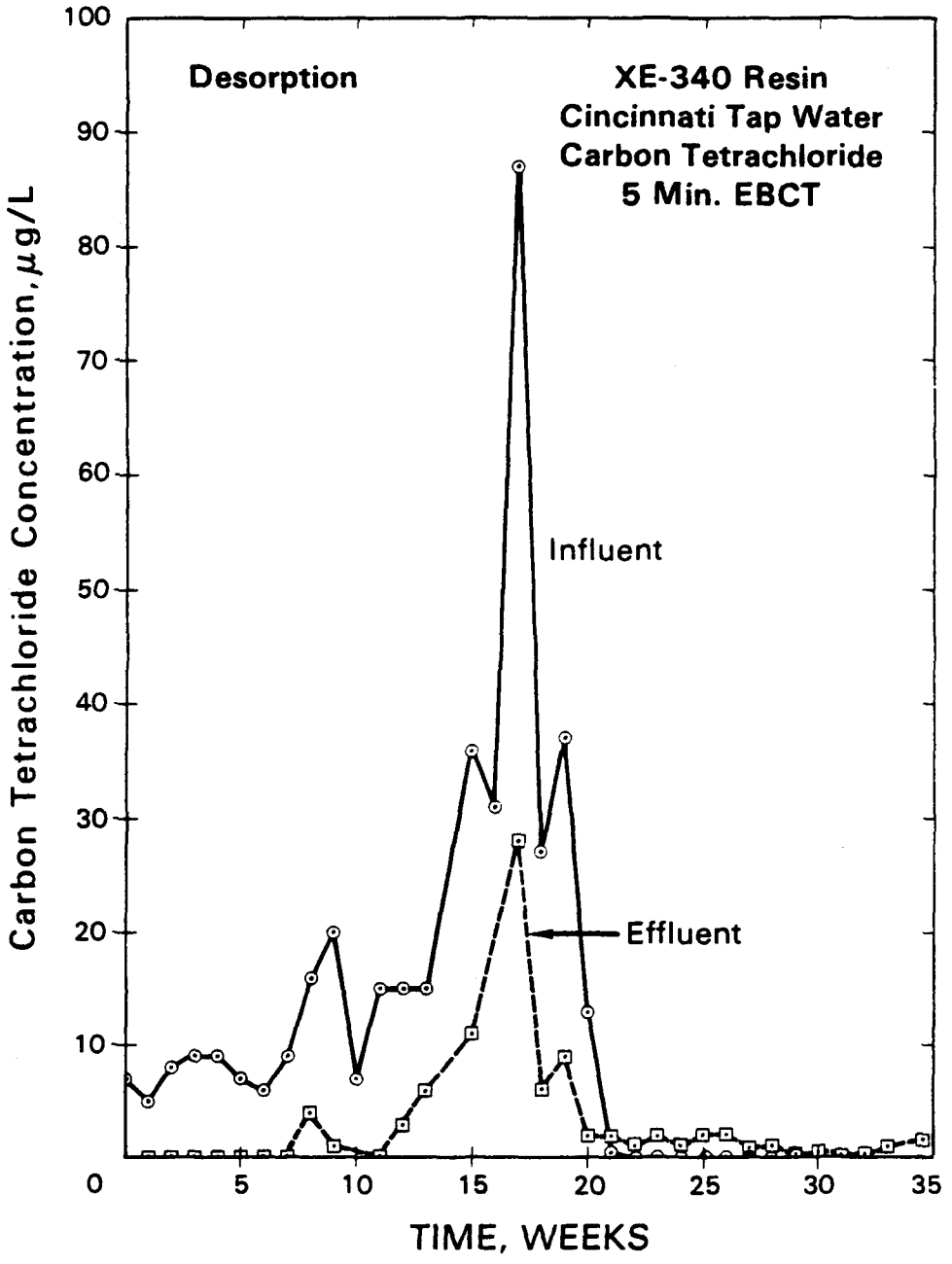


Figure 4. Desorption of Carbon Tetrachloride from XE-340

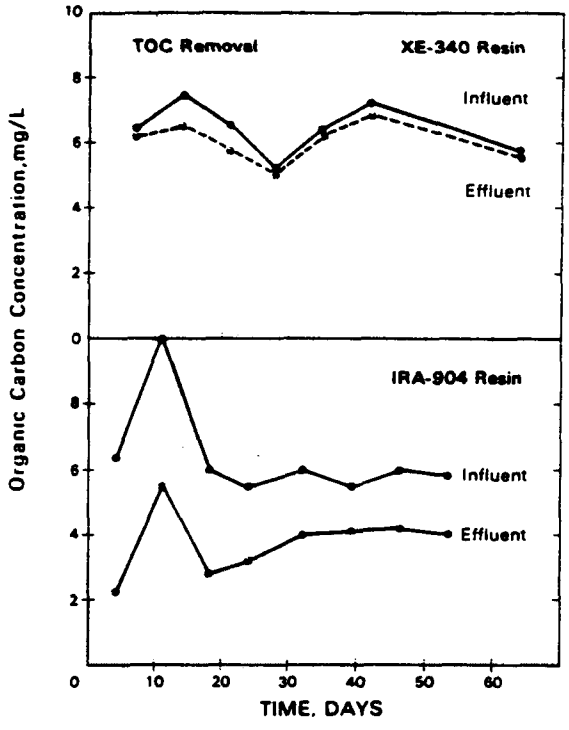


Figure 5. Removal of Organic Contaminants as Measured by TOC, by XE-340, and IRA 904 Resins

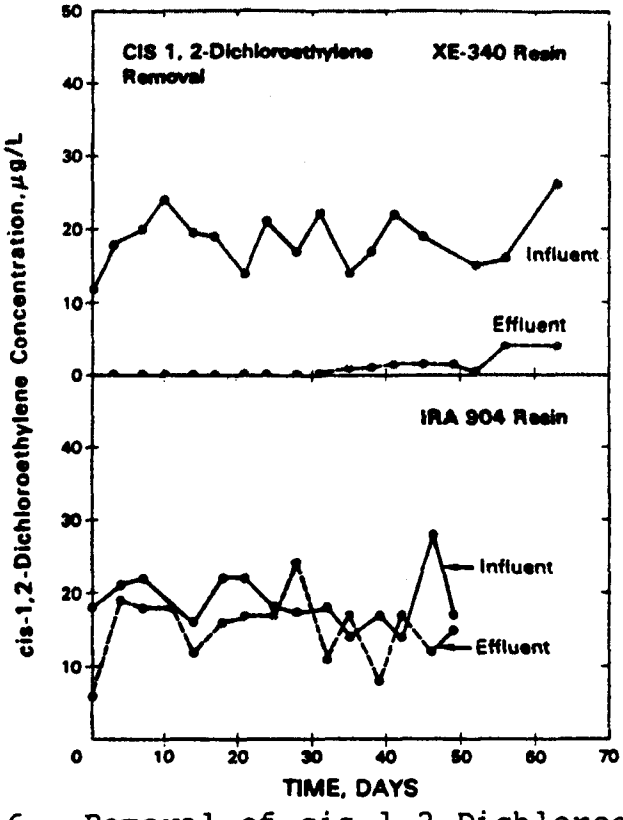


Figure 6. Removal of cis-1,2-Dichloroethylene by TOC, by XE-340, and IRA 904 Resins

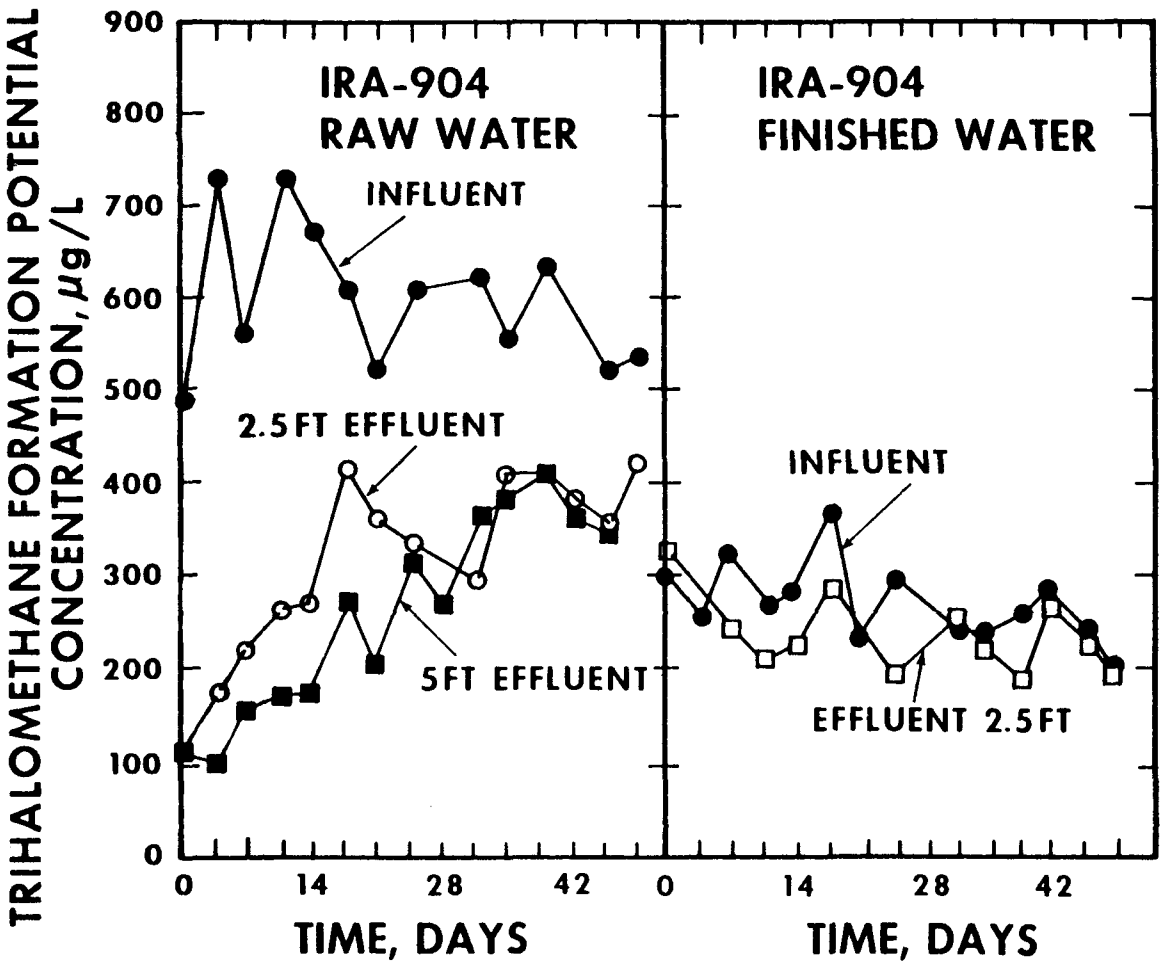


Figure 7. Removal of Trihalomethane Percursors by IRA 904 Resin

AERATION

Since many of the compounds found in contaminated groundwaters can be concentrated prior to gas chromatographic separation by purging from the liquid with an inert gas onto an adsorbent trap, aeration was investigated as a possible effective unit process for removing these compounds from water. Figure 8 demonstrates that for the trihalomethanes, good removal can be obtained, provided a sufficient air to water ratio is maintained. On the other hand, the removal of general organic contaminants as measured by the non-purgeable organic carbon concentration was largely unaffected by aeration in this diffused air system.

In one laboratory and one field experiment, the ability to remove eight chlorinated organic compounds was investigated. These studies were carried out in a diffused-air aeration system with a 10 minute contact time and an air to water ratio (volume to volume) of 4 to 1. The removal percentages for these eight compounds ranged from a high of 96 percent to a low of 20 percent. Plotting the percent removals vs. the solubility in water at 25°C in milligrams per liter, Figure 9 shows a general relationship between these two parameters. Other characteristics such as boiling point, molecular weight, and partition coefficient did not exhibit this relationship. Further study will indicate whether an approximate judgement can be made for removal of this type of organic contaminant by knowing its solubility in water.

Figure 10 shows that a relationship exists between percent remaining of an organic compound and the air to water ratio. Therefore, if aeration data were collected at one air to water ratio, and a different percent removal was required to meet a given effluent target concentration, this type of relationship could be used to determine what air to water ratio would be needed in order to reach this other treatment efficiency.

Finally, studies by McCarty, et al. (2) have indicated success using cascade type aerators. Studies of this type will be performed on contaminated groundwaters to determine whether or not the high air-to-water ratios in this type of tower would improve treatment as reported.

OXIDANTS PLUS ADSORBENTS

First Experiment

Several reports (3, 4, 5) have indicated that inserting ozone prior to an adsorption step in a drinking water treatment train will improve the performance of the combination of the two processes over the performance of either process alone. To

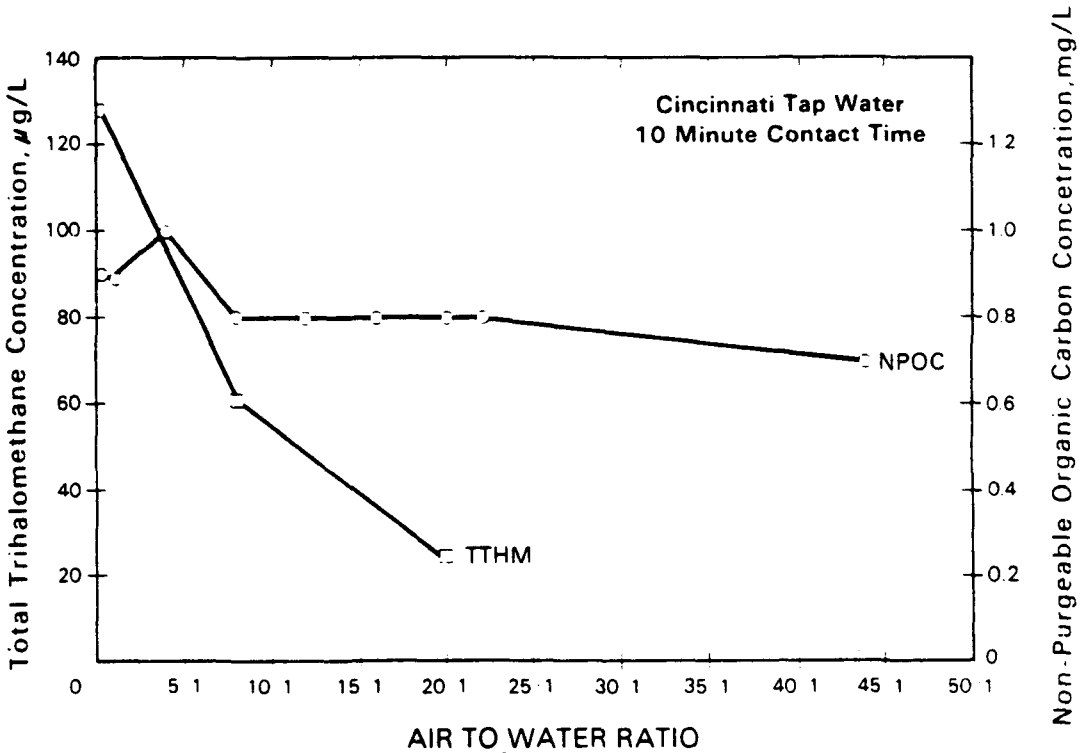


Figure 8. Influence of Aeration on Trihalomethane and Non-Purgeable Organic Carbon Concentrations

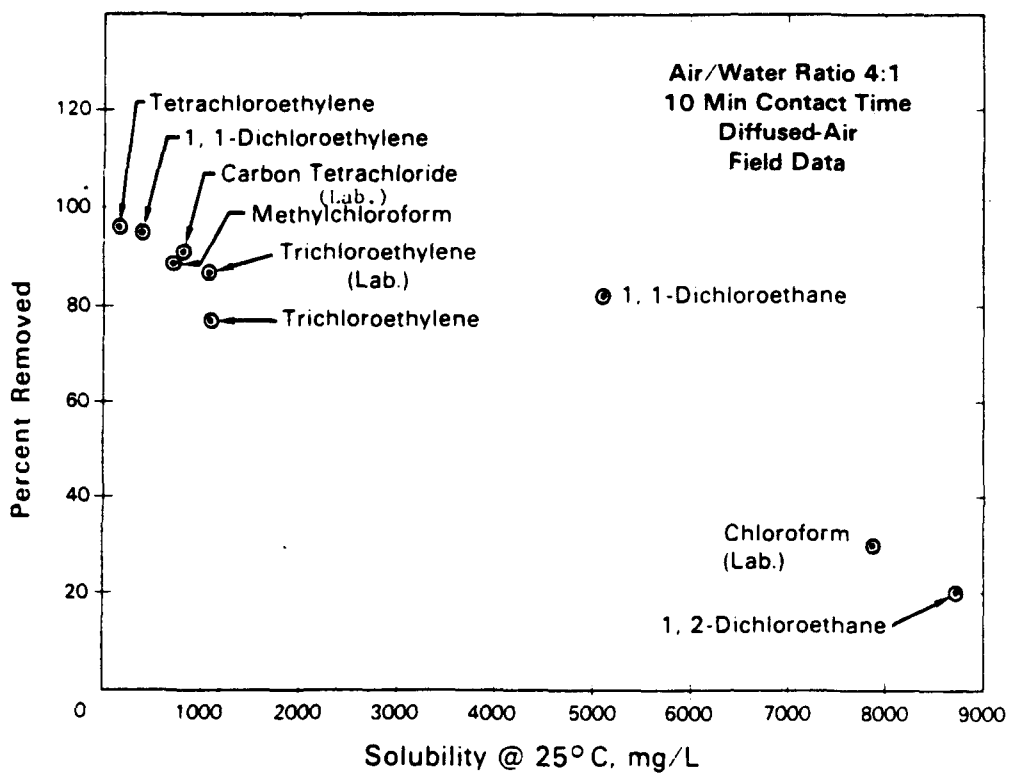


Figure 9. Relationship of Solubility to Effectiveness of Removal by Aeration

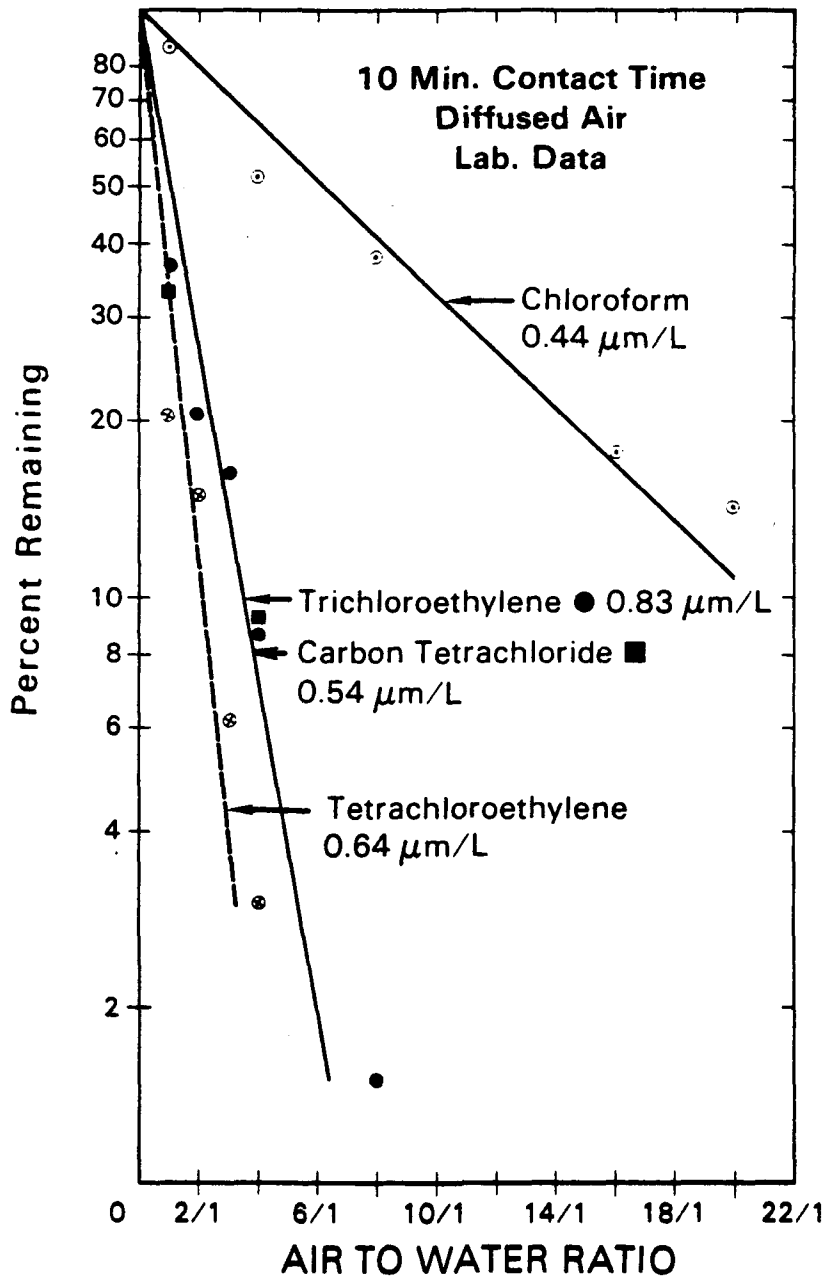


Figure 10. Removal of Four Organic Contaminants at Various Air to Water Ratios

investigate this possibility, a 75 gallon per day (290 liters per day) pilot column system was set up to treat coagulated and settled Ohio River water. Two parallel columns were used; in one, settled water was applied directly onto a granular activated carbon bed; in the other, an oxygen plus ozone* mixture was added to the water prior to the filter/adsorber such that the ozone dose was approximately 1.5 to 2.5 milligrams per liter.

Figure 11 shows that total organic carbon concentrations in the effluent of the column receiving oxygenated and ozonated water were always lower than in the effluent from the granular activated carbon column receiving untreated settled water. A similar "beneficial effect" was noted on the removal of disinfection byproducts formation potential (DB-PFP) as measured by total trihalomethane formation potential (see Figure 12). This "beneficial effect" was presumed to result from biodegradation of some organic compounds.

Second Experiment

This led to a second experiment in which coagulated and settled Ohio River water, 150 gal/d (580 l/d), was fed to four parallel treatment trains constructed of stainless steel, Teflon, and 1.5-inch (4 cm) diameter glass columns. Each treatment train consisted of a dual-media (anthracite coal over sand) filter followed by three granular activated carbon columns in series, each with a 10 minute empty bed contact time. One train received untreated settled water, a second train received water that was oxygenated only, at a rate equivalent to the oxygen in the "low ozone" system to be described below. A third train received oxygen plus ozone with the ozone dose approximately 5 mg/l ("high ozone"), and a fourth train received oxygen plus ozone with the ozone dose approximately 0.5 mg/l ("low ozone"). All four gas contactors are unpacked countercurrent flow glass columns with a stainless steel diffuser. The contact time is 18 minutes.

This experiment had four objectives: (1) to determine if the previous experiment could be confirmed; (2) to determine what minimum ozone dose was needed to produce the "ozone effect"; (3) to determine if oxygen alone would produce a similar "effect"; and, (4) to determine if the biological growths could be contained within the system.

*Because pure oxygen gas was used to generate the ozone, the gas fed into the gas contactor was an oxygen-ozone mixture. For accuracy, therfore, the term "oxygen plus ozone" is used for the system with oxidant added.

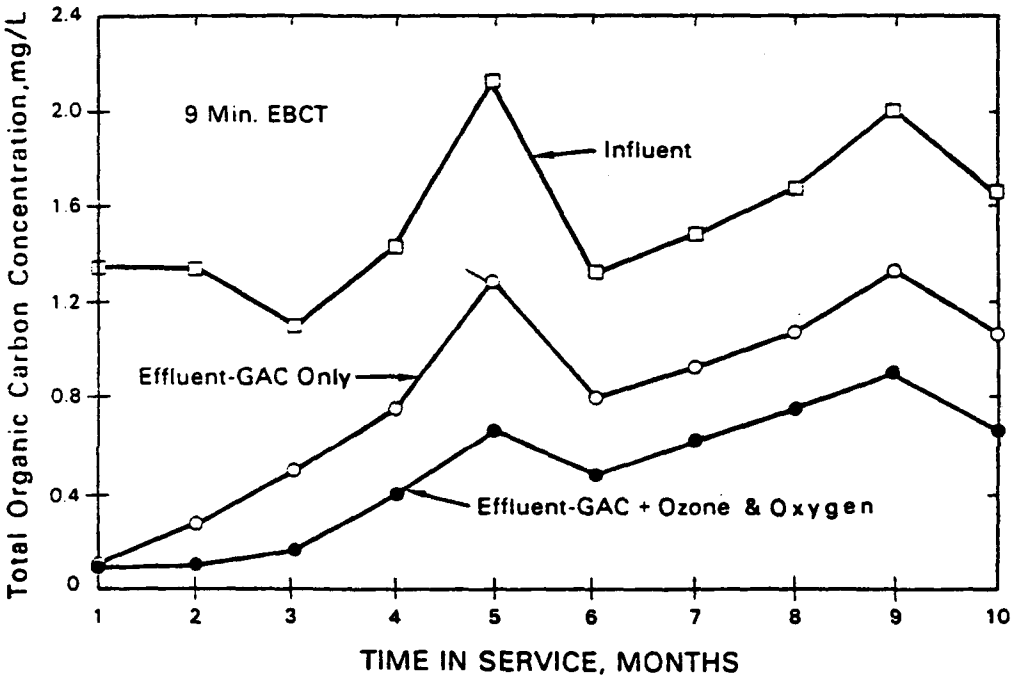


Figure 11. Influence of Ozonation Prior to Adsorption on Organic Carbon Removal

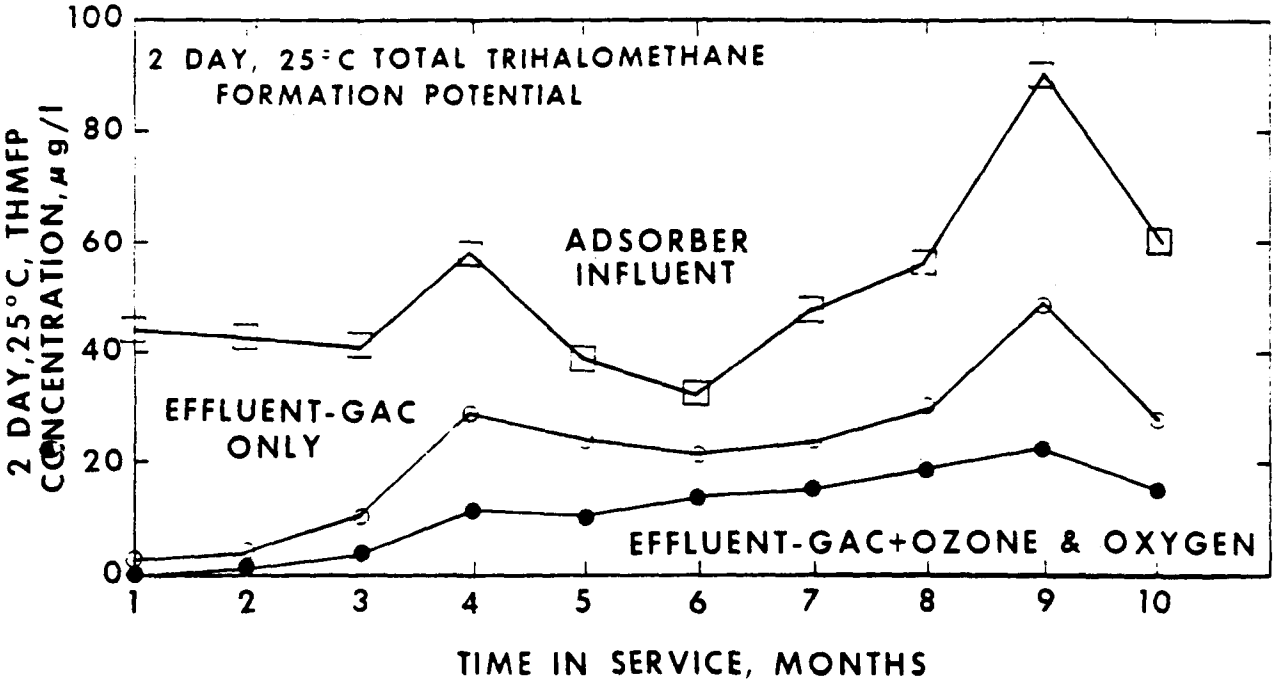


Figure 12. Influence of Ozonation Prior to Adsorption on Trihalomethane Formation Potential Removal

First Objective

Figure 13 shows that comparing the TOC removals, measured by "fraction remaining" (C_E/C_I), from the settled water to a point in the treatment train after the first of the three granular activated carbon columns in series, indicate that pretreating the water with oxygen plus ozone (5 mg/l) had some beneficial effect when compared to the control, as in Figure 11. This satisfied part of the first objective.

Note that in Figure 13, as in Figure 11, both treatment systems approached "steady-state" conditions toward the end of the test, and the TOC being removed reached some reasonably constant value greater than zero. Further, although this "steady-state" removal value is higher in the system with oxygen plus ozone pretreatment (the fraction remaining is lower), a "steady-state" condition is also reached in the control, indicating that biodegradation is also occurring in the control, even without any stimulation by pretreatment.

To investigate the reason for this effect, Figure 14 compares TOC "fraction remaining" for the oxygen plus 5 mg/l ozone system and the control at an intermediate point in the treatment train, between the dual-media filter and the granular activated carbon absorbent. Here again, a beneficial effect was noted, as indicated by a lower TOC "fraction remaining" through the dual-media filter in the system where the water had been pretreated with oxygen and 5 mg/l ozone. The top half of Figure 15 is a repeat of Figure 14 for comparison purposes. The lower half of Figure 15 shows that on a "fraction remaining" basis, the two parallel granular activated carbon columns were behaving similarly, regardless of the pretreatment. Therefore, although the combination of the dual-media filter and granular activated carbon adsorber in series showed a beneficial effect from oxygen plus 5 mg/l ozone as a pretreatment, this benefit manifested itself in improved removal of TOC in the dual-media filter, probably through biological action, and the performance of the adsorber itself was not enhanced by the pretreatment of oxygen plus 5 mg/l ozone. Note the evidence of biodegradation in both granular activated carbon adsorbers after about 175 days as shown by the lack of increase in the "fraction remaining" from then to the end of the test; see the lower portion of Figure 15.

Table 5 presents example calculations for the removal of organic carbon as measured by TOC for the control and the O_2 + 5 mg/l O_3 systems on two selected days. Note that although the percent passing (fraction remaining) is nearly the same for the two adsorbers, column 9 and Figure 15 (lower part), the load on the control adsorber and the quantity removed (column 8) is higher because of the lack of removal of TOC in the prior filtration step. Therefore, unless sufficient biological activity

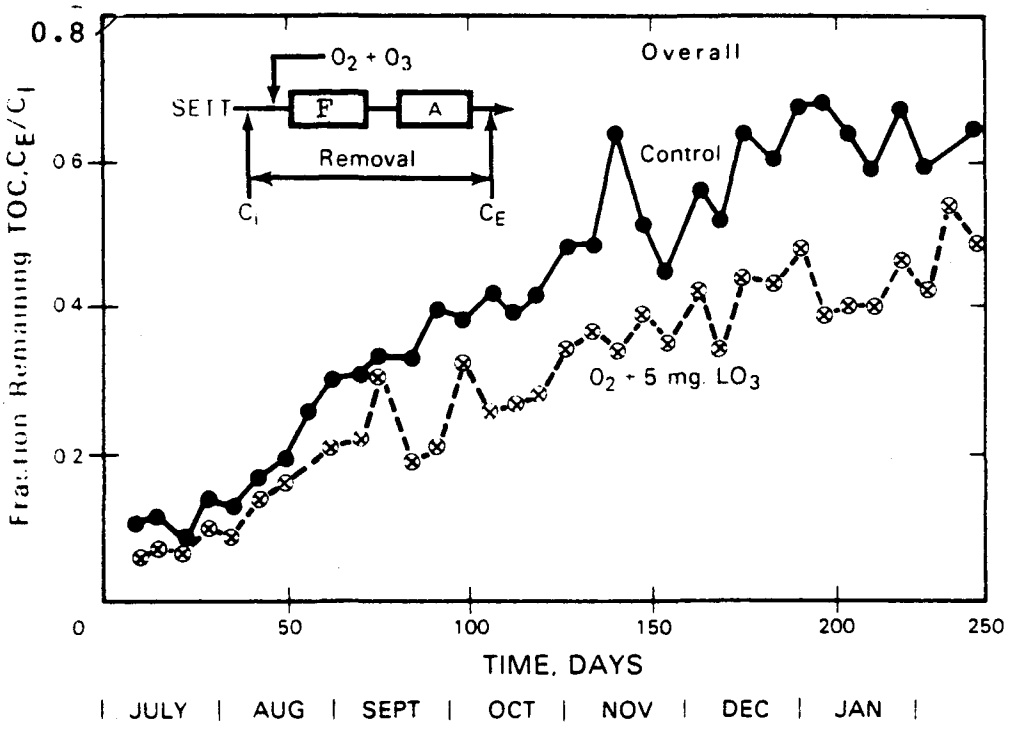


Figure 13. Removal of Organic Carbon By Granular Activated Carbon With and Without Pretreatment

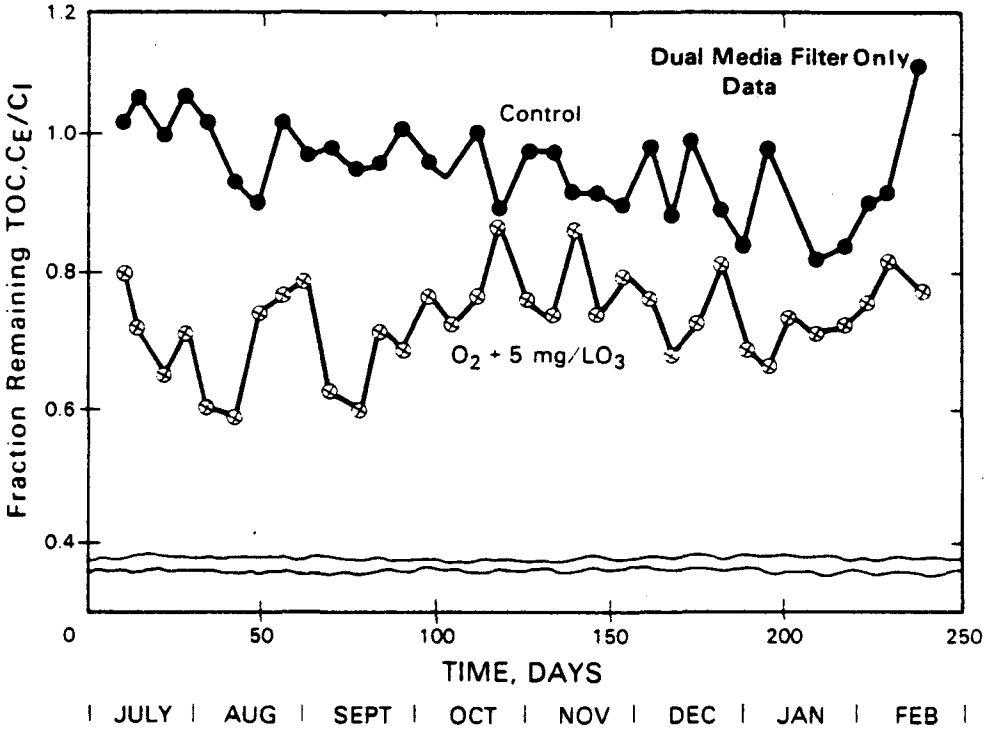


Figure 14. Removal of Organic Carbon By Dual Media Filtration With and Without Pretreatment

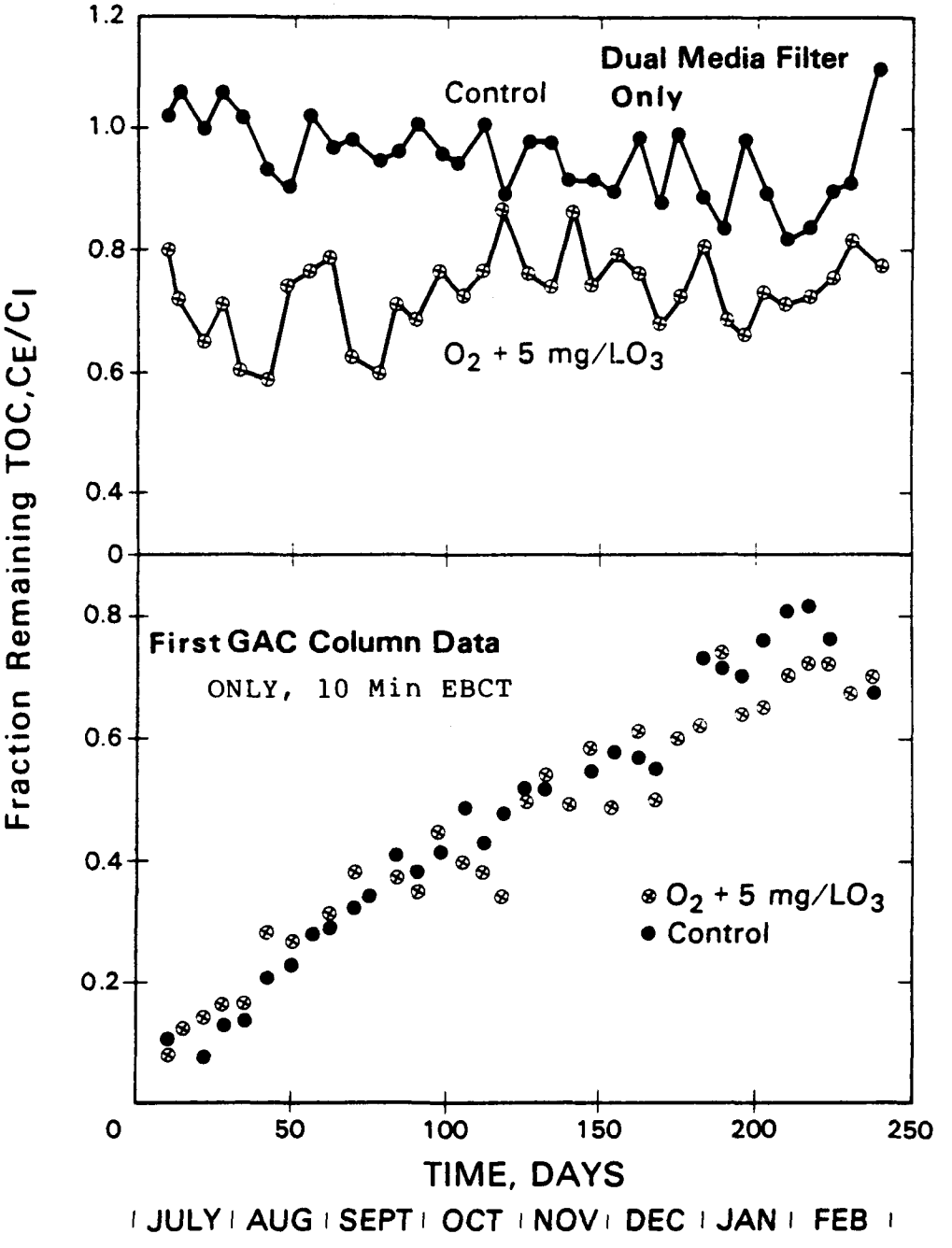


Figure 15. Removal of Organic Carbon Individually by the Dual-Media Filter and the First Adsorber with and without Pretreatment

Table 5. Concentrations of Organic Carbon at Various Points in the Treatment Train for Selected Days

System	Day	Influent	Contactor Effluent	Dual-Media Filter Effluent		First Granular Activated Carbon Adsorber Effluent			Percent Removal Overall System***
		TOC, mg/L	TOC, mg/L	TOC, mg/L	% Passing DM Only*	TOC, mg/L	ΔTOC, by GAC mg/L	% Passing GAC Only**	(1-CE/CI)X100
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Control	91	1.9	2.0	2.0	100	0.8	1.2	40	58
O_2 + 5 mg/L O_3	91	1.9	1.7	1.2	71	0.4	0.8	33	79
Control	133	2.1	2.0	1.9	95	1.1	0.8	58	48
O_2 + 5 mg/L O_3	133	2.1	2.0	1.4	70	0.8	0.6	58	62

*See Upper part Figure 15

**See Lower Part Figure 15

***See Figure 13

develops in the control adsorber to biodegrade this additional adsorbed organic carbon, as may have been happening after the 200th day (lower part of Figure 15), a given effluent concentration should be reached sooner in the control adsorber as compared to the O_2 + 5 mg/l O_3 system. Planned adsorption equilibrium studies should help determine whether the difference in the quantity of TOC adsorbed by the test system adsorber is a concentration effect or because the dual-media filter effluent contains a less adsorbable mixture of organic compounds.

Investigations were also carried out on the performance of this pilot column system for the removal of DB-PFP as measured by trihalomethane formation potential. The top section of Figure 16 shows that when oxygen plus 5 mg/l of ozone was added to the system as pretreatment, the net effect through the gas contactor, the dual-media filter, and the first granular activated carbon adsorber was beneficial. The effluent from that system had a consistently lower "fraction remaining" of THMFP than the control. This confirms the data from the previous experience shown in Figure 12 and satisfies the remainder of the first objective.

To investigate which unit process was responsible for the improved performance, the "fraction remaining" of THMFP in each of the unit processes, the gas contactor, the dual-media filter, and the granular activated carbon adsorber, were compared individually to their respective controls (lower three sections of Figure 16). In contrast to the situation that occurred with TOC removal, in this case oxygen plus 5 mg/l of ozone itself had some influence on THMFP, as shown by a lower "fraction remaining" in the gas contactor effluent as compared to the control (see second section of Figure 16). Note, the equivalent data for TOC removal were not plotted in Figure 15, as inspection of the data showed no removal of TOC occurred through the gas contactor.

The third section of Figure 16 shows that, similar to the situation with TOC removal, THMFP was being removed in the dual-media filter during the latter portion of the test, probably because of biological activity. Finally, as with TOC removal, little difference was shown in the performance of the granular activated carbon adsorber in spite of the addition of oxygen plus 5 mg/l of ozone (see fourth section of Figure 16). THMFP was evident in the control granular activated carbon adsorber as well as in the test system.

Second Objective

To determine what minimum ozone dose was required to produce the effect noted, the TOC removal data through the dual-media filter portion of the treatment train for the "low ozone" system, oxygen plus 0.5 mg/l ozone, was compared to the control.

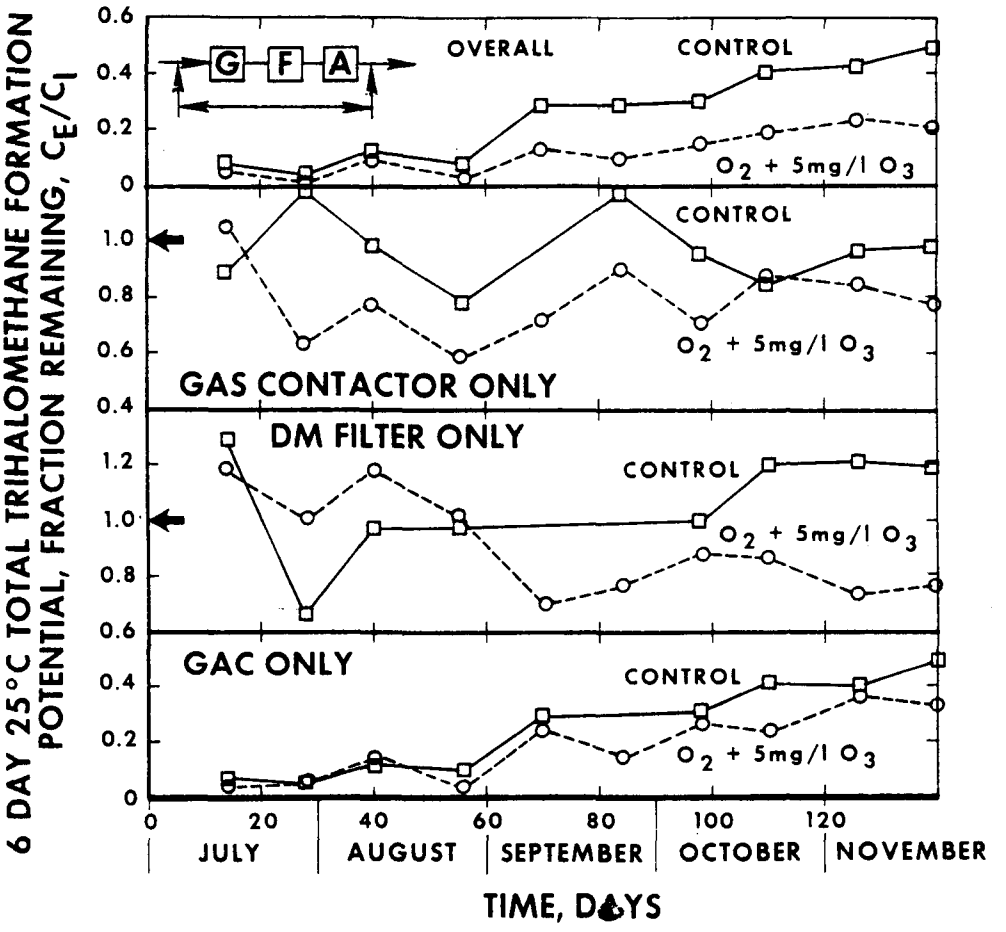


Figure 16. Removal of Trihalomethane Precursors by Various steps in the Treatment Train with and without Pretreatment

Throughout the first 175 days of the test an average of 87 percent TOC passed the dual-media filter in the "low ozone" system as compared to 93 percent passing in the control, indicating little difference. On day 175 the ozone dose was raised to 1 mg/l and on day 191 to 1.5 mg/l. Inspection of the TOC data at these increased doses showed some improvement in performance, but the data are too sketchy to draw firm conclusions as to the minimum dose required to produce some "effect" on TOC removal through the dual-media filter.

Although the TOC removal data were not conclusive, an attempt was made to determine the influence of raising the ozone dose on the system by examining the Standard Plate Count (SPC) in the effluent of the gas contactor. Table 6 compares the geometric mean SPC for the three periods. These data show that nearly complete elimination of the SPC in the gas contactor effluent did not occur until an ozone dose of 1.5 mg/l was reached. Although this study was halted in late February, 1979, it will be repeated in an attempt to determine what minimum ozone dose is necessary to produce a favorable effect on the removal of TOC and THMFP.

Table 6. Effect of Ozone Dose on Microbiological Content of Gas Contactor Effluent

	Control			Low Ozone System	
Sample Period Days	Geom. Mean SPC #/ml	No. of Samples n	O_3 Dose mg/l	Geom. Mean SPC #/ml	No. of Samples n
0-174	2,720	24	0.5	3,560	23
175-189	1,580	2	1.0	280	2
190-238	1,380	7	1.5	6	7

Third Objective

The treatment train in which "oxygen only" was added to the gas contactor was designed to determine whether any of the beneficial effect in the oxygen plus ozone system was caused merely by the presence of excess oxygen. For the first 175 days of the test, oxygen was added to this system at a rate equivalent to the oxygen in the treatment train receiving the lower ozone dose. On the 175th day, the oxygen gas flow rate was raised to match the quantity of oxygen being added to the gas contactor in the higher (5 mg/l) ozone system. Figure 17 suggests that before the change in the oxygen gas flow rate, with respect to TOC "fraction

remaining," the "oxygen only" system was behaving the same as the control. After the increase in the oxygen flow rate, however, the TOC "fraction remaining" data indicated an improvement in the performance of the "oxygen only" system to a point where it equalled the performance of the system to which oxygen plus 5 mg/l of ozone was being added.

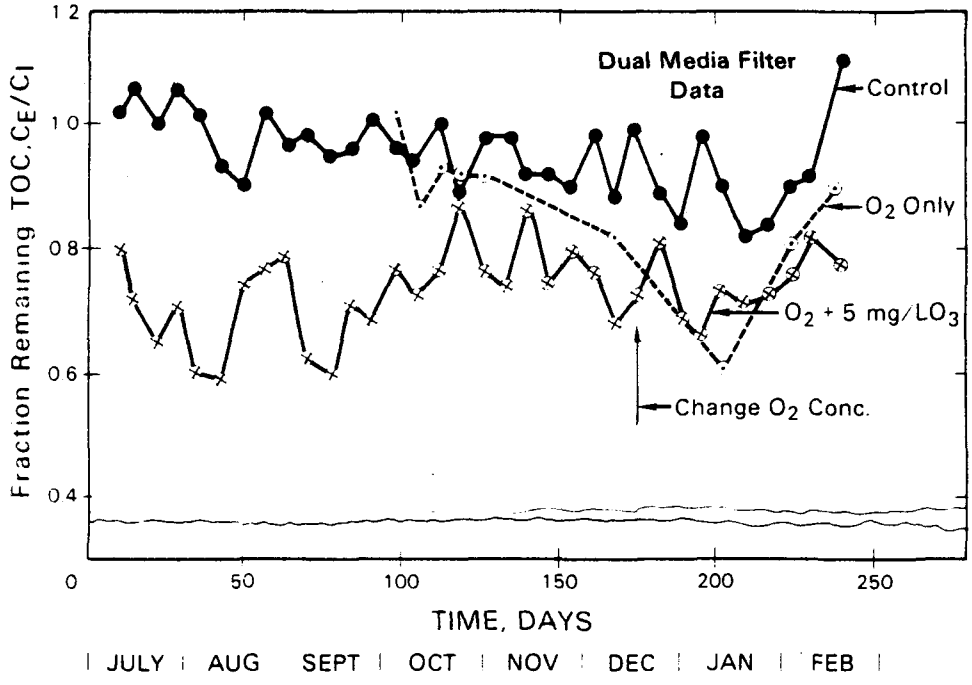


Figure 17. Removal of Organic Carbon by Dual-Media Filtration With and Without Pretreatment

Since this potentially important finding was only suggested by these data, a new experiment was begun in March, 1979 that consists of three parallel systems. In the control, settled Ohio River water is directly applied to a dual-media filter. In a second unit, settled water is oxygenated prior to filtration, and in a third system an equal amount of oxygen plus 5 mg/l of ozone is added to the water prior to filtration. Comparison of TOC and THMFP removals in these three systems should help demonstrate whether or not the presence of ozone is needed in the gas to produce an improvement in performance, at least in Ohio River water.

As previously shown, much of the improvement in performance of some of these systems was attributed to biological activity occurring in the dual-media filter. Therefore, if the suggested improved performance shown in Figure 17 did occur when the oxygen content was raised, the increased microbiological activity in the dual-media filter should have produced an increase in the SPC in the filter effluent. Table 7 showed that this did not occur. The reason for this is not known at this time (Spring, 1979) but may have been: (1) because only four samples were collected

following the change in oxygen dose, or (2) because the incubation temperature of the SPC test was so much higher than the temperature of the water in the test that low recoveries of organisms occurred, or (3) because the higher numbers of organisms were attached to the media and did not appear in the effluent. Detailed microbiological analyses will be made during the new experiment described above; this should help clarify this situation.

Table 7. Effect of Oxygen Dose on Microbiological Content of Dual-Media Filter Effluent

	Control			Oxygen Only System	
Sample Period Days	Geom. Mean SPC #/ml	No. of Samples n	O_2 Dose	Geom. Mean SPC #/ml	No. of Samples n
0-175	673	27	Low	615	23
175-283	470	8	High	288	4

Finally, efforts to assess the impact of increasing the oxygen gas flow rate on THMFP removal were thwarted because, during this cold weather period, the THMFP concentration was declining so rapidly in the influent to all of the systems, that any change in performance which might have been caused by increasing the oxygen gas flow rate was masked by this other occurrence. Again, the new experiment should help resolve the issue of the necessary presence of ozone in the gas to enhance DB-PFP removal.

Fourth Objective

In an effort to determine whether or not the expected biological growths could be contained in the filtration-adsorption system, standard plate counts were determined for the influent settled water and for samples taken at each intermediate point in the treatment train. For the summer (from the start of the experiment through September 21, 1978), these data show that 5 mg/l of ozone reduced the geometric mean SPC from 2,900/ml in settled water to 16/ml in the gas contactor effluent (see Figure 18) while essentially no change occurred in the control.

Following the dual-media filter, however, the geometric mean SPC had rebounded to 25,500/ml in the system receiving oxygenated and ozonated water (5 mg/l), while the geometric mean SPC actually declined somewhat through the dual-media filter of the control. This bacterial growth gives support to the contention that the organic removal occurring in the dual-media filter

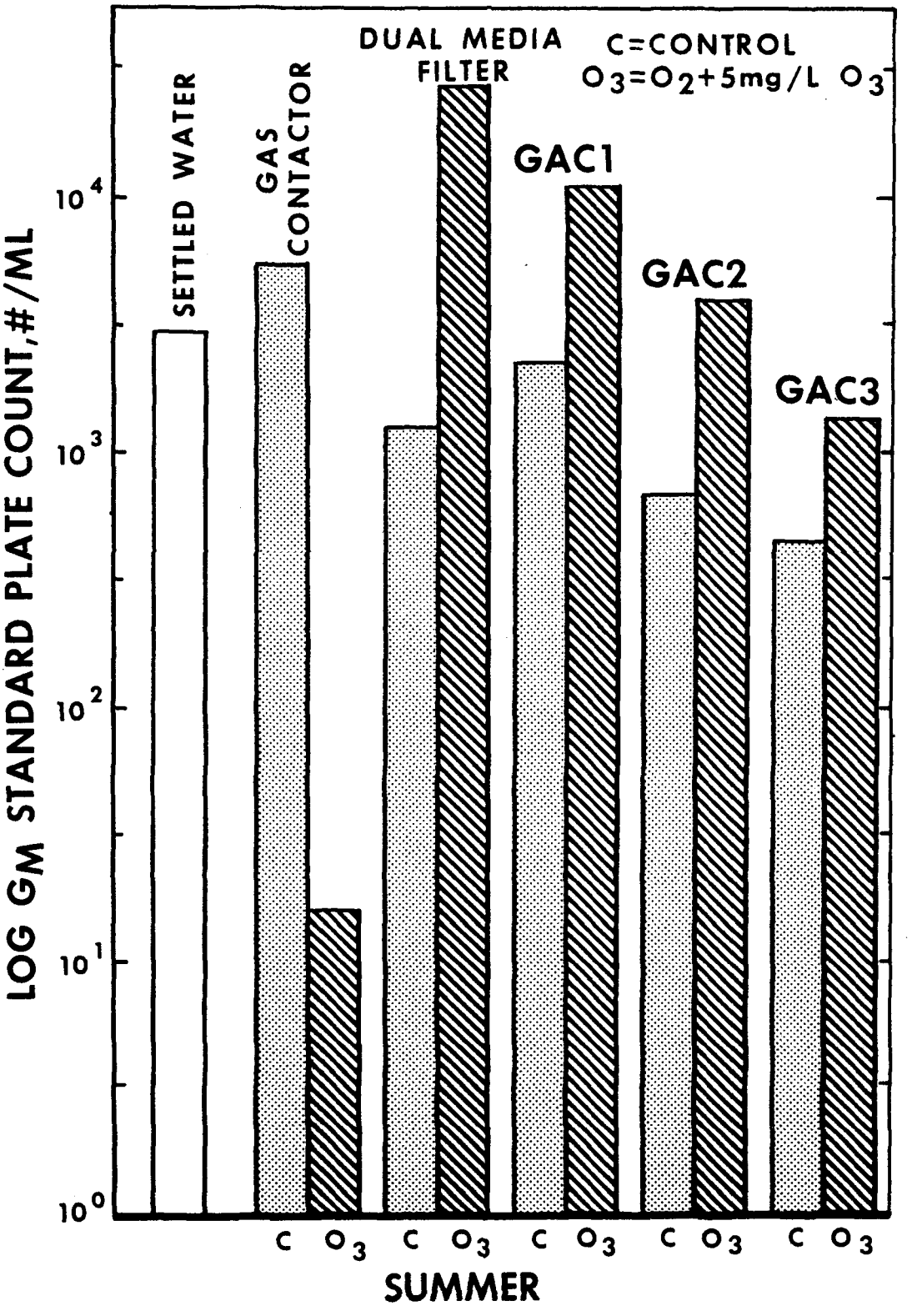


Figure 18. Standard Plate Count at Various Stages of Treatment

portion of the system is because of biodegradation. Measurement of the dissolved carbon dioxide content in the dual-media filters usually showed a higher concentration in the oxygen plus 5 mg/l ozone system as compared to the control, providing further evidence of biological activity.

In the oxygen plus 5 mg/l ozone system, sampling of the bacterial quality following each of the three granular activated carbon adsorbers showed a steady decline in the geometric mean SPC, indicating that microorganisms are being trapped in the adsorbers and, therefore, that the microorganisms are being contained in the system. These data do, however, reiterate the necessity for postdisinfection following a process such as this, and may indicate that a single granular media bed with a 10-minute empty bed contact time may not be sufficient to contain the microorganisms if growth is going to be so prolific in the first unit process.

Continued monitoring of the standard plate count in the effluent at various points in these two treatment trains through the fall (September 21, 1978 to December 21, 1978) and winter (December 22, 1978 through the end of the experiment in late February, 1979), indicated that temperature had a profound influence on the SPC in the various effluents. Table 8 shows that, although the geometric mean SPC did not decline much in the settled water through the seasons, a sharp drop occurred in these effluent values from the dual-media filter and various granular activated carbon adsorbers. These two systems, control and oxygen plus 5 mg/l ozone, will be continued through the spring and summer of 1979 and should indicate whether or not the microbiological content of these processes will rebound in the warmer weather.

Finally, some preliminary work on bacterial speciation indicates that although the number of bacteria in the effluents from the system treated with oxygen and 5 mg/l ozone increases in comparison to the control, the number of species of organisms tends to decrease. If this finding can be confirmed with further study, it would tend to indicate that certain species of organisms can predominate in the treatment processes and that these organisms are responsible for the major portion of the biodegradation that is occurring in these systems.

Future Studies

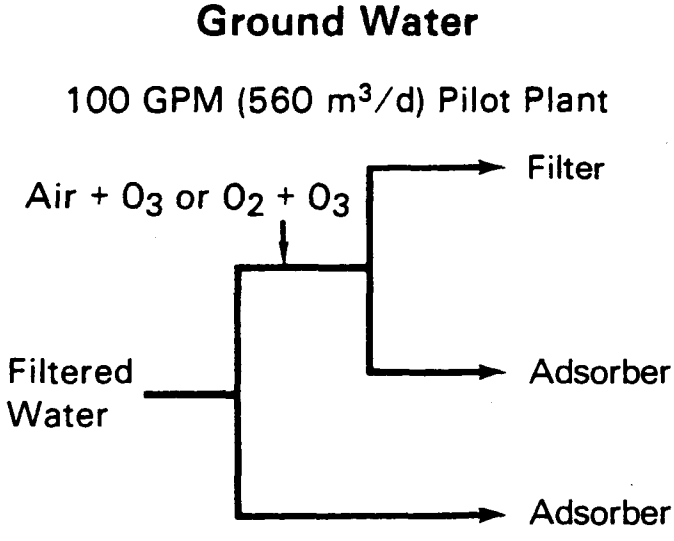
Future studies on these unit processes will involve both exploratory projects with Ohio River water and three field evaluation projects at other locations. Chlorination of coagulated and settled Ohio River water will determine whether or not the removal of organic halogenated compounds is influenced by the presence of oxygen or oxygen plus ozone as a pretreatment, which has been seen with other parameters such as TOC and THMFP

Table 8. Influence of Water Temperature on SPC in Effluents at Various Stages of Treatment

		Standard Plate Count (SPC) Geometric Mean (N/ml)					
Control	N	Inf. (Settled Water)	Gas Contactor	Dual Media Filter	GAC 1	GAC 2	GAC 3
Summer	15	2,900	5,140	1,230	2,170	650	420
Fall	12	1,500	1,370	350	202	165	134
Winter	9	1,440	1,420	469	67	41	48
Ozonated*							
Summer	15	2,900	161°	25,550	10,590	3,810	1,360
Fall	13	1,500	7†	10,440	595	330	205
Winter	8	1,440	5#	408	44	10	17

*Ozonated with 5 mg/l O_3 (together with excess O_2).
°Positive values only, 9 were 0/ml

†Positive values only, 2 were below detection limit
#Positive values only, 6 were below detection limit



High TOC and precursor, synthetic organics source data collection begins December, 1979.

Figure 19. Oxidant + Adsorbent Studies in Miami, Florida

(Figures 11, 12, 13, and 16). Additionally, oxidants other than ozone, such as hydrogen peroxide, will be investigated to determine whether or not similar effects to those described above will occur.

Figure 19 is the schematic diagram of a project being planned in Miami, Florida. Here, the raw water has high concentrations of TOC and THMFP, as well as the presence of synthetic organic contaminants. The major objectives are:

1. To compare the effectiveness of oxygen plus ozone before GAC vs. GAC alone for the removal of TOC, THM precursors and specific trace organic compounds of health concern from a groundwater supply.

2. To study the bacterial population types that exist in the various modes of treatment operations investigated. At this time (Spring, 1979) no decision has been made as to whether the ozone will be generated from oxygen or air. If air is used the test streams will be "air plus ozone" rather than "oxygen plus ozone" as in the pilot plant studies described above and the influence, if any, of oxygen itself will be reduced.

Figure 20 is a schematic diagram of the experimental set-up in Philadelphia, Pennsylvania. Here the TOC and THMFP concentrations of the river water are reasonably similar to those in the Ohio River, but synthetic organic contaminants are in somewhat higher concentration. In this case the ozone will be generated from air. The major objectives are:

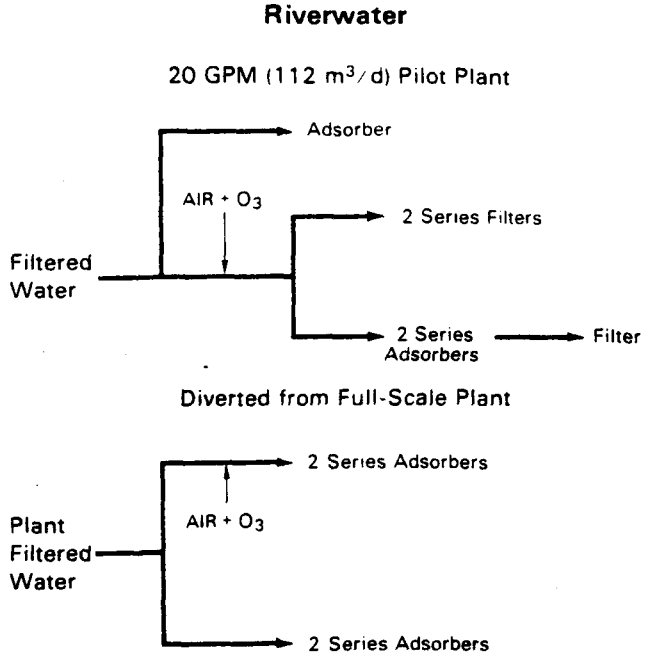
1. A bench- and pilot-scale study to determine the effectiveness of oxygen plus ozone before GAC to remove trace organic compounds of health concern from drinking water.

2. Compare the cost effectiveness of oxidant plus GAC vs. GAC only at this location.

Finally, Figure 21 is a schematic diagram of the study to be conducted in Shreveport, Louisiana. In this case, synthetic organic contaminants are nearly absent, but very high concentrations of TOC and THMFP are present. Here the ozone can be generated from either bottled oxygen or air. The major objectives are to:

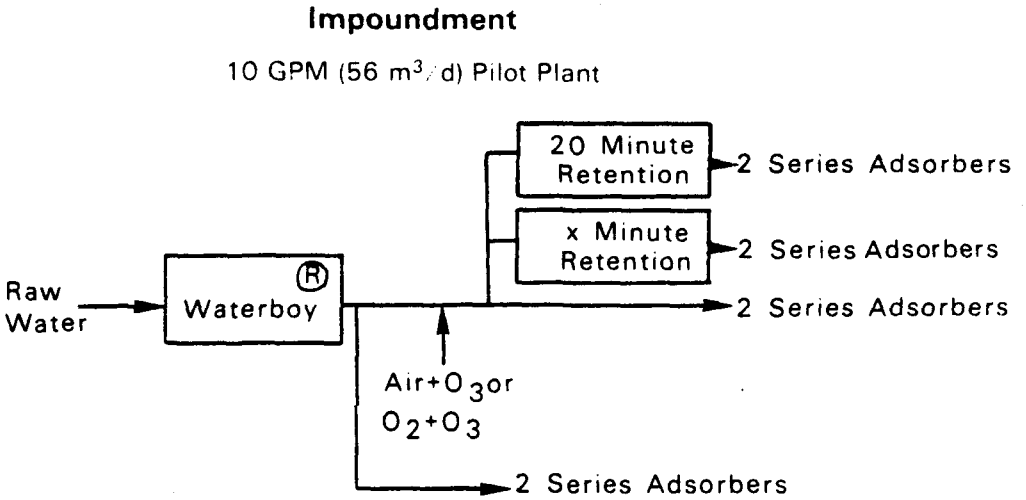
1. Compare the efficiency of oxygen plus ozone before GAC vs. GAC alone for the removal of THM precursors in a high TOC concentration surface water.

2. Compare the efficiency of ozone only vs. ozone and ultra-violet radiation (if current studies show it to



Medium TOC and precursor, synthetic organics source
data collection begins summer, 1979.

Figure 20. Oxidant + Adsorbent Studies in Philadelphia, Pennsylvania



High TOC and precursor, low synthetic organic source
data collection begins Fall, 1979.

Figure 21. Oxidant + Adsorbent Studies in Shreveport, Louisiana

be cost effective) as the preliminary oxidation step in the operation of the oxidant plus adsorbent columns for the removal of THM precursors in a high TOC concentration surface water.

3. Study the influence of contact time in the gas contactor on system performance.

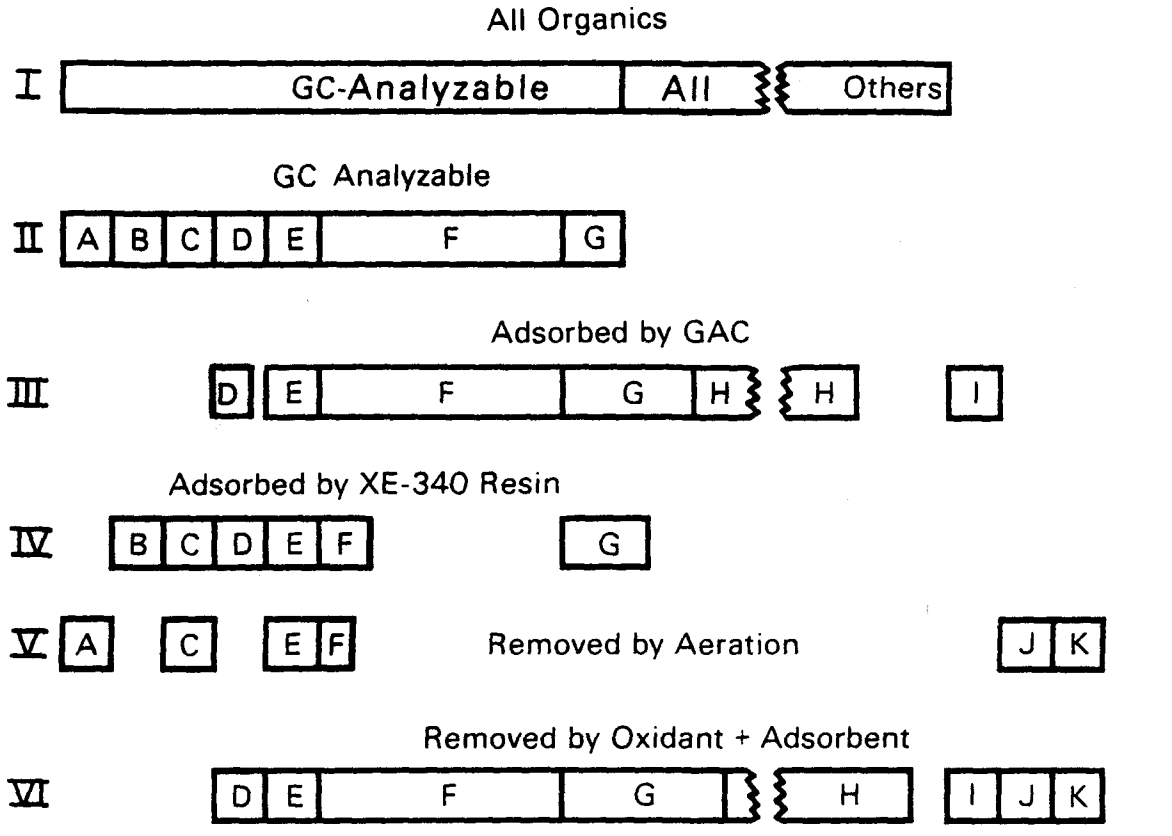
These three field evaluation projects, combined with the continued exploratory research using the pilot plant treating Ohio River water, should provide a wide range of data under a variety of operating circumstances related to the possibility of combining the unit processes of oxidation and adsorption.

SUMMARY

Considering the three organic contaminant removal unit processes reported in this paper, adsorption by synthetic resins, aeration, and a combination of oxidant and granular activated carbon adsorbent, along with what is already known about the performance of granular activated carbon alone as an adsorbent, leads to the conclusion that no one unit process is effective for the removal of all categories of organic contaminants. In a theoretical sense, all of the above named unit processes remove some fraction of all organic compounds, but in a practical sense many of these removals are so small as to be insignificant.

Figure 22 is an attempt to demonstrate the variability of the different unit processes for the removal of various types of organic contaminants. The first bar (I) shows that only a small portion of all organic compounds can be analyzed by gas chromatography and mass spectrometry. The second bar (II) breaks the analyzable portion of all organic contaminants down into seven categories that will be discussed below in relation to their treatability by the four unit processes under discussion.

Bar III, representing those organic contaminants adsorbed by granular activated carbon alone, shows that this unit process removes a wide range of organic contaminant types because of its ability to remove non-GC analyzable compounds measured typically as total organic carbon, AREA H, trihalomethane precursors, AREA G (only partially GC-analyzable, AREA G is smaller in Bar II), as well as a wide variety of synthetic organic chemicals, AREA F, such as polychlorinated biphenyls, polynuclear aromatic hydrocarbons, pesticides, and taste and odor producing compounds. Further, some chlorinated solvents, AREA E, such as trichloroethylene and tetrachloroethylene, and more soluble chlorinated solvents, AREA D, such as chloroform, are well removed by granular activated carbon adsorption when the adsorbent is fresh. Finally, granular activated carbon also adsorbs some heavy metals as indicated by AREA I.



AREA	EXAMPLES
A	Vinyl Chloride
B	1, 1- & 1, 2-Dichloroethane
C	Methyl Chloroform
D	Chloroform
E	Tri- and Tetrachloroethylene
F	PCB, PAH, Pesticides, Taste and Odor Compounds
G	THM Precursors
H	Compounds Measured Typically as TOC
I	Heavy Metals
J	Reduced Iron & Manganese, Sulfide
K	Ammonia

Note: Bar Length somewhat Related to Effectiveness

Figure 22. Summary of Treatment Effectiveness

Bar IV shows that the synthetic resin Ambersorb XE-340 removes some of the same materials that are reasonably well adsorbed by granular activated carbon, AREAS D and E, but is not effective for all compounds represented by AREA F (smaller than in Bar III) and not effective for organic compounds measured as TOC, AREA H. Also AREA G is smaller in Bar IV indicating that less trihalomethane precursor material is adsorbed by XE-340 than by granular activated carbon. Finally, heavy metals, AREA I, are not adsorbed by XE-340. On the other hand, XE-340 is effective for removing compounds represented by AREA B, for example, 1,1- and 1,2-dichloroethane, and AREA C, for example, methyl chloroform, which are compounds poorly adsorbed by granular activated carbon but well removed by XE-340. AREA D is larger than in Bar III showing the improved performance of XE-340 for chloroform removal.

Bar V demonstrates that aeration can remove a class of organic compounds that cannot be well removed by adsorption; AREA A, as represented by vinyl chloride. In addition, aeration removes some compounds that are well adsorbed on XE-340, AREA C, and adsorbed both by XE-340 and granular activated carbon, AREA E, and some taste and odor compounds from AREA F. In addition to removing these organic contaminants, aeration can remove two categories of inorganic contaminants; AREA J, representing iron, manganese, and sulfide; and AREA K, representing ammonia nitrogen.

Bar VI shows the demonstrated improvement of the combined treatment of oxidation and adsorption on granular activated carbon as compared to granular activated carbon adsorption alone. In Bar VI, AREA G and AREA H are larger than in Bar III indicating that this combination treatment is more effective for removing trihalomethane precursor compounds and compounds measured typically as total organic carbon than granular activated carbon adsorption alone. An economic analysis must be made, however, to determine whether or not the increase is great enough to justify the expense of the oxidant step (6). In addition, this combination treatment can remove ammonia nitrogen, AREA K, and reduced inorganics, AREA J.

Figure 22 shows that the broadest spectrum of organic contaminants can be removed by using granular activated carbon alone or granular activated carbon plus pretreatment with an oxidant, but if contaminants are present that are poorly removed by adsorption or biodegradation, then the alternative of aeration or adsorption on synthetic resins either alone or in combination with granular activated carbon adsorption may be a more effective method for controlling these specific compounds, depending on individual circumstances.

ACKNOWLEDGEMENTS

The authors wish to thank several people who contributed to the collection of data upon which this paper was based. These include: the local personnel at each site where data were collected, Mr. Bradford Smith, Mr. Dennis Seeger, and Ms. Clois Slocum who provided much of the organic analysis data; Mr. Kenneth Kropp who built much of the experimental apparatus and who, along with Ms. Dianne Hinderberger, operated the pilot plant; and Mr. Raymond Taylor and Prof. John Caruthers who provided the microbiological data. Finally the authors wish to thank Mr. Gordon G. Robeck, Mr. Alan A. Stevens and Mr. Edwin E. Geldreich for their valuable reviews and Ms. Patricia Pierson who typed the manuscript.

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A CONTRIBUTION TO THE DISCUSSION ON BIOLOGICAL PROCESSES IN GRANULAR ACTIVATED CARBON FILTERS

D. van der Kooij

Granular activated carbon (GAC) filters have been introduced and still are applied in drinking water treatment for the removal of taste and odor compounds and residual chlorine. More recently, the removal of specific toxic organic substances originating from wastewaters, as well as from chlorination processes, has become important. The specific applicability of GAC filtration for these purposes is based on the adsorptive capacity of GAC toward many organic compounds.

In the GAC filters, biological activity has generally been observed (1-5, 7-9, 13, 14). Many of the investigators suggested that the adsorption processes enhance the microbial degradation (oxidation) of organic compounds, by increasing both the substrate concentration in the filter bed and the contact time between the substrate and the organisms. In recent papers (3,8) it was emphasized that ozonation of water prior to GAC filtration results in an improvement of the biological oxidation processes in the GAC filters.

The general attention paid toward the biological activities in GAC filters might suggest that these processes are considered as being more important than the adsorption processes. In this context, the following remarks can be made:

1. An enhancement of biological degradation of organic compounds by adsorption processes in GAC filters used in drinking water treatment has never been directly proved. On the contrary, evidence has been presented (6, 10, 11), that microorganisms do not have the adsorbed compounds at their disposal. This evidence is based on the observation that the die-off rates of different types of microorganisms--coliforms, pseudo-monads and the bacteria assessed by the colony count--present on GAC (Norit ROW 0.8 Supra) and a non-activated carbon (NAC) taken from filters, which had been supplied with rapid sand filtered river water during a period of one year, were equal for identical groups on both types of the carbon (10).

   This observation indicated that the organic load of GAC did not influence the microorganisms. Moreover, it has been

shown (11) that the increase in the number of microorganisms on sand, NAC, and GAC in filters supplied with tap water was not influenced by the type of filter material. The final levels of the numbers of microorganisms on these materials were only slightly different, which is in contrast with the large difference in adsorption capacity between GAC on one hand and NAC and sand on the other. Experiments also revealed that microbiological activity on exhausted carbon does not restore the adsorption capacity (6), whereas phenol, which is both adsorbable and biodegradable, was oxidized only partially or not at all by bacteria in the presence of GAC (15). Based on these observations, it is concluded that the so-called biological regeneration of GAC in filters used for the preparation of drinking water is unlikely to occur. Moreover, it may be concluded that adsorption of biodegradable compounds results in an unnecessary load on the carbon and prevents the complete removal of these compounds by a biological process. For these reasons, GAC filtration should always be preceded by another filtration stage in which biological processes remove biodegradable compounds from the water.

2. The level of biological activity in GAC filters is influenced by easily biodegradable compounds coming onto the filter. Many of these compounds have low molecular weights and adsorb very poorly. A high filtration velocity results in a relatively large supply of these compounds per unit of filter volume. This partially explains why the bioactivity and numbers of microorganisms on GAC filters are larger than in slow sand filters (11). On the other hand, the biological activity in a GAC filter may be larger than in other filters in similar conditions because in the GAC filters a relatively large surface area per unit of filter volume is available for the attached growth of microorganisms. Indications of this aspect were obtained in experiments in which the performances of a GAC filter and a NAC filter were compared. In one experiment, these filters were supplied with river water pretreated by rapid sand filtration.

   Bacteriological investigations (Figure 1) revealed that the numbers of bacteria measured as colony-forming units per milliliter (c.f.u./ml) in the effluents did not differ. However, the numbers of bacteria on the filter materials (c.f.u./ml of carbon) sampled from the effluent end of the filters were two to three times higher on GAC than on NAC. Assuming a certain equilibrium between the number of microorganisms in the water (c.f.u./ml) and the number of microorganisms per unit of surface area of filter material, these observations may indicate that the specific surface area (cm^2/cm^3) available for attachment of microorganisms

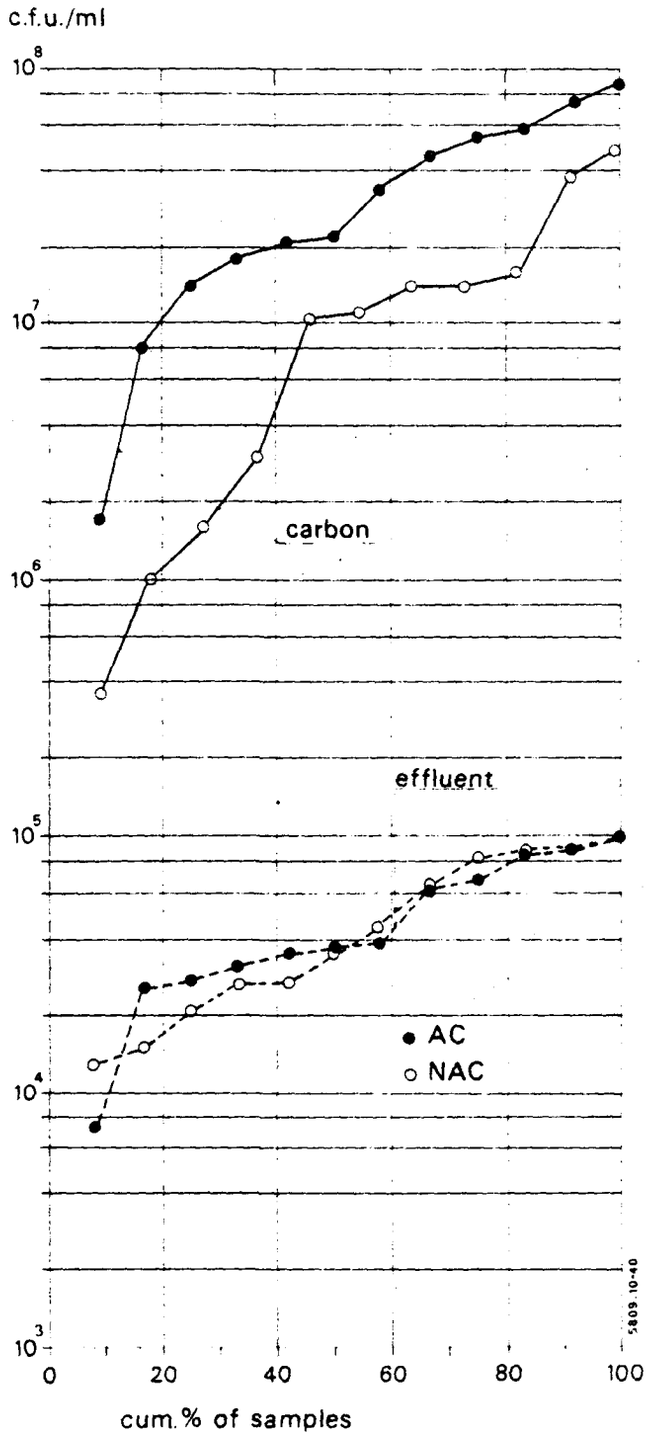

Figure 1. Cumulative Frequency Distribution of the Colony Counts on GAC and NAC and of the Effluents of Filters Supplied with Rapid Sand Filtered River Water

to GAC is two to three times higher than the corresponding value for NAC.

3. The stimulation of biological activity in the GAC filter by preozonation is not specific for these filters. Experiments performed by the author (12) showed that the amount of assimilatable (biodegradable) organic carbon (AOC) produced by ozonation was effectively reduced by a simple dual-media (anthracite-sand) filtration (v=15 m/h; h=2.2 m). An additional GAC filtration only resulted in a small additional AOC reduction (Table 1).

Table 1

The Effect of Ozonation and filtration (Waterworks of Rotterdam) on the Organic Substance in the Water as Measured by AOC, DOC, and UV

	Concentrations of Organic Substances		
	AOC† (g org. C/l)	DOC (mg org. C/l)	UV Absorbance* (m-1)
Raw water from storage reservoir	39	5.2	3.32
After ozonation	270	2.9	1.92
After double-layer filtration	41	2.9	1.68
After granular activated carbon filtration	15	2.4	1.16

†Assimilatable (degradable) organic carbon.
*Measured as absorbance at 254 nm.

Note: Average water temperature = 16°C.

4. Combination of ozonation and GAC filters results in an increased operating time, when the TOC concentration in the final effluent is used as a criterion. However, this increase in the allowable running time before TOC breakthrough may be irrelevant when the breakthrough criterion is keyed to specific organic compounds that are not influenced by ozonation.

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CLOSING REMARKS

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CLOSING REMARKS

PROF. DR. HEINRICH SONTHEIMER

For someone who has proposed such a conference, as I have done, who indicated some points of interest on which papers could be presented, who has helped to choose speakers, and so on, this meeting can be viewed in a very different manner than by someone who is only a participant. I have to ask, was it really worthwhile to have this meeting? Did people get enough information, particularly new information? Has the experience from pilot plants and large waterworks been presented in such a way that others really could use it? Or, since it is a NATO-CCMS meeting, did the papers presented for discussion really help to overcome the challenges to our modern society and help to foster a better understanding between nations and their people? I can only base my response to all these questions on my own impressions and on things I have learned myself during these 3 days.

There is a great deal of research going on in many countries on the best way to use granular activated carbon filters or other adsorption processes. Pilot plants are being used for this purpose and although methods and study goals are similar in some ways, there are enough dissimilarities so that it is possible to learn how one should proceed further in such studies to provide more reliable research.

I have derived many new ideas from the variety of very interesting reports presented, and it was interesting to realize that, in the long run, the best results are obtained by a sound combination of very practical studies and fundamental research. Some very good examples of this were given in one paper. For me, it confirms that this combination will be the best for the future.

I have to say that besides the effect of such studies, I am very impressed when real practical conclusions are drawn from such pilot studies, leading to real changes in existing plants, and through these to more safe and better drinking water. One example of this, in addition to many others, was demonstrated in the report of Mr. Schulhof from France. This special example also shows that we often don't need much money to rearrange our waterworks and to utilize new experience to optimize drinking water treatment. One could learn from Mr. Schulhof's, as well as other papers, that new techniques are not always more expensive than traditional treatment. This confirms my hope that the new

techniques really can help to solve some of our modern water quality problems; I think we should continue in this direction.

We all have learned during these 3 days that activated carbon filters and their optimum use has to be seen in context with all the other treatment methods. Best possible use of the activated carbon can also be achieved by promoting biological treatment within these filters. There will be many solutions for this combination in order to find the best solution in each case. I have found that we can also learn much from the experience gained in advanced wastewater treatment. I think this has been made very clear in Perry McCarty's paper on Water Factory 21.

We all know that much research has been done in the U.S.A., especially on advanced waste treatment technologies. I think we can apply much of the knowledge from this type of waste water treatment to drinking water treatment. I was especially happy to have Professor McCarty's paper confirm many of the findings of a research study we started a few months ago, using counter current aeration in conjunction with activated carbon filters for the total removal of organic trace contaminants, both volatile and nonvolatile.

I could add many more points to my concluding remarks, but I don't want to repeat information already mentioned and take up too much of your time. All of these papers will be published soon, in addition to the papers from the Karlsruhe conference, so you can read them and can see what is useful for each particular case.

Finally, I have to thank all of you for taking part in this meeting. I was really astonished to see so much interest in our lengthy program, and it speaks for this program that so many people are still here. I also want to thank all participants in the discussions; the only regret is that we did not have enough time for proper discussion. I apologize for that.

I especially have to thank all of the speakers, who did a very fine job involving a lot of preparation for their excellent slides and papers. It was worthwhile to listen to all of them.

Everything worked out well; I wish to thank all the people that prepared this conference. Today, I especially want to thank one person, Joe Cotruvo, who did a lot of work to assure that this conference would be a success. I think he has succeeded. I surely hope that this won't be the last time that we arrange such an international conference, and with this hope in mind I want to finish my remarks.

I hope you all had a good time and I wish all of you success in all of your undertakings and work. I'm very grateful that you have been here.

DR. COTRUVO

I thank you, Prof. Sontheimer, for the kind words, but as you know, there were many many people that put this symposium together. All of the people from the EPA's Office of Research and Development, the Municipal Environmental Research Laboratory, who put in so much time, Jim Symons, Gordon Robeck, their staffs, and all of the people from my office, including Craig Vogt and Bruce Capner. They have been with us throughout these past few days, and they deserve that credit.

I would like to turn the mike over to Victor Kimm for a few minutes; he wanted to say some words of farewell to you.

DR. VICTOR KIMM

I feel that there ought to be some kind of endurance award for the people who remain.

There are two or three specific things I'd like to mention. I feel compelled to say that, in a job like mine, you find one foot in the world of politicians and one foot in the science world, making you unqualified to address either world correctly. I find it much more productive to talk about science to the politicians and policy to the scientists. Perhaps it's best for me to stay in that mode to survive.

First I'd like to say something by way of a special vote of thanks to our international visitors who participated in the program. Few, if any of us, could attempt a technical presentation in a language other than our own. I suspect the preparations brought many anxious moments to our visitors. I thank them; we are indeed indebted.

One of the purposes of the conference is to open a dialogue on this new challenge to the water supply profession. Much of the discussion I have seen here has been along those lines. It appears that the conference has been very successful in introducing people with similar interests to one another, for which we are most thankful.

My final point, essentially directed more to my U. S. waterworks colleagues, was to try to return somewhat to our original theme. That is, if we are to remove trace organic contaminants from our

drinking waters, it is going to take a collaborative effort. It is something that will involve the water utilities, the academic community, consulting engineers, and regulatory officials at the Federal and State levels. I'm very pleased that all of those groups were represented here at this meeting and I hope that we can continue the dialogue that we have begun here as we face this challenge in our domestic regulatory framework.

DR. COTRUVO

I believe the theme of the program would have to be that, when one encounters contamination problems in drinking water, one has, indeed, a tremendous number of tools available to try to meet those problems. There really are no limits because there are choices among combinations of biological, chemical, and physical treatment processes which, when applied to the given problem, can be arranged to produce the optimum solution. This means that the present moment is an extremely exciting time to be a water supply engineer or scientist.

I think there is an opportunity to bring together all of the different technical tools that we presently have, chemistry, engineering, etc., to produce a product that is the best possible within the economic limitations that constrain us. There is an opportunity to let our imaginations range widely, to innovate and to see the products of our efforts actually brought to fruition to benefit the public.

I hope that the conference has been enjoyable. It's been an opportunity for you to let your imagination wander a bit, to meet many new people, to learn or at least to be introduced to many new concepts, and an opportunity to take those ideas home with you and let them ripen a bit before beginning to apply them in your own system.

I thank all of the participants, our foreign visitors, our American friends, and particularly Professor Sontheimer. Until the next time, I wish you farewell.

*U.S. GOVERNMENT PRINTING OFFICE : 1984 0-421-082/537