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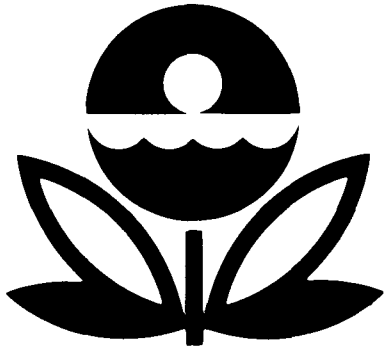
INTERIM TREATMENT GUIDE FOR CONTROLLING ORGANIC CONTAMINANTS IN DRINKING WATER USING GRANULAR ACTIVATED CARBON



Water Supply Research Division
Municipal Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio

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Supporting Documentation

for

U. S. Environmental Protection Agency
Interim Primary Drinking Water Regulations
"Control of Organic Chemical Contaminants in Drinking Water"

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INTERIM TREATMENT GUIDE FOR CONTROLLING ORGANIC CONTAMINANTS IN DRINKING WATER USING GRANULAR ACTIVATED CARBON

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EXECUTIVE SUMMARY

Low concentrations of organic compounds currently occurring in drinking waters are a hazard to the health of the consumers (see Basis and Purpose Dcoument) and in many cases cause drinking water to have an unpleasant taste and odor. This Guide concerns drinking water treatment unit processes that are available for the control of the concentration of organic contaminants. For the purposes of this Guide, organic contaminants are divided into five general classes:

Class I, organic compounds that cause taste and odor problems;

Class II, synthetic organic chemicals that are present in source waters from upstream discharges or runoff;

Class III, organic compounds (precursors) that react with disinfectants to produce "disinfection by-products";

Class IV, organic chemicals that are the disinfection by-products themselves; and

Class V, natural (non-Class III) organic compounds of little direct toxicological importance.

The Guide (including Appendices) is a compilation, both from the literature and from the research being conducted by the Water Supply Research Division, of treatment techniques for controlling these various classes of organic contaminants. This information then leads to a recommendation of how a water utility requiring additional treatment for organic contaminant control should proceed towards choosing the proper treatment design.

Four general categories of organic treatment unit processes are currently (Fall 1977) available. These are: precipitation, oxidation, aeration, and adsorption. In the Guide each of these general categories is reviewed and its advantages and disadvantages discussed. Although

all of these four processes do remove one class or another of organic contaminants to some degree, adsorption using granular activated carbon is chosen as the best "broad-spectrum" unit process for controlling concentrations of organic contaminants. Appendix A of the Guide details what is known about this unit process.

To summarize, the literature shows that Class I compounds, those producing taste and odor, are well removed by granular activated carbon adsorption. Class II compounds, synthetic source water contaminants, however, are variable in their adsorbability. Certain types of compounds such as pesticides, polynuclear aromatic hydrocarbons, polychlorinated biphenyls, and so forth are very strongly adsorbed, although low molecular weight halogenated compounds such as carbon tetrachloride are less strongly adsorbed. Therefore, although granular activated carbon is effective for the control of this latter type of compound when fresh, to maintain control, the granular activated carbon must be thermally reactivated more frequently than when more strongly adsorbed compounds are present in the water to be treated. A search of the literature shows that more than 50 different organic compounds have been investigated as to their adsorbability on granular activated carbon at concentrations approaching those that might be found in source or drinking waters. Unfortunately, many of these studies were conducted under conditions so dissimilar to those found in water treatment practice that they are not directly applicable to the current problem, but taken in total they do support the concept that granular activated carbon is a "broad-spectrum" adsorbent.

Because the problem of disinfection by-products and their precursors is relatively new, the literature does not contain much information on the adsorbability of these two classes of compounds. Some information

is, however, available on the treatability of organic compounds in general, as measured by some general organic parameters, and these results are related to the removal of Class III, disinfection by-product precursors. In general, granular activated carbon beds provide good removal of organic compounds as measured by these general organic parameters when fresh, but reactivation would be required more often than for control of taste and odor compounds. Many Class V compounds, low molecular weight organic acids and alcohols, are not readily adsorbable by granular activated carbon, but these compounds are of little toxicological significance.

The literature shows that currently (Fall 1977) four general types of reactivation devices are available, multiple-hearth, fluidized-bed, rotary kiln, and infra-red tunnel furnaces. Although some change in the reactivated carbon pore structure and subsequent loss in adsorption capacity during reactivation is possible, proper reactivation facility design will minimize this.

The in-house and extramural research program of the Water Supply Research Division is evaluating the performance of granular activated carbon adsorption for the control of the first four classes of organic compounds. This work is being carried out through bench-, pilot-, and field-scale research projects. These studies are an important adjunct to those found in the literature because they are being conducted under conditions of "low concentrations" and "adsorption in competition with other organics," both conditions that are found in practice.

Thus far, the results are supporting the literature and show that, when fresh, granular activated carbon can adsorb a wide variety of organic compounds, without significant measurable organic compounds initially leaching off of the adsorbent. Additionally, granular activated carbon has been shown to adsorb milligram per liter concentrations of organic carbon, even though the total concentration of specific organic compounds shown to be

adsorbed is only in the microgram per liter range (1000-fold less). This further indicates that many other individual organic compounds beyond those measurable at this time (Fall 1977) are also adsorbed. On the other hand, the research data show that capacity of granular activated carbon for the adsorption of some low molecular weight halogenated organic compounds, disinfection by-product precursors, and the disinfection by-product, chloroform, is on the lower end of the adsorption spectrum as compared to pesticides and taste and odor causing compounds. Contact times and reactivation frequencies must be adjusted to take this adsorption variability into account. Finally, excessive bacterial growths or endotoxin production does not occur in granular activated carbon beds to a significant extent.

Although research on the use of ozonation prior to granular activated carbon adsorption, called biological activated carbon, is not complete, initial results are promising. In summary, the data available, both from the literature, and from on-going research, support the recommendation of granular activated carbon adsorption as the best currently (Fall, 1977) available treatment for controlling organic contaminants.

Although granular activated carbon is chosen as the best available treatment, the design and operation of an adsorption system for a given utility must be site specific because of the variation in organic contaminants found from location to location. The technique a water purveyor should use to collect the data needed to design and operate a granular activated carbon facility in a given location is based on the principle of operating two small granular activated carbon pilot column systems, one with an empty bed contact time equal to that available in the existing filters at average flow and the other consisting of three columns in series to evaluate the benefits of additional contact time (see Appendix C for details) for a few months in the summer and winter to determine the necessary reactivation frequency.

To assess the performance of the granular activated carbon adsorbent, three performance criteria, based on weekly effluent sampling have been selected. These are:

1) the concentration of any of the low molecular weight halogenated organics (excluding the trihalomethanes) that are determinable by a purge and trap, gas chromatographic, halogen detector type analysis (see Appendix B) shall not exceed 0.5 μg/ℓ,

2) the increase in the total organic carbon concentration (see Appendix B) shall not exceed 0.5 mg/ℓ over the total organic carbon concentration in the granular activated carbon column effluent at the start of the test, and

3) the initial removal of total organic carbon must exceed 50 percent,

(Adsorber Inf. TOC Conc. - Adsorber Eff. TOC Conc/Adsorber Inf. TOC Conc.) x 100 > 50

In addition, the other organic maximum contaminant levels (MCL) must be met; therefore, the terminal "summation" trihalomethane concentration* (see Appendix B) and the pesticide concentrations (rarely involved) in the effluent shall not exceed the requirements specified in the Interim Primary Drinking Water Regulations.

Whichever of these criteria is exceeded first, as measured by a three-week running average $(W_i + W_{i+1} + W_{i+2})/3$, value assigned to $Week_{i+1}$) of weekly effluent analyses during the pilot granular activated carbon column tests shall determine the design factors for the granular activated carbon treatment system at that location.

Because the length of adsorber operating time (reactivation frequency) before the controlling criterion is exceeded will be related to the adsorber empty bed contact time in a given situation, the design empty bed contact time should be chosen such that the reactivation frequency will neither

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*Arithmetic sum of the concentration of the individual trihalomethane species measured. This parameter is called "Total Trihalomethane" in the Regulation.

be uneconomically short, nor so long as to allow the desorption of previously adsorbed organic contaminants. If an initial total organic carbon removal of 50 percent cannot be achieved in the pilot column using the empty bed contact time available in the existing filters at average flow at that location, even with the best available granular activated carbon for that situation, then replacing the media in the existing filter boxes with granular activated carbon will not be acceptable and post-filter adsorbers with longer empty bed contact times will have to be used. The pilot column tests will determine the most economical method of operation.

To estimate the cost of installing granular activated carbon adsorption treatment, calculations were made for both a sand replacement and a post-filter adsorption type design for two utility sizes based on a set of reasonable assumptions as detailed in the Guide. These total unit costs are as follows:

	10 mgd plant		100 mgd plant	
	Sand Replacement	Post-Filter Adsorption	Sand Replacement	Post-Filter Adsorption
cents/1000 gal.	13.2	16.7	6.9	8.7

Because alternative design and operation techniques yield different overall costs for treatment, examples of how a utility should make an economic analysis to choose the optimum design and operation configuration for that particular location is outlined in the Interim Treatment Guide. Specifically, this analysis shows, in general, that when a longer empty bed contact time adsorber system is considered, unless the increase in the period between reactivations is proportionally greater than the increase in empty bed contact time, total unit costs will rise. The data collected during the pilot column study outlined above will provide the information needed to make this analysis in a given location.

In addition, a technique for taking into account future inflationary trends is discussed, so that a water purveyor could make a choice of a design that would be cost effective over the life of the treatment facility. Because the use of post-filter adsorbers is less labor intensive than when the adsorbent is put in existing filter boxes, post-filter adsorbers will eventually become less expensive as that system is less influenced by inflation than are sand replacement systems, although a "present worth" analysis showed the sand replacement system to be a better investment for the assumptions in the example.

In summary, this Guide provides information that demonstrates that granular activated carbon adsorption is the best available treatment technology, Fall 1977, for treating water to remove organic contaminants, thereby improving finished water quality and providing the American consumer with a more healthful and esthetically pleasing drinking water.

INTERIM TREATMENT GUIDE FOR CONTROLLING ORGANIC CONTAMINANTS IN DRINKING WATER USING GRANULAR ACTIVATED CARBON

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INTERIM TREATMENT GUIDE FOR CONTROLLING ORGANIC CONTAMINANTS IN DRINKING WATER USING GRANULAR ACTIVATED CARBON

INTRODUCTION

Historically the problem of organic contamination of drinking water was related to taste and odor producing compounds. Although of only indirect health significance, these compounds are still important as they are the ones that make drinking water disagreeable and cause some consumers to use poorly controlled sources of drinking water, bottled water or water treated by home treatment devices. In the past five years, through advances in organic analytic techniques and understanding of organic reactions, three other classes of organics, although undetected by consumers, have been shown to be important in drinking water.

The second of the four classes of concern is contaminants found in source waters that are of industrial origin. These are contained in industrial wastes, municipal wastes, and urban and rural runoff and have a potential adverse health effect, (see Basis and Purpose). The third of the four classes of organic compounds is that with which disinfectants react to produce disinfection by-products (precursors). These are largely, but not entirely, of natural origin, arising from urban and rural runoff and municipal wastes and have a potential secondary health effect, creating carcinogens and toxicants when reacting with disinfectants. The fourth class of organic chemicals is the disinfection by-products themselves, (trihalomethanes if chlorine is the disinfectant), either in the source water from upstream disinfection practices or created in the water treatment process itself. These too have a direct potential adverse health effect (see Basis and Purpose). A fifth class, of little concern, is the organics of natural origin that are not disinfection by-product precursors.

Because such a small percentage of the total organic contaminants in drinking water can be identified and quantified, estimated to be less than 10 percent, other classes may be identified in the future.

Therefore, the first four classes of organic compounds should be controlled to provide consumers with a wholesome and taste-and-odor-free drinking water. The purpose of this Interim Guide is to summarize what is known about organic removal unit processes and to recommend a procedure that will allow those utilities requiring additional organic contaminant control to select an appropriately sized treatment facility.

REVIEW OF ORGANIC REMOVAL UNIT PROCESSES

The advantages and disadvantages of each of the four general types of organic removal unit processes will be briefly reviewed.

Precipitation

The addition of a metal coagulant for the removal of particulates or raising the pH for removal of calcium and magnesium results in the removal of some organic matter. This can be measured both by the reduction in the organic carbon concentration, see Figure 1, and color. Although partially effective for the removal of disinfection by-product precursors, see Figure 2 using chloroform formation as an example, this process does little for the reduction of the other classes of organic compounds that are in true solution.

Oxidation

A second possibility for organic removal is to treat the organics with an oxidizing agent. If oxidation could be complete, this would be an attractive approach as the major end-products would be carbon dioxide and water. Although some organic oxidation has been demonstrated when oxidants such as ozone, chlorine dioxide, chlorine, and potassium permanganate are added to water,

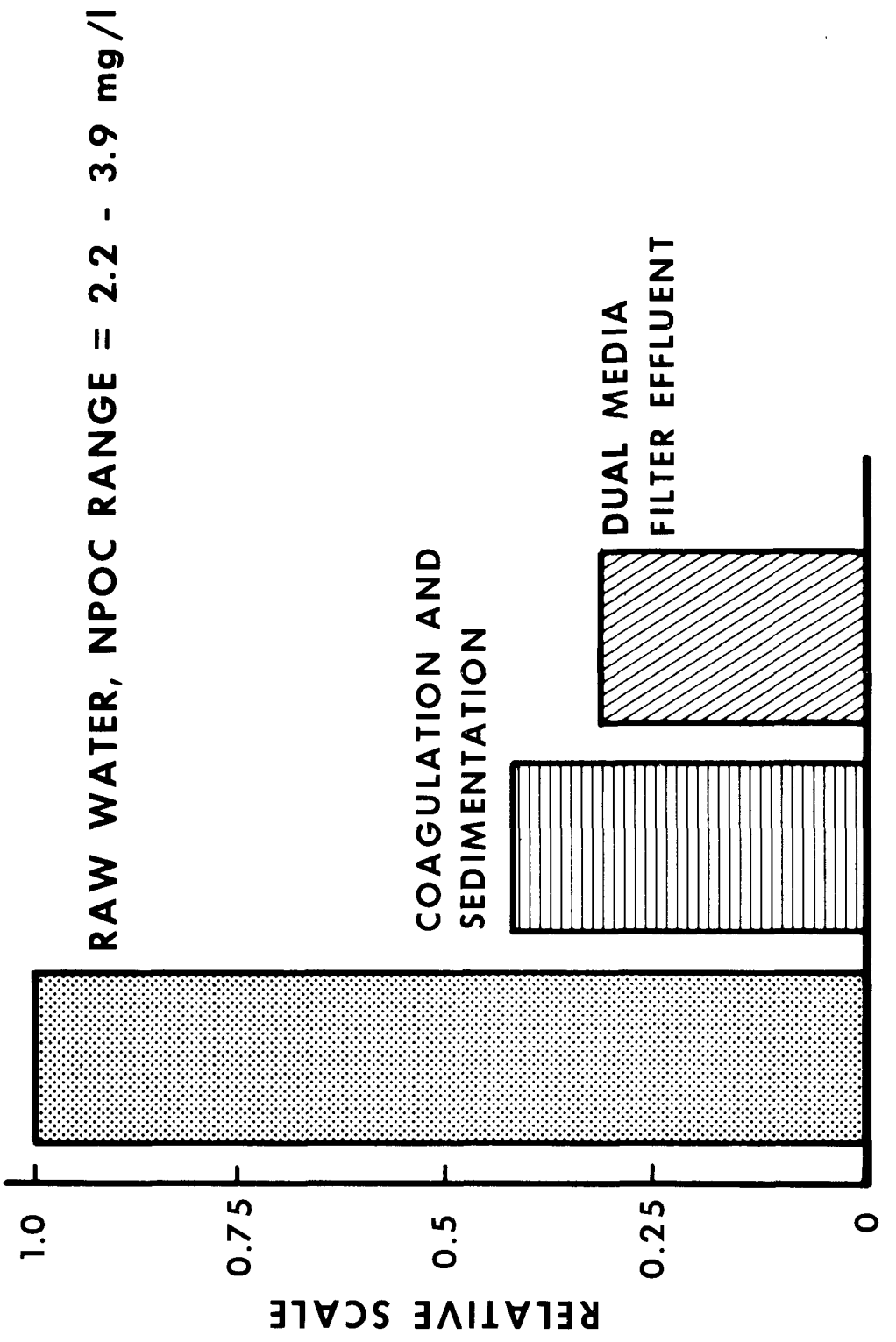

FIGURE 1. RELATIVE NON-PURGEABLE ORGANIC CARBON REMOVAL DURING WATER TREATMENT IN THE PILOT PLANT

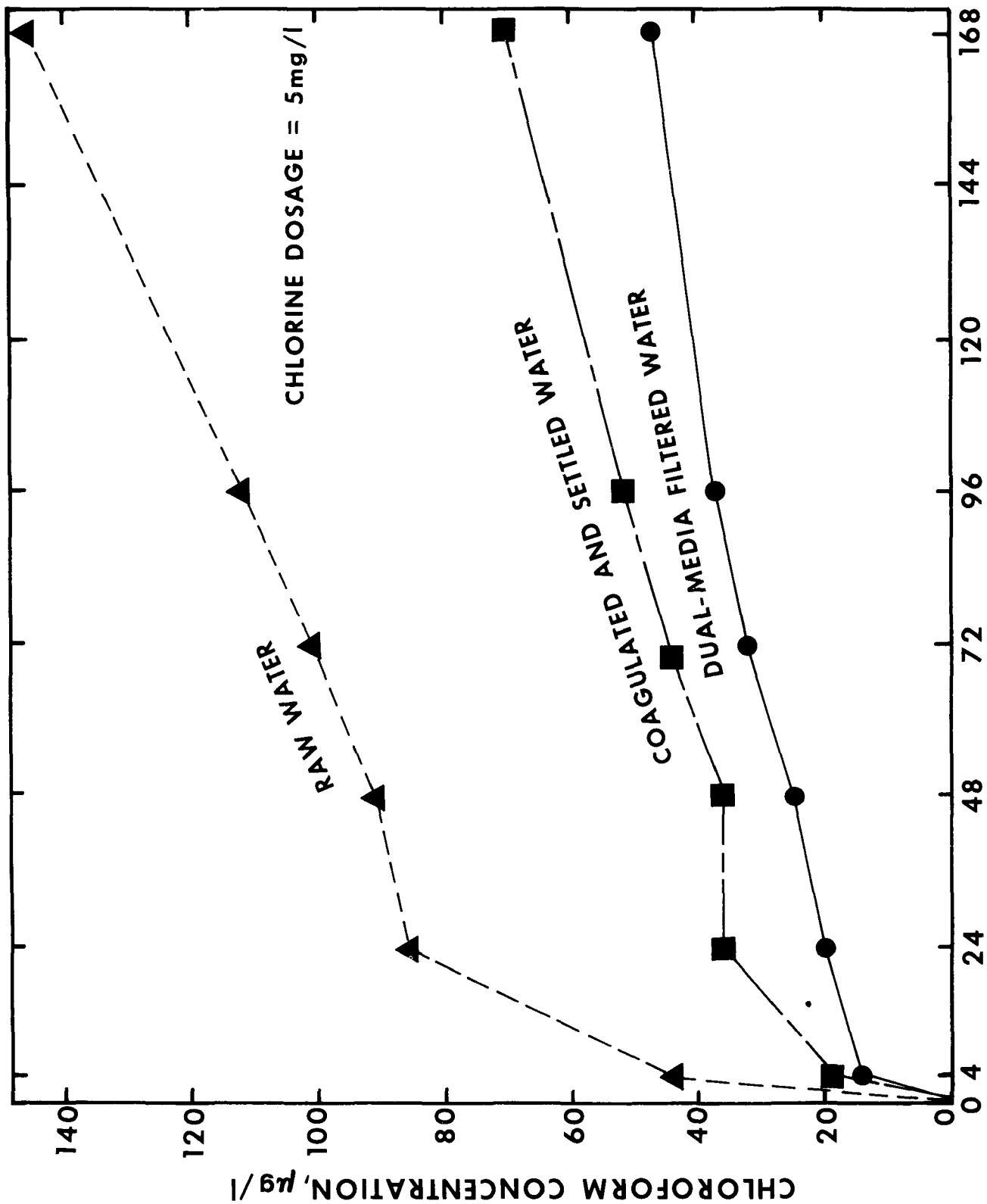

FIGURE 2 INFLUENCE OF WATER QUALITY ON CHLOROFORM FORMATION POTENTIAL

doses must be uneconomically high to insure nearly complete oxidation, see Figure 3. If oxidation is incomplete, the organic compounds will not be oxidized to carbon dioxide and water, but only to some intermediates of unknown toxicologic hazard. Thus far, even the addition of ultra-violet radiation to an ozonation process has not been demonstrated to cause nearly complete oxidation for many compounds.

Aeration

Because many of the organic compounds of concern that have recently been shown to occur in drinking water were determined by a procedure that employs a concentration step based on purging the compounds from the sample with diffused gas, aeration, either diffused air or spray, was considered as a possible organic removal process. The advantage of such a process would be that the organic compounds are truly removed from the water without the formation of by-products or intermediates. The disadvantages are at least two-fold; one, the removed materials are transferred from the water phase to the air phase, possibly causing another problem, and two, only organic substances with certain characteristics are removable even with excessive quantities of air, see Figure 4. Therefore this approach is self-limiting.

Adsorption

A fourth possible approach to control of organic contaminants is to remove them from the water by adsorption onto a surface. Two types of adsorbents are currently commercially available in the United States. These are: 1) synthetic resins and 2) activated carbon, either in the powder or granular form.

Synthetic Resins

Synthetic resins of the Amberlite XAD type (a class of macroreticular divinylbenzene-styrene or acrylic copolymers) have a very limited capacity for

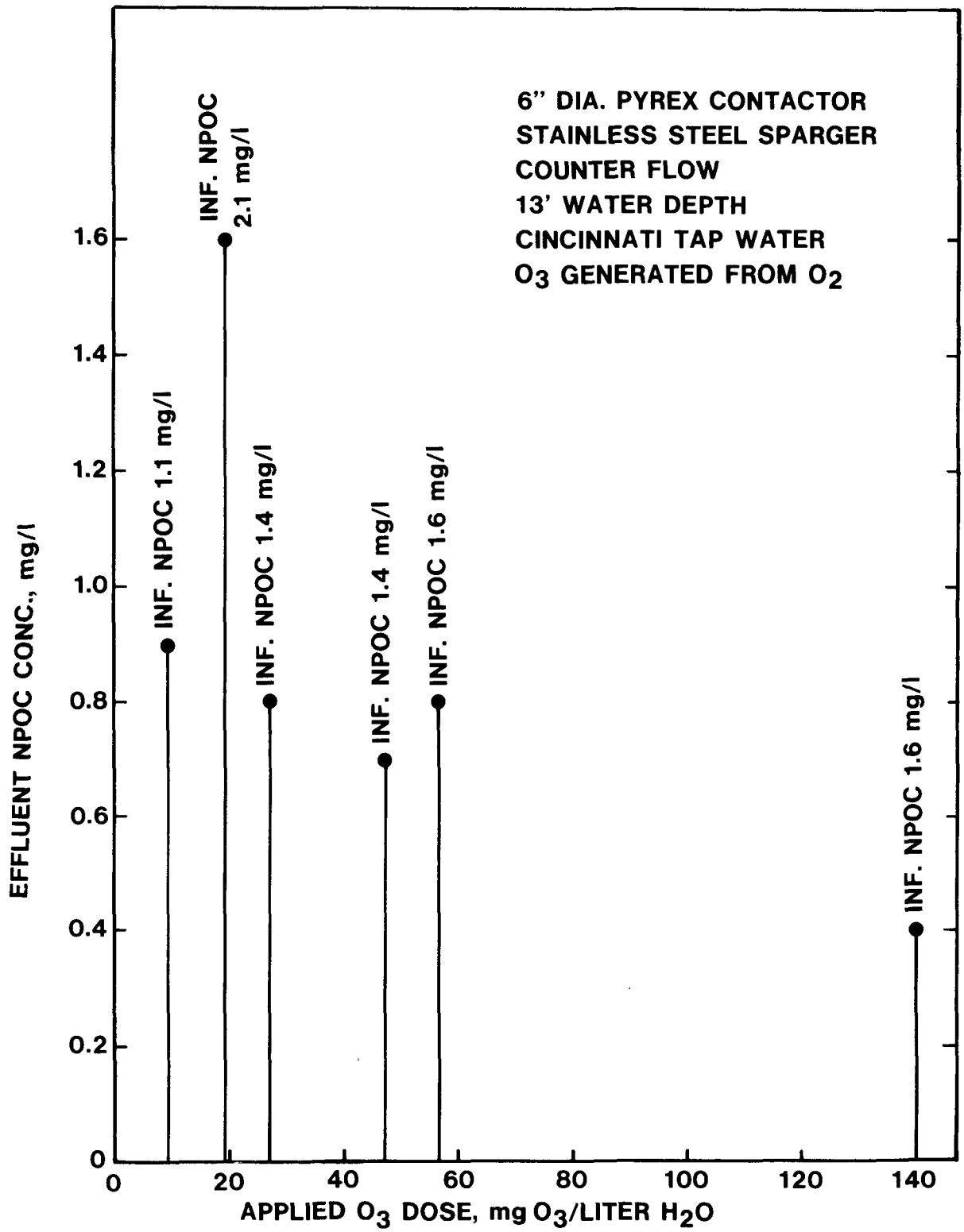

FIGURE 3. REDUCTION IN NON-PURGEABLE ORGANIC CARBON CONCENTRATION BY OZONATION

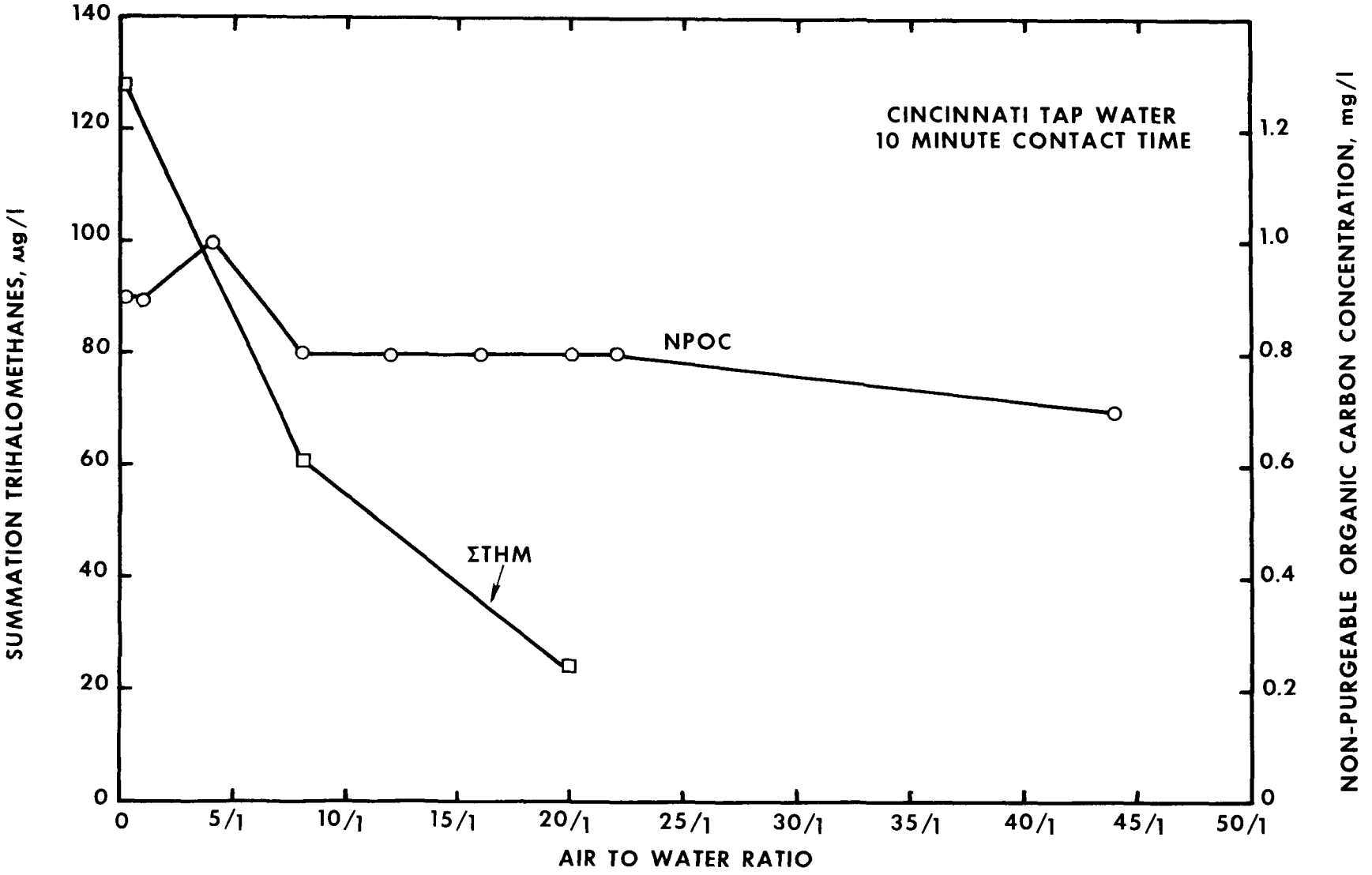

FIGURE 4. INFLUENCE OF AERATION ON TRIHALOMETHANE AND NON-PURGEABLE ORGANIC CARBON CONCENTRATIONS

adsorption, although Ambersorb XE-340 (a carbonaceous adsorbent, chemically intermediate between the XAD type and activated carbon and manufactured by Rohm and Haas*), has a high adsorption capacity for organic compounds such as chloroform and carbon tetrachloride, but does not have much capacity for the removal of a wide range of organic compounds as measured by organic carbon concentrations, see Figure 5.

Activated Carbon

Activated carbon is a form of carbon that is activated by a carefully controlled oxidation process to develop a porous carbon structure with a large surface area. This large surface area gives the activated carbon a high capacity to adsorb dissolved organic materials from water. The major raw materials used in the manufacture of granular activated carbons are petroleum coke, bituminous coal and lignite. After preliminary processing, these materials are heated to a high temperature and reacted with steam to develop the extensive internal pore structure required for adsorption. The substance is then crushed, graded, screened, and packaged. The raw material and activating conditions used affect adsorption and physical properties of the carbons produced. For additional information the reader is referred to the Journal of the American Water Works Association, 66, No. 11, 672-681 (1974) for the AWWA Standard for Granular Activated Carbon, AWWA, B604-74.

Powdered activated carbon is a good adsorbent with a high surface area per gram of material, but as it is usually added to the water to be treated in a single dose, an equilibrium is established between the organic compounds and the adsorbent, thereby limiting the extent of removal possible. Table I shows that high doses of powdered activated carbon were unable to reduce the Threshold Odor Number to acceptable levels (three or less)[1] in this instance. Further, Figure 6 shows that high doses of powdered activated carbon were

*Mention of commercial firms does not imply endorsement by the U.S. Environmental Protection Agency.

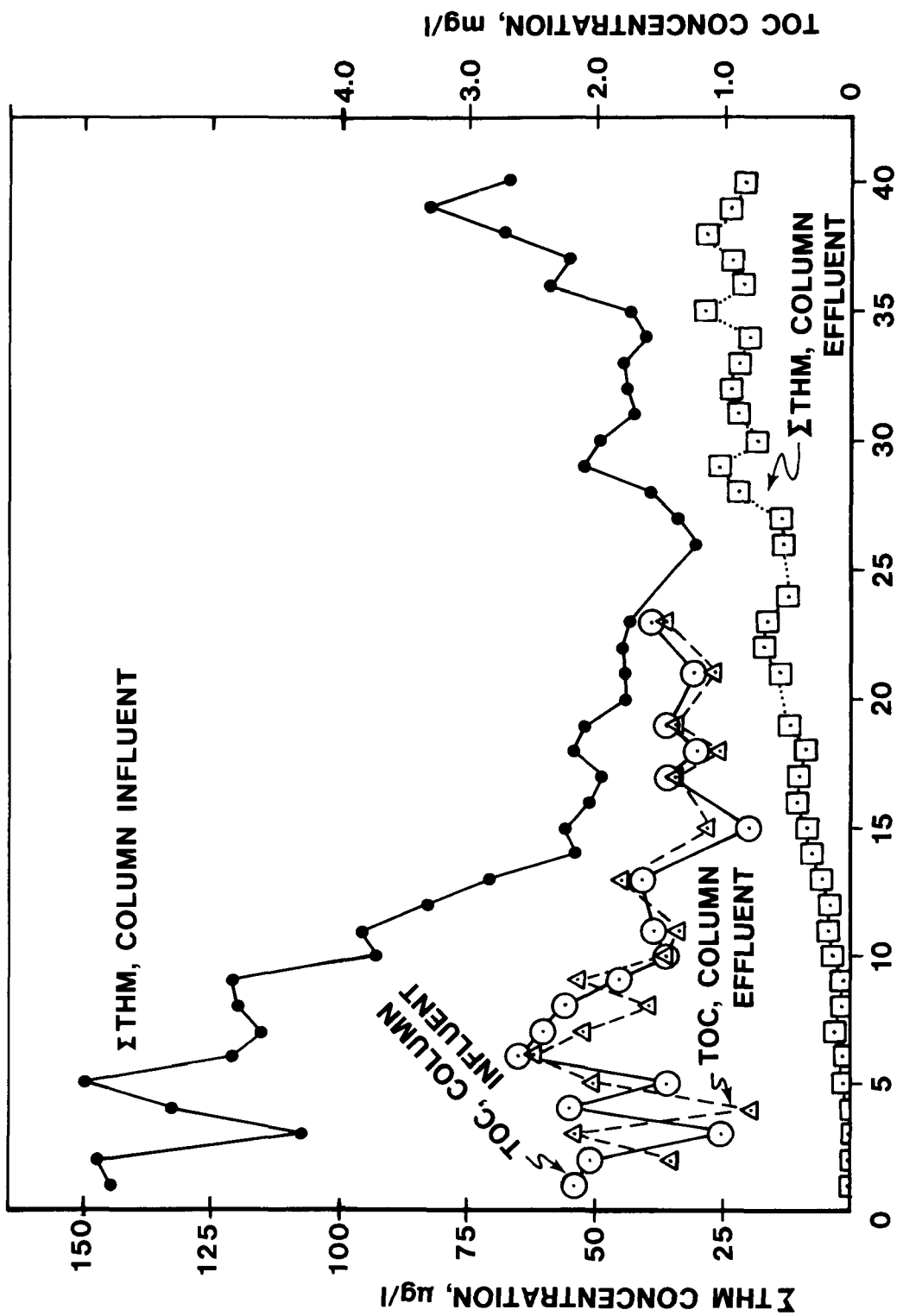

FIGURE 5. REMOVAL OF TRIHALOMETHANES AND ORGANIC CARBON BY AMBERSORB® XE-340 (empty bed contact time=10 min)

TABLE I

Powdered Activated Carbon Dose for Nitro, West Virginia Water Plant - 1963[1]

Month	Average Monthly Powdered Activated Carbon Dosage mg/ℓ	Finished-Water Threshold Odor No.*		
		Min.	Max.	Avg.
January	21	8	35	21
February	27	8	50	25
March	21	6	26	12
April	19	10	60	17
May	20	8	30	14
June	20	8	19	11
July	19	7	14	9
August	22	5	26	12
September	22	8	26	12
October	42	8	40	13

*At 60°C.

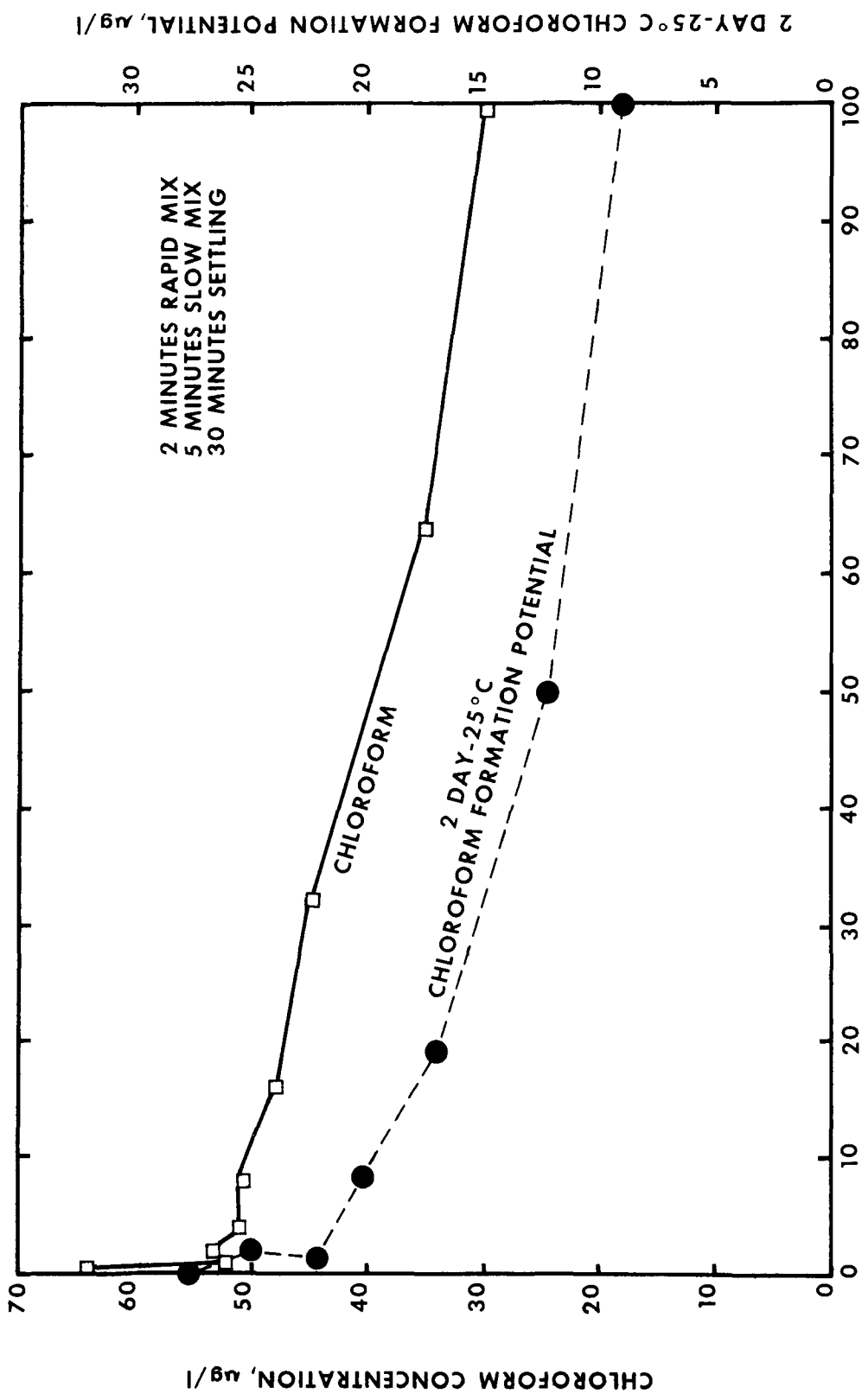

FIGURE 6. INFLUENCE OF POWDERED ACTIVATED CARBON ON CHLOROFORM CONCENTRATION AND CHLOROFORM FORMATION POTENTIAL

required to greatly reduce the concentration of chloroform in tap water, as well as the concentrations of the disinfection by-product precursors as measured by the trihalomethane formation potential test.[2] Note, because of the problem of interference of residual powdered activated carbon with the total organic carbon test, evaluating the ability of powdered activated carbon to remove organic carbon is difficult.

In contrast, when activated carbon is used in a column, it acts like a series of powdered activated carbon "doses" being applied to water of continually improving quality as the water passes through the column. This "plate effect" permits an activated carbon column to produce water containing much lower concentrations of organic matter when contrasted to reasonable additions (10 mg/ℓ or less) of powdered activated carbon.

An example of excellent performance of granular activated carbon for removing Class I type organic compounds, taste and odor producing, is shown in Figure 7. In this installation, the granular activated carbon replaced the sand in existing filter boxes and under these circumstances controlled tastes and odors for more than 1 year.

An early example demonstrating the ability of granular activated carbon beds to adsorb Class II type organic compounds, source water contaminants, showed that seven compounds, listed below, present in the Kanawha River after aeration could be reduced to below detectable concentrations by fresh (2-day old) granular activated carbon beds.[1]. These compounds were bis-(2-chloroethyl) ether, 2-ethylhexanol, bis-(2-chloroisopropyl) ether, α-methylbenzyl alcohol, acetophenone, isophorone, and tetralin. A recent review of the literature (see Table II) has expanded this list considerably.

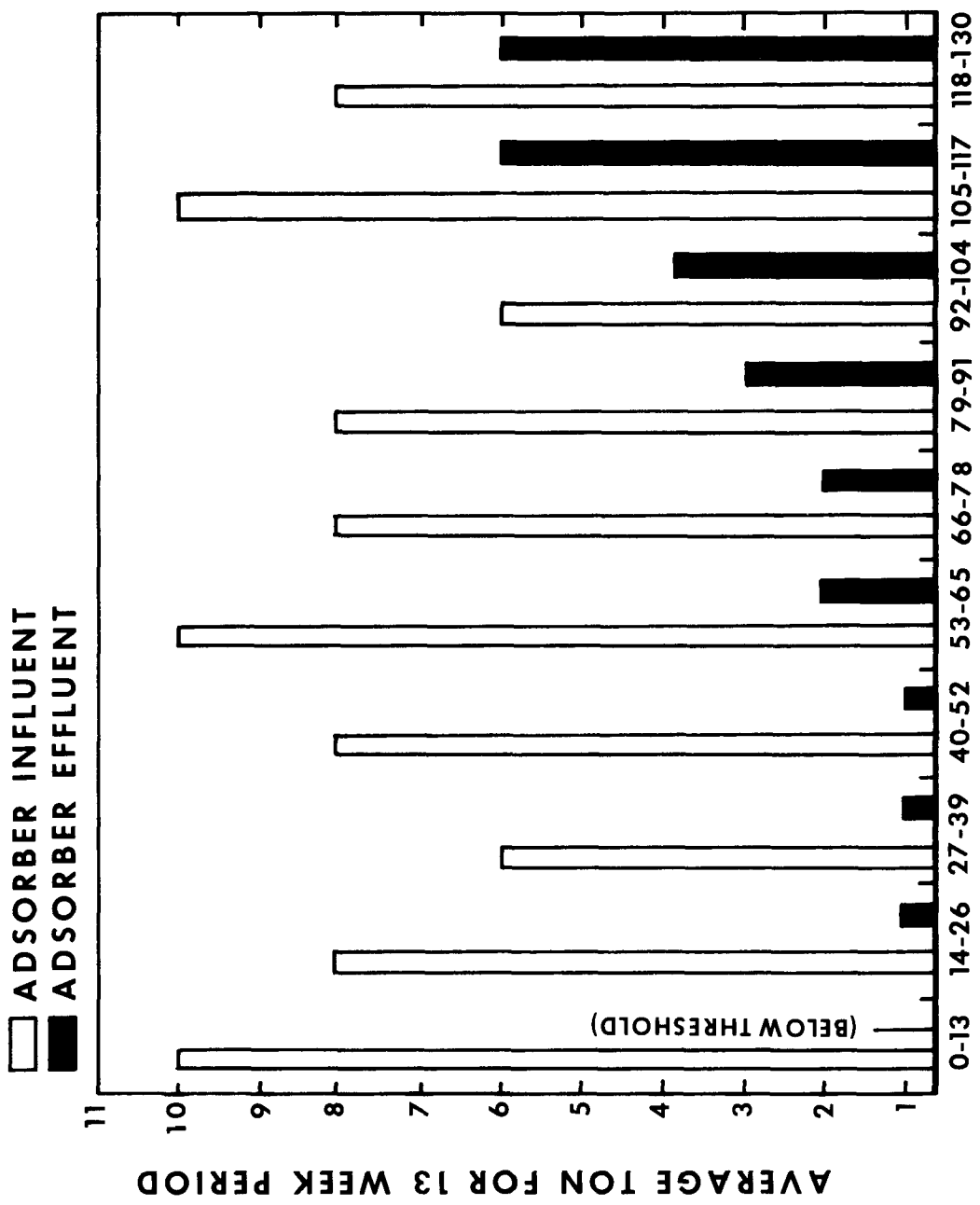

FIGURE 7 THRESHOLD ODOR NUMBER BREAKTHROUGH PATTERN FOR NEW ACTIVATED CARBON FILTER, LAWRENCE, MASS.

TABLE II

ORGANIC COMPOUNDS THAT HAVE BEEN REPORTED IN THE LITERATURE* TO BE ADSORBABLE ON GRANULAR ACTIVATED CARBON

acetophenone
aldrin
baygon
α-BHC
benzocaine
benzoic acid
butyric acid
bis-(2-chloroethyl) ether
bis-(2-chloroisopropyl) ether
dibrom
dieldrin
di (n-butyl) phthalate
di (2-ethylhexyl) phthalate
diuon
diquat
dimethoate
m-dinitrobenzene
DDT
endosulfan
endrin
gasoline
heptachlor
heptachlor epoxide
hexachlorobenzene
isophorone
juglone
lindane
linuron
MS-222
malathion
α-methylbenzyl alcohol
methyoxychlor
nitrobenzene
oil (fuel)
paraquat
parathion
phenylacetic acid
phenols
p-nitrophenol
propionic acid
pyridine
PCB
rotenone
sevin
simazine
strychnine
3-trifluoromethyl-4-nitrophennol (TFM)
2-ethylhexanol
2,4-D
2,4-dinitrophenol
2,4,5-T (ester)
toxaphene
tetrachlorobenzene
telodrin
triazine
tetraline

*References given in Appendix A. Studies with original concentration 1 mg/ℓ or less.

Current research efforts by the Water Supply Research Division continue to demonstrate the ability of granular activated carbon to adsorb a variety of synthetic organic contaminants. Figure 8 is an example of these data, showing the adsorption of carbon tetrachloride by granular activated carbon. The data in Table III indicate the adsorbability of other low molecular weight halogenated organic compounds by granular activated carbon. The data in Figure 9 demonstrate that with Ohio River water, granular activated carbon adsorption treatment can initially produce an effluent containing only approximately 0.1 mg/ℓ of organic carbon. This shows that under these circumstances, when fresh, the granular activated carbon adsorbed over one milligram per liter of organic carbon. Because most of the specific organic contaminants found in drinking water occur at μg/ℓ concentrations, 1000-fold less, this further indicates the ability of granular activated carbon to adsorb a wide variety of organic contaminants. Finally, the data in Figure 10 further demonstrate this point, as indicated by the absence in the granular activated carbon bed effluent of many of the organic compounds that show up as "peaks" on the capillary gas chromatogram of the influent to the granular activated carbon column.

Figure 11 is an example of data collected by the Water Supply Research Division at one of its large-scale field research projects. These data show the ability of granular activated carbon to adsorb Class III type organic compounds, disinfection by-product precursors. The data in Figures 12A and 12B show that, when fresh, granular activated carbon has the ability to adsorb Class IV type organic compounds, disinfection by-products. The bromine-containing trihalomethanes are well adsorbed, chloroform breaking through the granular activated carbon treatment systems first.

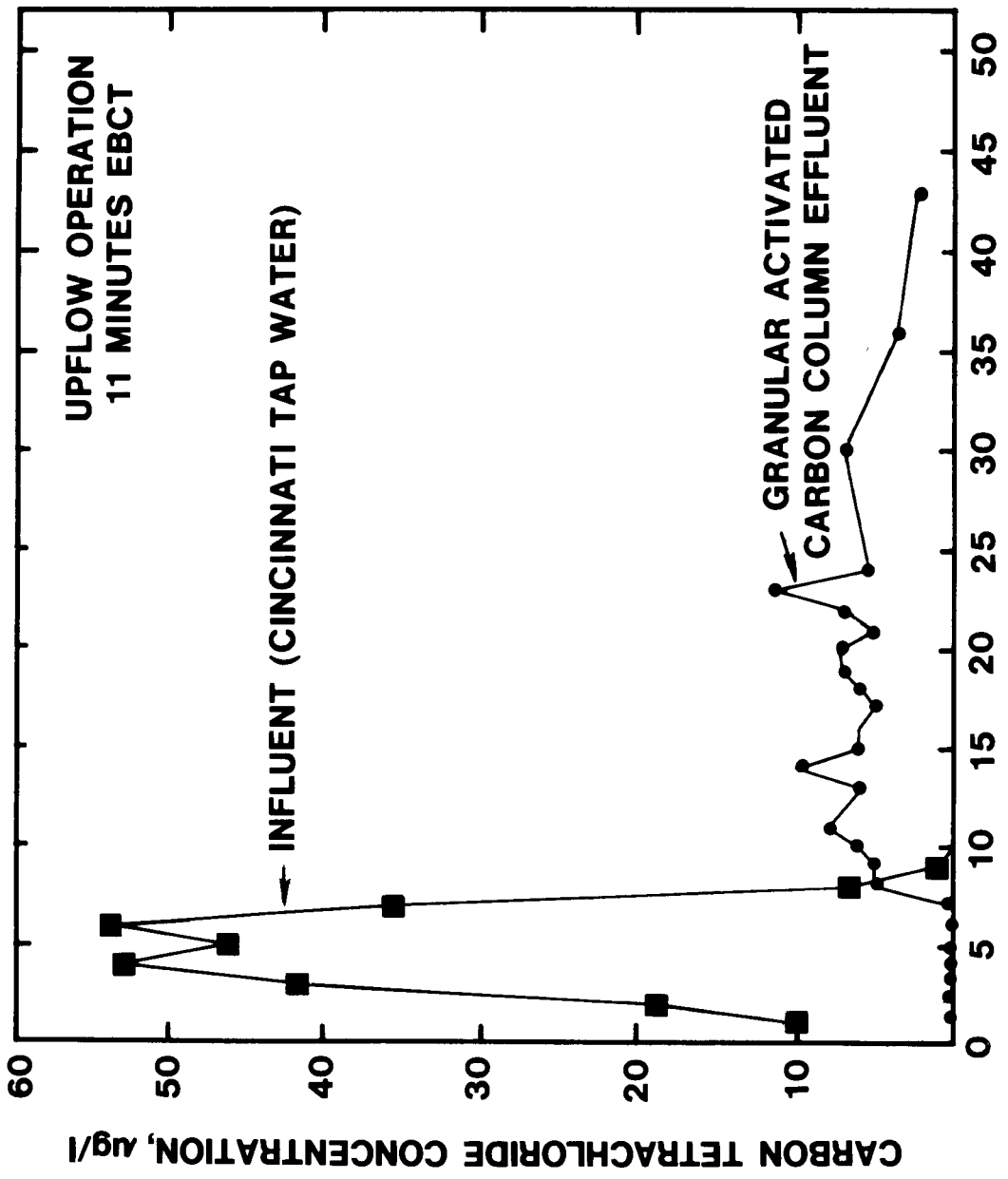

FIGURE 8. PERFORMANCE OF GRANULAR ACTIVATED CARBON BED FOR CARBON TETRACHLORIDE REMOVAL

TABLE III

USE OF GRANULAR ACTIVATED CARBON BEDS TO REMOVE ORGANIC CONTAMINANTS FROM A GROUND WATER SUPPLY

Contaminant	Influent Concentration Range, µg/ℓ	Average Effluent Conc., µg/ℓ 0-4 weeks	4-8 weeks	8-12 weeks
1,1,1-trichloroethane	10.9-36.7	NF	NF	0.4
trichloroethylene	1.9-7.7	NF	<0.1	<0.1
tetrachloroethylene	0.1-16.9	NF	<0.1	<0.1

NF = None found

Note: After six weeks of testing, two new contaminants, 1,1-dichloroethane and cis-1,2-dichloroethylene began appearing in the influent to the granular activated carbon column. No cis-1,2-dichloroethylene has yet been detected in the treated water, but the average concentration of 1,1-dichloroethane in the effluent for the 4 to 8 week period after first appearing was 0.7 µg/ℓ.

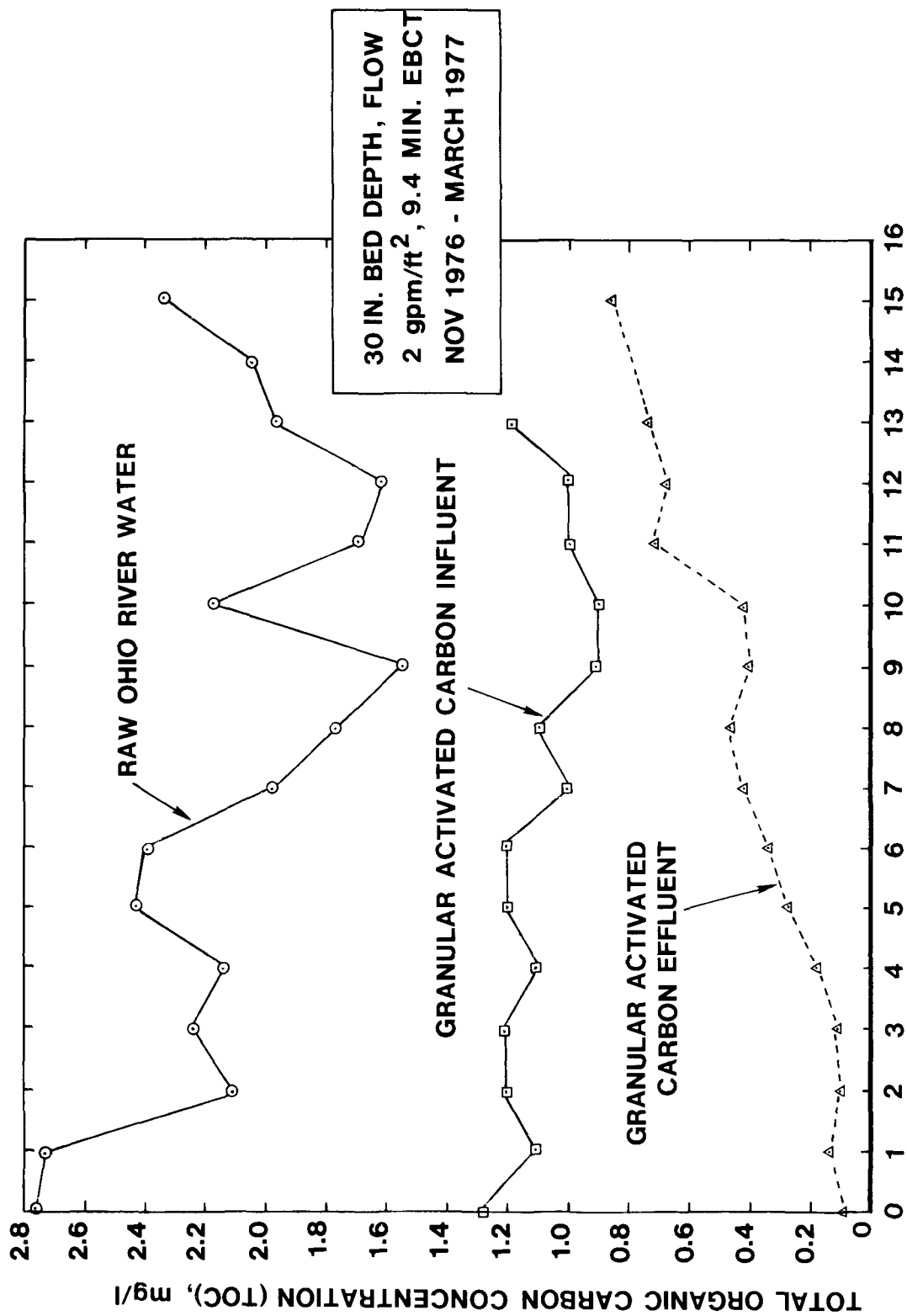

FIGURE 9 ORGANIC CARBON BREAKTHROUGH CURVE FOR PILOT WATER TREATMENT PLANT

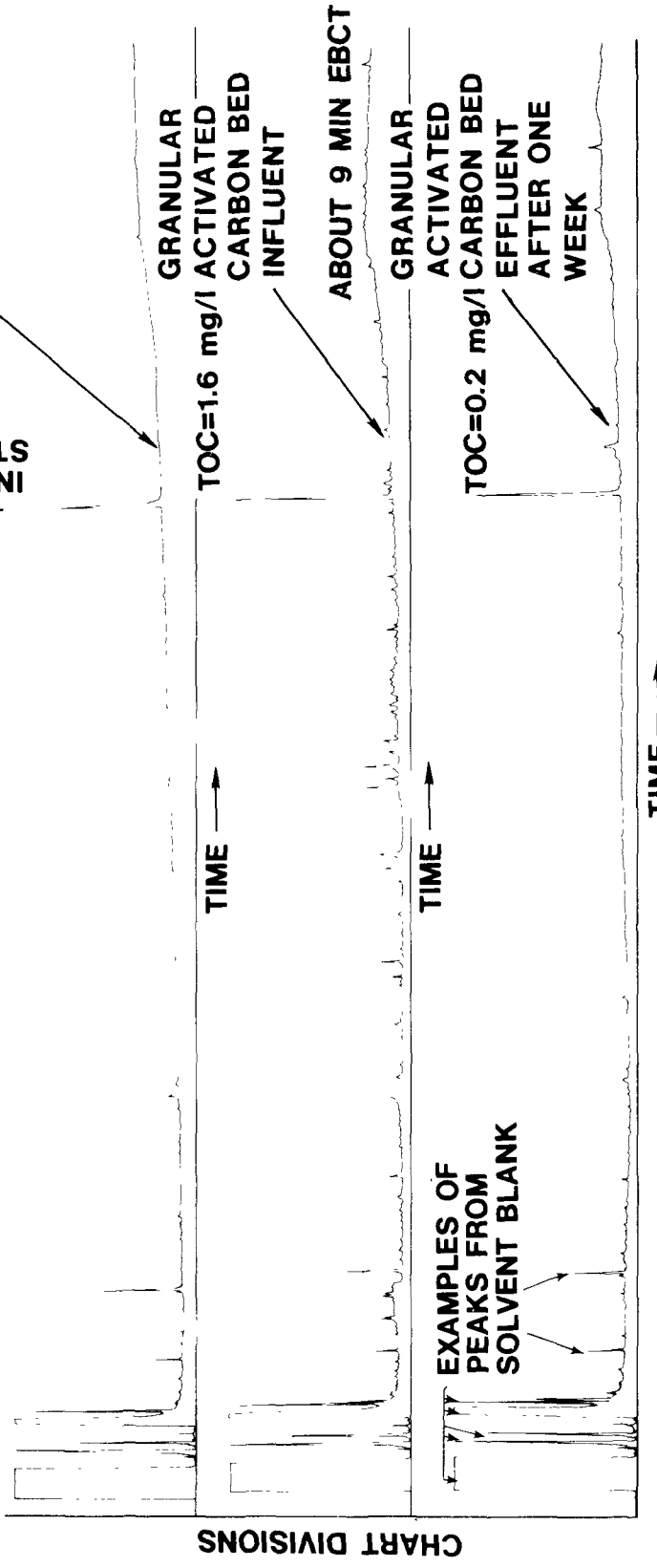

FIGURE 10. COMPARISON OF ORGANIC CONTENT OF A GRANULAR ACTIVATED CARBON EFFLUENT BY SOLVENT EXTRACTION AND CAPILLARY GAS CHROMOTOGRAPHY

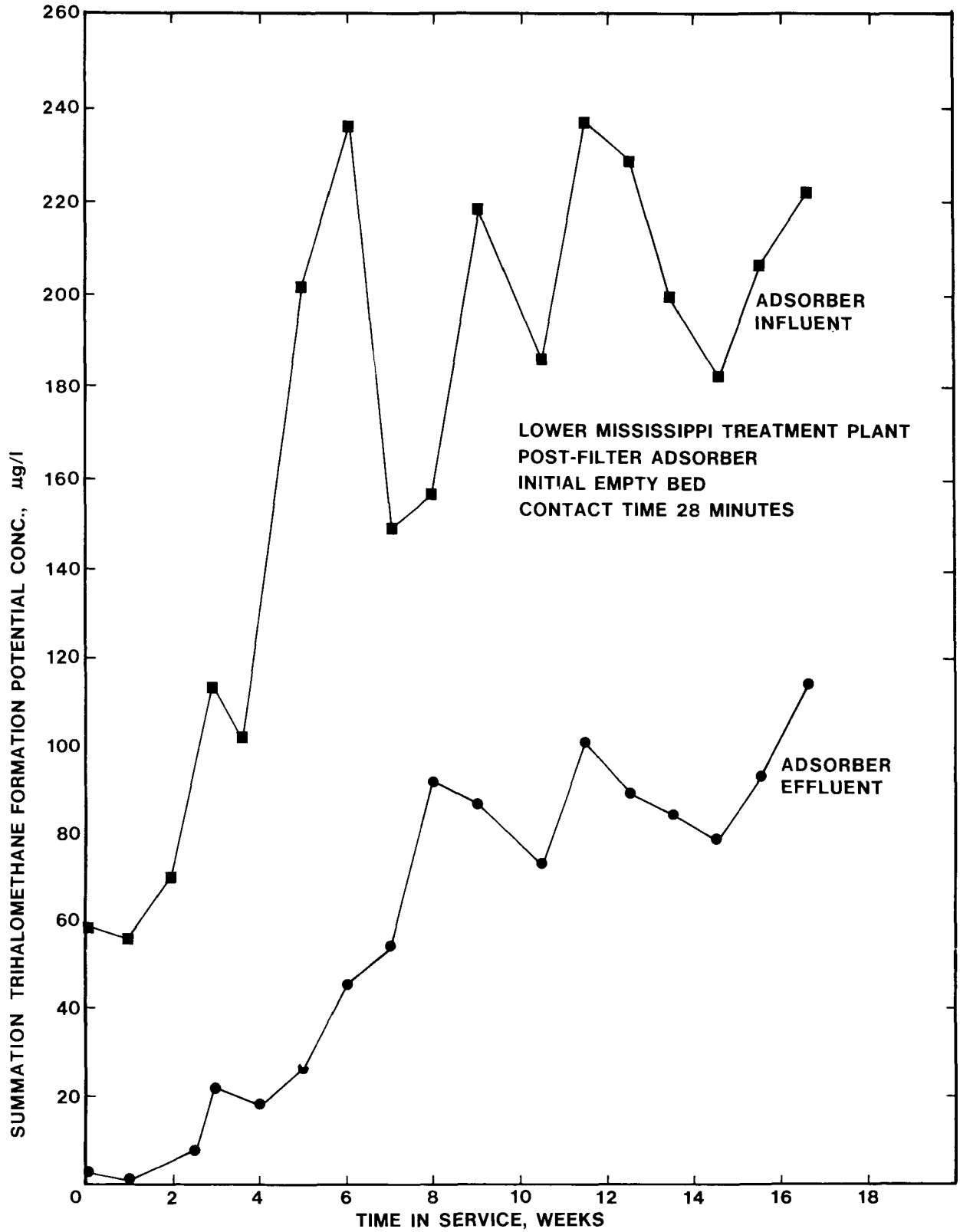

FIGURE 11. BREAKTHROUGH PATTERN OF CLASS III ORGANIC CONTAMINANTS,DISINFECTION BY-PRODUCT PRECURSORS

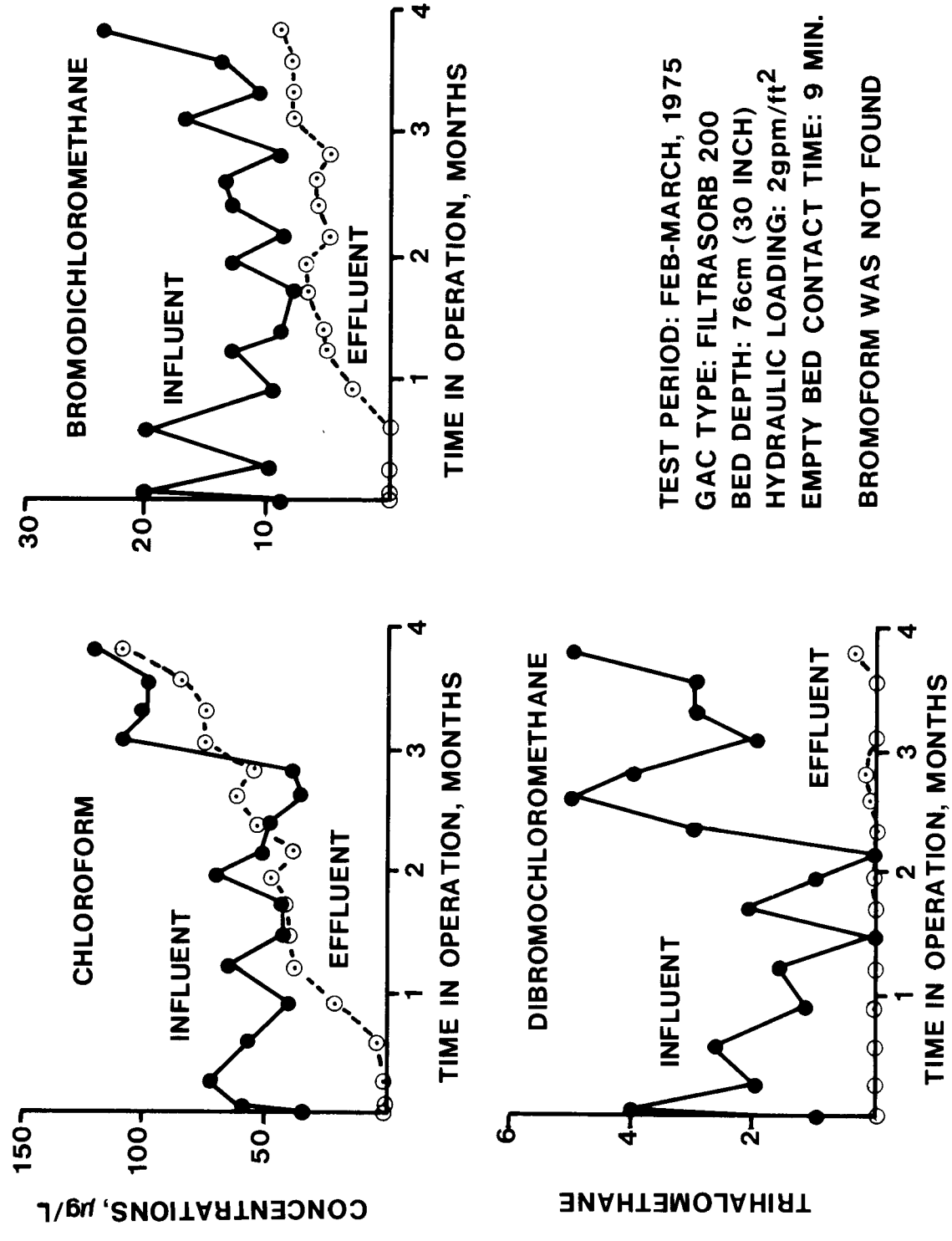

FIGURE 12 A. REMOVAL OF TRIHALOMETHANES FROM CINCINNATI, OHIO TAP WATER BY COAL-BASE GRANULAR ACTIVATED CARBON

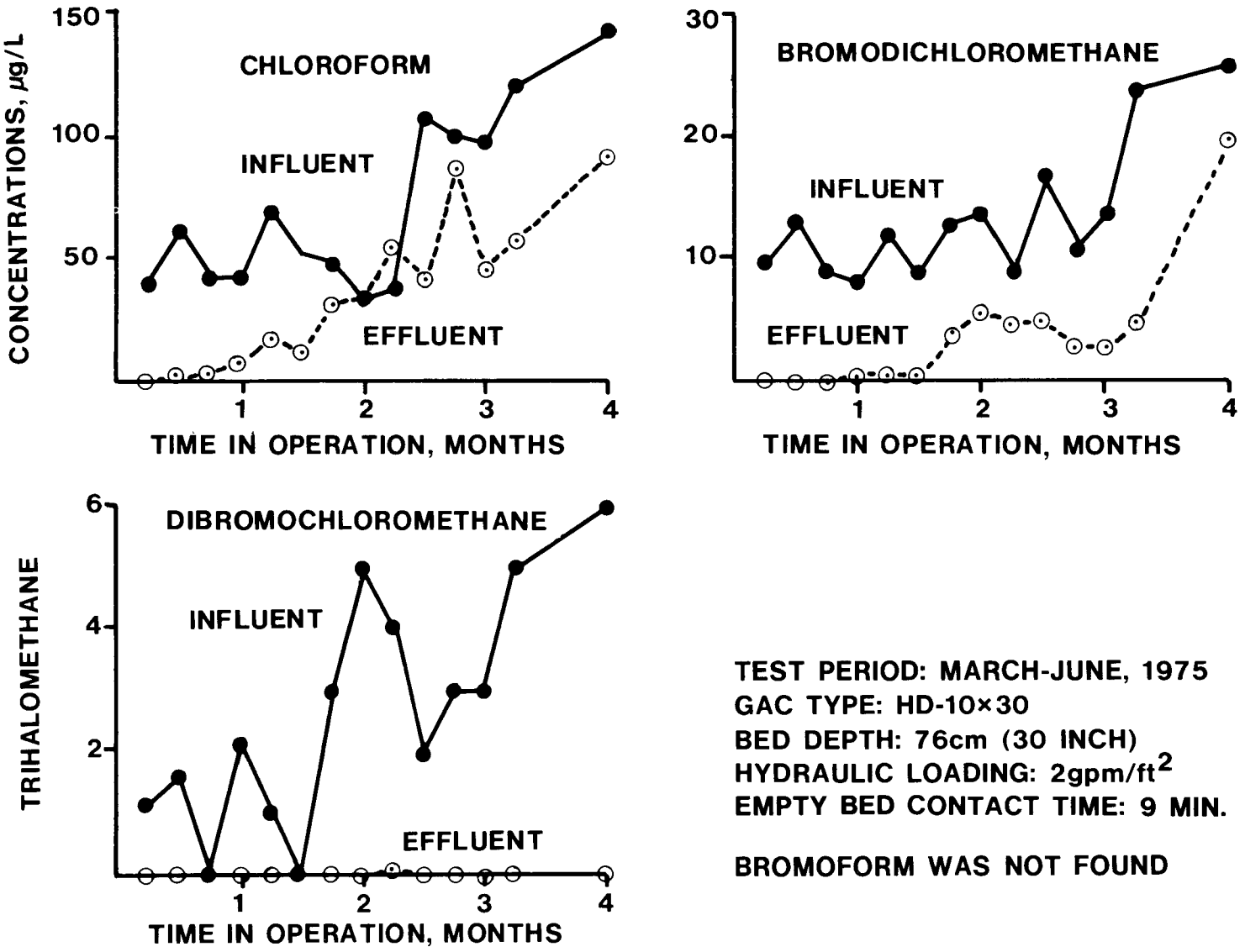

FIGURE 12 B. REMOVAL OF TRIHALOMETHANES FROM CINCINNATI, OHIO TAP WATER BY LIGNITE BASE GRANULAR ACTIVATED CARBON

The disadvantage of any adsorption process is that the adsorbent's capacity has a finite limit. This means that the adsorbent either must be replaced, or processed in a manner that will restore its adsorptive capacity. In the case of granular activated carbon, as it is contained in a vessel, in contrast to powdered activated carbon, it can be removed, dried and thermally reactivated such that the adsorbed organic materials are driven off the activated carbon and the surfaces reactivated for further use. Note, proper treatment of the off-gases is necessary to avoid an air pollution problem.

Summary

Taking into account all of the advantages and disadvantages of the various organic removal unit processes briefly discussed above, granular activated carbon has been selected as the best "broad-spectrum" process for the removal of organic compounds, without the production of by-products, currently available at this time (Fall 1977). Appendix A contains the detailed analysis of the literature and the Water Supply Research Division research findings that support this conclusion. In addition, Appendix A contains a brief review of a variation of the usual granular activated carbon adsorption process called biological activated carbon employing ozonation preceding adsorption. The next section of this Guide will present the technique a water purveyor should use to develop the necessary design and operation data needed to install a granular activated carbon adsorption system.

PROCEDURE FOR COLLECTION OF SITE SPECIFIC DESIGN DATA

Collection of Treatability Data

Performance Criteria

Having chosen granular activated carbon as the best "broad-spectrum" organic removal unit process currently (Fall 1977) available, several questions still remain for a given utility required to install this form of treatment. These are: 1) how should the facility be designed and operated to optimize performance and 2) which of the currently commercially available granular activated carbons are best for a given location. To begin to answer these questions, the objective of treatment must be defined. In general terms, the treatment process should remove, to the degree possible, four of the classes of organic compounds defined above; taste and odor producing components, source water synthetic contaminants, disinfection by-product precursors, and disinfection by-products. The fifth class, natural organic compounds that are not disinfection by-product precursors, are not easily controlled by granular activated carbon adsorption, but are of little public health concern. Further, the reactivation cycle should neither be uneconomically short, nor so long as to allow the desorption of previously adsorbed material, see Figure 8.

Within these general constraints, how are the two basic questions to be answered? Some performance criteria for the adsorption process must be chosen so that it can be properly designed and operated. Experience has shown that wide differences exist in the adsorbability of various organic compounds, see Appendix A. Some toxic chemicals such as pesticides, and polynuclear aromatic hydrocarbons are strongly adsorbed as are taste and odor compounds and should not be a limiting performance factor. Toward the other end of the adsorption spectrum are the low molecular weight halogenated compounds, chloroform, carbon tetrachloride and so forth.

Because of the variability of adsorption among organic compounds and of adsorption competition among different organic compounds, the design and operation of an adsorption facility must be site specific. To allow the evaluation of granular activated carbon as a treatment process in any given location, performance criteria have been chosen, as detailed below, beyond the established maximum contaminant levels (MCLs) for trihalomethanes and pesticides. In a given location, any one of these performance factors may be the one that controls design and operation, because to assure maximum protection for consumers, all three and the MCLs must be met.

The first performance criterion is: Although EPA is not now setting MCL's for other specific organic compounds, reduction of exposure to known or suspected carcinogens in drinking water to the extent possible is encouraged. Because evidence is mounting that low molecular weight halogenated compounds such as carbon tetrachloride, tri- and tetrachloroethylene, vinyl chloride, and so forth are a health hazard, and are adsorbable by granular activated carbon, the treatment process should be designed and operated so that the granular activated carbon is reactivated* when the concentration of any organic compound of this type (excluding the trihalomethanes) exceeds 0.5 µg/ℓ in the effluent. Additionally, these organic compounds can be measured by a single analytic procedure, see Appendix B.

This criterion leaves a gap in contaminant control. Neither known carcinogens, such as benzene (an unchlorinated compound), nor toxicants that are unable to be analyzed at this time (Fall 1977) would necessarily be controlled if only the above criterion were used. Therefore, the second performance criterion must be related to some group parameter(s). As a group parameter, organic carbon has merit, as any deterioration in granular

*For this discussion reactivation of the granular activated carbon is assumed rather than replacement.

activated carbon bed performance with respect to this parameter would indicate an increase in the concentration of some unknown organic compound(s) of unknown hazard in the treated water. Therefore, to maximize protection for the consumer, the treatment process should be designed and operated so that the granular activated carbon is reactivated when the increase in the concentration of total organic carbon (TOC) exceeds 0.5 mg/ℓ over the initial effluent TOC concentration (see Appendix B), the second performance criterion.

Finally, to assure that the granular activated carbon is performing adequately at the start of the test, the third performance criterion is that the initial TOC removal ((Adsorber Influent TOC Conc. - Adsorber Effluent TOC Conc.)/Adsorber Influent TOC Conc.)) x 100, must exceed 50 percent.

In addition to these criteria, to meet the maximum contaminant level (MCL) portion of the Regulation, the treatment process should be designed and operated so that the granular activated carbon is reactivated when: 1) the arithmetic sum* of the terminal trihalomethane concentrations, a technique for estimating compliance with the Regulations, (see Appendix B), or 2) the pesticide concentrations (rarely involved) exceed the MCLs (0.10 mg/ℓ proposed for the trihalomethanes) specified in the Interim Primary Drinking Water Regulations.

These performance criteria should be applied as follows. The simplest method of retrofitting a large water treatment plant with granular activated carbon would be to replace the present filter media with granular activated carbon (sand replacement) and add a reactivation facility. To investigate this mode of operation in a particular location, a small granular activated carbon column with an empty bed contact time, volume/flow (EBCT), similar to that available in the existing filter boxes during average flow should be fabricated (see Appendix C) and used to treat settled water. The effluent concentration of: 1) Any low molecular weight halogenated compounds present, 2) Total Organic Carbon, and 3) Terminal summation trihalomethane (see Appendix B)

*Called "Summation" Trihalomethanes in the Guide and Appendices and "Total" Trihalomethanes in the Regulations.

should be determined weekly to show how long good performance can be maintained with that particular adsorbent and EBCT. When Criterion one or two or the MCL are exceeded, using a three week running average, $(W_i + W_{i+1} + W_{i+2}/3$, value assigned to $Week_{i+1})$ the granular activated carbon would have to be reactivated. If Criterion three is exceeded initially, this EBCT is not adequate.

To investigate the use of a granular activated carbon system with a longer EBCT, a second system consisting of three pilot granular activated carbon columns in series each with a 10 minute EBCT should be operated simultaneously with the one described above on filtered water (see Appendix C). Sampling after each of these three additional columns will show the influence of longer contact time on reactivation frequency as measured by all the Criteria. Pages A69 to A76 of Appendix A present an example of making this type of investigation and an analysis of these data are presented below. Finally, because experience has shown that Terminal ΣTHM concentrations are likely to be greater in the summer and the concentration of the types of organic compounds related to Criterion one are often higher in source waters in the winter, collecting these pilot column data in both seasons would be very helpful.

Another major question beyond mode of operation, empty bed contact time, and reactivation frequency is which commercially available granular activated carbon is most cost effective for a given location. A utility wishing to evaluate the performance of competitive commercial products could do so by expanding the test procedure outlined above to include parallel units containing different kinds of adsorbents. Possibly the adsorbent suppliers would help in this evaluation.

Example Data

Data collected by the Water Supply Research Division in three locations, the lower Mississippi River, the central Ohio River, and a southern Florida ground water will be used to show how these performance criteria would be

applied. Tables IV and V contain data from a full-scale installation in the lower Mississippi Valley, rather than the recommended pilot granular activated carbon columns, but do show that for this installation Criterion 1 and 2 are exceeded after two plus weeks for the sand replacement system, while the reactivation frequency could be extended to six weeks through the use of post-filter adsorbers. The difference in EBCT is too small to account for this difference. For the data in Table VI, collected with a pilot column operating on tap water from the central Ohio Valley, Criterion 1 controlled after 7 weeks, followed by Criterion 2 on the 8th week. The MCL was not exceeded until the 24th week.

The data in Tables VII, VIII and IX were prepared from pilot granular activated carbon column studies conducted in southern Florida on a ground water containing high concentrations of organic carbon and trihalomethane formation potential, as well as several low molecular weight halogenated organic compounds. These data show that the short EBCT does not provide good performance for very long and leads to the conclusion that longer EBCTs are necessary. Pilot columns with longer EBCTs are now being employed at this site (see pages A69 to A76 in Appendix A). Tables VIII and IX present data from repeat runs and indicate the general reproducibility of this approach.

Calculation of Adsorbent Use Rate

The data collected by the procedure summarized above can be used to calculate the use rate (dose) in weight per unit volume of water of granular activated carbon needed to meet the controlling criterion for any empty bed contact time. Adsorbent use rate 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(s) until each criterion and the MCL is exceeded.

TABLE IV

APPLICATION OF PERFORMANCE CRITERIA FROM LOWER MISSISSIPPI PROJECT

SAND REPLACEMENT - AVERAGE EBCT - 21 min.

Time, Weeks	Criterion 1: 1,2-Dichloroethane Conc.	Criterion 1: Trichloroethylene Conc.	Criterion 2: TOC Conc.	Criterion 3: TOC Removal Percentage	MCL: Term. ΣTHM Conc.
Performance Criteria:	µg/ℓ < 0.5	µg/ℓ < 0.5	mg/ℓ < Δ0.5 over TOC_o	% Initial > 50%	mg/ℓ < 0.10
0	-	NF	0.8	77	-
1	0.25	NF	-		< 0.01
2+	0.7*	NF	2.0*		0.05
3	1.5	NF	2.0		0.07
4	3.7	NF	1.9		0.11*
5		NF			0.13
6		NF			
7		NF			
8		NF			
9		0.03			
10+		0.03			
11+		0.03			
12+		NF			
13+		NF			
14+		NF			
15+		NF			
16+		NF			

NF - None found

* - Performance criterion exceeded

Note: All data are three week running averages, except for TOC_o

TABLE V

APPLICATION OF PERFORMANCE CRITERIA FROM LOWER MISSISSIPPI PROJECT

POST-FILTER ADSORBER, AVERAGE EBCT - 24 min.

Time, Weeks,	Criterion 1: 1,2-Dichloroethane Conc.	Criterion 1: Trichloroethylene Conc.	Criterion 2: TOC Conc.	Criterion 3: TOC Removal Percentage	MCL: Term. ΣTHM Conc.
Performance Criteria:	µg/ℓ < 0.5	µg/ℓ < 0.5	mg/ℓ < Δ0.5 over TOC_o	% Initial > 50%	mg/ℓ < 0.10
0	-	NF	0.8	73	-
1	0.2	NF	0.9		<0.01
2+	0.1	NF	0.8		0.01
3	0.0	NF	0.8		0.02
4	0.1	NF	0.8		0.02
5	0.5	NF	1.0		0.02
6	0.7*	NF	0.9		0.03
7	0.9	NF	1.0		0.04
8		NF	1.1		0.07
9		NF	1.3*		0.08
10+		0.1	1.3		0.09
11+		0.1			0.09
12+		0.1			0.09
13+		NF			0.09
14+		NF			0.09
15+		NF			0.10
16+		NF			-

NF - None Found

* - Performance criterion exceeded

Note: All data are three week running averages, except for TOC_o.

TABLE VI

APPLICATION OF PERFORMANCE CRITERIA FROM OHIO RIVER TAP WATER

POST-FILTER ADSORBER - UPFLOW MODE - EBCT - 11 minutes

Time, Weeks	Criterion 1 Carbon Tetrachloride Conc.	Criterion 2 TOC Conc.	Criterion 3 TOC Removal Percentage	MCL Term. ΣTHM Conc.
Performance Criteria	µg/ℓ < 0.5	mg/ℓ <Δ 0.5 over TOC_o	% Initial > 50%	mg/ℓ < 0.10
0	ND	ND	ND	ND
1	NF	0.34	77	NF
2	NF	0.28		< 0.01
3	NF	0.31		< 0.01
4	NF	0.40		< 0.01
5	NF	0.41		< 0.01
6	NF	0.57		< 0.01
7	1.7*	0.71		0.01
8	3.3	0.85*		0.02
9	5.3	1.21		0.02
10				0 .03
11				0.04
12				0.04
13				0.05
14				0.06
15				0.06
16				0.07
17				0.07
18				0.08
19				0.08
20				0.09
21				0.10
22				0.10
23				0.10
24				0.11*

ND - Not determined

NF - None Found

* - Performance Criterion Exceeded

Note: All data are three week running averages, except for TOC_o.

TABLE VII

APPLICATION OF PERFORMANCE CRITERIA FROM SOUTHERN FLORIDA GROUNDWATER

RAW WATER APPLIED TO COLUMN, EBCT - 6.2 minutes

	Criterion 1				Criterion 2	Criterion 3	MCL
Time, Weeks	A Conc.	B Conc.	C Conc.	D Conc.	TOC Conc.	TOC Removal Percentage	Term. ΣTHM Conc.
Performance Criteria	µg/ℓ <0.5	µg/ℓ <0.5	µg/ℓ <0.5	µg/ℓ <0.5	mg/ℓ < Δ0.5 over TOC_o	% Initial > 50%	mg/ℓ < 0.10
0	-	-	-	-	3.3	67	-
1	NF	NF	0.13	NF	4.9*		0.33*
2	NF	<0.01	1.0*	<0.01	6.1		0.51
3	<0.01	0.3	2.4	<0.01	7.6		0.59
4	<0.01	0.04	4.9	<0.01			
5	<0.01	0.03	5.8	NF			
6	<0.01	0.01		NF			
7	0.01	0.02		NF			
8	0.02	0.02		NF			
9	0.04	0.03		NF			
10	0.05	0.06		<0.01			
11	0.06	0.05		<0.01			
12	0.27	0.15		0.03			
13+	0.39	0.17		0.05			
14	0.67*	0.30		0.06			
15	0.70	0.30		0.06			
16	-	-		-			

NF = None found

* = Performance criterion exceeded

Note: All data are three week running average, except for TOC_o.

A = trans -1,2-Dichloroethylene

B = 1,1-Dichloroethane

C = cis-1,2-Dichloroethylene

D = Trichloroethylene

Note: These data are for illustrative purposes only and are not indicative of final design and operation based on longer EBCTs, see pages A69 to A76.

TABLE VIII

APPLICATION OF PERFORMANCE CRITERIA FROM SOUTHERN FLORIDA GROUNDWATER

FILTERED WATER APPLIED TO COLUMN, EBCT - 6.2 minutes

	Criterion 1					Criterion 2	Criterion 3	MCL
Time, Weeks	A Conc.	B Conc.	C Conc.	D Conc.	E Conc.	TOC Conc.	TOC Removal Percentage	Term. ΣTHM Conc.
Performance Criteria	µg/ℓ <0.5	µg/ℓ <0.5	µg/ℓ <0.5	µg/ℓ <0.5	µg/ℓ <0.5	mg/ℓ < Δ0.5 over TOC_o	% Initial >50%	mg/ℓ <0.10
0	NF	NF	NF	NF	ND	-	-	-
1	0.13	NF	3.57*	0.20	0.40	1.5	76	0.16*
2	0.13	0.18	4.30	0.21	0.38	4.3*		0.22
3	0.13	0.18	5.25	0.21	0.32	5.2		
4	0.04	0.39	4.65	0.01	1.68*	4.5		
5	0.04	0.21	6.85	<0.01	2.65	4.5		
6	0.04	0.21	9.19	<0.01	3.27	4.8		
7	-	-	-	-	-	-		

ND = Not Determined

NF = None Found

* = Performance criterion exceeded

Note: All data are three week running average, except for TOC_o.

A - trans-1,2-Dichloroethylene

B = 1,1-Dichloroethane

C = cis-1,2-Dichloroethylene

D = Trichlorethylene

E = Vinyl chloride

Note: These data are for illustrative purposes only and are not indicative of final design and operation based on longer EBCTs, see pages A69 to A76.

TABLE IX

APPLICATION OF PERFORMANCE CRITERIA FROM SOUTHERN FLORIDA GROUNDWATER

FILTERED WATER APPLIED TO COLUMN, EBCT - 6.2 minutes

	Criterion 1					Criterion 2	Criterion 3	MCL
Time, Weeks,	A Conc.	B Conc.	C Conc.	D Conc.	E Conc.	TOC Conc.	TOC Removal Percentage	Term. ΣTHM Conc.
Performance Criteria	µg/ℓ <0.5	µg/ℓ <0.5	µg/ℓ <0.5	µg/ℓ <0.5	µg/ℓ <0.5	mg/ℓ <Δ0.5 over TOC_o	% Initial >50%	mg/ℓ <0.10
0	-	-	-	-	-	0.4	93	-
1	NF	NF	NF	NF	3.80*	2.3*		0.12*
2	NF	0.37	0.43	NF	3.80	3.5		0.23
3	NF	0.43	1.70*	NF	4.47	3.9		0.37
4	NF	0.43	5.40	NF	1.73	3.6		
5	NF	0.17	6.80	0.07	2.30	3.0		
6	NF	0.37	9.53	0.17	1.17	4.4		
7	0.2	0.60*	8.87	0.37	2.00	-		
8	-	-	-	-	-	-		

NF = None found

* = Performance criterion exceeded

Note: All data are three week running average, except for TOC_o.

A = trans-1,2-Dichloroethylene

B = 1,1-Dichloroethane

C = cis-1,2-Dichloroethylene

D = Trichloroethylene

E = Vinyl chloride

Note: These data are for illustrative purposes only and are not indicative of final design and operation based on longer EBCTs, see pages A69 to A76.

If the adsorbent use rate decreases with increasing empty bed contact time then a more than proportional improvement in performance is gained by increasing the empty bed contact time. The next sub-section on "Economic Analysis" will show the importance of knowing whether or not this proportionally between empty bed contact time and performance occurs in a given location. Further, the adsorbent use rate can be used to estimate one of the major components of cost associated with a granular activated carbon adsorption treatment system, the cost of adsorbent reactivation. Figures 42 and 43 in Appendix A, pages A109 and A110, present the unit costs that can be multiplied by the adsorbent use rate to calculate the reactivation cost per unit volume of water produced.

The data in Table X, based on Figures 24 to 27, pages A69 to A76 in Appendix A, can be used an as example of this type of analysis.

TABLE X

ADSORBENT USE RATES FOR TREATING A SOUTHERN FLORIDA GROUND WATER

Empty Bed Contact Time Minutes	Criterion 1 VC Use, mg/l	Criterion 1 Cis Use, mg/l	Criterion 2 TOC Use, mg/l	MCL Use, mg/l
6.2	560	90	1,340	860
12.4	370	70	880	430
18.6	170	NR	530	410
24.8	230	NR	430	410

VC - Vinyl Chloride
Cis = cis-1,2-Dichloroethylene
NR = Criterion Not Reached
Note: Data are from Figures 24 to 27, pages A69 to A76, Appendix A. These data are for example purposes only. Calculated adsorbent use rates at other locations are much lower.

These data show that the adsorbent use rate declined for all criteria as the empty bed contact time increased from 6.2 - 18.6 minutes, (more than proportional performance improvement), but that the next increment of empty bed contact time to 24.8 minutes did not lower the adsorbent use rate for the MCL requirement. Therefore, for these data, an empty bed contact time of about 19 minutes was optimum.

Summary

In summary several points are important:

1) Granular activated carbon treatment performance criteria have been selected that will permit collecting the data from pilot granular activated carbon columns that is necessary for; a) the economical design and operation of a granular activated carbon adsorption unit process, and b) choosing an adsorbent in any given location requiring organic contaminant control.

2) This scheme is also flexible enough to serve other purposes such as evaluation of the combination of ozone and granular activated carbon (biological activated carbon), including an evaluation of the microbiological content of the effluent, and the performance of reactivated carbon compared to virgin material, if a sample of reactivated carbon is available for study.

3) Because of changing seasons and possible changes in the quality of source waters, continued monitoring of the full-scale treatment plant will be necessary for good process control.

4) Although the pilot granular activated carbon column tests should give a good indication of full plant performance, some adjustments in reactivation frequency should be expected.

5) Although the above outlined approach may not be the ultimate solution, operation of the full-scale granular activated carbon beds to meet the established performance criteria consistently will provide a large measure of protection for consumers against the health hazards and esthetic problems of organic compounds in drinking water.

Economic Analysis

The final selection of a water treatment plant design based on the "Collection of Treatability Data", previous sub-section, may involve an economic analysis of alternatives. This sub-section will summarize recommended economic analysis procedures to aid utilities and consulting engineers in arriving at a cost-effective design. More details are included in Appendix A, pages A91 to A111.

Basic Costs

For these analyses, as in the "Interim Treatment Guide for the Control of Chloroform and other Trihalomethanes"[3,4], two types of granular activated carbon systems will be considered, one using the granular activated carbon in separate contactors after sand filters (hereafter called post-filter adsorber) and the other using the granular activated carbon as a replacement for the media in existing filter beds (hereafter called sand replacement). Both systems will be considered with on-site reactivation. The economics of using truck transport combined with centralized reactivation furnaces has been explored in the Trihalomethane Interim Treatment Guide.[3,4]

When the assumption is made that granular activated carbon will replace the media in existing filters, the need to consider the cost of separate granular activated carbon contactors is eliminated. For purposes of the sand replacement analysis, a water treatment plant is assumed to consist of a number of one mgd filters. Table XI shows the design parameters that were assumed for the sand replacement systems. Table XII contains typical design assumptions for post-filter adsorber systems of 10 and 100 mgd.

Note that, for the sand replacement, a granular activated carbon loss of 10 percent per reactivation cycle is assumed, but a granular activated

TABLE XI

DESIGN PARAMETERS FOR GRANULAR ACTIVATED CARBON

(Sand Replacement)

Design Parameters	Level
Activated Carbon Cost	$.45/lb
Activated Carbon Loss per Reactivation Cycle	10 percent
Fuel Cost	$1.50/mil BTU
Construction Cost Index	273.8 (6/77)
Wholesale Price Index	194.6 (6/77)
Direct Hourly Wage Rate	$5.58/hr (5/77)
Amortization Rate	7 percent
Amortization Period	20 years
Volume per Filter	856 ft^3
Loss in Adsorptive Capacity	0 percent
Design Capacity	70 percent
Empty Bed Contact Time	13.4 minutes
Reactivation Frequency	Every 1.2 months

Note: The influence of variations in these assumptions on the final cost is discussed in detail in the Interim Trihalomethane Control Guide.[3,4]

TABLE XII

PARAMETERS FOR GRANULAR ACTIVATED CARBON

(Post-filter Adsorption)

Design Parameters	Level
Activated Carbon Cost	$0.45/lb
Activated Carbon Loss per Reactivation Cycle	5 percent
Fuel Cost	$1.50/mil BTU
Construction Cost Index	273.8 (6/77)
Wholesale Price Index	194.6 (6/77)
Direct Hourly Wage Rate	$5.58/hr (5/77)
Amortization Rate	7 percent
Amortization Period	20 years
Filter Configuration	
10 mgd plant	
No. of filters	8
Diameter of filters	12 feet
Vol. per filter	1470 ft^3
Empty Bed Contact Time	18 minutes at 5.4 gpm/ft^2
100 mgd plant	
No. of filters	28
Diameter of filters	20 ft.
Vol. per filter	4396 ft^3
Empty Bed Contact Time	19 minutes at 5.5 gpm/ft^2
Loss in adsorptive capacity	0 percent
Design capacity	70 percent
Reactivation Frequency	Every 2.4 months

Note: The influence of variations in these assumptions on the final cost is discussed in detail in the Interim Trihalomethane Control Guide.[3,4]

carbon loss of only 5 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 granular activated carbon loss because the activated carbon is changed manually. In post-filter adsorption systems, the activated carbon transfer is assumed to be accomplished hydraulically, leading to fewer possibilities for handling losses. Representative costs for both types of systems based on the design parameters in Tables XI and XII are summarized in Table XIII.

The costs for the post-filter adsorber system in Table XIII are assumed as if the system might be added to an existing 100 mgd plant. In this case, the post-filter adsorber is assumed to supply an average flow of 70 mgd rather than for the peak capacity of the plant at 100 mgd.

Table XIV contains the unit costs for three possible granular activated carbon system design configurations. Lines 1 through 3 show the costs associated with a 100 mgd sand replacement system with an average flow of 70 mgd. Lines 4 through 6 are associated with a 70 mgd sand replacement plant treating 70 mgd, and lines 7 through 9 contain unit costs for a post-filter adsorption system that is designed for and produces an average flow of 70 mgd. Therefore, the first sand replacement system has a load factor of 70 percent, while the other two systems have load factors of 100 percent.

Each system illustrates a set of conditions that might be met under field conditions. Designing a plant for peak capacity, for example 100 mgd, with an average load factor of 70 percent is common. The second set of data illustrates a condition in which the peak capacity and average flows are equal. Figure 13 shows the cost penalty of excess capacity. In Figure 13, for given equivalent reactivation frequencies, the cost in cents per thousand gallons is plotted for the smallest contact time in each plant design, lines 1 and 4 from Table XIV. The cost penalty decreases as the time between reactivations increases.

TABLE XIII

COSTS FOR GRANULAR ACTIVATED CARBON SYSTEMS

System	10 mgd Sand Replacement	10 mgd Post-filter** Adsorption	100 mgd Sand Replacement	100 mgd Post-filter** Adsorption
Capital Costs				
Project Costs				
Furnace ($)	834,000	703,000	2,300,000	2,016,000
Contactors ($)	-	1,451,000	-	7,373,000
Initial Activated Carbon Charge ($)	230,000	316,000	2,300,000	3,210,000
Total Project Cost ($)	1,064,000	2,470,000	4,600,000	12,599,000
Total Capital (Project and Interest) Cost*	2,009,000	4,663,000	8,685,000	23,787,000
Amortized Unit Capital Cost (cents/1000 gal)	3.94	9.12	1.70	4.65
Unit Operating Cost (cents/1000 gal)	9.23	7.61	5.18	4.01
Total Unit Cost (cents/1000 gal.)	13.17	16.73	6.88	8.66

*Amortized Capital Cost at 7%, 20 years yields a capital recovery factor of 0.0944.

**The post-filter adsorber system is assumed as an incremental addition to an existing treatment plant and its maximum capacity was assumed to be 70 percent of the original plant capacity.

TABLE XIV

COST COMPARISON AMONG GRANULAR ACTIVATED CARBON SYSTEMS

System Type	Design Flow (mgd)	Peak Capacity (mgd)	Empty Bed Contact Time (minutes)	Reactivation Frequency (Months Between) Costs in cents/1000 gal.									
				0.1 mo	0.25 mo	0.5 mo	0.75 mo	1 mo	2 mo	3 mo	4 mo	5 mo	6 mo
Sand	70	100	14.3	62.4	27.9	15.8	11.5	9.3	5.8	4.5	3.9	3.4	3.1
Replacement	70	100	28.6	118.6	52.0	28.8	20.8	16.7	10.2	7.9	6.7	5.9	5.4
	70	100	42.9	173.6	75.4	41.4	29.7	23.7	14.4	11.1	9.4	8.3	7.6
Sand	70	70	10	45.1	20.4	11.7	8.6	7.0	4.4	3.5	2.9	2.6	2.4
Replacement	70	70	20	85.1	37.7	21.1	15.3	12.3	7.6	5.9	5.0	4.5	4.1
	70	70	30	124.1	54.3	30.1	21.7	17.4	10.6	8.2	7.0	6.2	5.6
Post-	70	70	10	32.7	17.4	11.8	9.8	8.7	6.9	6.2	5.9	5.6	5.5
Filter	70	70	20	57.8	28.9	18.6	14.9	13.0	9.9	8.7	8.1	7.7	7.5
Adsorber	70	70	30	82.0	39.8	24.9	19.6	16.9	12.5	10.9	10.1	9.5	9.2

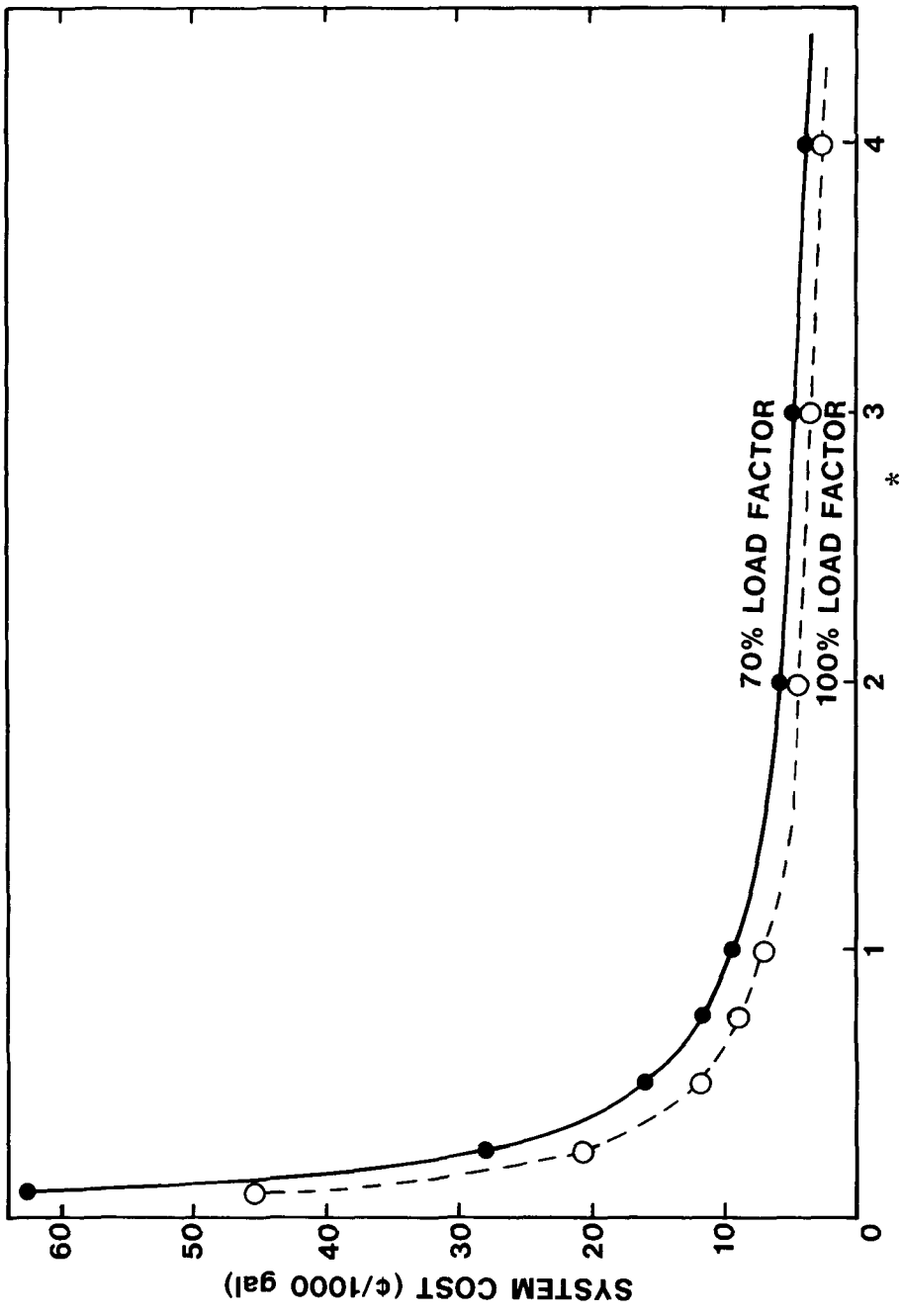

FIGURE 13. THE COST OF EXCESS CAPACITY FOR SAND REPLACEMENT SYSTEMS

*Time Between Reactivations.

Influence of Empty Bed Contact Time

The tradeoff between bed depth (empty bed contact time) and reactivation frequency for a given quality of water is an important relationship. To make this comparison the ratio between reactivation frequency in months and the EBCT in minutes was calculated. For example, for one of the systems in Table XIV with an EBCT of 10 minutes and a reactivation frequency of 0.5 months, the ratio, "R", is as follows:

$$R = \frac{0.5 \text{ months}}{10 \text{ minutes}} = 0.05 \qquad (1)$$

The R values were calculated for the sand replacement systems in Table XIV XIII with contact times of 10 and 20 minutes (lines 4 and 5). The system with 20 minutes contact time has twice the bed depth of the system with 10 minutes contact time.

The cost in cents per thousand gallons is plotted versus R in Figure 14 for these two systems. These data show that the longer contact time bed is always more expensive for the same value of R. When the R value remains the same, this means that a direct proportionally exists between empty bed contact time and reactivation frequency, which may or may not be true in a given situation. The data collected with the pilot columns described in the previous sub-section will provide the necessary information for this analysis.

For a given value of R and a given EBCT (P_1) the straight line drawn horizontally to the curve representing the longer contact time bed (P_2), represents the increase in the period between reactivations that is required for the longer contact time to be economically equivalent to the shallower bed. In Figure 14 at P_1, R = 0.01, the total unit cost for the 10 minute empty bed contact time bed is 45.1 cents/1000 gal. Drawing a horizontal line to the 20 minute contact time curve yields an R at P_2 of 0.0124. The necessary reactivation frequency for cost equivalancy can be calculated as follows:

$$\frac{P_2}{20} = 0.0124 \qquad (2)$$

$$P_2 = 0.25 \text{ months}$$

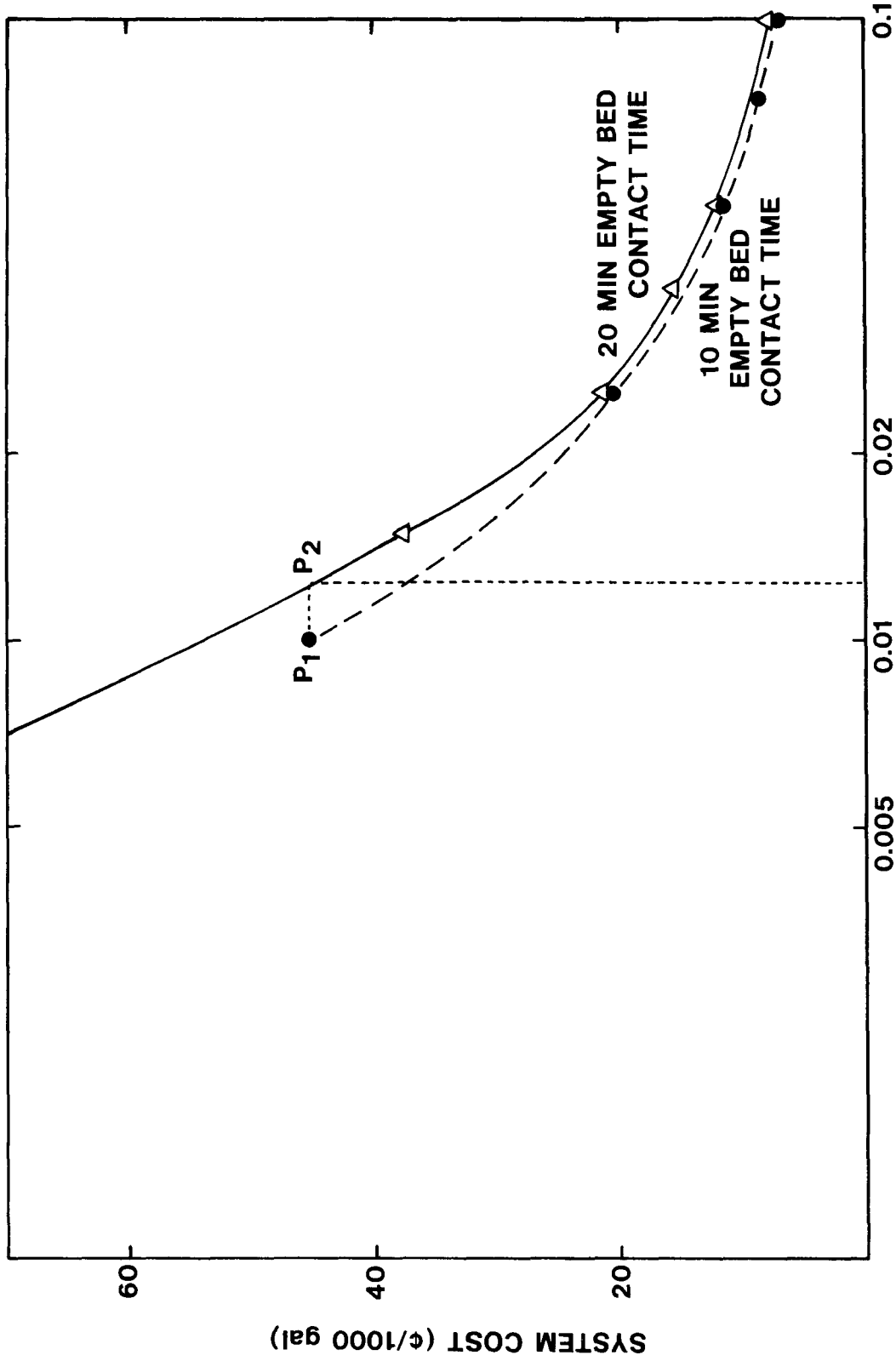

FIGURE 14. EFFECT OF EMPTY BED CONTACT TIME AND REACTIVATION FREQUENCY ON COST FOR SAND REPLACEMENT SYSTEM

Therefore, the period between reactivations would have to increase by 150 percent to be able to use a 100 percent longer EBCT system at the same cost. This non-proportional relationship between EBCT and reactivation frequency is caused by the increased activated carbon inventory that must be maintained for deeper beds.

At larger values for R (longer periods between reactivation), however, the difference between systems becomes small so that little economic penalty occurs when choosing a system with a longer EBCT and a longer period between reactivations. Performance data from the recommended pilot column test (see previous sub-section), to determine whether or not a more than proportional lengthening in reactivation frequency will occur with an increase in contact time, can be used to make this type of analysis in a given location.

Influence of Type of System Chosen

In the following analysis when post-filter adsorbers and sand replacement systems are compared, the comparison will be made between the last two systems in Table XIV because the design empty bed contact times are equal. Figure 15 shows the cost in cents per thousand gallons for a sand replacement system and the post-filter adsorber having equal empty bed contact times (10 minutes). For very short reactivation periods (less than 2 weeks) post-filter adsorbers are always less expensive than sand replacement. When the reactivation period is greater than 0.5 months, however, sand replacement becomes less expensive because of less capital expense.

Figure 16 shows the relationship between a sand replacement system with a 10 minute EBCT and a post-filter adsorber with a 20 minute EBCT. As might be expected from the previous analysis, with smaller R values the longer EBCT post-filter adsorber is less costly than the shorter EBCT -sand replacement system, but as the period between reactivations increases, the sand-replacement system becomes relatively less expensive. Therefore, under this set of

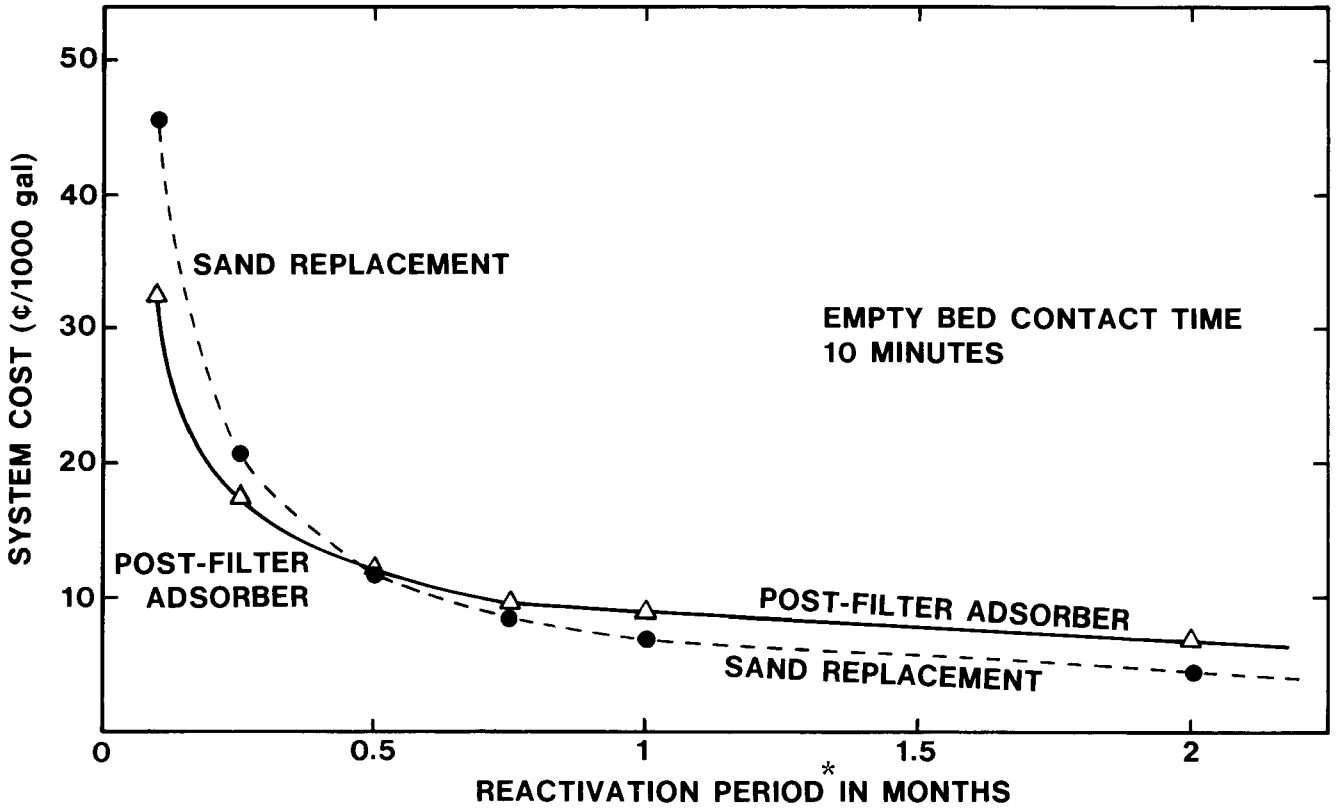

FIGURE 15 COMPARISON OF COST OF SAND REPLACEMENT AND POST-FILTER ADSORPTION SYSTEMS

*Time Between Reactivations.

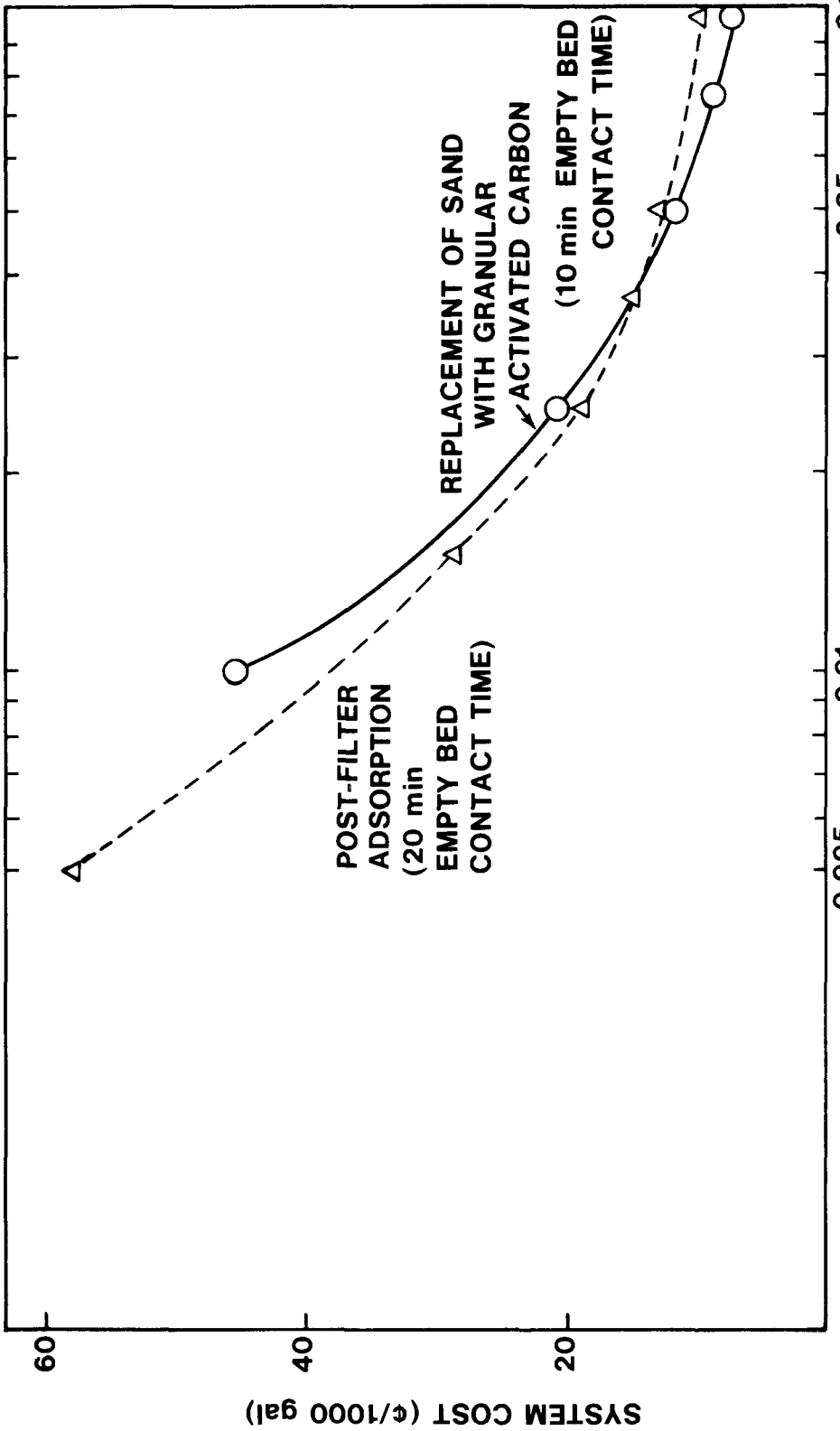

FIGURE 16. EFFECT OF EMPTY BED CONTACT TIME AND REACTIVATION FREQUENCY ON COST FOR SAND REPLACEMENT AND POST-FILTER ADSORPTION SYSTEMS

assumptions, the increased cost of building post-filter adsorbers cannot be overcome by obtaining longer periods between reactivations through the use of longer EBCTs, if the reactivation frequency is greater than 0.4 months. Because the cost differential is not great, however, other considerations may dictate final designs. Note: the cost comparisons of other combinations than those presented in Figures 13-16 can be made using the data in Table XIV.

Influence of Granular Activated Carbon Cost

To minimize costs, a water purveyor might consider the use of the least expensive granular activated carbon available. A lower cost activated carbon, however, may also require shorter periods between reactivation, if its performance is reduced. For example, using the data shown in Figure 17, for a 10 mgd post-filter adsorption plant, if a pound of activated carbon costs $0.70 and the reactivation frequency is three months, then the system cost would be 17.5 cents/1000 gal. With a less expensive activated carbon, perhaps one costing $0.30/pound, the reactivation frequency would have to be 2 months or greater to achieve a favorable economic tradeoff under these assumed conditions.

Influence of Inflation

Table XIII shows that under static economic conditions, sand replacement systems are slightly less expensive than post-filter adsorption systems. Because post-filter adsorption is less labor intensive than sand replacement, it might become less expensive some time in the future because of inflation. Figure 18 illustrates the impact of inflation on the two 100 mgd systems (one of each type) assuming an inflation rate of 5 percent per year and shows that sand replacement system does become more expensive than post-filter adsorption in year 18.

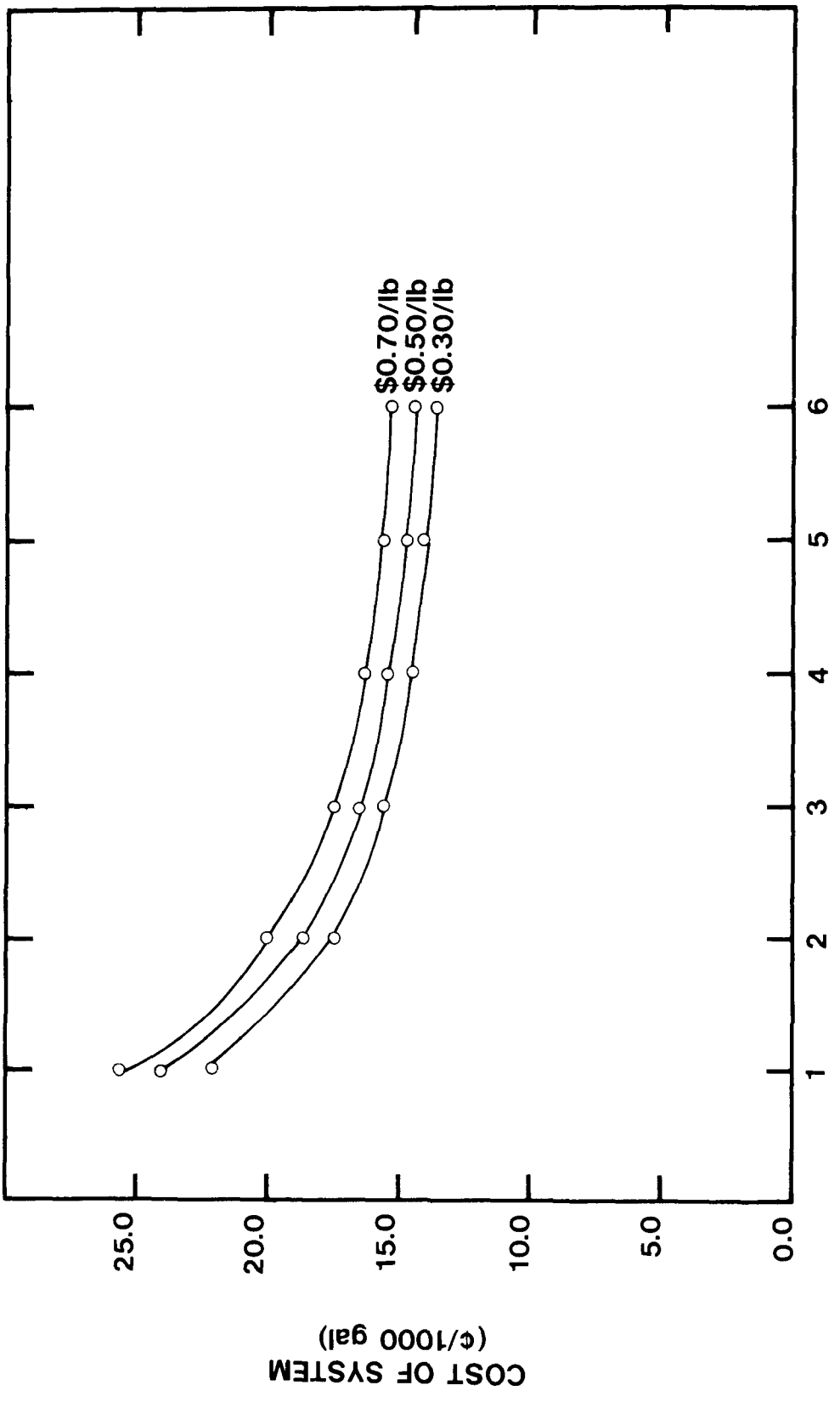

FIGURE 17. EFFECT OF ACTIVATED CARBON COST AND REACTIVATION PERIOD ON SYSTEM COST FOR 10 mgd POST-FILTER ADSORPTION PLANT

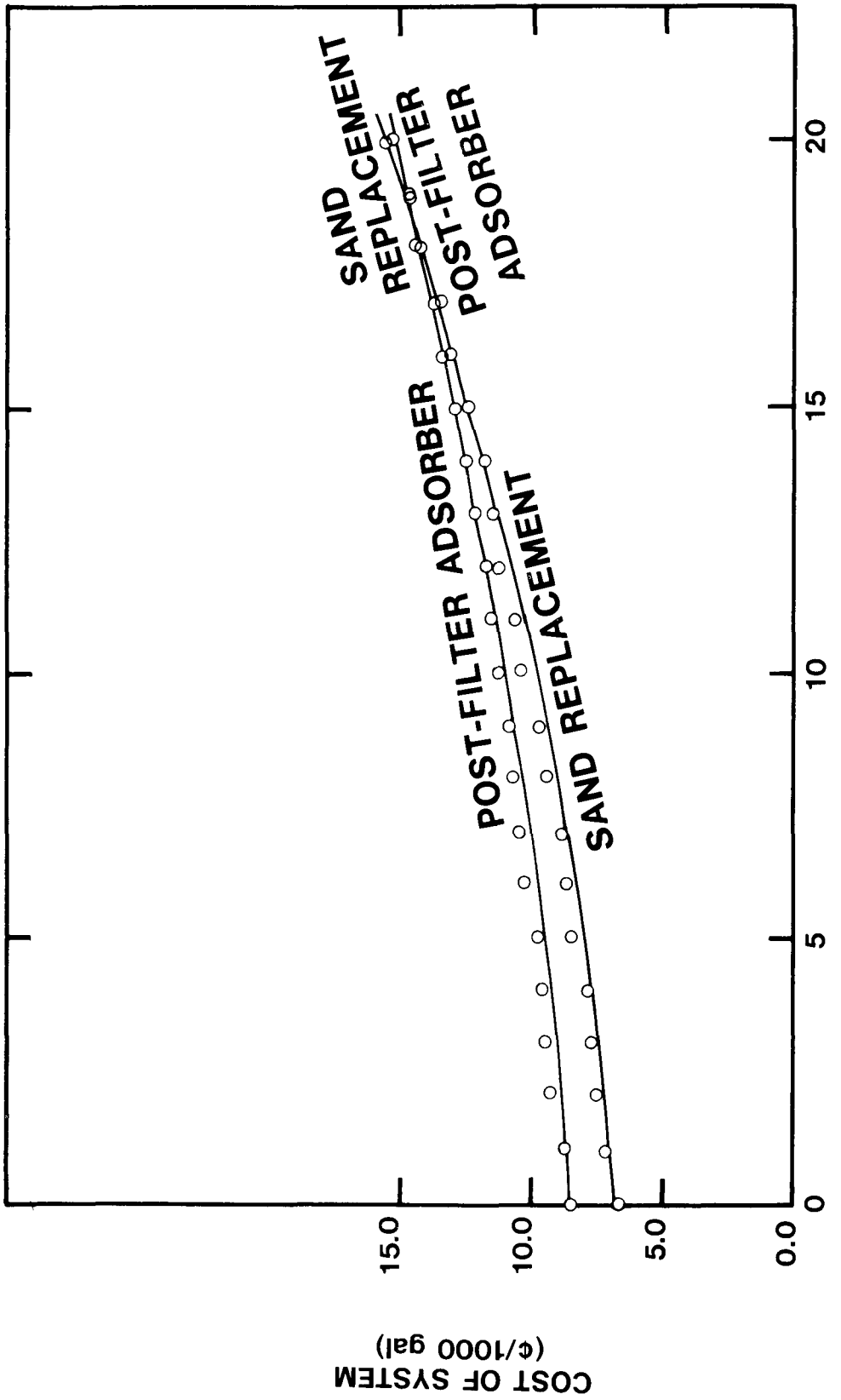

FIGURE 18. EFFECT OF 5% INFLATION RATE ON COST OF 100 mgd POST-FILTER-AND SAND REPLACEMENT ADSORPTION SYSTEMS

Figure 19 shows the impact of inflation on the two granular activated carbon configurations, over a 20-year period assuming inflation at 7 percent per year. Post-filter adsorption becomes less expensive than sand replacement in year 12 under this set of assumptions for a 100 mgd plant.

Figures 18 and 19 illustrate that over the life of the two types of systems, because of the labor intensive nature of the sand replacement type, it eventually becomes more expensive than a post-filter adsorber on a yearly expenditure basis. This phenomenon occurs, of course, because the capital expenditure remains fixed over the life of the investment, while operating costs, particularly labor costs, are subject to inflation.

Figures 18 and 19 also illustrate that the total expenditure over time is less for the sand replacement system than for post-filter adsorbers. To account for total expenditures, a "present value" analysis was made for the systems listed in Table XIII. Two discount rates (6% and 8%) and three inflation rates (5%, 7% and 9%) were used in the analyses. The results are summarized in Table XV. As can be seen from the Table, for the larger plant, at the highest inflation rate, for both discount rates, the difference in present value for the two systems is small. In no case, however, is the present value of the expenditure for post-filter adsorbers less than those for sand replacement.

The unit costs in Table XIII show that small treatment systems in general are more expensive,on a per unit of product basis, than larger systems. These costs can be reduced significantly, however, by the use of truck transport and regional reactivation systems. This effect is illustrated in the Trihalomethane Interim Treatment Guide.[3,4]

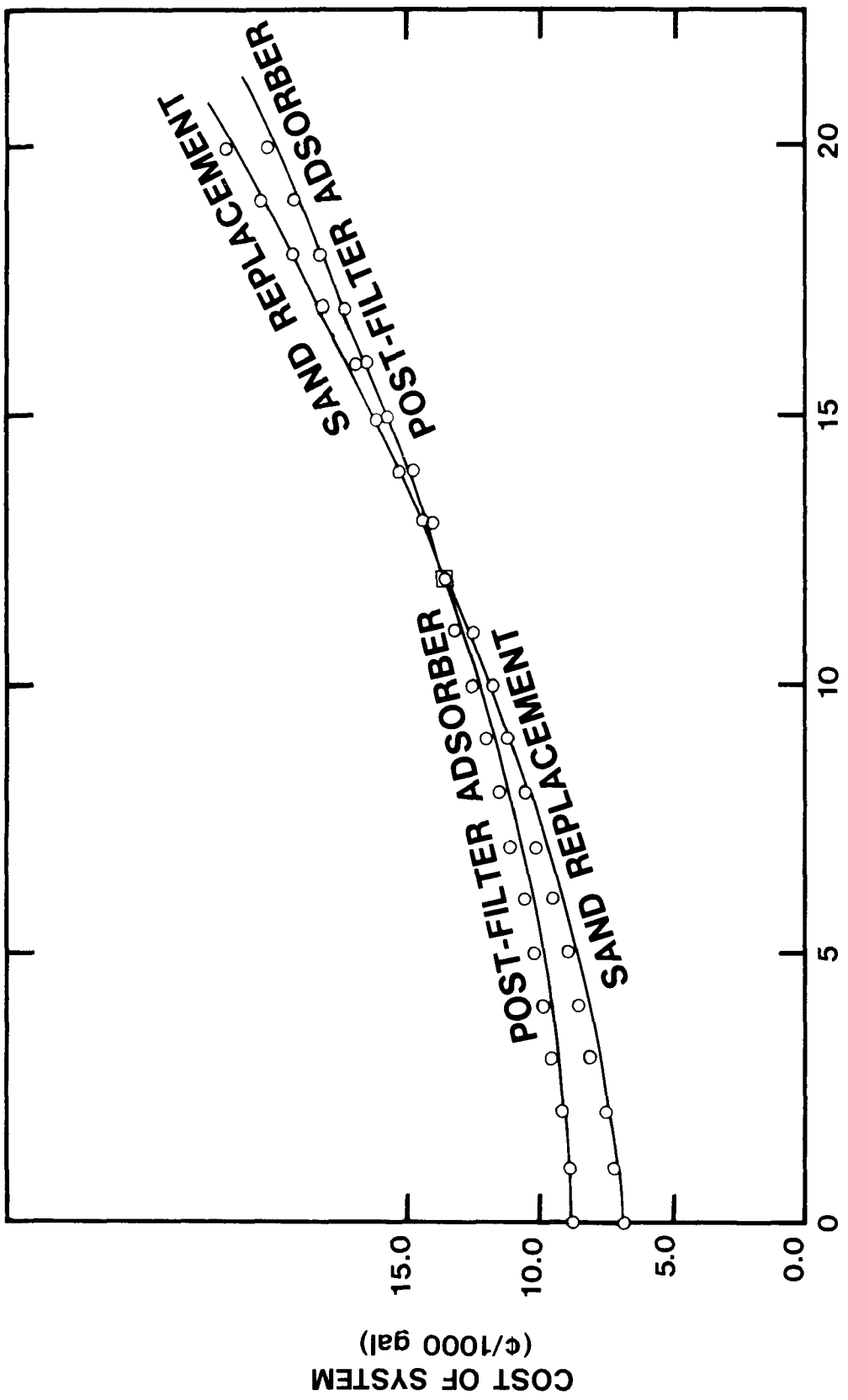

FIGURE 19. EFFECT OF 7% INFLATION RATE ON COST OF 100 mgd POST-FILTER AND SAND REPLACEMENT ADSORPTION SYSTEMS

TABLE XV

SUMMARY OF PRESENT VALUE ANALYSIS

FOR POST-FILTER ADSORPTION AND SAND REPLACEMENT SYSTEMS

System	10 mgd Discount at 6%	10 mgd Discount at 8%	100 mgd Discount at 6%	100 mgd Discount at 8%
Sand Replacement				
Inflation at 5%	225.67	190.96	119.43	101.67
Inflation at 7%	262.37	219.50	140.86	117.64
Inflation at 9%	305.30	252.58	166.12	137.13
Post-Filter Adsorber				
Inflation at 5%	259.96	221.20	134.69	114.76
Inflation at 7%	289.80	244.72	150.63	127.15
Inflation at 9%	323.35	270.50	169.12	141.40

Summary

This sub-section has discussed some of the important factors that a water purveyor must consider when making decisions regarding the use of granular activated carbon systems for removal of organic contaminants. Because the economics of choosing and designing a granular carbon system are complicated, individual utilities or their consultants, or both may need assistance in developing cost and economic design criteria. The Water Supply Research Division is prepared to assist those utilites affected by treatment regulations. Computer programs currently being utilized by WSRD and instructions in the use of these programs will be made available to interested parties. The Water Supply Research Division is prepared to provide a limited economic analysis for individual utilities affected by the treatment regulations. This assistance will aid the utility in making general decisions regarding overall implementation strategies, but will not be sufficient for specific designs.

SUMMARY

In summary, the Interim Treatment Guide provides information that demonstrates that granular activated carbon adsorption is the best available treatment technology, Fall 1977, for treating water to remove organic contaminants, thereby improving finished water quality and providing the American consumer with a more healthful and esthetically pleasing drinking water. For a more detailed summary the reader is referred to the Executive Summary at the front of this document. Three Appendices with more detailed information on various aspects of this subject follow this Guide.

ACKNOWLEDGMENTS

The Authors wish to extend their special appreciation to Ms. Maura M. Lilly without whose dedication, secretarial skill, diligence and patience, this Guide could not have been completed in a timely manner. They also wish to thank the Organic Contaminants Research Staff, J.K. Carswell, J. DeMarco, P. Dorsey, W.C. Elbert, W.A. Feige, D.L. Guttman, D. D. Hinderberger, K.L. Kropp, O.T. Love, Jr., B.W. Lykins, L.A. Moore, D.R. Seeger, C.J. Slocum, B.L. Smith, A. A. Stevens and R. Stevie, all of whom contributed to this document.

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See Also:

"Activated Carbon in Water Treatment" Proceedings of a Water Research Association Conference at the University of Reading, April 3-5, 1973, Water Research Centre, Medmenham, United Kingdom, Available from the Water Research Centre, Henley Road, P.O. Box 16, Medmenham, Marlow, United Kingdom, SL7 2HD.

Translation of Reports on Special Problems of Water Technology - Volume 9 - Adsorption" Proceedings of a Conference in Karlsruhe, Federal Republic of Germany, 1975, EPA-600/9-76-030, December 1976.

APPENDIX A

PERFORMANCE OF GRANULAR ACTIVATED CARBON FOR THE REMOVAL OF ORGANIC COMPOUNDS

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APPENDIX A

TABLE OF CONTENTS

PERFORMANCE OF GRANULAR ACTIVATED CARBON FOR THE REMOVAL OF ORGANIC COMPOUNDS

The purpose of Appendix A is to summarize the current state of knowledge concerning the performance of granular activated carbon adsorption as a treatment unit process. Appendix A will be in two major parts, one, a review of the literature, and two, a summary of the current status of the Water Supply Research Division's projects on this subject. The literature review will not be exhaustive, but will be a summary of the subject. Because many of the research projects discussed in the second portion of Appendix A are on-going, the research findings to date (Fall 1977)* will be presented as progress reports. Detailed papers on these studies will be published in the technical literature as they are completed.

Literature Review

Taste and Odor Control

Many water treatment plants in the United States are practicing taste and odor control by the addition of powdered activated carbon, which also removes some organic matter. Currently (Fall 1977) however, about 35 plants are using granular activated carbon, either alone or on top of some sand, as both a filter media for particulate control and an adsorption media for organic contaminant control. This type of system is hereafter called a sand replacement system and is used primarily for taste and odor control. A few water purveyors installed these granular activated carbon beds because of the organic pollution in their raw water as well as taste and odor problems.

In their 1964 paper, Woodward, Dostal, and Robeck[1] reported on five installations of granular activated carbon beds during the 1930's. A more recent survey[2] of the known granular activated carbon installations in this country, see Table I, shows that approximately 80 percent of the water

*Some data collected beyond that contained in the November 1977 draft of Appendix A has been included in the report.

TABLE I

DATE GRANULAR ACTIVATED CARBON FIRST INSTALLED[2]

	Experimental Use (9 Plants)	Routine Use (38 Plants)
1935	0	1
1961	0	1
1967	0	1
1968	0	2
1969	0	1
1970	1	4
1971	3	6
1972	1	7
1973	1	7
1974	1	5
1975	1	3
1976	0	1

treatment plants routinely using granular activated carbon beds have been installed since 1970.

A discussion of some of the early installations is of interest. In the fall of 1963 the management of the Nitro, West Virginia, water utility installed two beds of granular activated carbon to investigate treatment for removal of taste and odor. During the 3-month testing period the Threshold Odor Number (TON) of the raw water varied between 500 and 1000. During this same time period the TON of the influent water to the experimental granular activated carbon beds varied between 100 and 200, with one excursion to 400. These beds, with empty bed contact times (EBCT) of about eight minutes, were able to produce an odor-free water for as long as 26 days.[3] The success of these tests encouraged the water purveyor to convert the entire plant to granular activated carbon beds in 1965. Another interesting feature of this installation was the construction of an on-site 10,000 lb/day multiple-hearth reactivation furnace. From that time, until the plant was closed several years later, because the municipality obtained a different source of water, the granular activated carbon was reactivated approximately every six months.

The success of granular activated carbon beds for controlling taste and odor demonstrated at Nitro, West Virginia, has been duplicated at many other water utilities. For example, at Piqua, Ohio; Mt. Clemens, Michigan; Lawrence, Massachusetts[4]; and Davenport, Iowa, the water purveyors were having difficulty providing their consumers with an acceptable drinking water in spite of the use of large doses of powdered activated carbon. After conversion to granular activated carbon beds, these purveyors reported successful control of their taste and odor problems. Figure 1 shows that at Lawrence, Massachusetts, during a time period when the TON in the settled water was in the 6-10 range, the granular activated carbon beds controlled the effluent TON to acceptable levels for over a year.

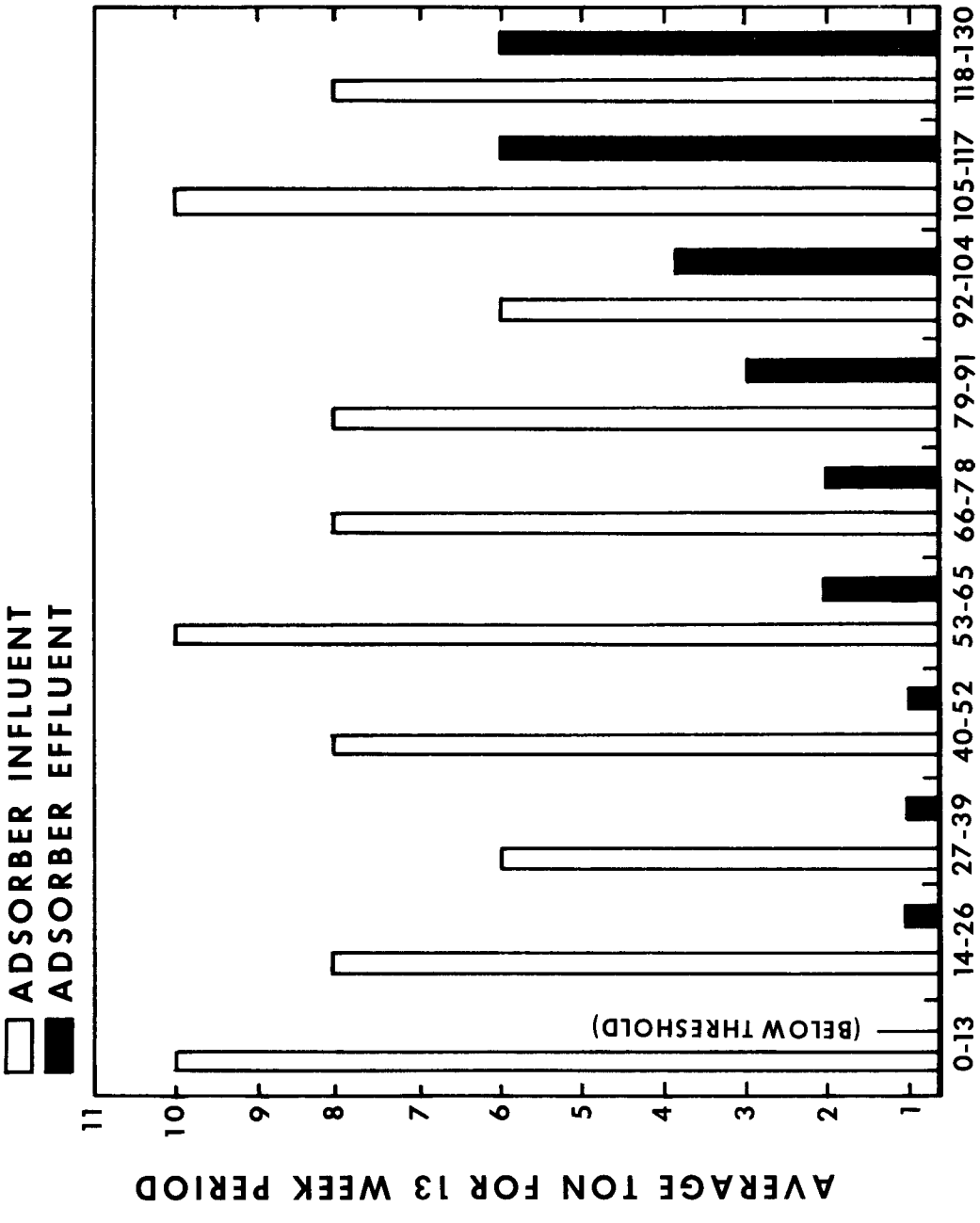

FIGURE 1 THRESHOLD ODOR NUMBER BREAKTHROUGH PATTERN FOR NEW ACTIVATED CARBON FILTER, LAWRENCE, MASS.

When conversion was first contemplated, the Massachusetts State Health Department insisted that some sand be left in the bottom of the filters to avoid any problems with particulate (turbidity) breakthrough. A six-month comparison of the turbidity in the effluent of a conventional sand filter and an all granular activated carbon system, see Figure 2, showed that their performance was equal. Note, pilot plant scale comparisons by the Water Supply Research Division Laboratory has confirmed this finding.[5] When the entire plant was converted to granular activated carbon, no sand was left in the filter boxes.

In the survey cited above[2] the water purveyors were asked how long their current charge of granular activated carbon had been in service and whether or not the beds were still effective for taste and odor removal. The shortest effective life reported was 23 months and some beds had been in service for four years and were still effective. Reports from the United Kingdom[6] substantiate these findings from United States practice.

Removal of Organic Compounds as Measured by General Organic Parameters

The previous sub-section detailed the performance of granular activated carbon beds for the removal of taste and odor causing compounds, but investigators have also been interested in the performance of the granular activated carbon adsorption process with respect to the removal of analytic parameters that would be reflective of the "total" organic content of water. As pointed out by Stevens and Symons,[7] no analytic test currently available measures the "total concentration of organic compounds" in water. Several tests have been proposed to approximate or be proportional to this parameter. A few of these are: 1) the organics-carbon adsorbable test producing a carbon chloroform extract (CCE), 2) chemical oxygen demand (COD), and 3) total organic carbon (TOC).

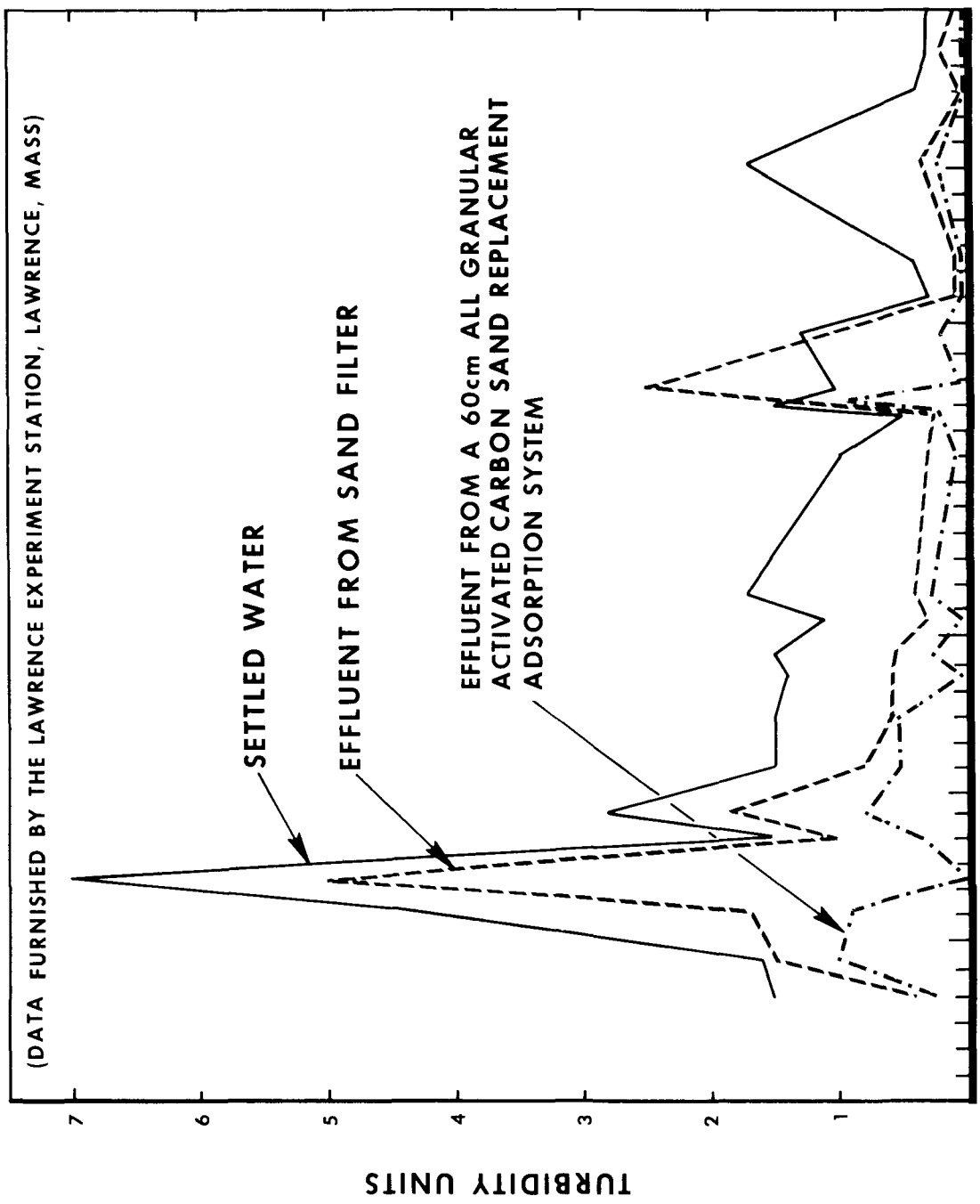

FIGURE 2. COMPARISON OF SAND vs. GRANULAR ACTIVATED CARBON FOR TURBIDITY REMOVAL

These tests have been used to monitor various operating granular activated carbon adsorption beds.

In 1965, Dostal, Pierson, Hager and Robeck[3] reported that the percent removal of chemical oxygen demand declined from 72 percent at the start of the test to 56 percent after 31 days at the Nitro, West Virginia water treatment plant, mentioned previously, while 97.5 percent of the odor was still being removed after 31 days. More recently, monitoring of operating granular activated carbon beds has been carried out at five field locations: Nitro, West Virginia; Piqua, Ohio; Mt. Clemens, Michigan; Lawrence, Massachusetts; and Davenport, Iowa. This monitoring began in September 1968 and spanned several years. Because analytic capabilities have changed and improved gradually, the same monitoring techniques were not used at all of these installations. In general, however, the purpose of the monitoring was to compare the time of breakthrough (first detectable increase) of organic compounds as measured by a general organic parameter with the time of odor breakthrough.

In every case, the breakthrough of odor occurred much later than the breakthrough of the parameter measuring the removal of general organic compounds. Except for the Nitro, West Virginia situation, the control of odor was successful for years, whereas control of organic compounds as measured by a general organic parameter was successful only for weeks. The following are some typical data: Nitro, West Virginia, CCE-hf* removal** lasted 5 weeks; Piqua, Ohio, CCE-lf removal lasted 10 weeks; Mt. Clemens, Michigan, CCE-m removal lasted less than 28 weeks; Lawrence, Massachusetts, CCE-m removal lasted 16 weeks, and Davenport, Iowa, CCE-m removal lasted 6 weeks. Figure 3 from Lawrence, Massachuetts, is a typical data plot of the breakthrough curve for a general organic parameter.

*The lower case letters refer to the method of operation of the activated carbon adsorption collection and the chloroform extraction system and are defined in Reference 8.
**Effluent concentration approximates influent concentration.

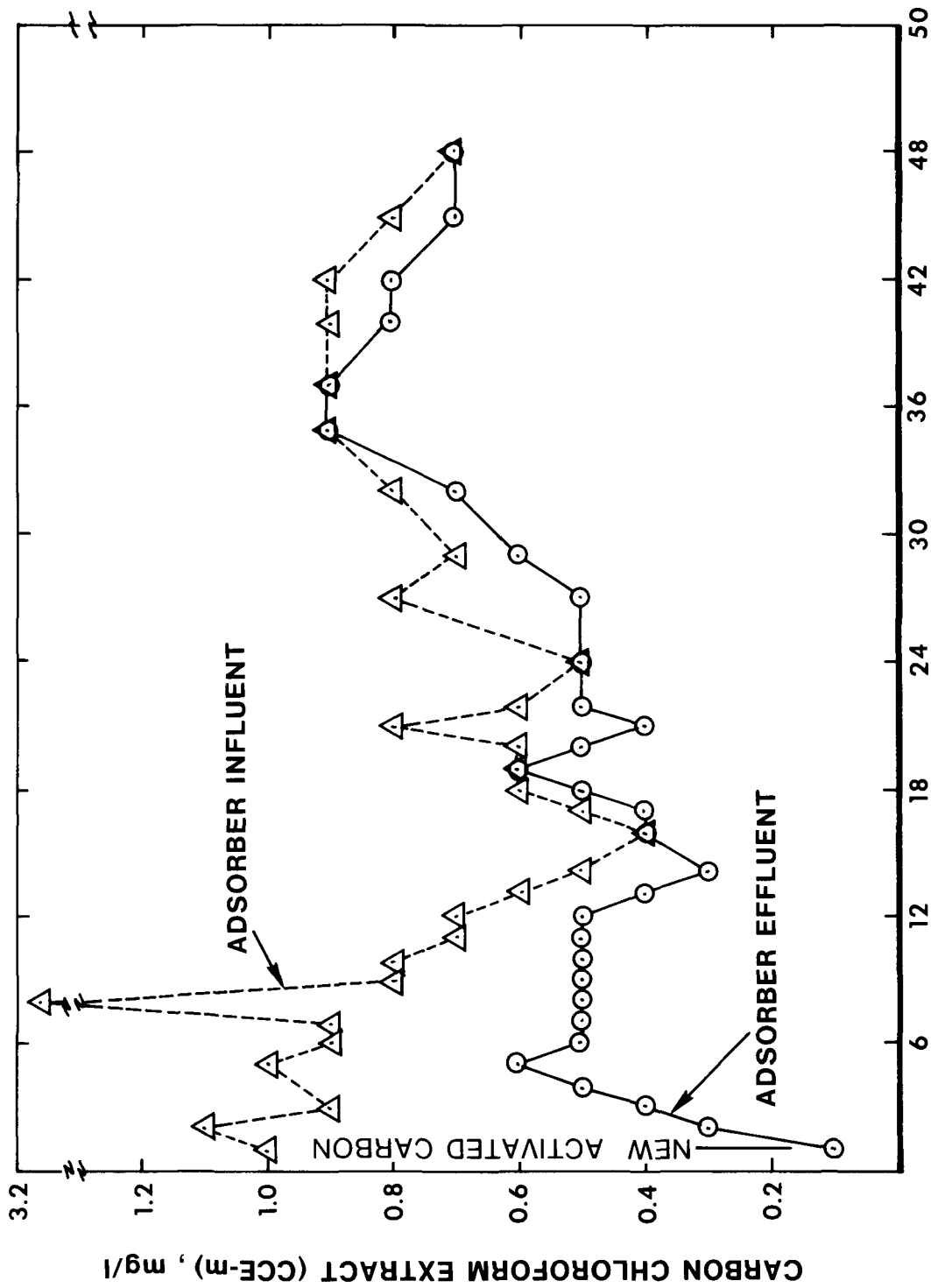

FIGURE 3. CCE-m REMOVAL AT LAWRENCE, MASS. BY SAND REPLACEMENT TYPE GRANULAR ACTIVATED CARBON ADSORPTION UNIT

Figure 4 from Ford[6] * indicates that experiences in the United Kingdom are similar to those in the United States. The experience in Germany is similar to that in the United Kingdom as shown by Heymann[9]* of Duisburg who investigated the breakthrough pattern of the parameter dissolved organic carbon (DOC) through a granular activated carbon bed with sampling points at various depths. Figure 5 shows that the maximum depth, corresponding to an empty bed contact time of 4 minutes, showed some increase in DOC after about 4 to 5 days. These reports lead to the generalized conclusion that if controlling the general organic content of drinking water is desirable, the useful life of a given charge of granular activated carbon in an adsorption bed will be much shorter than might be anticipated from performance based on taste and odor compound control.

Removal of Specific Organic Compounds

Early demonstrations of granular activated carbon's ability to remove specific organic compounds from water came from its use as an analytic procedure in which organics were adsorbed on granular activated carbon and desorbed (extracted) with a solvent, chloroform or ethyl alcohol. Analysis of these extracts revealed what organic compounds that were in the original sample were able to be adsorbed onto granular activated carbon under prescribed conditions, and then be desorbed with a solvent. For example, in 1956, Middleton and Rosen[10] found the following organic compounds or classes of compounds in a carbon chloroform extract (CCE) from a surface water:

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*Note, the entire document "Activated Carbon in Water Treatment," a Water Research Association conference held at the University of Reading, April 3-5, 1973 and available from the Water Research Centre, P.O. Box 16, Henley Rd., Medmenham, U.K., SL7 2HD, is an outstanding volume well worth reviewing. A second document "Translation of Reports on Special Problems of Water Technology - Volume 9 - Adsorption" a conference held in Karlsruhe, Federal Republic of Germany, 1975, EPA-600/9-76-030, December 1976 is an excellent companion document to the one just previously cited and summarizes the experiences of water purveyors in continental Western Europe with activated carbon.

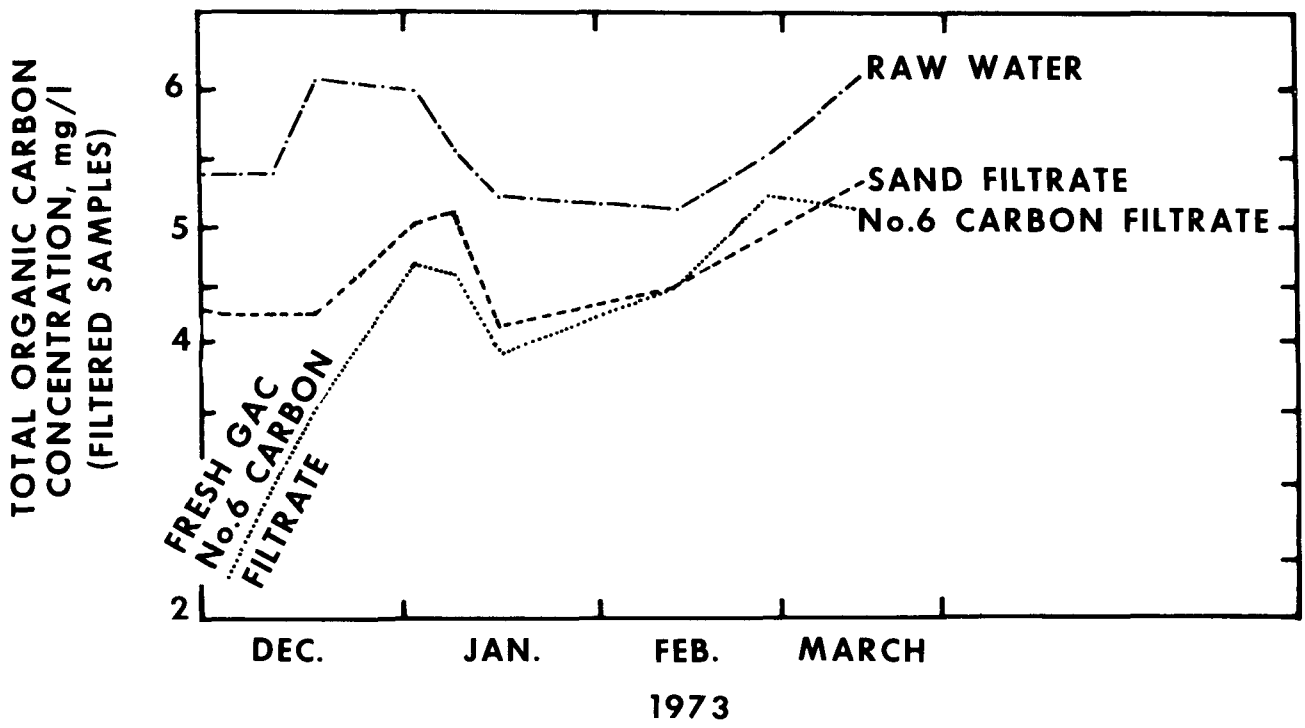

FIGURE 4. REMOVAL OF DISSOLVED ORGANIC CARBON BY GRANULAR ACTIVATED CARBON

CARBON RENEWED IN No.6 FILTER 29-11-72
REFERENCE 6

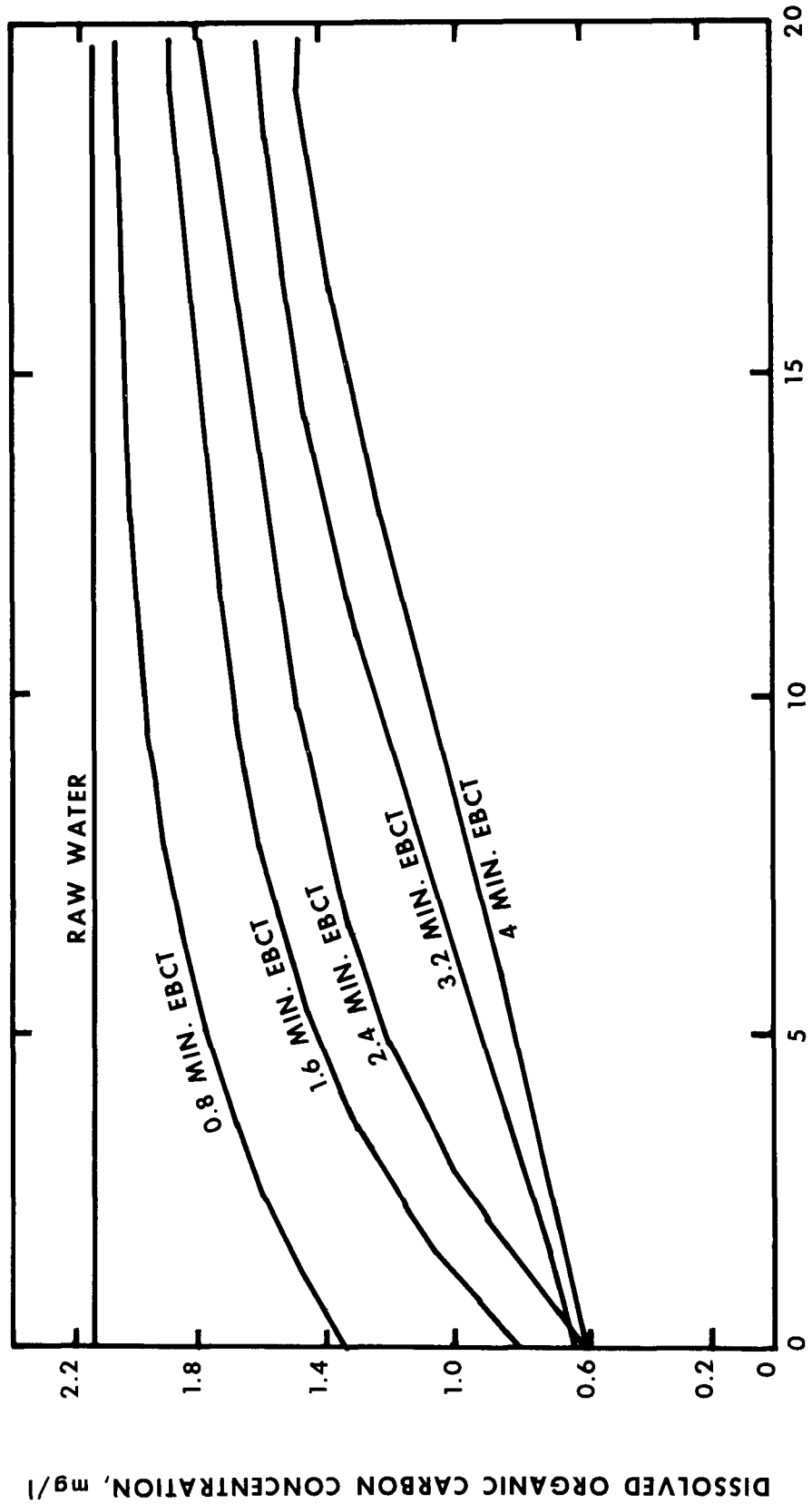

FIGURE 5. BREAKTHROUGH OF DOC
GRANULAR ACTIVATED CARBON BEDS
DUISBURG, FED. REP. OF GERMANY
REFERENCE 7

Substituted benzene compounds
Polycyclic hydrocarbons
Acrylonitrile
Aldehydes
Organic acids
DDT
Kerosene
Phenyl ether
Alcohols
Ketones
Esters

In the same year, Rosen, Middleton and Taylor[11] isolated alkyl benzene sulfonate from a carbon-alcohol (ethyl) extract (CAE). In 1963 Rosen, Skeel and Ettinger[12] isolated the following organic compounds from a river water CCE.

Naphthalene
Styrene
Ethyl benzene
2-Ethylhexanol
Di-isobutyl carbinol
2-Methyl-5-ethylpyridine
Tetralin
Acetophenone
Bis- (2-chloroisopropyl) ether
Bis- (2-chloroethyl) ether
Phenyl methyl carbinol

In 1970, Rosen, Mashni and Safferman[13] reported on finding both geosmin and 2-methyl-isoborneol in a CCE from an Ohio Lake. In 1972 a report was published[14] concerning studies on organic contamination of drinking water conducted in the lower Mississippi River area. Organic compounds were collected on granular activated carbon and desorbed by both heat and solvents. One sample contained the following compounds:

acetylene dichloride
benzene
carbon tetrachloride
chloroform
1,2-dichloroethane
dimethyl sulfoxide
ethyl benzene
methyl chloride
propyl benzene
toluene
vinyl benzene

A second series of samples contained the following organic materials:

acetone

acetophenone

benzene

bromobenzene

bromochlorobenzene

bromoform

bromophenyl phenyl ether (positional isomer?)

butyl benzene

a-camphanone

chlorobenzene

chloroethyl ether

chloromethyl ether*

chloroform

chloronitrobenzene

chloropyridine

dibromobenzene

dichlorobenzene (positional isomer?)

1,2-dichloroethane

dichloroethyl ether

dimethoxy benzene

2,6-dinitrotoluene

endo-2-camphanol

ethyl benzene

exo-2-camphanol

hexachlorobenzene

1-isobromobenyl-4-isopropyl benzene (1,2 isomer)

isocyanic acid

methyl biphenyl

methyl chloride

nitrobenzene

o-methoxyphenol

p-menth-en-1-8-ol

tetrachloroethylene

toluene

1,1,2-trichloroethane

vinyl benzene

---

*The identity of this compound is very questionable.

Also in 1972 Kleopfer and Fairless[15] found the following compounds in CCE's from drinking water taken from the Ohio River at Evansville, Indiana, using gas chromatographic - mass spectrometric techniques.

Bromodichloromethane
Dibromochloromethane
Bromoform
Ethylbenzene
Styrene
Hexachloroethane
Chlorohydroxybenzophenone
Toluene
Tetrachloroethylene
Xylene
Bis-(2-chloroisopropyl) ether
Bis-(2-chloroethyl) ether
Hexachlorobenzene

Finally, Symons and Stevens[7] reported on organic compound identification from an ethyl alcohol extract of granular activated carbon (CAE) that included the following:

Trichlorobiphenyl
Tetrachlorobiphenyl
Pentachlorobiphenyl
Hexadecane
Octadecane
Eicosane
Docosane
Diethylphthalate**
Di (2-ethylhexyl) phthalate**
Methyl Ester of Benzoic Acid*
Methyl Ester of Benzene Sulfonic Acid
Methyl Ester of Palmitic Acid*
Methyl Ester of Stearic Acid*
Methyl Ester of Lignoceric Acid*

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* - Probably esterified during extraction.
** - Plasticizers

These reports show some of the types of organic compounds that can be adsorbed from water by granular activated carbon as evaluated by this technique.

Below are typical references reporting on the removal of specific organic compounds in conjunction with other organics by granular activated carbon beds in use at operating water treatment plants. In 1965, Robeck, Dostal, Cohen and Kreissl[16] demonstrated that coal-base granular activated carbon, partially exhausted for CCE-hf removal, could reduce the concentration of endrin, dieldrin, lindane, 2,4,5-T ester, DDT, and parathion dosed into river water. In the same year, Dostal, Pierson, Hager and Robeck[3] showed that the seven compounds listed below that were present in the Kanawha River water after aeration could be reduced to below detectable concentrations by fresh (2-day old) granular activated carbon beds. These compounds were bis-(2-chloroethyl) ether, 2-ethylhexanol, bis-(2-chloroisopropyl) ether, a-methylbenzyl alcohol, acetophenone, isophorone and tetralin.

Forty days later, however, all of these compounds with the exception of acetophenone were detected at a bed depth equal to an empty bed contact time of about 8 minutes. Providing an additional 2 minutes of empty bed contact time did remove these seven compounds at this time (40 days), although another organic compound, ethyl benzene, was detected at a bed depth equal to 15 minutes of empty bed contact time.

Stieglitz, et al.[17] reported on removals by 2 month-old granular activated carbon beds of 61 organic compounds amenable to analyses by the Grob closed loop stripping and gas chromatographic procedures[18]. The granular activated carbon appeared to have lost its effectiveness for adsorbing compounds eluting from the chromatograph early, such as chloroform and trichloroethylene, but was still quite effective for later eluting chlorinated aromatics. Some questions remain as to documentation of analytical recovery efficiencies and the operation of the adsorption beds, however. The authors claim that some higher concentrations of

a few aliphatic and aromatic hydrocarbons in the adsorber effluent can be explained by chromatographic or biological effects on the adsorber. Dissolved organic chlorine (DOCl) was still being reduced from 85 to 2 µg/ℓ through the adsorber at this time. The sum, as organic chlorine, of the concentration of chloroform, carbon tetrachloride, trichloroethylene, and tetrachloroethylene in the treated water accounted for all the DOCl. To summarize, after two months of operation, all of the typical low molecular weight chlorinated compounds were breaking through the bed although DOCl was significantly removed from a chlorinated influent.

In 1965 Kolle, Sontheimer, and Stieglitz[19] reported on studies of pilot granular activated carbon adsorbers receiving ozonated pre-filtered Rhine River water. Two or three adsorbers in series were used, each one meter in depth. Each meter of depth represented four minutes of empty bed contact time. After six months of operation, granular activated carbon samples were taken from the top of each section and from the bottom of the last section. These activated carbon samples were extracted with dioxane and the extracts analyzed for specific organics. The following organics were found in various concentrations: chloroform, 1,2-dichloroethane, 1,2-dichloropropane, tetrachloroethylene, trichloroethylene, bis-(2-chloroisopropyl) ether, o-dichlorobenzene, hexachlorobutadiene, hexachlorocyclohexane, and tris-(2-chloroethyl)-phosphate.

According to the authors, the substances identified in these extracts can be classified into three groups, the aromatic chlorohydrocarbons, (o-dichlorobenzene) that were completely adsorbed by the uppermost layer of the adsorber, the aliphatic chlorohydrocarbons (hexachlorobutadiene and hexachlorocyclohexane) that were much less strongly adsorbed, but still are adsorbed well enough so that the lowest filter layers do not contain these substances, and the oxygen-containing organic

chlorine compounds, bis-(2-chloroisopropyl) ether and tris-(2-chloroethyl) phosphate, that were breaking through the activated carbon beds and were identified in the bottom layer of the filter.

In addition to the above information, chloroform, 1,2-dichloroethane, and 1,2-dichloropropane were present at various levels throughout the adsorbers, although tri- and tetrachloroethylene were confined to the upper and middle layers of the three-layered adsorber. The presence of these first three compounds throughout the depth of the adsorber would tend to weaken the authors' gross classification of the adsorption of aliphatic hydrocarbons (see above).

In 1977 Suffet, et al.[20] reported on the performance of granular activated carbon and some adsorbent resins for the removal of trace organics from Philadelphia drinking water. Suffet used computer-reconstructed gas chromatographic profiles plus mass spectrometric identifications to assess the ability of the adsorbents to remove twenty-seven identified organic compounds. For the activated carbon column (Calgon F-400*, 9.7 minute empty bed contact time) in one experiment, the adsorbent was shown to be quite effective for removal of most of the compounds identified although exhaustion was noted for the organic compounds with lower boiling points by the 18th week of the run. Gas chromatographic profile analysis of the F-400 column effluent indicates chloroform and trichloroacetone first broke through after 3 weeks and dibromochloromethane and tetrachloroethane first broke through after 4 weeks.

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* Mention of commercial products does not imply endorsement by the U.S. Environmental Protection Agency.

In a second experiment, breakthrough patterns were presented for 1,2,7,9 and 15 weeks of the run plus the respective organic profiles for the influent water. Twenty-nine compounds were identified from the gas chromatographic profiles for this experiment. Empty bed contact time in this experiment was 7.3 - 7.5 minutes. Again, detection in the effluent of organic species with lower boiling points occurred sooner than organic compounds with higher boiling points. Suffet[20] cautions the reader, however, that the data are largely qualitative and interpretation of results is complicated by the highly variable nature of the organic content of the influent to the adsorbent column.

In 1977 McCarty, et al.[21] reported on the performance of "Water Factory 21" for removal of organic materials. Water Factory 21 is an advanced waste treatment facility designed to reclaim wastewater to provide injection water needed for a sea water barrier system to protect ground waters in Orange County, California. Part of the treatment train includes packed-bed, upflow pressure adsorbers filled with Calgon Filtrasorb 300. The empty bed contact time is 30 minutes.

During a period when the plant was operating on a continuous basis, single activated carbon adsorber influent and effluent samples were taken and subjected to a rather rigorous organic analysis by closed loop stripping.[18] Relative influent and effluent concentrations were reported for sixteen compounds and absolute concentrations for twelve of these. The general trend was toward removal of these compounds to widely varying degrees. An examination of the gas chromatograms verifies this trend for a large number of unidentified compounds (see section on "Unidentified Compounds" , page A52, for results of a similar comparison). The meaning of the results presented by McCarty, et al., however, are difficult to interpret in the context of predicting activated carbon adsorber life for removal of the specific compounds identified, because few data are presented on

the condition of the activated carbon itself (time in-place, reactivation frequency, and so forth). Measurement of influent/effluent organic concentration profiles vs. time is part of the planned future Water Factory 21 work, however.

Most of the information on reducing various concentrations of trace organics has been gathered through laboratory studies and pilot-scale experiments. The National Interim Primary Drinking Water Regulations[22] established maximum contaminant levels for six organic chemicals: endrin, lindane, methoxychlor, toxaphene, 2,4-D and 2,4,5-TP (Silvex). These six specific organic contaminants can be grouped under the general term "pesticides." The "Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations"[23] reported that adsorption on granular activated carbon is the most effective treatment process for reducing the concentrations of these contaminants.

The U.S. EPA library in Cincinnati made a computer search of the literature on the subject of adsorption of organic contaminants on granular activated carbon. Listed below in Table II are 50 organic compounds in addition to those reported in the text that have been reported to be reduced in concentration through granular activated carbon treatment. Only those studies where the concentration of the specific organics before treatment were below the one mg/ℓ level were included, thus eliminating studies on industrial wastes where the concentrations are usually much higher. Even these concentrations are higher than usually found in source waters, making direct extrapolation or prediction of adsorption behavior speculative when low concentrations are present. These data are based on both isotherm and column type studies.

TABLE II

ADDITIONAL ORGANIC COMPOUNDS THAT HAVE BEEN REPORTED IN THE LITERATURE TO BE ADSORBABLE ON GRANULAR ACTIVATED CARBON

acetophenone[29]
aldrin[39,43,49]
baygon[36]
a-BHC[43,49,50,54]
benzocaine[32]
benzoic acid[29]
butyric acid[29]
dibrom[32]
dieldrin[25,39,43,49]
di (n-butyl) phthalate[48]
di (2-ethylhexyl) phthalate[48]
diuon[50]
diquat[30,51]
dimenthoate[49,50]
m-dinitrobenzene[38]
DDT[27,39,43,46,49]
endosulfan[49,52]
endrin[50,53]
gasoline[26]
heptachlor[49]
heptachlor epoxide[49]
hexachlorobenzene[49]
juglone[32]
lindane[27,31,49,50]
linuron[49]
MS-222[32]
malathion[43,49]
methyoxychlor[49,95]
nitrobenzene[38]
oil (fuel)[26,35,37,45]
paraquat[30,51,52]
parathion[50]
phenylacetic acid[29]
phenols[33,34,40,42,45]
p-nitrophenol[42]
propionic acid[29]
pyridine[29]
PCB[39,41,49]
rotenone[24,32]
sevin[36]
simazine[28,31,50]
strychnine[53]
3-trifluoromethyl-4-nitrophenol (TFM)[32]
2,4-D[44,50]
2,4-dinitrophenol[44]
2,4,5-T (ester)[43,50]
toxaphene[24,50]
tetrachlorobenzene[49]
telodrin[49]
triazine[28]

A report by Giusti, et al.[55] includes a list of 12 alcohols, 8 aldehydes, 11 amines, 4 pyridines (and morpholines), 8 aromatics (benzene derivatives), 11 esters, 3 ethers, 14 glycols and glycol ethers, 2 halogenated hydrocarbon solvents, 10 ketones, 8 acids, and 2 oxides that were studied. Single dose studies (isotherms not determined) were carried out on each of the compounds with 100 ml of a 1000 mg/ℓ solution being dosed with 0.5 g of activated carbon (equivalent dose 5000 mg/ℓ). Concentrations of solute dosed were less where solubilities so dictated. These data were used to draw conclusions and test hypotheses about effects of pH, polarity, functional groups, molecular weight, and other differences in physical and chemical characteristics, in-so-far as amenability to adsorption is concerned. These data might relate to relative adsorbability of the respective compounds at these very high concentrations, but do not evaluate competitive effects of mixtures or the relative effects of 5 to 6 order of magnitude lower concentrations of organic matter and adsorbent that are experienced in the drinking water treatment situation.

Isotherm tests were run for only 5 compounds at varying pH and although linear, the isotherms were determined only at high concentrations. Parallel column studies and multi-solute isotherm studies were conducted on these compounds and the authors claim a fairly high level of predictability of the column capacities from the isotherm data. Whether this translates well to lower concentrations (where isotherms may become non-linear) or to real systems where the solute species number in the hundreds, cannot be determined from these studies.

In summary, although the individual literature citations are often vague on critical details of the study, and data have been collected under a variety of circumstances, many atypical, in total they do demonstrate that granular activated carbon is correctly described as a "broad-spectrum" adsorbent.

Reactivation of Granular Activated Carbon

Although the internal pore structure providing a large surface area per unit weight is developed during initial manufacture (thermal activation) of granular activated carbon, the surface area is finite and eventually becomes covered with adsorbate, and adsorption ceases. To continue with effective adsorption the granular activated carbon is processed to remove these adsorbed materials (reactivation). The most common technique for processing granular activated carbon to renew the adsorption capacity of its surfaces is to drive off and oxidize the adsorbed organic compounds in environment containing steam and little oxygen at high temperature (approaching 1000°C). The problem is to design a facility and choose reactivation conditions, such that the maximum amount of adsorbed materials is removed with a minimum of change in the properties of the granular activated carbon.

The four basic types of furnaces currently (Fall 1977) in use for the reactivation of granular activated carbon are: the multiple-hearth, the rotary-kiln, the infra-red-tunnel, and the fluidized-bed furnace. Of the five currently operating on-site reactivation facilities in Europe, two are multiple-hearth furnaces and three are various designs of the fluidized bed furnace. Figure 6 is a schematic diagram of a multiple-hearth furnace, Figure 7 is a cross-section of a one-bed fluidized bed furnace, Figure 8 is a diagram of the infra-red-tunnel furnace, and Figure 9 shows a rotary-kiln furnace. The Water Supply Research Division currently has underway three projects for the evaluation of reactivation factilites.

Proper design and operation of a thermal reactivation facility is necessary to avoid any unwanted change in the properties of granular activated carbon. For example, Juhola[56] reported a change in pore size distribution upon several cycles of reactivation as shown in Table III.

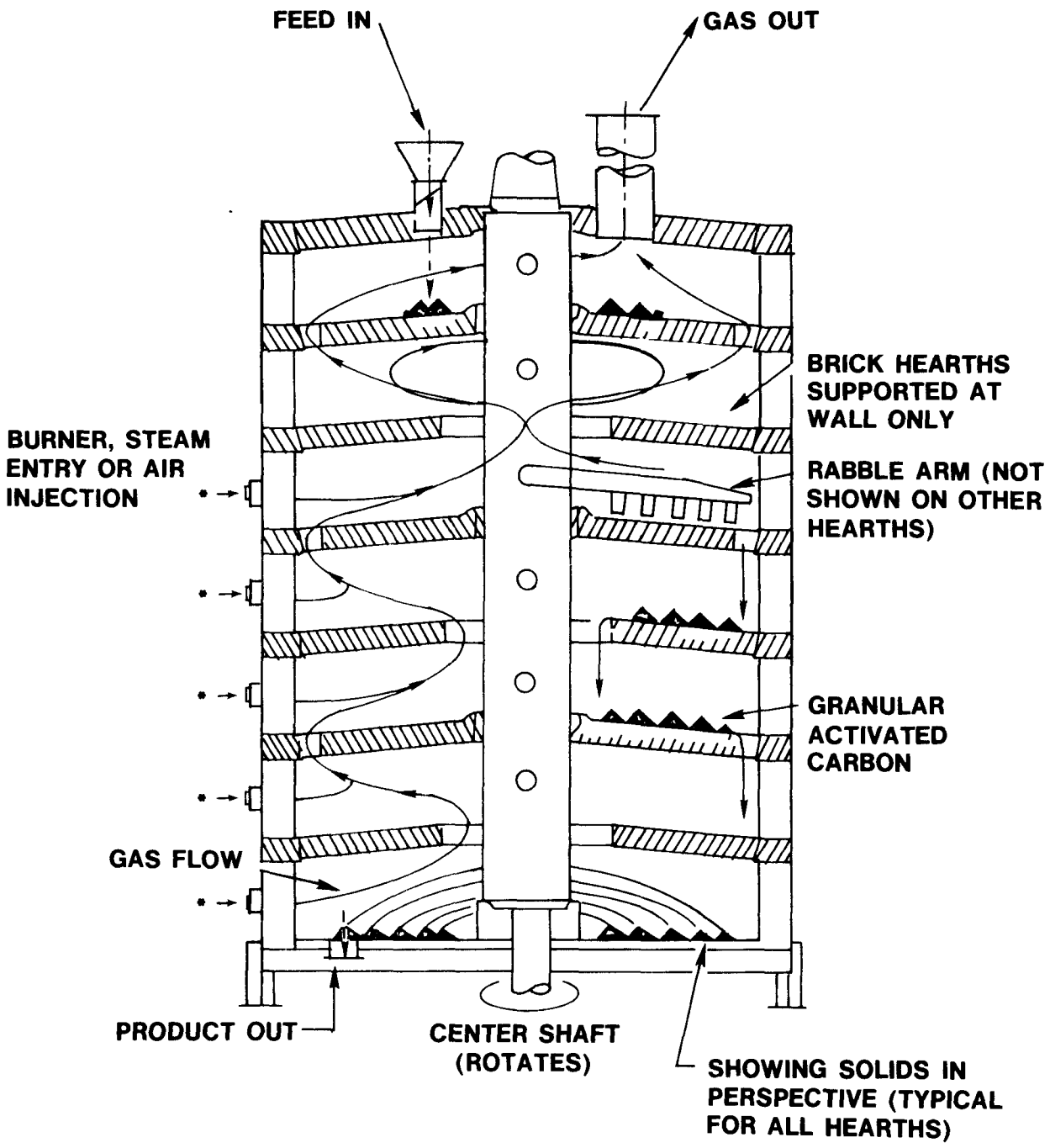

FIGURE 6 CROSS SECTION MULTIHEARTH FURNACE

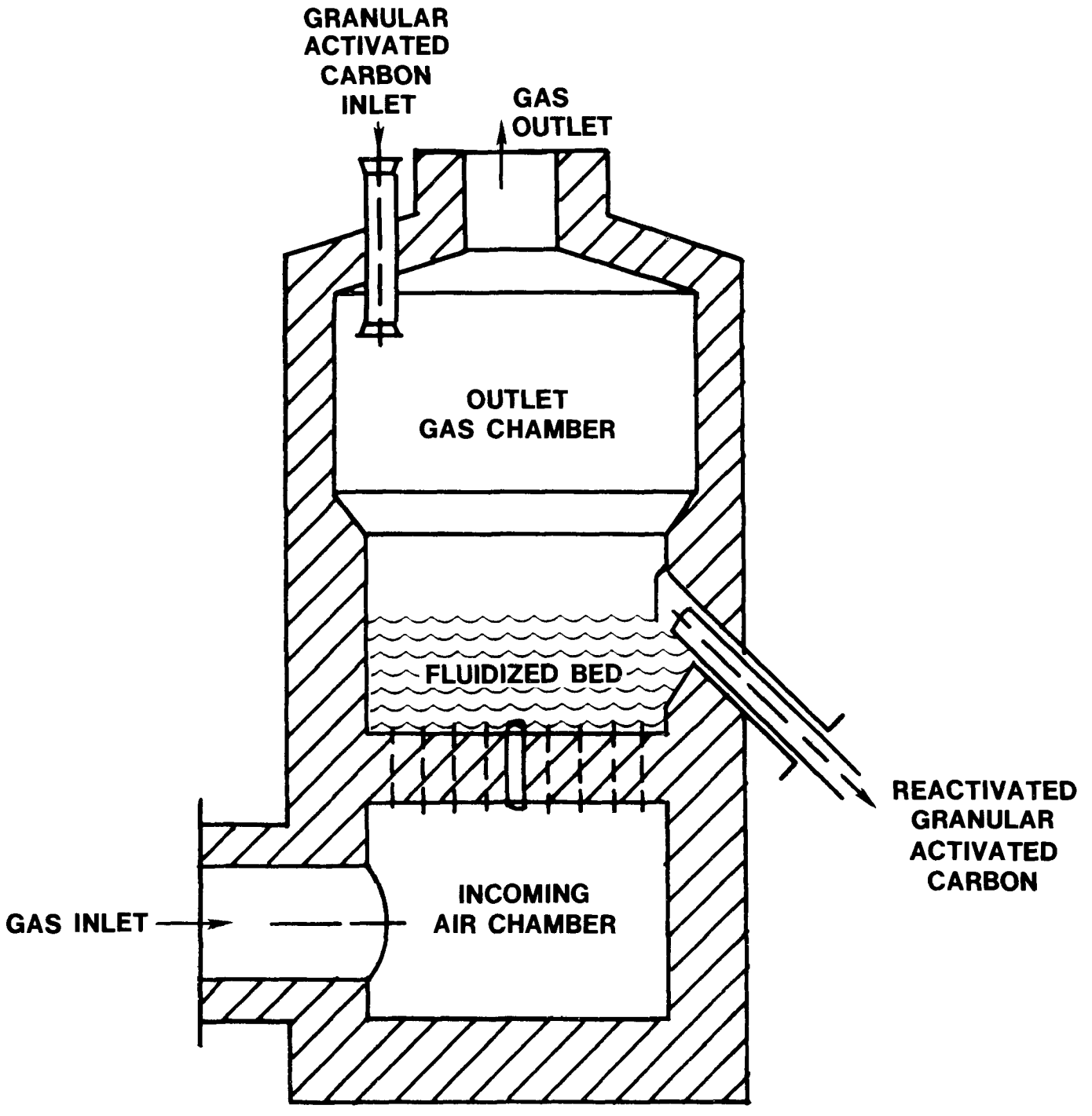

FIGURE 7 CROSS SECTION OF FLUIDIZED BED FURNACE

NOTE: THIS DIAGRAM DEPICTS A ONE-BED FURNACE AS AN EXAMPLE. OTHER DESIGNS OF FLUIDIZED BED FURNACES ARE COMMERCIALLY AVAILABLE.

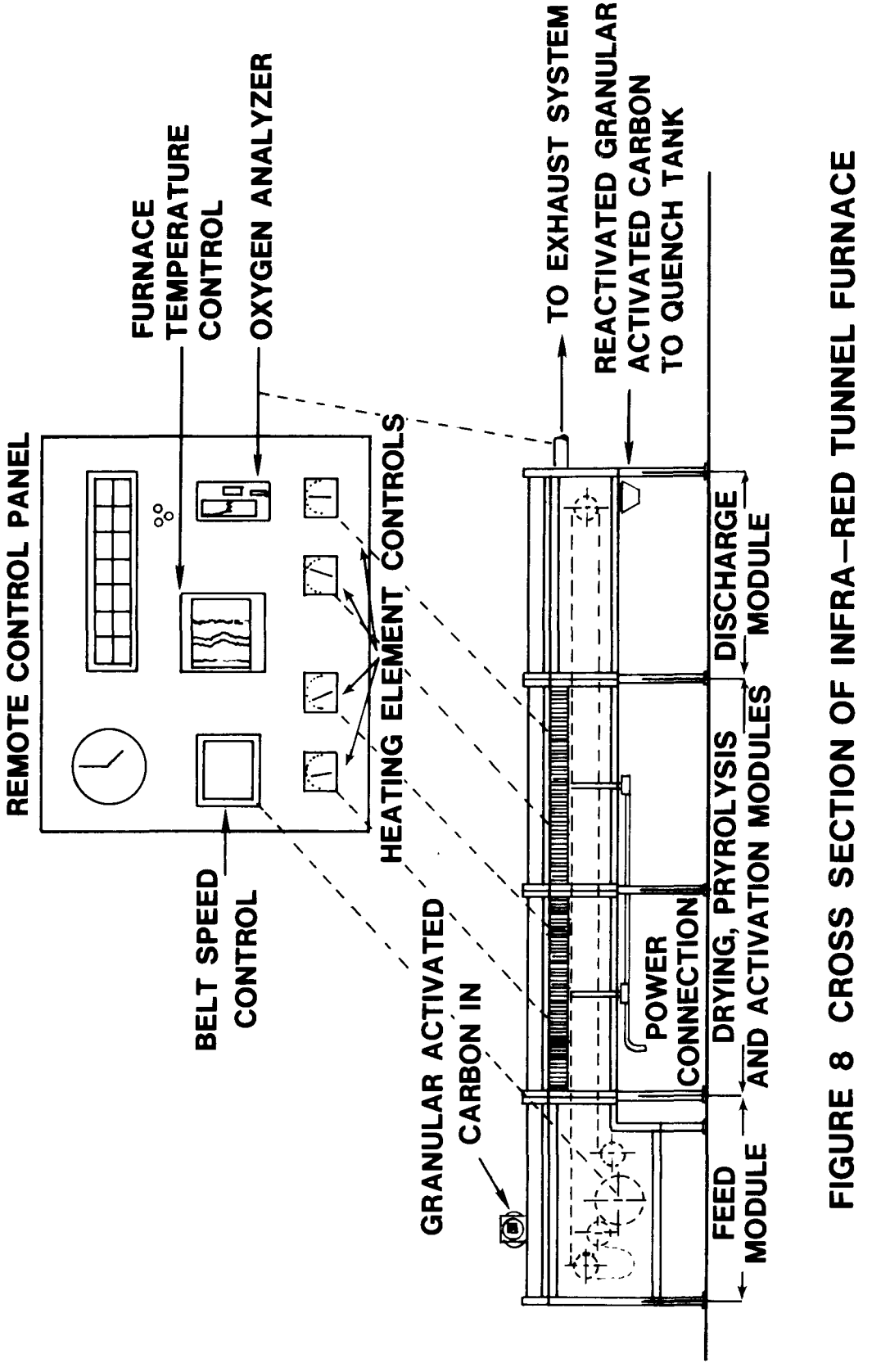

FIGURE 8 CROSS SECTION OF INFRA-RED TUNNEL FURNACE

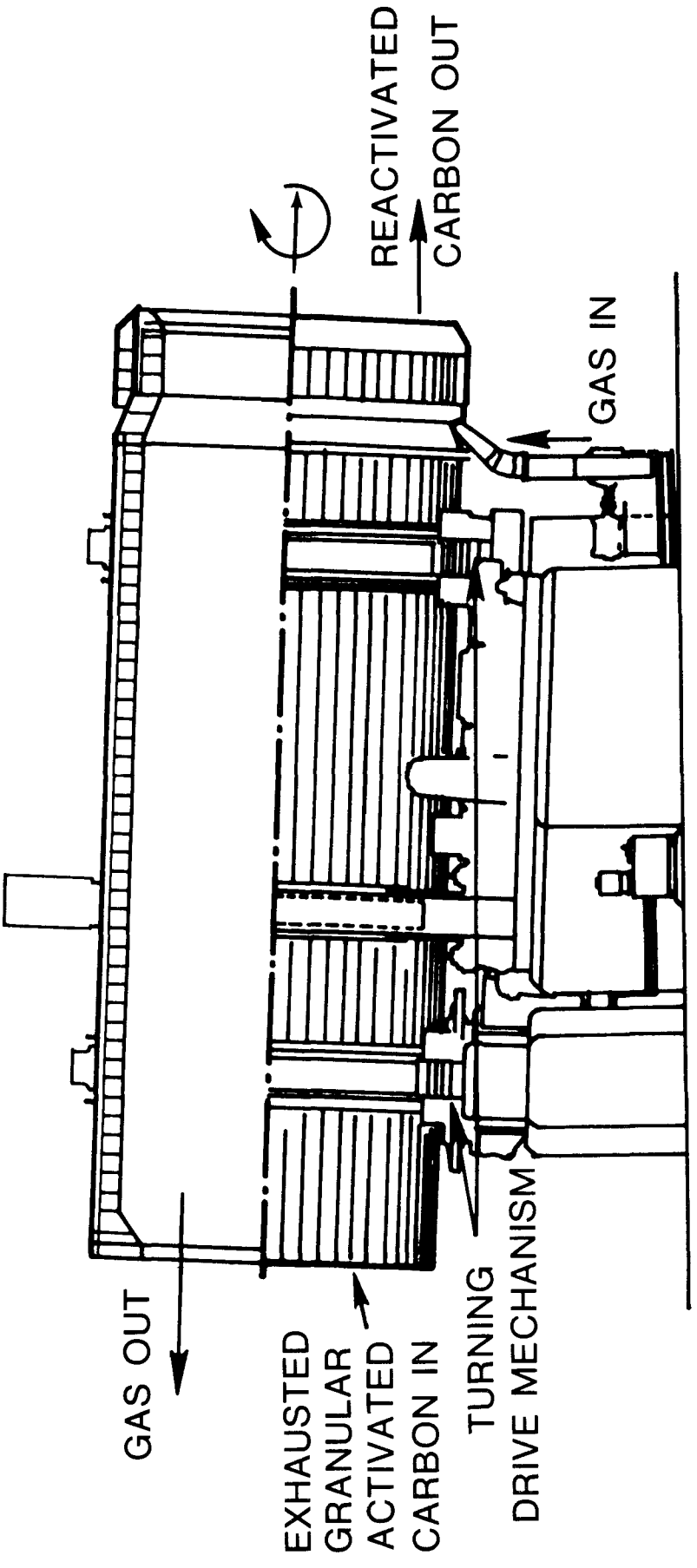

FIGURE 9. CROSS SECTION OF ROTARY KILN FURNACE

TABLE III

CHANGES IN GRANULAR ACTIVATED CARBON PROPERTIES ON SUCCESSIVE REACTIONS

Cycle	Ash Content - %	Iodine Number* Measure of Pores Between 1 nm and 2.5 nm	Molasses Number* Measure of Pores Greater than 2.8 nm	Bulk Density
Initial	5.7	1090	250	0.469
1	7.6	1040	310	0.468
2	8.6	935	290	0.469
3	9.5	940	350	0.473

*These numbers are based on the adsorption of the respective material under a standard set of conditions.

This change in pore structure was then reflected in a decrease in performance as measured by a decrease in initial percent chemical oxygen demand reduction from 55 percent to 40 percent over eight reactivation cycles.

Smith[57] agreed pointing out that based on Figure 10, practically no change occurred in pore size distribution in the 1 to 1.9 nm diameter range, although a marked change occurred in the pores between 1.9 and 2.5 nm in diameter. He also noted that from 2.5 nm diameter and above, again, very little change occurred in the pore structure. Finally, DeJohn and Hutchins[58] also reported that the effect of thermal reactivation may be to reduce the surface area in the micropores of granular activated carbon. They further state that the properties of granular activated carbon derived from lignite are not changed as much as the properties of granular activated carbon derived from another source, bituminous-coal. Their data showed a decline in specific surface area of bituminous-coal based activated carbon from 1100 m^2/gm for virgin material to 700 m^2/gm (36 percent) after four reactivations, although lignite-based activated carbon only declined from 650 m^2/gm for virgin material (initially lower) to 500 m^2/gm (23 percent) after five reactivations.

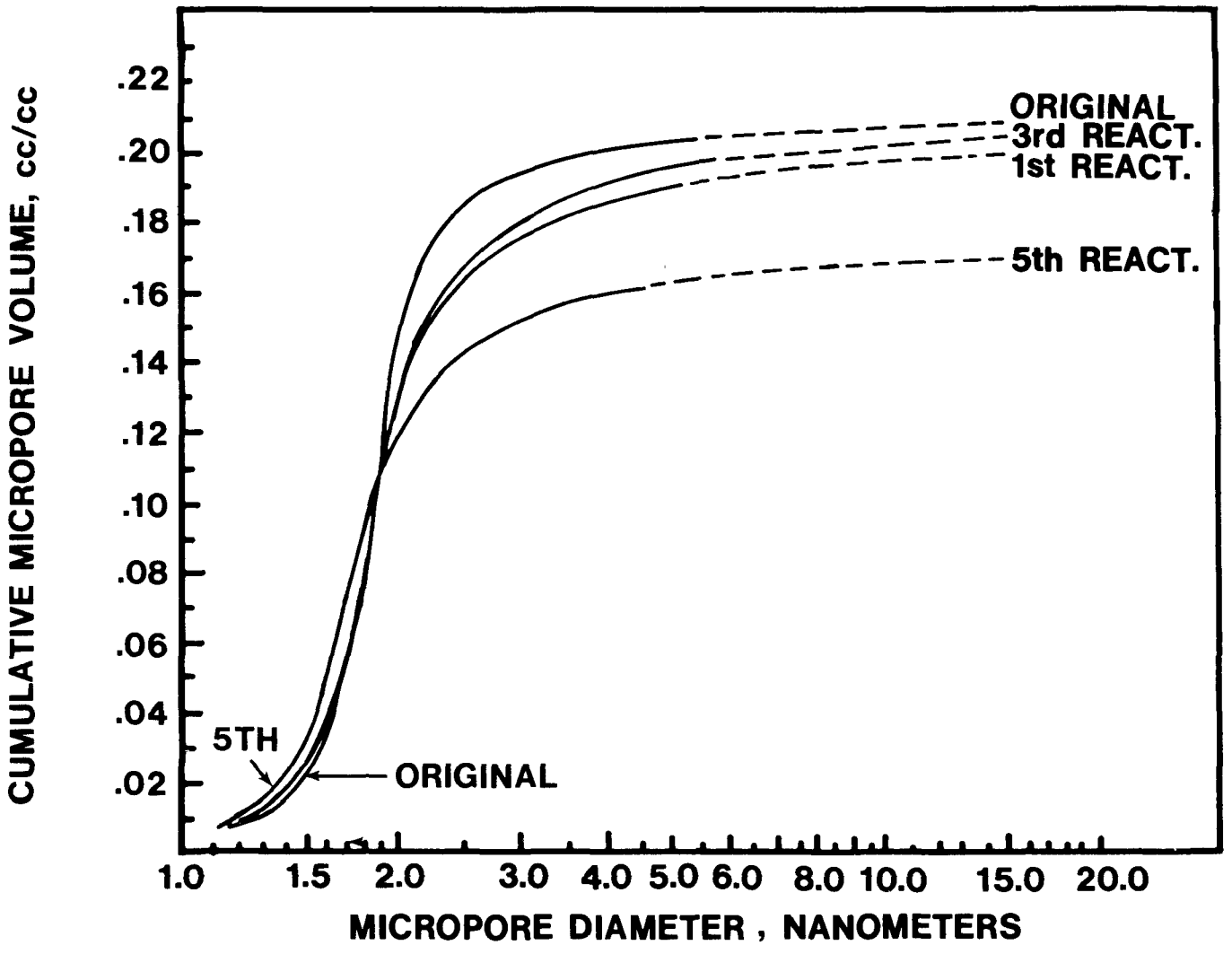

FIGURE 10. CUMULATIVE MICROPORE VOLUMES AS A FUNCTION OF MICROPORE DIAMETER REFERENCE 57

In contrast to these reports, Juntgen[59] noted that, based on Figure 11, an appropriate time-temperature relationship (800°C - 20 min.) during reactivation can be developed that will not alter activated carbon significantly from its virgin state. In support of this, Weissenhorn[60] collected data on the decline of granular activated carbon performance as measured by ultraviolet absorbance of the effluent with relation to the volume of water treated per unit volume of granular activated carbon and showed, according to Figure 12, that virgin activated and reactivated carbon were nearly equivalent. Finally, the Shirco Company of Dallas, Texas, claims to have collected data as shown in Figure 13 and Table IV. (unpublished promotional literature).

TABLE IV
TYPICAL RESULTS OF CARBON REACTIVATION IN THE SHIRCO ELECTRIC INFRARED FURNACE

Activated Carbon	Apparent Density (g/cc)	Iodine Number	Molasses Number
ICI HYDRODARCO 3000			
Virgin	0.352	550	333
Spent	0.458	413	302
Reactivated	0.397	596	380
CALGON FILTRASORB 400			
Virgin	0.48	1167	355
Spent	0.62	480	250
Reactivated	0.48	1122	376
WESTVACO NUCHAR WV-L			
Virgin	0.594	834	371
Spent	0.678	588	178
Reactivated	0.593	868	380
CARBORUNDUM			
Virgin	0.525	950	220
Spent	0.667	320	137
Reactivated	0.523	1132	230

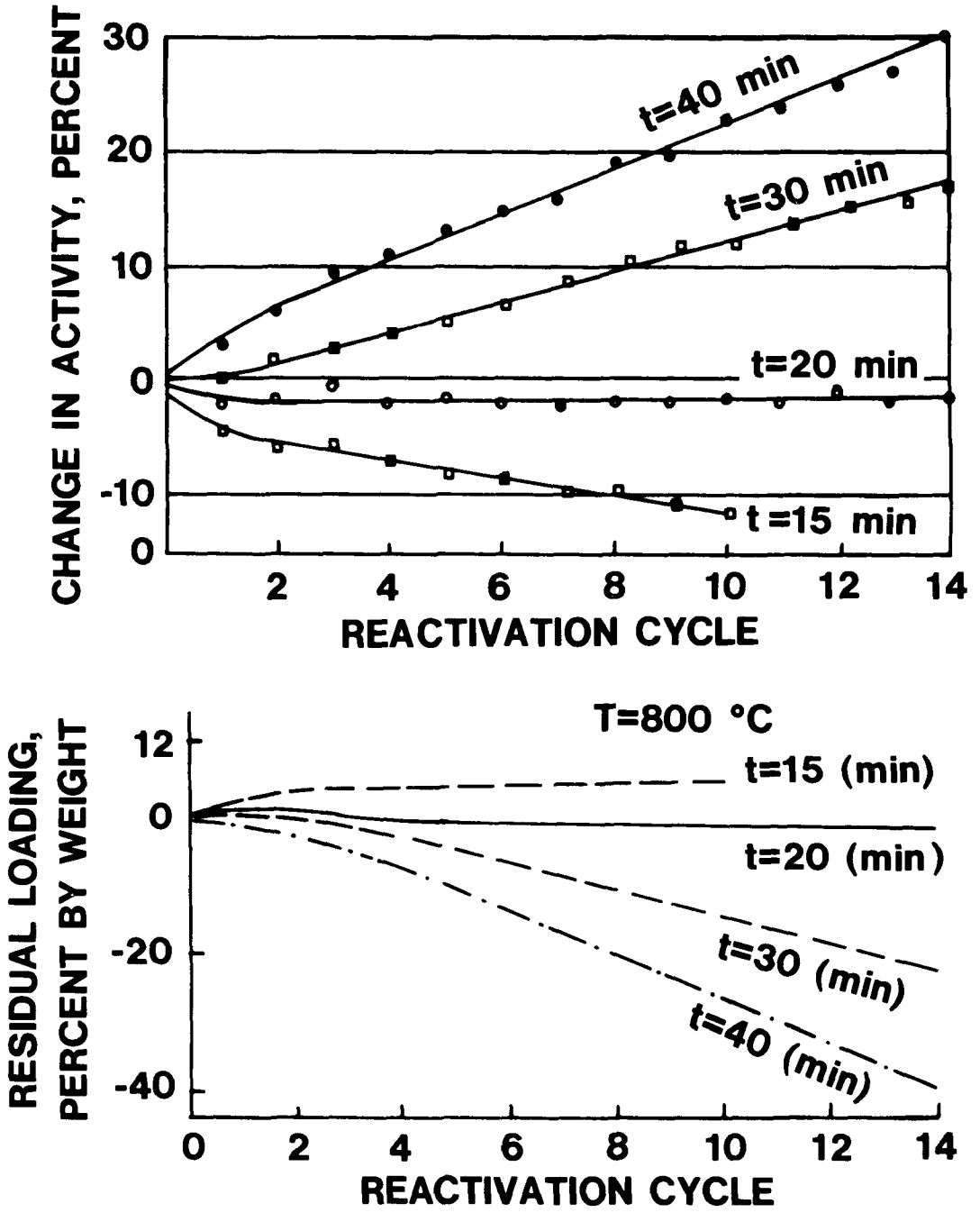

FIGURE 11. EFFECT OF RESIDENCE TIME ON ACTIVITY AND CHANGE OF WEIGHT OF ACTIVATED CARBON REFERENCE 59

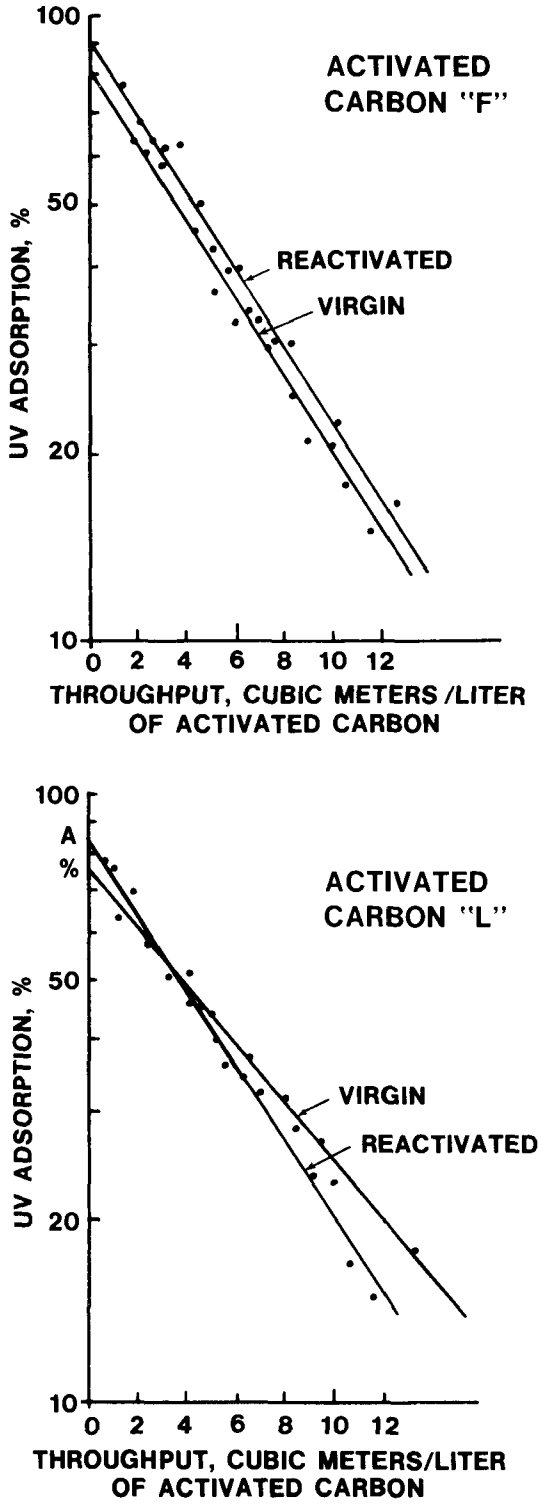

FIGURE 12 INFLUENCE OF REACTIVATION ON GRANULAR ACTIVATED CARBON PERFORMANCE REFERENCE 60

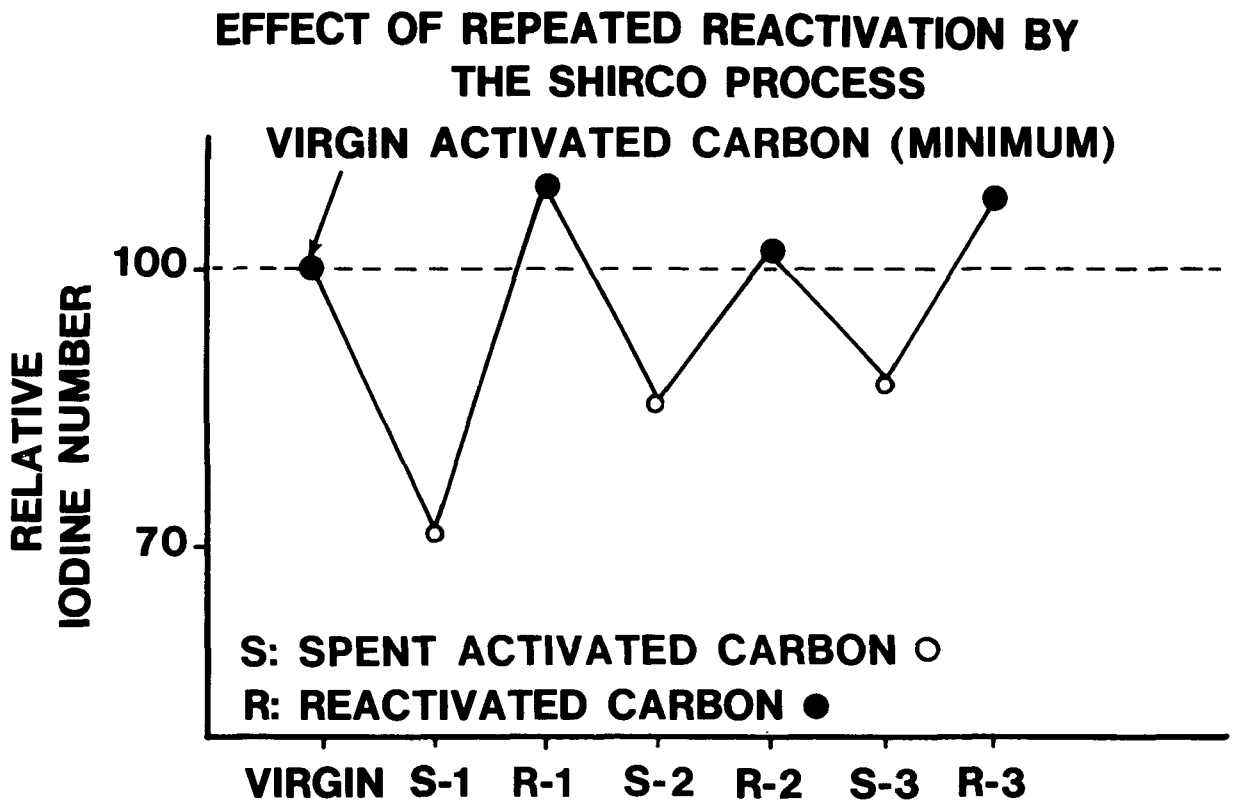

FIGURE 13 INFLUENCE OF REACTIVATION ON IODINE NUMBER FROM SHIRCO, INC. PROMOTIONAL LITERATURE

In summary, some changes may occur in granular activated carbon properties during thermal reactivation, and any reactivation system should be carefully designed to minimize the changes. Because some granular activated carbon losses occur through burn-off and mechanical attrition, fresh granular activated carbon will be added during each operating cycle. The addition of this fresh material will help overcome any losses in performance of the reactivated granular carbon, as compared to virgin material.

A final design consideration for any reactivation system must include proper consideration of handling the off-gases. Both dust collecting devices and gas after-burners may have to be considered in certain circumstances. Reactivation systems, however, can be designed in order to avoid any possible problems of air pollution during the reactivation process.

Because, as discused above, most water utilities using granular activated carbon as part of their water treatment process are doing so to control tastes and odors, and because tastes and odors are removed by granular activated carbon adsorption beds for periods of several years, reactivation of granular activated carbon for drinking water purposes is not widespread. In most cases, when a water purveyor changes the granular activated carbon charge in its treatment plant, the material that is replaced in the beds is virgin rather than reactivated granular carbon. The only known on-site reactivation facility at a water treatment plant in the Unted States was at Nitro, West Virginia, a plant that has now been closed for several years because the utility built a new plant on a cleaner source of water. At this writing (Fall 1977) the five known on-site reactivation facilities at water treatment plants are all in Europe, one in Switzerland, two in the

Federal Republic of Germany, one in Sweden, and one in the United Kingdom.

If granular activated carbon adsorption systems are to be used to control other organic contaminants beyond taste and odor producing compounds, as noted in the literature review above and as will be discussed in the sub-sections below, the period between reactivations will be much shorter than currently practiced.

Current Water Supply Research Division Research Findings

In an attempt to provide additional information not currently in the literature on the performance of granular activated carbon as an adsorption medium, the Water Supply Research Division has an active in-house and extramural research program on this subject The results of these experiments, many still on-going, are summarized below. Detailed papers on many of these projects will eventually be published in the technical press.

Class I Compounds (Taste and Odor Producing)

Snoeyink at the University of Illinois, working under EPA sponsorship found that the odorous compounds 2-methylisoborneol (MIB) and geosmin are both strongly adsorbed by activated carbon.[61,62] When present, humic substances significantly reduce the capacity of activated carbon for adsorption of these compounds, more so before equilbrium is achieved than at equilibrium. Commmercial humic acid (HA) and the humic substances from well water each had differing competitive effects on MIB. The capacity of activated carbon for geosmin adsorption was reduced by commercial HA to a greater extent than was observed for MIB. The performance of laboratory columns was consistent with the isotherm results. Application of distilled water to a partially saturated activated carbon bed resulted in almost no elution of MIB indicating that it was strongly adsorbed.

Using the data collected in this study and assuming, 1) complete saturation of the activated carbon, 2) no desorption and 3) no biological activity, Snoeyink predicted the bed life for the reduction of MIB or geosmin from 10 μg/ℓ to its threshold odor level of 0.1 μg/ℓ in a 7-8 minute empty bed contact time bed to be much greater (several months to years) than the predicted life for the reduction of humic substances from 5 to 1 mg/ℓ (1 to 2 months). When both MIB, or geosmin, and humic substances must be removed, humic substance removal will control the life of the bed.

Chlorophenols are adsorbed very strongly by activated carbon at the μg/ℓ level, which is near the threshold odor limit for these compounds. The extent of adsorption of 2,4-dichlorophenol (DCP) and 2,4,6-trichlorophenol (TCP) is a function of pH. The neutral species of these compounds predominate at pHs below the pK_a (pH at which the concentrations of the free acid and the acid anion are equal) values (7.85 and 6.00, respectively, at 25°C) and are adsorbed more strongly than the anionic species. As the number of chlorine atoms substituted on the phenol increases, the solubility of the neutral species decreases and the adsorbability increases. As substitution increases, the pK_a of the species is lowered, however.

When water containing phenol is chlorinated with low levels of chlorine, a mixture of chlorophenols will form and thus the extent of adsorption of one chlorophenol in the presence of another chlorophenol is an important consideration. Significant reductions in adsorption capacity (up to 50 percent) of one chlorophenol was caused by the presence of a second chlorophenol. Evaluation of the competitive effects of commercial HA, soil fulvic acid (FA) and leaf FA showed that the presence of these materials decreased the capacity of activated carbon for chlorophenol adsorption and that each of the materials competed somewhat differently.

Even in the presence of humic substances and another chlorophenol species, however, the adsorption capacity is even greater for chlorophenol than it is for MIB and that bed life for chlorophenol adsorption will be greater than for MIB and much greater than for humic substances.

In another study, a joint effort between the AWWA Research Foundation, 14 water utilities, the EPA Water Supply Research Division, and the Universities of Illinois, Iowa State and Missouri-Columbia, is underway to determine the removal of trace organics (particularly taste and odor compounds and haloforms) on granular activated carbon and polymeric adsorbents.

In this study, pilot scale columns containing seven different adsorbents are located at the Kansas City Water Treatment Plant, Kansas City, Missouri. The adsorbents include granular activated carbon made from bituminous coal, lignite, petroleum, and peat, and carbonaceous anion exchange resins. The adsorbers are presently arranged so that both a coal-base-and a lignite-base granular activated carbon system can provide up to 33 minutes empty bed contact time (EBCT). The applied water is unstable because of precipitative lime softening and a lack of recarbonation, resulting in calcium carbonate deposition on the adsorbents. The effect of this will be evaluated. Work will continue on the pilot column studies until the spring of 1978 and the final report will be available by early summer. Taste and odor removal results are not available at this time (Fall 1977).

Class II Compounds (Synthetic Source Water Contaminants)

Naphthalene

A long-term (started July 7, 1974) experiment comparing the adsorption of naphthalene with that of background organic content of Cincinnati tap water on granular activated carbon beds was terminated during June 1975.

330-day span of the experiment, 18,500 liters of Cincinnati tap water spiked with an average concentration of 30 μg/ℓ of naphthalene were passed through the granular activated carbon column (16.9 min EBCT). Although the non-purgeable organic carbon (NPOC) 50 percent removal front had penetrated the entire 27-inch length of the column by May 1975, the maximum penetration of the naphthalene 50 percent removal front was only about 6.5 inches (this was quite variable throughout the experiment). Therefore granular activated carbon columns can be expected to remove compounds of low polarity and solubility such as naphthalene for a much longer period of time than they can remove the diverse organic group represented by NPOC.

The variability of the depth of the naphthalene penetration into the adsorbent (1-6.5 inches) is something of a mystery. Suspected causes are (1) variable influent concentrations, (2) variable constitution of NPOC (competitive adsorption), (3) biological activity, (4) variable flow, (5) variable temperature, or (6) influence of backwashing.

Other Polynuclear Aromatic Hydrocarbons

Snoeyink, at the University of Illinois, reported[62] that limited experimentation with the polynuclear aromatic hydrocarbon (PAH) anthracene led to the conclusion that no significant association between its adsorption and that of humic substances occurred. Thus the possibility of PAH passage through granular activated carbon beds because of its association with the less adsorbable humic substances is not a cause for concern.

Carbon Tetrachloride

The adsorption of this contaminant on granular activated carbon beds was observed in the U.S. EPA Cincinnati Laboratory during the fall and winter of 1976-77 when carbon tetrachloride was in the tap water. At that time, granular activated carbon columns that had been in service for two months were being monitored for trihalomethane reduction. Table V shows the monthly average carbon

tetrachloride concentrations in the tap water and corresponding monthly average concentrations in the effluent. In spite of being in service for two months, the granular activated carbon was effective for 3 to 5 months, probably because this contaminant was "new" to the adsorbent when it occurred during the third month. Low level desorption of the carbon tetrachloride continued for several months after the contaminant disappeared from the influent.

TABLE V

ADSORPTION OF CARBON TETRACHLORIDE ON GRANULAR ACTIVATED CARBON

	Time in Service, months										
	1	2	3	4	5	6	7	8	9	10	11
Monthly Average Influent, µg/ℓ	NF	NF	5	8	13	15	44	NF	NF	NF	NF
Monthly Average Effluent, µg/ℓ	NF	NF	NF	NF	NF	<6*	14	16	13	6	6

Filtrasorb 400 granular
activated carbon
10 min. Empty bed contact time
NF = none found
* - Single Value during month

During the first week of January 1977 a 6-inch diameter by 30-inch depth bed (11 minutes EBCT) of virgin Calgon Filtrasorb 400 granular activated carbon was placed in upflow operation treating Cincinnati tap water. Coincidently with the start of operation, the concentration of carbon tetrachloride in the tap water began to increase.

Figure 14 shows the performance of the adsorbent bed during the first 43 weeks of 1977. During the first 7 weeks, the granular activated carbon effectively removed carbon tetrachloride during the period of extremely high influent concentrations. As the influent concentration returned to the limit of detection (0.1 µg/ℓ), the adsorbent, acting under the influence of the adsorption-desorption equilibrium phenomenon, began to desorb carbon

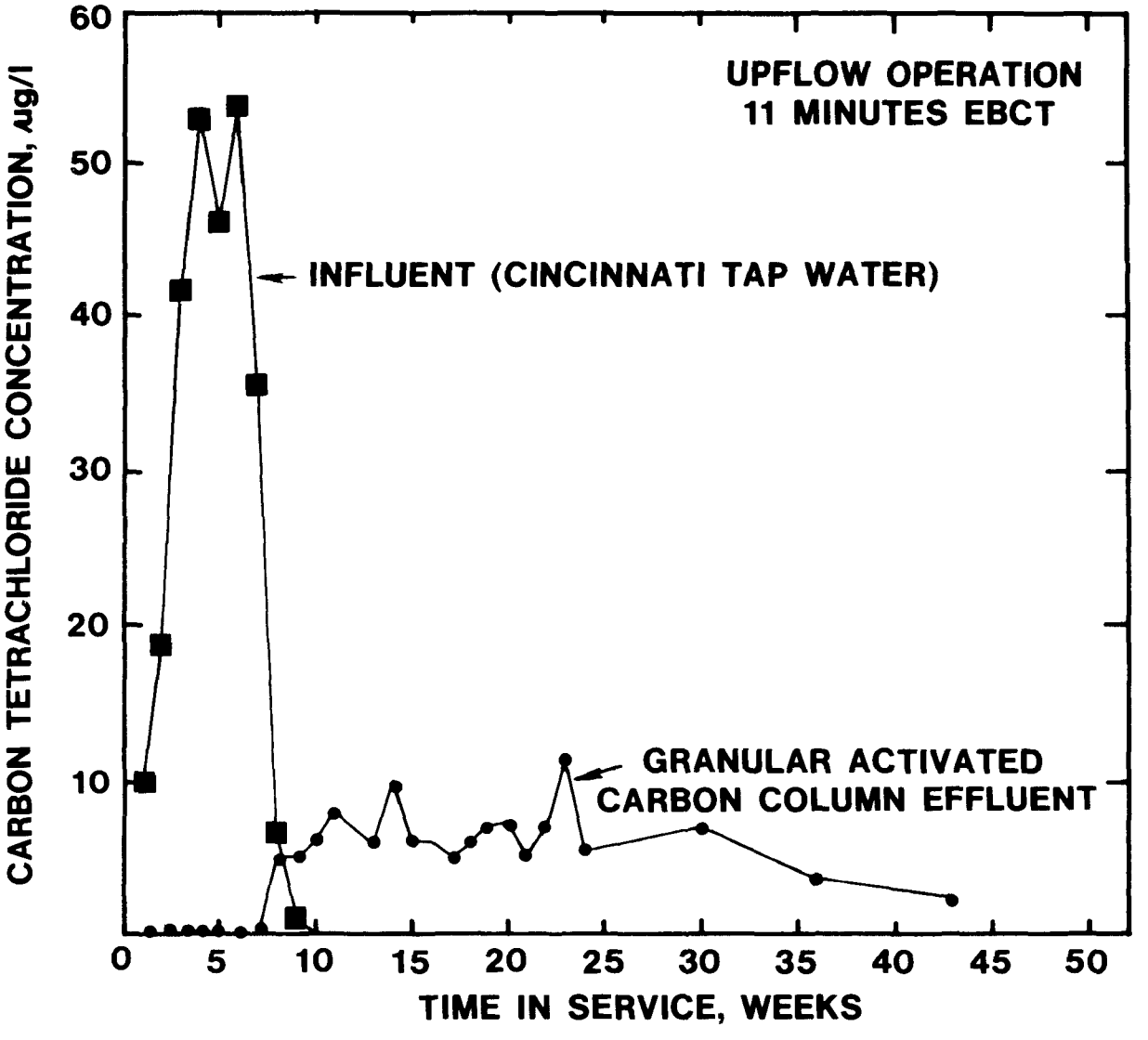

FIGURE 14 PERFORMANCE OF GRANULAR ACTIVATED CARBON BED FOR CARBON TETRACHLORIDE REMOVAL

tetrachloride. This desorption, which was monitored approximately every 6 weeks, has continued for about 9 months.

Figure 14 is important because it illustrates the protection a granular activated carbon adsorption barrier can afford the consumer during periods of sudden contamination of the raw water supply. These data also demonstrate that granular activated carbon reactivation will probably be necessary fairly frequently to afford continuing consumer protection and guard against desorption of unwanted contaminants.

Trichloroethylene, Tetrachloroethylene and Similar Chlorinated Organics

Because several incidences of tri- and tetrachlorethylene contamination of drinking water supplies have been reported, the Water Supply Research Division is currently (Fall 1977) studying the effectiveness of granular activated carbon beds for removing these pollutants. In most instances the water source is ground water and the contamination can be linked to some industrial activity involving the present or past use of cleaning solvents in the aquifer recharge area. Columns containing granular activated carbon (10 minute empty bed contact time) have been installed in three locations in New England and the first few weeks of data indicate that tri- and tetrachloroethylene are very well removed when the adsorbent is fresh, see Table VI. As indicated in the footnote to Table VI, the contaminant, 1,1-dichloroethane was not as well removed. At another location (not shown in Table VI) the tetrachloroethylene contamination has exceeded 2500 µg/ℓ, yet the granular activated carbon bed produced an effluent with less than 0.5 µg/ℓ tetrachloroethylene, for 15 weeks. These tests are continuing.

TABLE VI

USE OF GRANULAR ACTIVATED CARBON BEDS TO REMOVE ORGANIC CONTAMINANTS FROM A GROUND WATER

Contaminant	Influent Concentration Range, µg/ℓ	Average Effluent Con., µg/ℓ 0-4 weeks	4-8 weeks	8-12 weeks
1,1,1-trichloroethane	10.9-36.7	NF	NF	0.4
trichloroethylene	1.9-7.7	NF	<0.1	<0.1
tetrachloroethylene	0.1-16.9	NF	<0.1	<0.1

NF = None Found

Note: After six weeks of testing, two new contaminants, 1,1-dichloroethane and cis-1,2-dichloroethylene began appearing in the influent to the granular activated carbon column. No cis-1,2-dichloroethylene has yet been detected in the treated water, but the average concentration of 1,1-dichloroethane in the effluent for the 4 to 8 week period after first appearing was 0.7 µg/ℓ.

Prediction of Granular Activated Carbon Bed Performance, Studies with Humic Acid and Carbon Tetrachloride, Dieldrin, PCB, Benzene, and p-Dichlorobenzene

Weber, at the University of Michigan, is studying the adsorption of several specific organic compounds on granular activated carbon. The main thrust of this WSRD grant activity is to investigate the possibility of predicting activated carbon column adsorber performance on the basis of mathematical parameters obtained from simple batch kinetic and equilibrium (isotherm) studies. Although the studies include only the use of model systems (humic acids as the competitive species), certain general conclusions about relative activated carbon adsorber operating life can be drawn on the basis of some of the data obtained to date from the modeling studies.

The results of the work with carbon tetrachloride support the in-house work reported above in that an adsorber life of several weeks to months can be expected. The work with dieldrin indicates that this compound is very strongly adsorbed, supporting evidence to that effect previously reported in the literature.[23] PCB mixtures resemble pesticides in properties and are also strongly adsorbed.

Adsorber operating life for PCB's are likely to be on the order of months to one year. Adsorber operating periods for treatment of benzene and p-dichlorobenzene are likely to range somewhere between carbon tetrachloride and the PCB mixtures.

Mixtures from Actual Waters

In an attempt to further evaluate the capability of granular activated carbon beds to remove actual mixtures of raw water organic contaminants in competition with other organics, several studies are being conducted on actual waters at locations other than Cincinnati, Ohio. One of these research projects, using bench scale pilot granular activated carbon columns is being performed with a ground water in Southern Florida. The granular activated carbon columns are 1-inch in diameter and contain 30-inches of activated carbon. The bed was loaded at 3 gpm/ft^2, which resulted in a 6.2 minute empty bed contact time. The influent to the granular activated carbon column was untreated ground water for the first phase of the study and finished water for the second and third phase. The source has a color of approximately 50 color units, a TOC concentration of about 10 mg/ℓ, and a pH of about 7.1.

The project includes routine analysis for the concentration of 19 organic compounds, total organic carbon, and trihalomethane formation potential, both before and after the granular activated carbon column. The average influent concentration to the granular activated carbon bed for the duration of the study is shown in Tables VII, VIII, and IX. Tables X, XI, and XII show the corresponding effluent concentrations for specific substances with time over the duration of each study. These data show that at these short contact times, some organic compounds did break through fairly early in the test, but that the chlorinated aromatic compounds were well removed. Longer empty bed contact time tests are now underway, see pages A69 to A78.

TABLE VII

AVERAGE CONCENTRATIONS OF TENTATIVELY IDENTIFIED ORGANICS INFLUENT TO GRANULAR ACTIVATED CARBON BED

(Jan. 18 - May 20, 1977)

Compound		µg/ℓ
Vinyl chloride		0.8
Methylene chloride		0.08
Methyl iodide		nil
trans-1,2-Dichloroethylene		1.3
1,1-Dichloroethane		0.3
cis-1,2-Dichloroethylene		29.0
Chloroform	(Tr. to 2.1)	0.16
1,1,1-Trichloroethane		
1,2-Dichloroethane	(Sum)	0.11
Carbon tetrachloride		
Trichloroethylene		0.13
Bromodichloromethane	(Tr to 0.9)	0.11
Tetrachloroethylene		0.06
Dibromochloromethane	(Tr. to 0.4)	0.04
Chlorobenzene		0.19
Bromoform	(Tr. to 0.19)	0.02
p-Chlorotoluene		0.11
o,m,p-Dichlorobenzene (sum)		1.1

TABLE VIII

AVERAGE CONCENTRATION OF TENTATIVELY IDENTIFIED ORGANIC COMPOUNDS IN INFLUENT TO GRANULAR ACTIVATED CARBON BED (Aug. 26 to Oct. 18, 1977)

EBCT = 6.2 minutes

Chemical Name	µg/ℓ
Vinyl chloride	5.4
Methylene chloride	not determined
trans-1,2-Dichloroethylene	1.0
1,1-Dichloroethane	0.3
cis-1,2-Dichloroethylene	19
Chloroform	57
1,1,1-Trichloroethane	
1,2-Dichloroethane — (Sum)	5.3
Carbon tetrachloride	
Trichloroethylene	0.1
Bromodichloromethane	39
Tetrachloroethylene	nil
Dibromochloromethane	27
Chlorobenzene	0.8
Bromoform	2.5
p-Chlorotoluene	0.2
m-Dichlorobenzene	
p-Dichlorobenzene — (Sum)	0.3
o-Dichlorobenzene	

TABLE IX

AVERAGE CONCENTRATIONS OF TENTATIVELY IDENTIFIED ORGANIC COMPOUNDS IN INFLUENT TO GRANULAR ACTIVATED CARBON BED, EBCT = 6.2 min.

(Run No. 2, Nov. 1, 1977 - Jan. 3, 1978)

Compound	µg/ℓ
Vinyl chloride	7.4
Methylene chloride	-
trans-1,2-Dichloroethylene	0.63
1,1-Dichloroethane	0.11
cis-1,2-Dichloroethylene	24.5
Chloroform	76.6
1,1,1-Trichloroethane	
1,2-Dichloroethane → (sum)	7.9
Carbon tetrachloride	
Trichloroethylene	0.52
Bromodichloromethane	48.4
Tetrachloroethylene	nil
Dibromochloromethane	29.0
Chlorobenzene	0.56
Bromoform	1.95
p-Chlorotoluene	nil
m-Dichlorobenzene	nil
p-Dichlorobenzene	0.19
o-Dichlorobenzene	0.09

TABLE X

CONCENTRATIONS OF TENTATIVELY IDENTIFIED ORGANICS PRESENT IN EFFFLUENT FROM ADSORBER, EBCT = 6.2 min. (Jan. 18 - May 20, 1977)

All data in µg/ℓ - Compare to Table VII

Time, Weeks	A	B	C	D	E	F	G	H	I	J
0	N	N	N	N	0.007	N	N	0.02	-	0.07
1	N	N	0.18	N	0.006	N	N	N	-	0.003
2	N	N	0.2	N	0.004	N	N	0.02	-	N
3	0.002	0.02	2.7	0.002	0.001	0.01	N	N	-	0.003
4	N	0.08	4.2	N	0.002	N	N	N	-	N
5	0.002	0.007	7.8	N	N	N	N	N	-	0.006
6	N	0.013	5.3	N	N	N	N	N	-	N
7	0.002	0.015	12.0	N	N	N	N	N	-	0.002
8	0.04	0.02	18.0	N	N	0.001	N	N	-	0.003
9	0.02	0.03	17.3	N	N	N	N	N	-	0.003
10	0.05	0.04	21.6	N	N	N	N	N	-	0.002
11	0.07	0.1	10.2	0.01	N	N	N	N	-	N
12	0.07	0.02	18.7	0.006	N	N	N	N	-	0.03
13+	0.66	0.32	25.7	0.06	N	N	N	N	0.79	0.01
14	0.45	0.17	30.4	0.07	N	N	N	N	0.70	0.10
15	0.90	0.38	23.3	0.05	N	N	N	N	0.81	0.06
16	0.76	0.34	21.9	0.06	N	N	N	N	0.75	0.05
17	0.60	0.23	21.3	0.028	N	N	N	N	0.78	N

- = Not determined
N = None found
A = trans-1,2-Dichloroethylene
B = 1,1-Dichloroethane
C = cis-1,2-Dichloroethylene
D = Trichloroethylene
E = Tetrachloroethylene
F = Chlorobenzene
G = p-Chlorotoluene
H = m,p,o-dichlorobenzene
I = Vinyl chloride
J = 1,1,1-Trichloroethane
1,2-Dichloroethane
Carbon tetrachloride

TABLE XI

CONCENTRATIONS OF TENTATIVELY IDENTIFIED ORGANICS PRESENT IN EFFLUENT FROM ADSORBER

EBCT = 6.2 min., (Run No. 1, Aug. 26 - October 18, 1977)

All Data in µg/ℓ - Compare to Table VIII

Time Weeks	A	B	C	D	E	F	G	H	I	J
0	N	N	N	N	N	N	N	N	-	N
1	N	N	N	N	N	N	N	N	0.165	N
2	0.40	N	10.7	0.59	N	N	N	N	0.64	N
3	N	0.55	2.19	0.03	N	N	N	N	0.33	N
4	N	N	2.87	N	N	N	N	N	N	0.31
5	0.12	0.62	8.9	0.003	N	N	N	N	4.7	0.34
6	N	N	8.77	N	N	N	N	N	3.25	0.09
7	N	N	9.91	N	N	N	N	N	1.85	N

N = None found

A = trans-1,2-Dichloroethylene
B = 1,1-Dichloroethane
C = cis-1,2-Dichloroethylene
D = Trichloroethylene
E = Tetrachloroethylene
F = Chlorobenzene
G = p-Chlorotoluene
H = m,p,o-Dichlorobenzene
I = Vinyl chloride
J = 1,1,1-Trichloroethane
1,2-Dichloroethane
Carbon tetrachloride

TABLE XII

CONCENTRATIONS OF TENTATIVELY IDENTIFIED ORGANICS IN EFFLUENT FROM ADSORBER

EBCT = 6.2 min. (Run No. 2, Nov. 1, 1977 - Jan. 3, 1978)

All data in µg/ℓ, Compare to Table IX

Time Weeks	A	B	C	D	E	F	G	H	I	J	K	L
0	N	N	N	N	N	N	N	N	0.30	N	N	N
1	N	N	N	N	N	N	N	N	N	N	3.2	1.28
2	N	N	N	N	N	N	N	N	N	N	8.2	N
3	N	1.05	1.28	N	N	N	N	N	N	N	N	N
4	N	0.21	3.8	N	N	N	N	N	N	N	5.2	N
5	N	N	11.1	N	N	N	N	N	N	N	N	N
6	N	0.30	5.5	0.22	N	N	N	N	N	N	1.7	1.5
7	N	0.8	12.0	0.29	N	N	N	N	N	N	1.8	4.9
8	0.58	0.66	9.1	0.57	N	N	N	N	N	N	2.5	4.0
9	0.97	N	9.1	0.04	N	N	N	N	N	N	4.4	4.7

N = None found

A = trans-1,2-Dichloroethylene
B = 1,1-Dichloroethane
C = cis-1,2-Dichloroethylene
D = Trichloroethylene
E = Tetrachloroethylene
F = Chlorobenzene
G = p-Chlorotoluene
H = m-dichlorobenzene
I = p-Dichlorobenzene
J = o-Dichlorobenzene
K = Vinyl chloride
L = 1,1,1-Trichloroethane
1,2-Dichloroethane
Carbon tetrachloride

Another actual plant site research project is being performed using full-scale granular activated carbon beds located at a water treatment plant in the lower Mississippi Valley. In this project one bed is used as a post-filter adsorber and another as a sand replacement system in parallel operation. The post-filter adsorber is an existing conventional rapid sand filter that had the 30 inches of sand replaced by 30 inches of 12x40 mesh granular activated carbon. The post-filter adsorber is in series after a rapid sand filter, so that the granular activated carbon received coagulated, settled, softened, and filtered water. The empty bed contact time was 27 minutes at the start of the test and 20 minutes at the end because of granular activated carbon loss, caused by inadvertent excessive backwashing.

The sand replacement system is an existing rapid sand filter that had the top 24 inches of the 30 inches of sand replaced by 24 inches of 12x40 granular activated carbon. This unit receives coagulated, settled and softened water directly from the precipitator of the full-scale plant. The empty bed contact time was 24 minutes at the start of the test and 18 minutes at the end because of granular activated carbon loss caused by inadvertent excessive backwashing.

The project includes routine analysis for the concentration of at least 35 organic substances and total organic carbon and trihalomethane formation potential both before and after the granular activated carbon beds. Table XIII shows the effluent concentration for each substance found, as contrasted to the influent concentrations listed at the bottom of the Table for the duration of the study, 25+ weeks. For this report only the post-filter adsorber data will be shown as an example. Note, for this project, too, all data is preliminary in nature as the gas chromatograph-mass spectrometry confirmations have not yet been evaluated for consistency of identification (Fall 1977).

TABLE XIII

REMOVALS OF TENTATIVELY IDENTIFIED ORGANICS BY POST-FILTER GRANULAR ACTIVATED CARBON ADSORBER

Empty Bed Contact Time, 27 min. Start, 20 min. End

Time, Weeks	Benzene Effl. Conc. µg/ℓ	1,2-Dichloroethane Effl. Conc. µg/ℓ	Trichloroethylene Effl. Conc. µg/ℓ	Toluene Effl. Conc. µg/ℓ
0	ND	0.4	ND	ND
1	0.1	0.2	ND	0.1
2+	ND	ND	ND	ND
3	ND	0.1	ND	ND
4	ND	ND	ND	ND
5	0.1	0.3	ND	0.1
6	ND	1.1	ND	ND
7	ND	0.7	ND	ND
8	ND	0.8	ND	ND
9	ND	1.3	0.4	ND
10+	ND	1.4	ND	ND
11+	0.1	1.0	ND	0.2
12+	ND	2.0	ND	ND
13+	ND	3.5	ND	ND
15+	ND	4.5	ND	ND
20+	ND	10.1	ND	ND
25+	ND	9.4	ND	ND
Avg. Inf. Conc. µg/ℓ	0.3	8.0	0.3	0.2
Range Inf. Conc. µg/ℓ	ND-2.1	1.2-23.7	ND-0.9	ND-0.9

ND = Not detected

Within the precautions stated, Table XIII can be used to show the trends for removal by the granular activated carbon bed. The adsorber removed the ambient concentrations of toluene, benzene and trichloroethylene more efficiently than other substances consistently present during the first 10+ weeks of operation. The 1,2-dichloroethane was removed at an average of greater than 80 percent for about 8 weeks, but the effluent concentration consistently exceeded 0.5 µg/ℓ after six weeks. Desorption occurred from about the 16th week to the end of the test. Preliminary data show that trace concentrations (ng/ℓ) of chlorinated hydrocarbon insecticides were generally reduced to below detectable concentrations throughout the 25+ week study. Finally, the sand replacement system performed similarly to the post-filter adsorber, but the removals were not as long-lasting.

A third study on the performance of granular activated carbon beds is being conducted in full scale at a water treatment plant in the upper Ohio Valley. As this project is just starting, the data are preliminary, mainly because the identification of specific organics thus far is based only on gas chromatographic retention times without mass spectrometry confirmation.

The following generalizations are made after 52 days of virgin granular activated carbon being on-line. Compounds for which granular activated carbon adsorption may serve as a control mechanism and their influent concentration ranges are: 1,1,1-trichloroethane or carbon tetrachloride or both (0.17 - 1.14 µg/ℓ, not resolved); 1,2-dichloropropane or trans-1,3-dichloropropylene or both (0.10-0.64 µg/ℓ) (not resolved); trichloroethylene (0.16-0.96 µg/ℓ); cis-1,3-dichloropropylene or 1,1,2-trichloroethane or both (0.15-24.0 µg/ℓ)(not resolved); dichloroiodomethane (0.10-1.22 µg/ℓ) and chlorobenzene (0.24-3.36 µg/ℓ). Although present occasionally, these compounds were not consistently present in the influent to the adsorber, therefore removals could not be calculated.

Unidentified Compounds

After concentration, gas chromatography can be used to separate many organic compounds, producing a gas chromatogram in which the separated organic compounds are represented by "peaks" on a chart. Although unidentified, the absence of certain peaks after a given type of treatment gives an indication of the success of the treatment. In 1972, influent and effluent carbon chloroform extracts[8] from an operating granular activated carbon sand replacement system in Lawrence, Massachusetts were compared gas chromatographically. Figure 15 shows the reduction of many of the organic peaks when the granular activated carbon was fresh, but after 16 weeks of operation the influent and effluent gas chromatograms were similar, Figure 16. Note, Figure 3, page A8, shows the breakthrough pattern of the general organic parameter CCE-m from this same treatment unit.

Recently, in the WSRD laboratories this approach was repeated using improved analytic procedures. Weekly one gallon samples of influent and effluent from a virgin granular activated carbon bed (about 9 minute EBCT), receiving coagulated, settled, and dual media filtered Ohio River water, were collected and extracted with one 250 ml and two 100 ml portions of redistilled methylene chloride. After concentration of the extract 2 µg of anthracene, in methylene chloride was added as an internal standard.

In-house analyses are being conducted on a gas chromatograph employing a 30 meter SP-2100 wall coated glass capillary column. Injections are made at 20°C, and after 5 minutes the oven temperature is programmed at 2°/min to 240°C. Detection limits for anthracene (internal standard) using a flame ionization detector is approximately 0.4 ng or approximately 20 ng/ℓ for similarly responding compounds from the original 4ℓ sample. Preliminary results, Figure 17, indicate that after one week almost all of the compounds present in the influent were not detectable in the effluent. Further, no major new peaks occurred, indicating that organics detectable by this procedure were not leaching off the granular

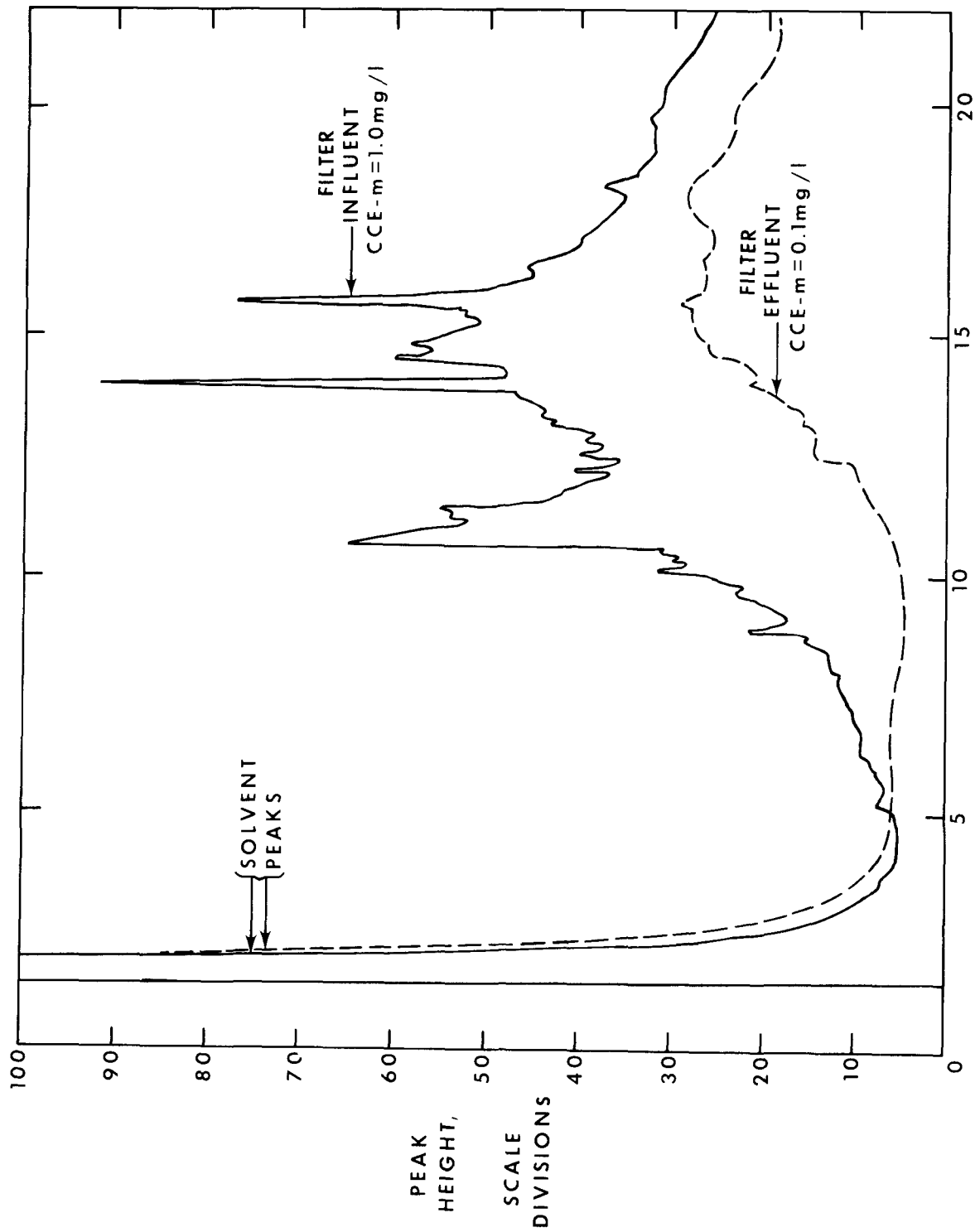

FIGURE 15 COMPARSION OF GAS CHROMATOGRAMS OF CCE-m's COLLECTED DURING 1st WEEK OF OPERATION AT LAWRENCE, MASS.

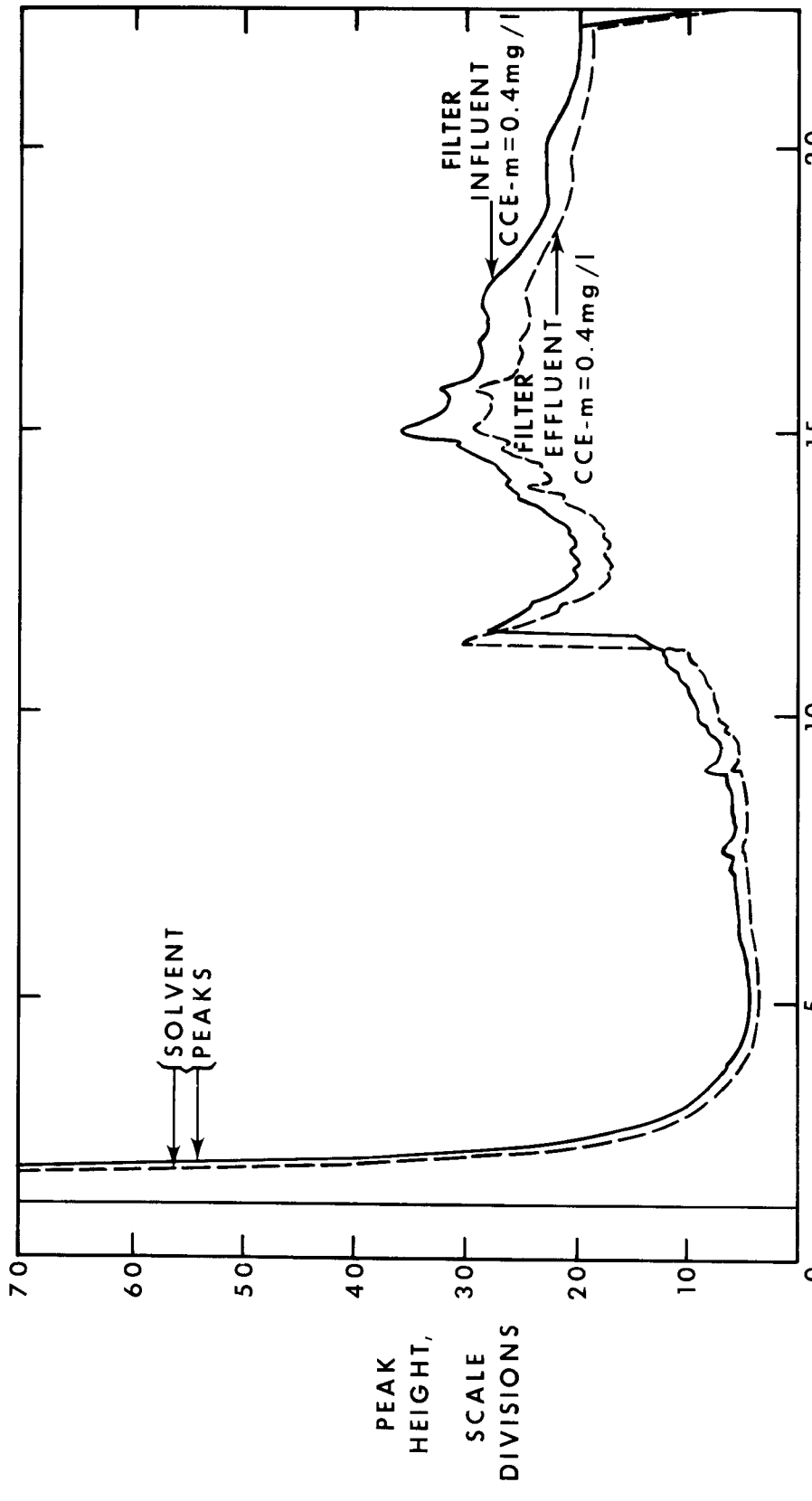

FIGURE COMPARSION OF GAS CHROMATOGRAMS OF CCE-m's COLLECTED DURING 16th WEEK OF OPERATION AT LAWRENCE, MASS.

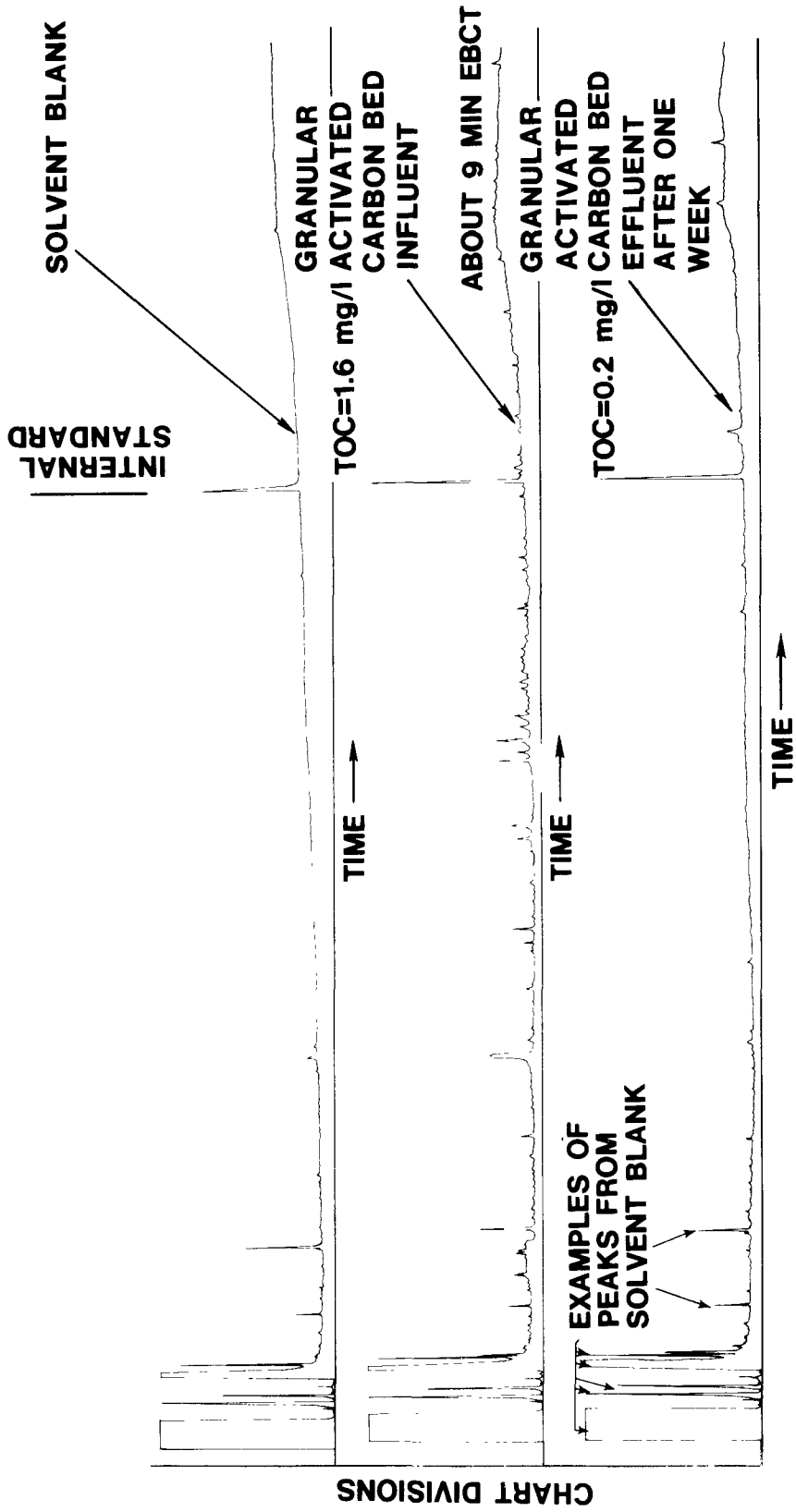

FIGURE 17 COMPARISON OF ORGANIC CONTENT OF A GRANULAR ACTIVATED CARBON EFFLUENT BY SOLVENT EXTRACTION AND CAPILLARY GAS CHROMOTOGRAPHY

activated carbon. Analysis of later samples showed; 1) that the influent quality was very variable and 2) that although some "peaks" began occurring in the effluent it always contained fewer "peaks" than the influent, even after 3 months. These studies are continuing. Figure 18 shows the increase in effluent NPOC concentration during the time of the collection of the above samples. Similar data have been collected by Heymann[9] in Duisburg, Federal Republic of Germany.

Note, because the influent to the pilot plant (Ohio River water) is stored in open tanks for several days prior to treatment, relatively volatile chlorinated organics were not present in the influent to the granular activated carbon bed.

Summary

Taken in total, these results, which were collected under conditions representative of those found in drinking water, support the concept of granular activated carbon adsorption being a "broad-spectrum" organic removal unit process. These data do, however, indicate the variation adsorbability of different organic compounds and show the importance of site specific evaluations of granular activated carbon performance as outlined in the Interim Treatment Guide (see pages 23 to 26).

Class III Compounds (Disinfection By-Product Precursors)

Because no direct measurement exists for Class III organics (for example, trihalomethane precursors), the degree of precursor removal can be judged by comparing trihalomethane concentrations upon chlorination of an untreated control water (called the terminal trihalomethane concentration)[63] to similar data collected on a treated water after similar chlorination and storage. For example, if the effluent from a sand filter that was chlorinated and stored for two days yielded 50 µg/ℓ chloroform and the same effluent passed through an adsorbent, then chlorinated and stored under similar conditions produced 25 µg/ℓ chloroform, the adsorbent would be 50 percent effective in removing chloroform formation potential. This example assumes that no

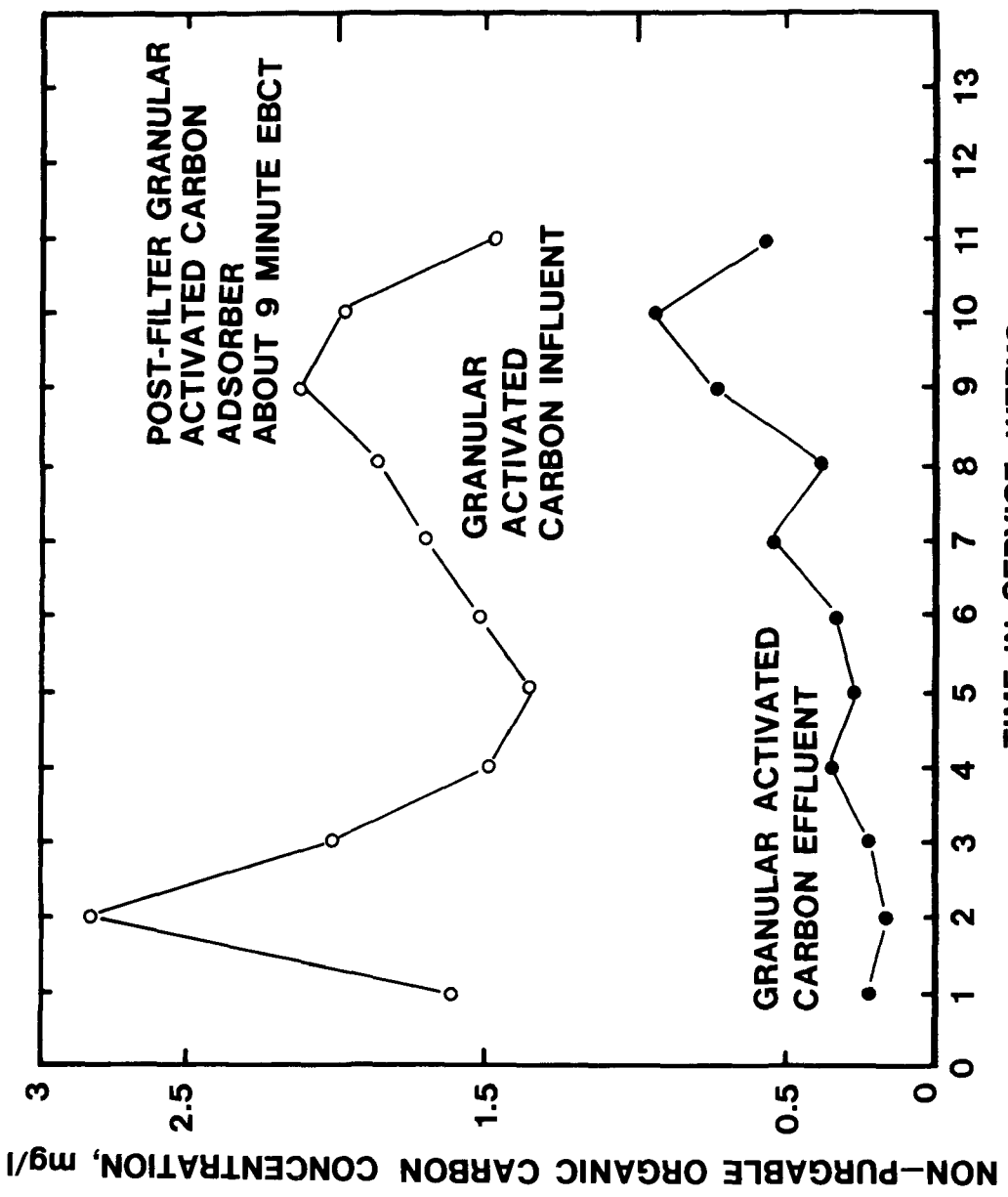

FIGURE 18 BREAKTHROUGH OF NON-PURGEABLE ORGANIC CARBON

trihalomethanes were present in the filter effluents, that is the terminal trihalomethane concentration and trihalomethane formation potential are equal.

Using Ohio River water as source, Love et al.[64] observed that the relative effectiveness of granular activated carbon adsorbers to prevent the formation of trihalomethanes was highest for chloroform and lowest for dibromochlormethane. A granular activated carbon bed receiving coagulated, settled, but undisinfected water was initially effective for preventing trihalomethane formation upon subsequent chlorination (see Figure 19).

Similar pilot plant studies have been carried out by Sylvia at the Lawrence Experiment station in Lawrence, Massachusetts under a WSRD research Contract. The Merrimac River receives considerable industrial contamination upstream from the Lawrence study site, however, relative to the Ohio River, the Merrimac has a very low turbidity (2-4 NTU vs 10-75+ NTU, for the Ohio River at Cincinnati), and experimentation has shown that trihalomethane precursors in the Merrimac are only slightly reduced in concentration through coagulation and settling, yet are removed for long periods by granular activated carbon adsorption. For example, three different types of granular activated carbons exposed to treated yet undisinfected Merrimac River water were found to reduce the trihalomethane formation potential (2 day) of 40-60 μg/ℓ to less than 1 μg/ℓ after 6 months of operation. Details on this will be contained in the final project report, which is due in early 1978.

Work by Snoeyink[63] at the University of Illinois on the adsorption of humic and fulvic acids, major trihalomethane precursors, relates to this phase of the overall problem of organic contamination. He found that activated carbon adsorbed humic substances in all cases that were studied, but the adsorption properties of the substances from different sources varied widely as did the extent

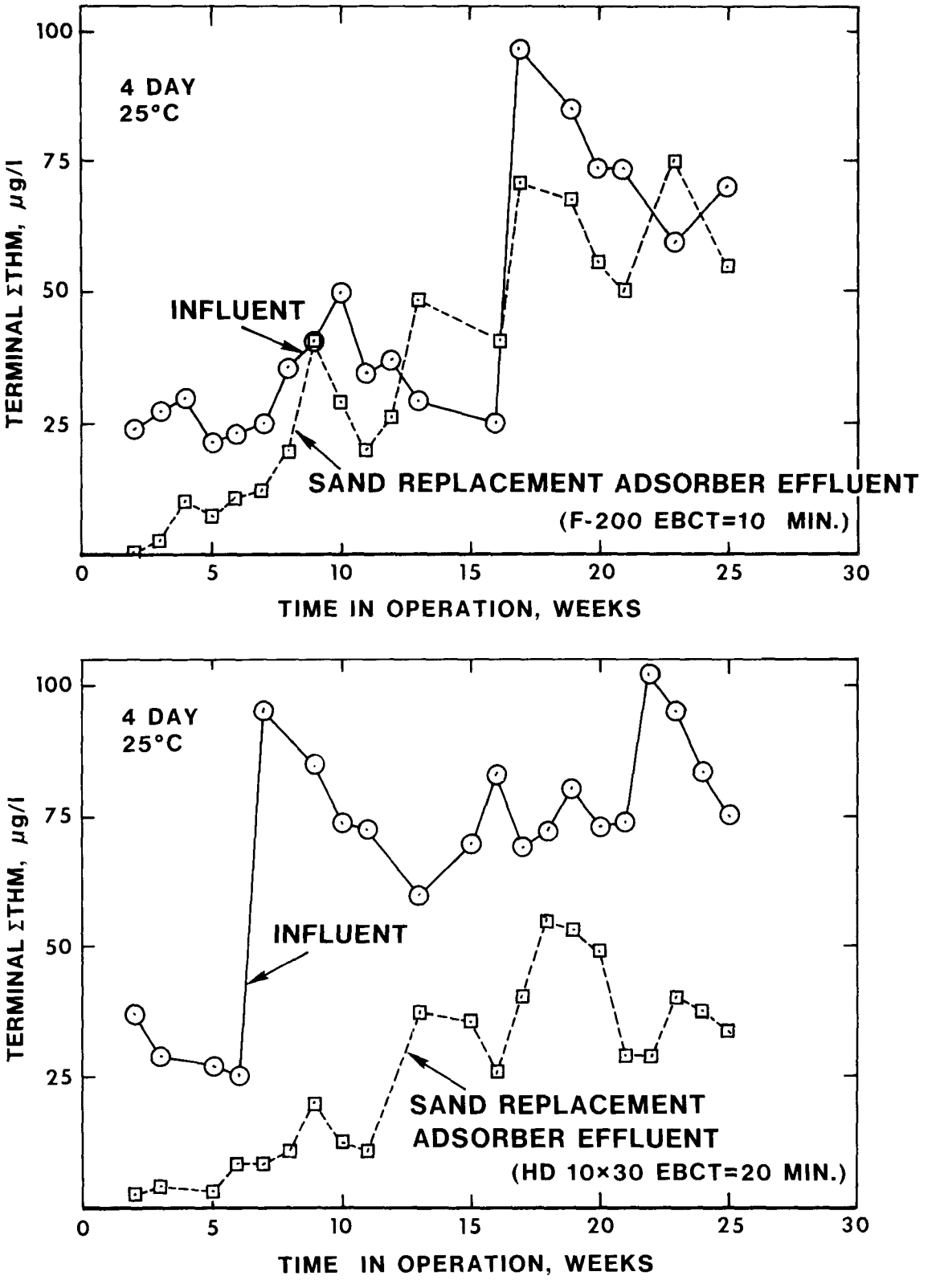

FIGURE 19 USE OF GRANULAR ACTIVATED ACTIVATED CARBON FOR REMOVING TRIHALOMETHANE FORMATION POTENTIAL. REFERENCE 64

to which they competed with selected trace organics for adsorption sites on activated carbon.

Humic substances from leaf- and soil extract, a well water, and a commercial source were examined in detail. Extent of adsorption depended upon solubility, with the less soluble humic acid (HA) fraction being more adsorbable than the fulvic acid (FA) fraction from the same source. The lower molecular weight species from a given FA or HA fraction are more adsorbable than the high molecular weight species, presumably because more surface area is accessible to them.

The adsorption characteristics of the humic substances are also dependent on the method of analysis used to quantify them. The species that fluoresce the most were found to be the lower molecular weight species and these adsorb best. Ultra-violet absorbing species did not adsorb as well as those that fluoresce. Solution pH and phosphate concentration also had a marked effect on adsorbability of the humic materials, with adsorption generally improving with decreasing pH and increasing phosphate concentration. The trihalomethane formation potential of the humic substances varied widely from source to source, with only one exception, but no dependence on molecular weight was found for fractions of FA or HA. This work reemphasizes the need for on-site pilot studies to determine adsorbability for that particular location.

The removal of disinfection (chlorination) by-product precursors was also studied at the three projects operating at the actual water treatment plants cited above. The data in Table XIV and Figure 20 show the same variability in the treatability of trihalomethane precursors as noted in the previous studies. Note: The data in Table XIV show that although breakthrough did occur, complete exhaustion for the removal of trihalomethane formation potential did not, at least during the time of the study. In summary, removal of trihalomethane precursors by adsorption on granular activated carbon beds is variable and site specific.

TABLE XIV

REMOVAL OF SUMMATION** TRIHALOMETHANE FORMATION POTENTIAL (THMFP)

BY GRANULAR ACTIVATED CARBON BEDS

Southern Florida Ground Water 6.2 min. EBCT				Lower Mississippi River Water EBCT-28 min. start, 20 min. end			
Time Weeks	Inf. THMFP µg/ℓ	Eff. THMFP µg/ℓ	Percent Reduction	Time Weeks	Inf. THMFP* µg/ℓ	Eff. THMFP* µg/ℓ	Percent Reduction
0	384	11	97	0	59	2.3	96
1	485	335	34	1	56	1.3	98
2	758	558	28	2+	70	6.7	91
3	878	560	37	3	113	22	80
4	807	579	30	4	104	18	82
5	733	557	27	5	203	25	87
6	710	524	29	6	239	44	81
7	936	437	53	7	151	49	68
8	617	342	45	8	159	92	42
9	639	424	34	9	217	86	60
10	616	445	39	10+	184	73	60
11	348	397	-17	11+	240	100	58
12	655	452	33	12+	236	89	62
17+	575	394	31	15+	205	93	54
				20+	297	148	50
				25+	218	157	28

*Note: These data are shown in Figure 11, page 20, of the Interim Treatment Guide.

**The arithmetic sum of the individual trihalomethane species determined. This parameter is called "Total" Trihalomethane Formation Potential in the Regulations.

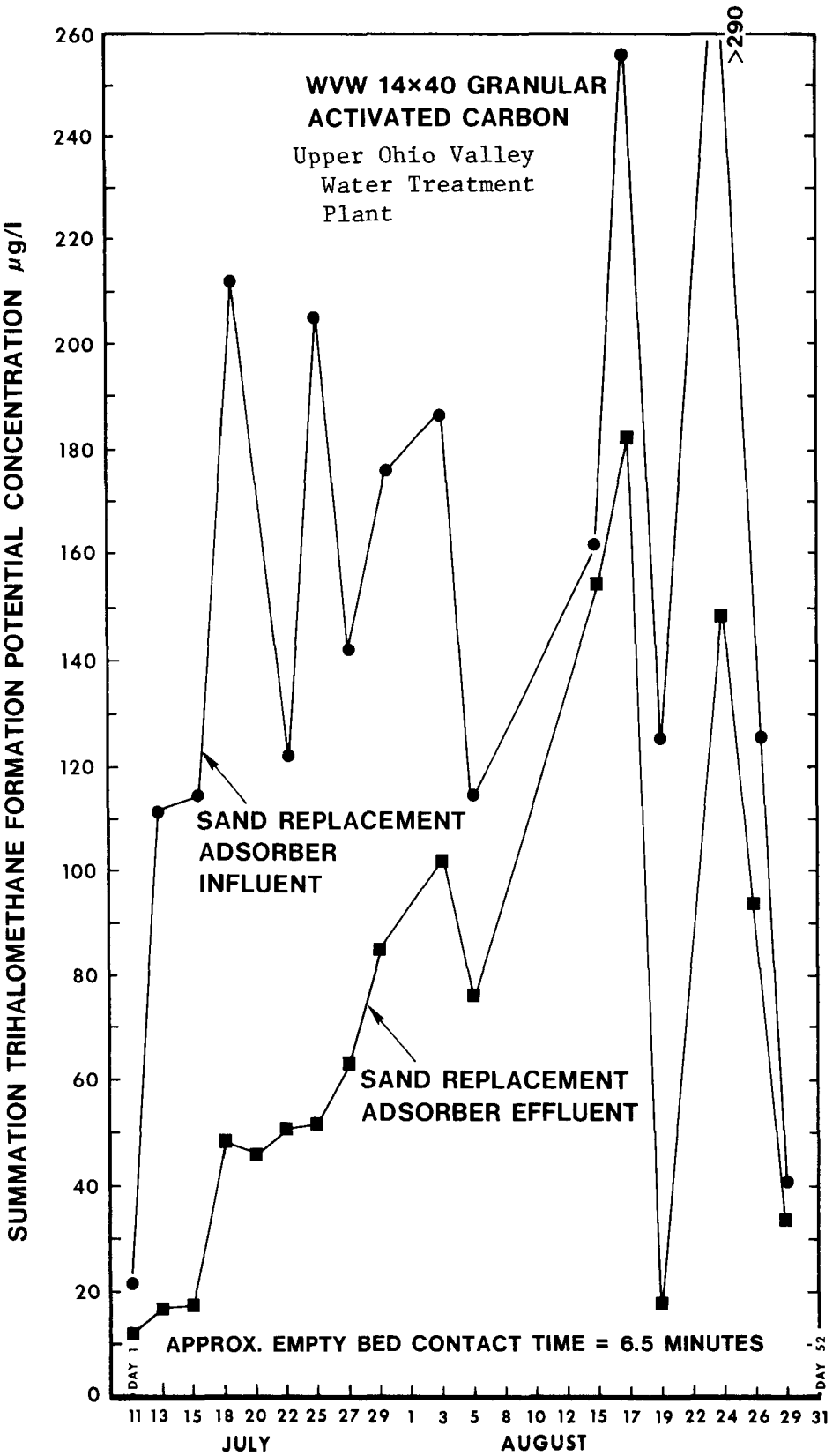

FIGURE 20 REMOVAL OF TRIHALOMETHANE PRECURSORS BY GRANULAR ACTIVATED CARBON BEDS

Class IV Compounds (Disinfection By-Products)

To determine the effectiveness of granular activated carbon to remove trihalomethanes, Cincinnati tap water, which contains these compounds, was exposed to granular activated carbon columns at various hydraulic loadings (different contact times). Chloroform was reduced 90 percent or more for about three weeks, (10 min. EBCT), then breakthrough was steady until the adsorber was exhausted at about the ninth or tenth week. The trihalomethanes containing bromine were effectively reduced by the granular activated carbon for 30 or more weeks. Figure 21 shows the difference in effectiveness of six different types of granular activated carbon for removing all of the trihalomethanes summed together.[64] In earlier field studies[65] where the applied water and the effluent from granular activated carbon beds were sampled, the findings regarding trihalomethane reductions were very similar to the laboratory results.

The second phase of the Florida study, which studied adsorption of organics from chlorinated water, also showed that chloroform was the trihalomethane least effectively adsorbed, while bromoform was adsorbed the best of the trihalomethanes. At the lower Mississippi River water treatment plant, ammonia is added after the addition of chlorine so the concentrations of trihalomethanes reaching the granular activated carbon bed were low, chloroform (1.8-46 µg/ℓ), bromodichloromethane (NF-6.2 µg/ℓ), dibromochloromethane (NF-12.8 µg/ℓ), bromoform (NF). Under these conditions the bromine-containing trihalomethanes were well removed, although chloroform began to appear consistently in the adsorber effluent at low concentrations after the fifth week. Adsorption-desorption cycles began after 13 weeks.

Figure 22, data from the water treatment plant in the upper Ohio Valley, shows a breakthrough pattern for the trihalomethanes very similar to the pilot plant data described above and shown in Figure 21. Here too, the bromine-containing trihalomethanes were removed better than chloroform.

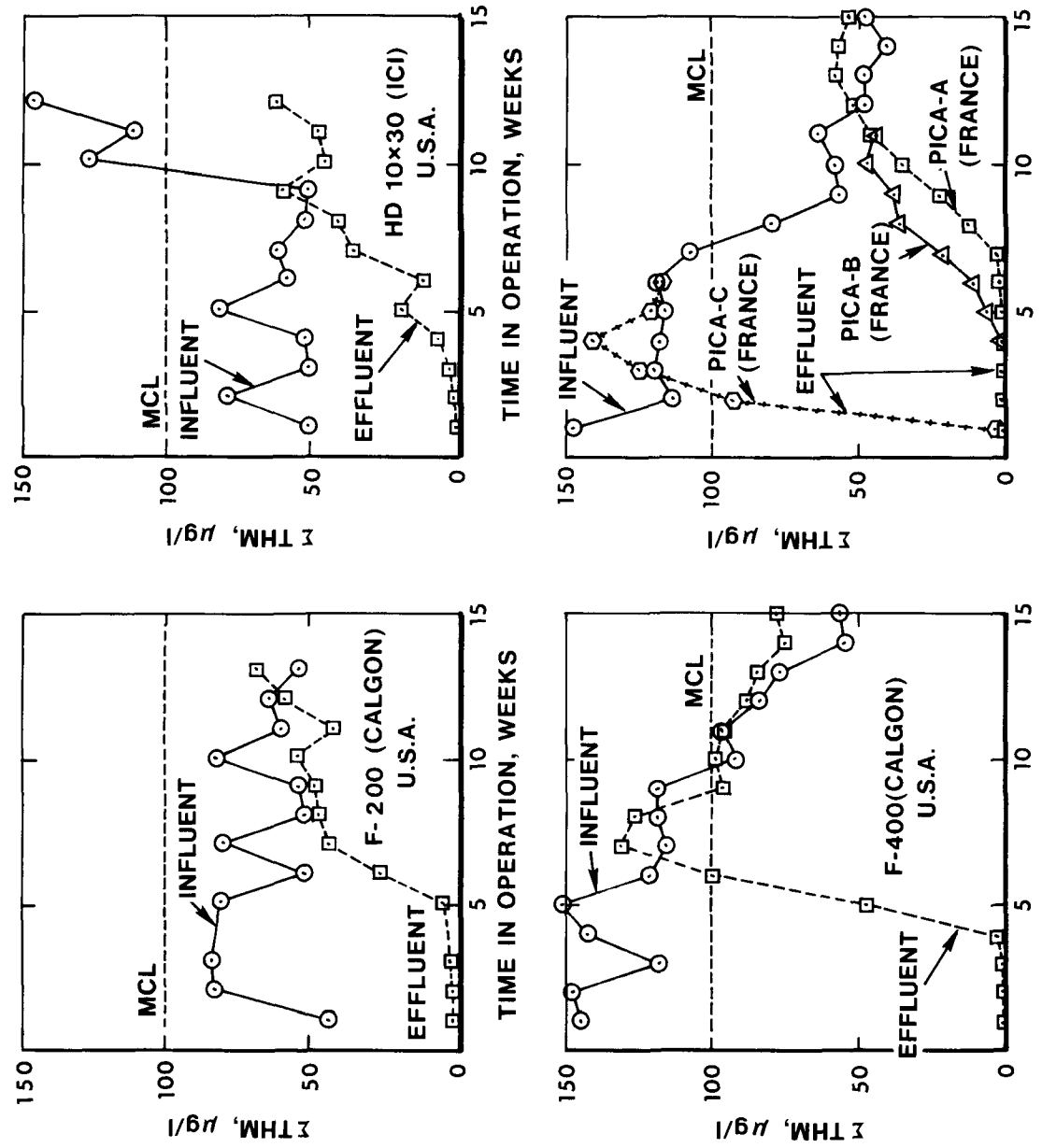

FIGURE 21 REMOVAL OF TRIHALOMETHANES FROM CINCINNATI, OHIO TAP WATER USING SIX TYPES OF GRANULAR ACTIVATED CARBON (EMPTY BED CONTACT TIME=10 MIN.)

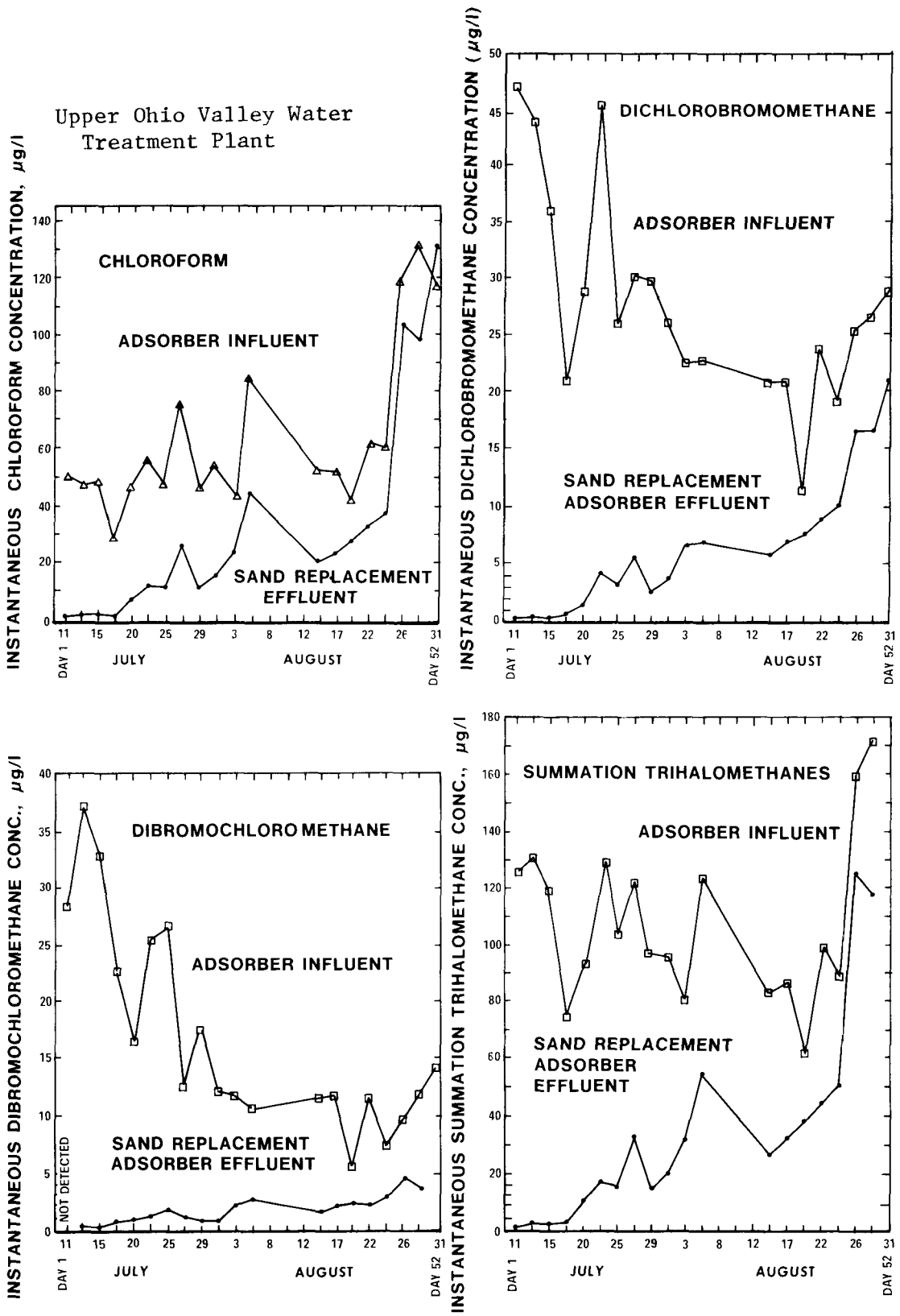

FIGURE 22. REMOVAL OF TRIHALOMETHANES BY GRANULAR ACTIVATED CARBON BEDS-6.5 MINUTE EMPTY BED CONTACT TIME-VIRGIN WVW 14×40 GRANULAR ACTIVATED CARBON

In summary, if the aromatics, taste and odor compounds, and certain pesticides can be categorized as strongly adsorbed onto granular activated carbon, then chloroform is located near the other end of the adsorption spectrum.

General Organic Parameters

Although not directly related to any single class of organic compounds discussed above, the use of an easily measured general parameter to monitor the performance of an adsorption treatment system is appealing from the standpoint of convenience and cost. The Water Supply Research Division pilot plant studies routinely include the following general organic measurements: non-purgeable organic carbon (NPOC)[66], ultra-violet absorbance (UV) at 254 nm[66], and fluorescence -- both the emission scan (EMS)[66] and the fixed wavelength procedure described by Silvia as the rapid fluorometric method (RFM)[67].

Figure 23 shows the pattern of each general organic parameter for the first 15 weeks after a fresh granular activated carbon adsorber was put into service. In an attempt to develop a simple test to predict the organic carbon content of effluents, UV, RFM and EMS data were correlated to NPOC. Table XV summarizes the regression analysis. The most promising relationship thusfar is between RFM and NPOC. A clearer understanding of these relationships and others, such as between some general parameter and trihalomethane (Class IV) or by-product precursor (Class III) concentrations is being sought through additional statistical analyses and should be available in the near future.

TABLE XV

RELATIONSHIP BETWEEN NPOC AND OTHER GENERAL ORGANIC PARAMETERS FOR MONITORING A GRANULAR ACTIVATED CARBON ADSORBER

	UV	RFM	EMS
(R^2) Coefficient of Determination	0.22	0.67	0.52
(R) Correlation Coefficient	0.47	0.82	0.72
Significant at 95% by F and t test	Yes	Yes	Yes
95% Confidence, interval, mg/ℓ	±0.73	±0.48	±0.58

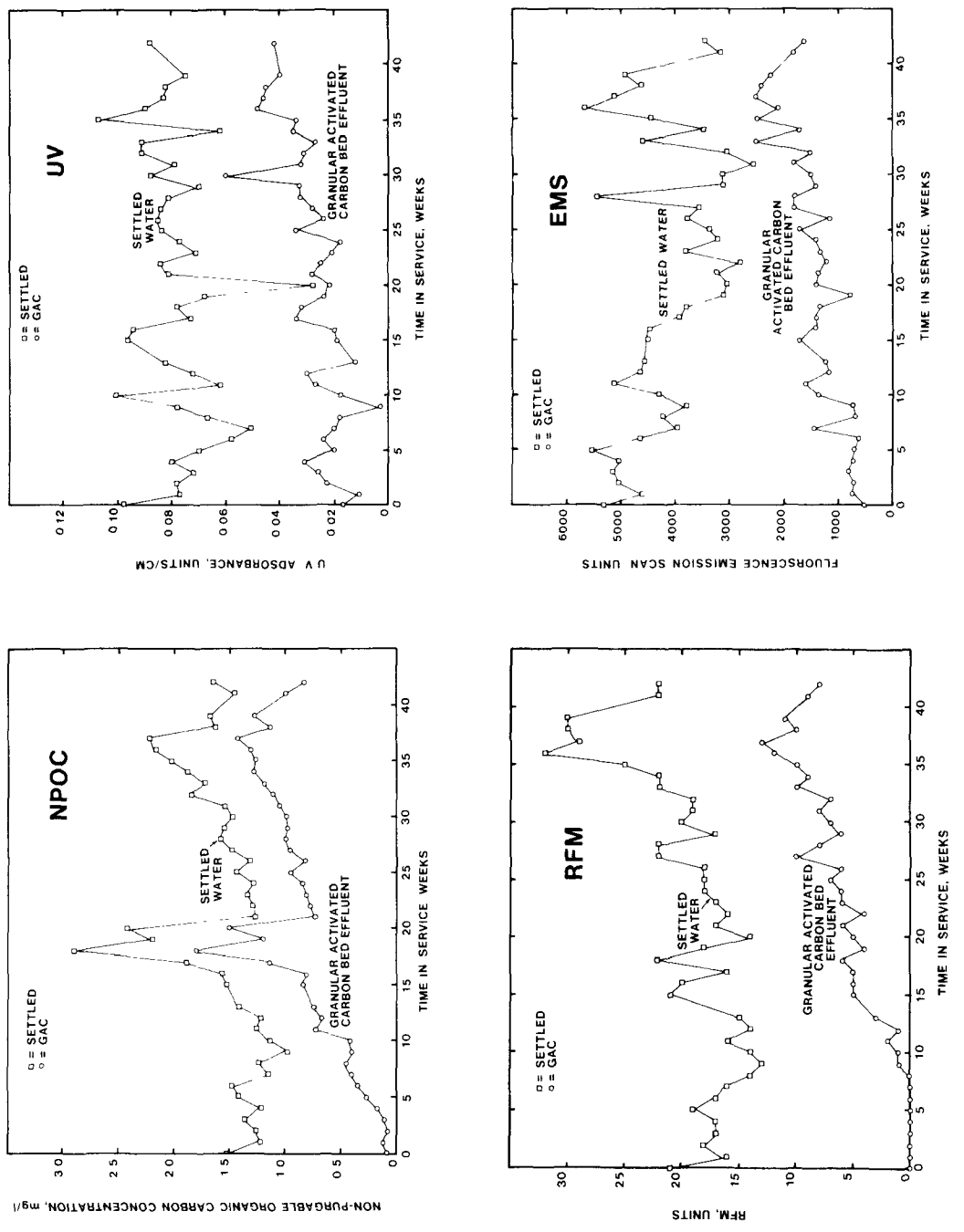

FIGURE 23. COMPARISON OF VARIOUS GENERAL ORGANIC PARAMETERS AS POSSIBILITIES FOR OPERATIONAL CONTROL OF GRANULAR ACTIVATED CARBON BEDS.

Thusfar, the best predictor of NPOC, RFM, has such a high 95 percent confidence interval ($\pm$0.48 mg/ℓ) that its potential use is discouraging. Sylvia[64], however, obtained better results correlating RFM measurements with granular activated carbon bed performance as measured by CCE-m, so some possibilities for this approach may exist in certain waters .

As noted above, in addition to correlating a more easily measured general organic parameter against NPOC, the use of a general parameter to predict performance of a granular activated activated carbon bed with respect to breakthrough of a specific organic compound or group of specific organic compounds is also an attractive concept. In the lower Mississippi River water treatment plant study, four general parameters have been correlated to total trihalomethanes, trihalomethane formation potential, and the sum of all of the non-trihalomethane chlorinated organic compounds in the adsorber effluent. Table XVI shows that, except for UV adsorbance, the correlation coefficients have good statistical significance. The confidence limits on these data are, however, not available at this time (Fall 1977). This effort will continue at this field site, as well as in the Water Supply Research Division pilot plant, and at other water treatment plant project locations.

TABLE XVI

RELATIONSHIP BETWEEN VARIOUS GENERAL ORGANIC PARAMETERS AND THREE CLASSES OF ORGANIC CONTAMINANTS

	NPOC (50 OBS)		EMS (42 OBS)		RFM (47 OBS)		UV (50 OBS)	
	r[a]	Signif.[b]	r	Signif.	r	Signif.	r	Signif
Class II Total Non-Trihalo-methane Organics	0.585	.00001	0.622	.00001	0.740	.00001	0.282	.047
Class III ΣTHMFP	0.723	.00001	0.658	.0001	0.770	.00001	0.366	.009
Class IV ΣTHM	0.631	.00001	0.745	.00001	0.747	.00001	0.306	.031

a - "r" is the correlation coefficient

b - "Signif" is the significance of the correlation coefficient, r (the smaller the value for "Signif" the greater the significance.)

OBS - Observations

Influence of Empty Bed Contact Time

One phase of the project studying the use of adsorbents to remove organics from a southern Florida groundwater includes the effect of empty bed contact time on organic removal using the techniques similar to those outlined in the "Procedure for Collection of Site Specific Design Data" in the Interim Treatment Guide (pages 23 to 26) and Appendix C. Finished water from the treatment plant was diverted to four pilot granular activated carbon columns connected in series. Each column contained 30 inches of 12x40 mesh activated carbon and was operated at a hydraulic loading of 3 gpm/ft^2. The nominal empty bed contact time for each column was 6.2 min. and thus the contact times were 6.2 min., 12.4 min., 18.6 min., and 24.8 min., respectively for the four columns. Twenty purgeable halogenated organic substances were monitored at the inlet and outlet of each column. Also TOC and Terminal THM concentration data were collected.

The ability to achieve a given quality of effluent for longer time periods (larger water volumes) is related to longer empty bed contact times (larger activated carbon volumes), Figures 24, 25, 26 and 27. Figure 26 for vinyl chloride is an exception as the relationship is not as definite for the data collected to date. Prior experience also showed that vinyl chloride removal by granular activated carbon adsorption was the most sporadic of all substances tested at this site. So far this has been the only substance to show such an erratic pattern. Figures 24, 25, and 27 show a "broad-wave" front for the substances tested, thus providing a more gradual approach toward equilibrium concentration than if a more "narrow-wave" front had occurred.

In order to assess the period of time between activated carbon reactivations for a given empty bed contact time, the three performance criteria discussed in the Interim Guide were applied to the data in Figures 24-27. Whenever a performance criterion was consistently exceeded, the first time at which the criterion was exceeded (see arrow on Figures) was used and the corresponding operating time and water volume treated calculated. The concentrations between data points were taken as linear.

Table XVII presenting the maximum duration of time in days of operation and liters treated when complying with each criterion shows that the TOC criterion is the most limiting of the three at all contact times for the conditions tested. TOC would have limited the operating time to 1.5 days, 4.5 days, 11.2 days and 18.6 days for the respective empty bed contact times.

Table XVIII is a different display of the prior data in which the activated carbon volumes used and water volumes treated are recalculated using the 6.2 min EBCT data as unity and presenting all data as ratios. Thus for the most stringent criterion, TOC, if two times the activated carbon volume is used,

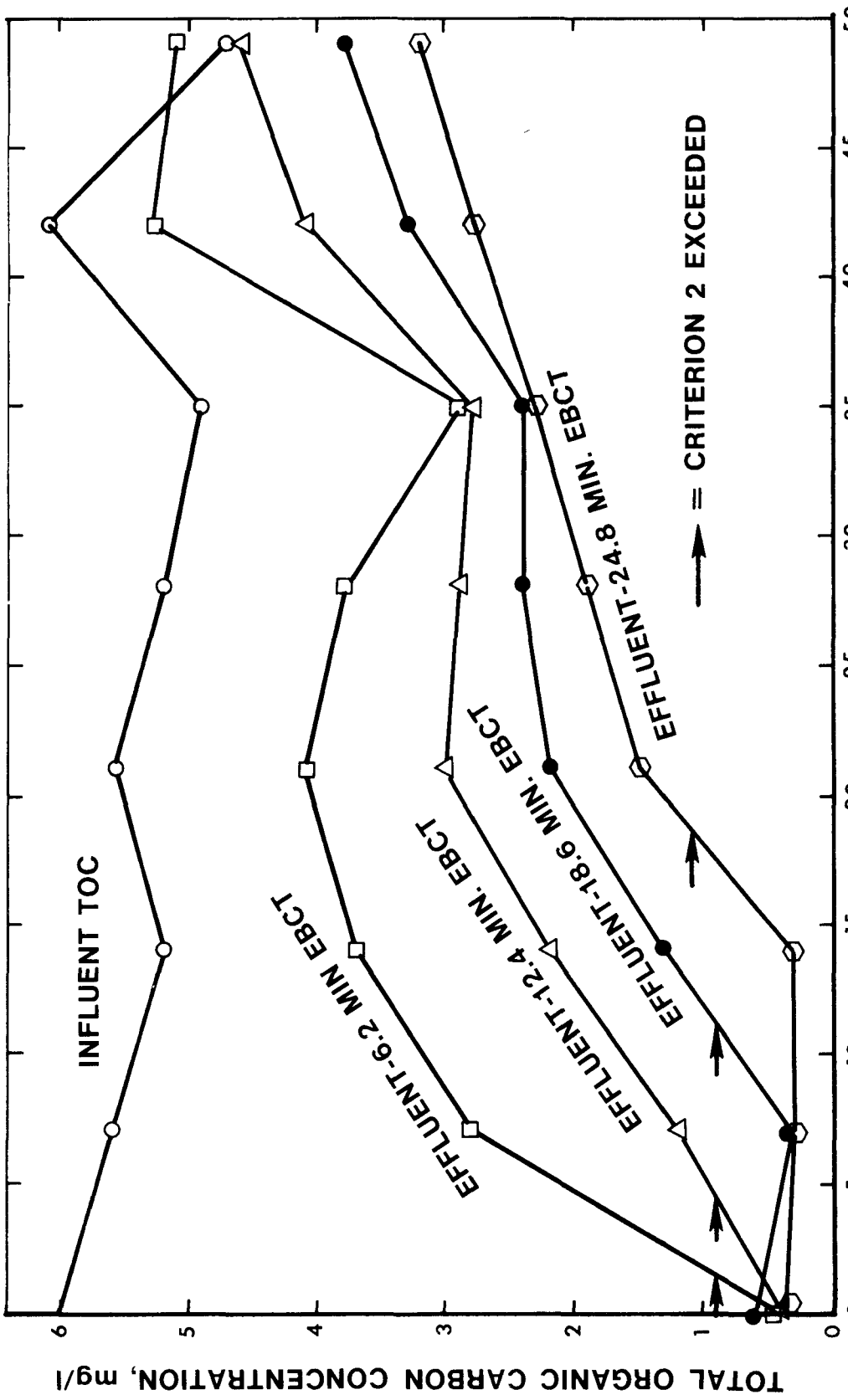

FIGURE 24. EXAMPLE OF THE INFLUENCE OF EMPTY BED CONTACT TIME ON ORGANIC CARBON REMOVAL

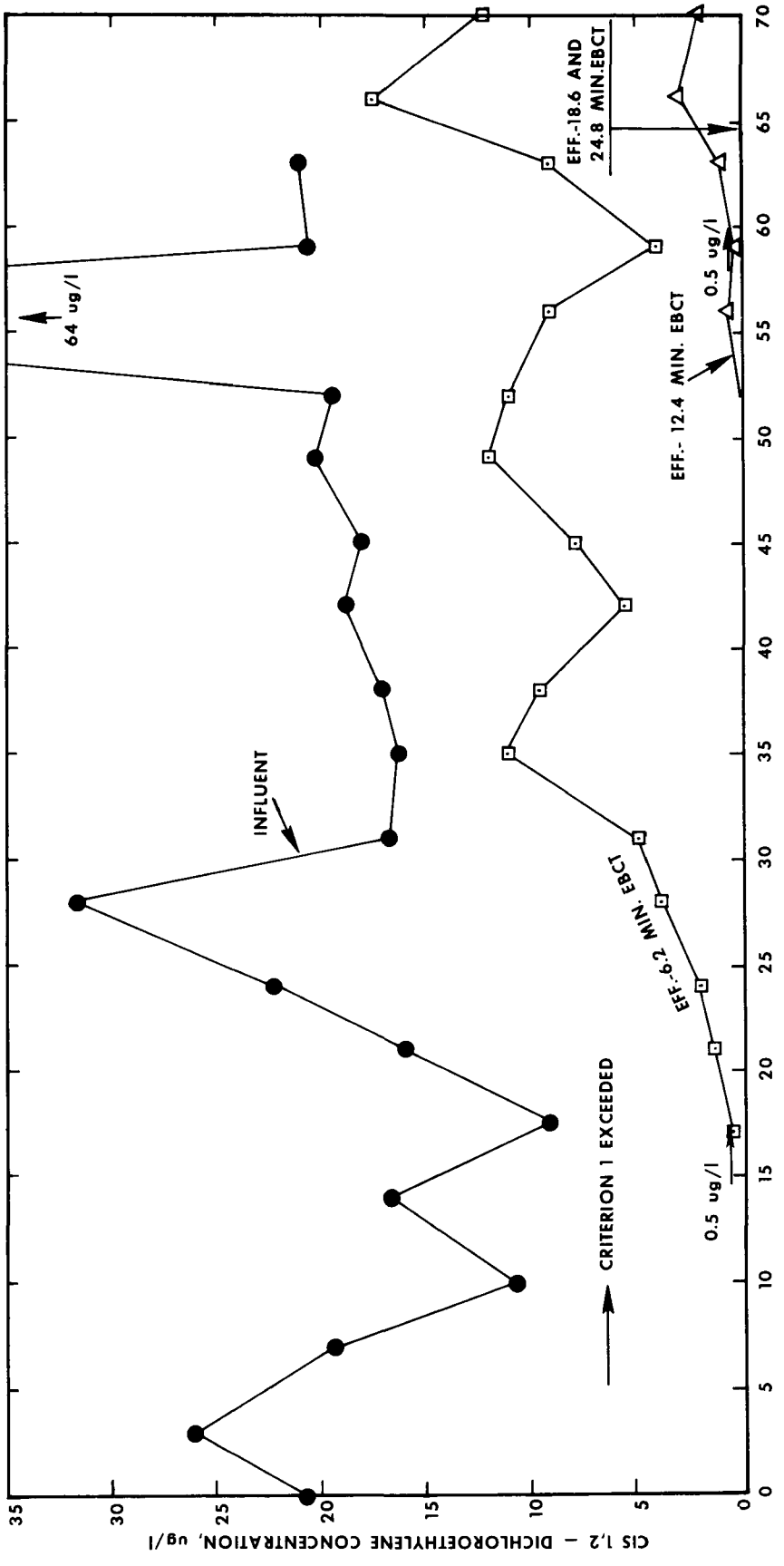

FIGURE 25 EXAMPLE OF THE INFLUENCE OF EMPTY BED CONTACT TIME ON CIS 1,2 - DICHLOROETHYLENE REMOVAL

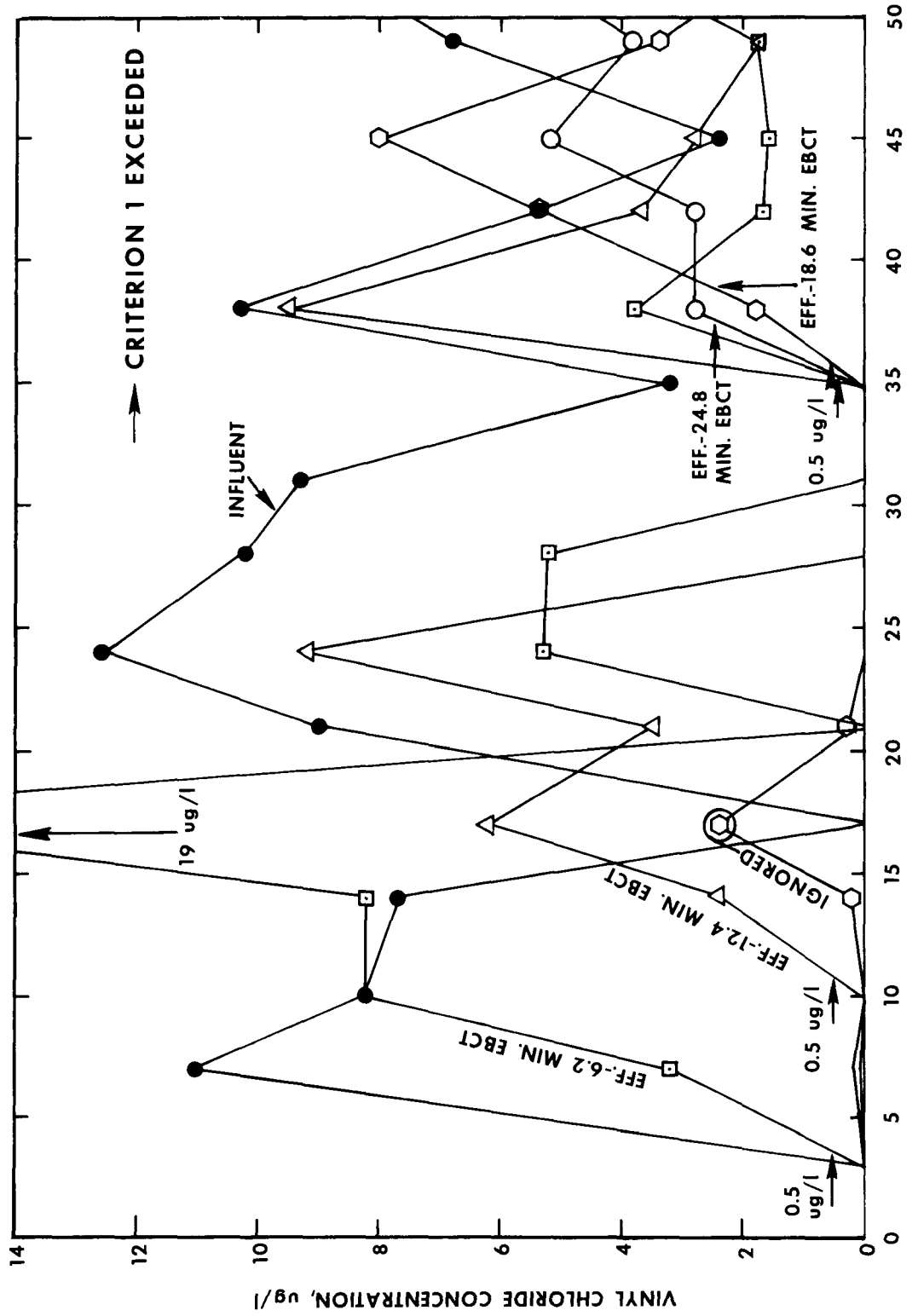

FIGURE 26 EXAMPLE OF THE INFLUENCE OF EMPTY BED CONTACT TIME ON VINYL CHLORIDE REMOVAL

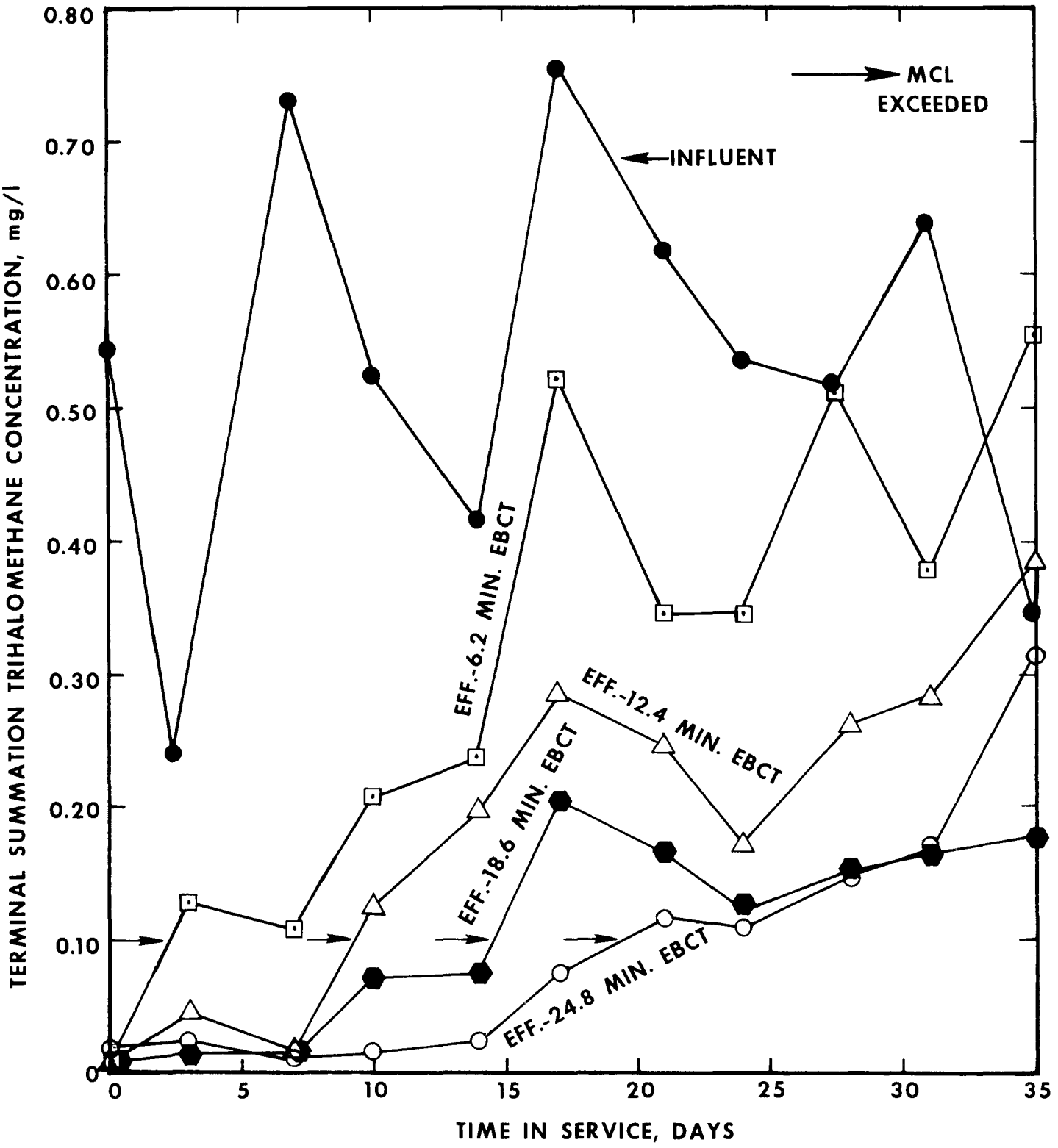

FIGURE 27 EXAMPLE OF THE INFLUENCE OF EMPTY BED CONTACT ON TERMINAL SUMMATION TRIHALOMETHANE REMOVA

TABLE XVII

DURATION OF RUN ALLOWED BY EACH CRITERION

Empty Bed Contact Time Minutes	Criterion No. 1 (Vinyl Chloride)		Criterion No. 1 (cis-1,2-Dichloro-ethylene)		Criterion No. 2 (TOC)		MCL	
	Days	Liters	Days	Liters	Days	Liters	Days	Liters
6.2	3.5	313.8	17.5	1573.3	1.5	132.5	2.3	204.8
12.4	10.8	966.4	60.5	5437.4	4.5	402.3	9.3	832.7
18.6	35.7	3196.1	-	-	11.2	999.6	14.5	1297.1
24.8	35.3	3096.5	-	-	18.6	1653.7	19.5	1733.2

- = Not yet exceeded criterion.

TABLE XVIII

RATIO OF VOLUME OF WATER TREATED IN COMPLIANCE WITH EACH CRITERION

EBCT Min.	Ratio of Act. Carbon Required	Criterion No. 1 Specific Organics (V.C.)	(cis)	Criterion No. 2 TOC	MCL
6.2	1	1	1	1	1
12.4	2	3.1	3.5	3.0	4.1
18.6	3	10.2	-	7.5	6.3
24.8	4	9.9	-	12.5	8.5

V.C. = Vinyl chloride

cis = cis-1,2-Dichloroethylene

- = Not yet exceeded criterion

three times the amount of water can be treated before the criterion is exceeded. Further, again doubling the empty bed contact time increases the length of time of operation over six more times, a favorable improvement. Similar beneficial results occurred relative to criterion one and the MCL requirements with a doubling of the "base" empty bed contact time, but redoubling produced only a proportional increase in operating time according to the MCL requirement.

This evaluation of empty bed contact time shows that increased quantities of activated carbon, at fixed flow conditions, resulted in the ability to treat more water before exceeding a given criterion. In each case the first doubling of empty bed contact time resulted in adsorber operating times that were proportionately greater than the increase increse in empty bed contact times for all criteria. This has an important impact on the economics of treatment, see pages 43-45 in the Interim Guide.

Two in-house studies on the influence of empty bed contact time on adsorber operating times, Figures 28 and 29, showed that for the two organic compounds, chloroform and carbon tetrachloride, the time to reach a given breakthrough point was approximately proportional to the empty bed contact time. Because of these different results in two different locations, this type of information should be collected in the location under study, as indicated on pages 23-26 of the Interim Treatment Guide.

Biological Growth and Endotoxin Production

Standard Plate Count

Controlling bacterial populations (and particularly killing or inactivating pathogenic microorganisms) is a primary goal of water treatment. Some concern, therefore, has been expressed about the possibility of bacteria proliferating within granular activated carbon beds. To investigate this, the bacterial quality of the untreated and treated water from the WSRD pilot plant was

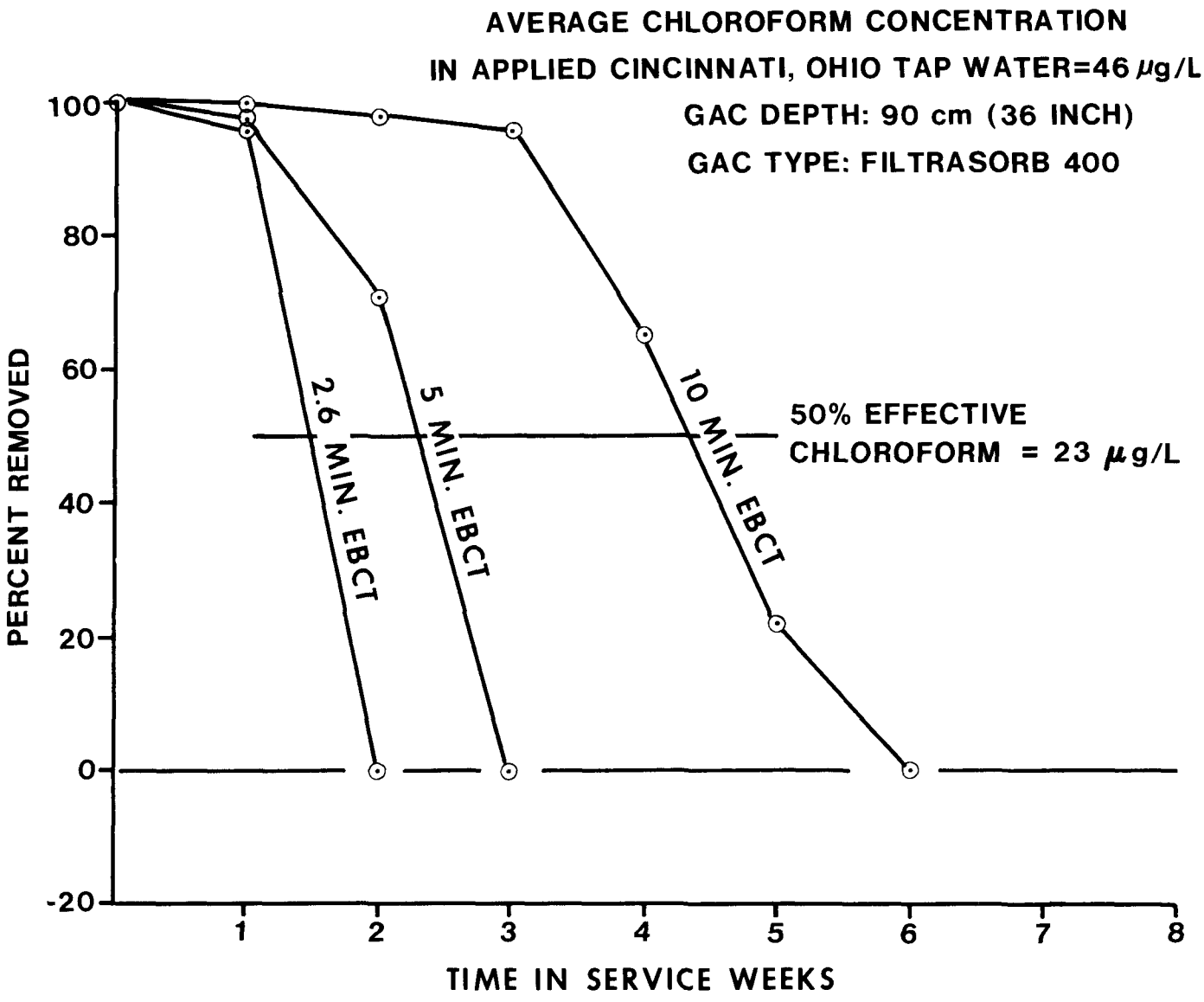

FIGURE 28. EFFECT OF EMPTY BED CONTACT TIME ON CHLOROFORM REMOVAL FROM TAP WATER.

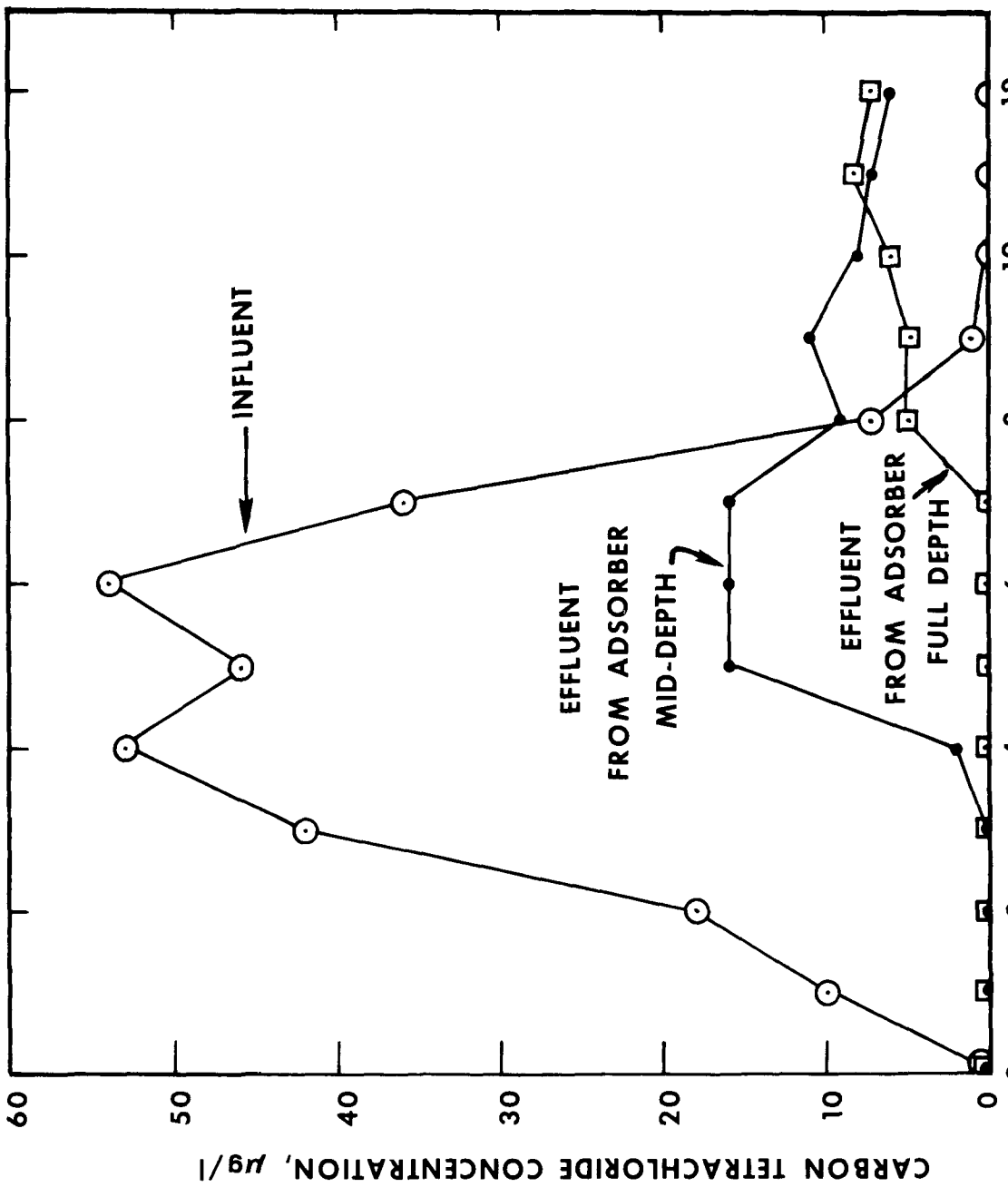

FIGURE 29 INFLUENCE OF EMPTY BED CONTACT TIME ON CARBON TETRACHLORIDE REMOVAL

routinely monitored over a four-month period by the staff of the WSRD Microbiological Treatment Branch using the Standard Plate Count (SPC) test. Samples were also collected intermittently and analyzed for total and fecal coliforms, however, these indicator organisms seldom survived the coagulation and settling processes and were never detected in the filter or adsorber effluents. The monthly average SPC (expressed as the geometric mean) for the pilot plant studies (see Table XIX), in general, show a two log (99 percent) reduction in the bacterial count through the treatment plant. Note that no disinfectant was added anywhere in the treatment process. Although an increase in bacterial populations was expected a priori, the SPC of the effluent from the granular activated carbon adsorber was slightly lower than the SPC in the companion sample taken from the dual media filter effluent. No attempt was made to measure attached growths. An attempt was made, however, to isolate and identify the predominant populations in the pilot plant. From the adsorber effluent, five or six different types of colonies could be recognized and two genera, Flavobacterium and Xanthomonas were identified from smear plates.

TABLE XIX

MONTHLY MEAN (G_m) STANDARD PLATE COUNT

(Pilot Plant Studies - Ohio River Water)

all bacterial counts are No./1 ml

Time in operation, Months,	Raw	Settled	Effluent from Dual Media Filter	Effluent from Granular Activated Carbon Adsorber
1	19,600	1650	137	63
2	12,000	1000	270	72
3	7,170	790	80	29
4	6,680	700	100	37

Endotoxins

Endotoxins are lipopolysaccharide-protein complexes produced in the cell walls of Gram-negative bacteria. The lipopolysaccharide portion of the complex is pyrogenic and as little as 1 μg can produce fever in a 700 kg horse.[68] Concern, therefore, has been expressed regarding the possible formation of endotoxins in granular activated carbon adsorbers because of bacteriological activity. For a 6-month period in 1977, the U.S. EPA Health Effects Research Laboratory (HERL) monitored bacterial endotoxin concentrations in untreated and treated water from the WSRD organics removal pilot plant. These were companion samples with those collected for Standard Plate Count analyses.

Using the Limulus lysate bioassay[69], HERL scientists observed a marked reduction in pyrogenic activity as a result of chemical coagulation (and settling) and a slight additional decrease through filtration by either dual media or granular activated carbon. The encouraging finding was that no increase in pyrogenic activity occurred in the effluent from the granular activated carbon bed. These data are shown in Table XX. An extramural project entitled "Pyrogenic Activity of Carbon-Filtered Waters" (EPA Grant No. R-804420010) is underway at Texas A&M University. Samples for endotoxin concentrations are being collected from full-scale water treatment plants utilizing granular activated carbon adsorption and the results from this definitive study should provide further evidence as to whether or not a problem exists.

TABLE XX

MONTHLY MEAN ENDOTOXIN CONCENTRATIONS IN OHIO RIVER WATER
(Pilot Plant Studies)

Time in Operation, Months	Endotoxin Concentration, μg/ℓ			
	Raw	Coagulated/Settled	Dual Media Effl.	Granular Activated Carbon Adsorbent Effluent
2	158	16	16	9
3	236	63	7	6
4	205	36	41	11
5	500	66	16	15
6	45	20	5	4
7	35	11	11	11

Ozone Enhanced Granular Activated Carbon Adsorption (Biological Activated Carbon)

One organic removal unit process being used in some locations has not yet been discussed in this report. It is currently (Fall 1977) receiving much attention, therefore, although much still needs to be known about the process, a discussion of a variation of granular activated carbon adsorption for organic contaminant control in which ozonation precedes the granular activated carbon treatment processes is included here. These two processes in combination are frequently called biological activated carbon.

Literature Review

As part of a research grant with the WSRD, Dr. Rip Rice, in collaboration with Public Technology, Inc., Washington, D. C. prepared a chapter of the final report on the "Status of Ozonation and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies" project summarizing what is known about biological activated carbon. The first few pages of that chapter, with some editing, are presented below.

A REVIEW OF THE STATUS OF OZONATION PRIOR TO GRANULAR ACTIVATED CARBON FOR REMOVAL OF DISSOLVED ORGANICS AND AMMONIA FROM WATER AND WASTEWATER

1. Introduction

In a recent article that discusses the use of granular activated carbon in water treatment, McCreary & Snoeyink[70] state that "beds of granular activated carbon (GAC) are a convenient place for microorganisms to grow because bacteria attach themselves to the irregular external surfaces of the activated carbon particles and are very difficult to dislodge via backwashing procedures." In the presence of soluble carbonaceous matter, which serves as food for these organisms, and in the absence of oxygen, anaerobic bacteria can develop. There are numerous instances in which sulfidic odors have been reported emanating from granular activated carbon columns used for the removal of dissolved organic materials contained in sewage treatment plant effluents[71,72] and drinking water supplies.[73]

On the other hand, with sufficient dissolved oxygen and carbonaceous matter, the bacteria that develop in activated carbon beds will be aerobic. These do not produce sulfidic odors.

Many of the advantages of biological granular activated carbon (BAC) were first recognized by German water treatment scientists in the 1960's in drinking water plants along the Rhine River in the Dusseldorf area. Subsequently, BAC processes also have been installed in Swiss and French drinking water treatment plants, and are subjects of active pilot studies in Holland and Belgium. In the United States, the U.S. Environmental Protection Agency's Water Supply Research Division in Cincinnati, Ohio has been testing a pilot BAC column since late in 1976 (see below.)

2. Fundamental Principles

Granular activated carbon is made biologically active by the deliberate introduction of sufficient dissolved oxygen (DO) to aqueous streams just before they are passed through GAC columns. As long as the water contains sufficient DO to maintain aerobicity of the bacteria and sufficient dissolved carbon to provide food, the aerobic bacteria will thrive in this environment. Eberhardt[74] has likened bacterial activity in such an ideal environment to a "herd of cows grazing in a luscious meadow." Pre-ozonation can convert larger, less biodegradable organic molecules into smaller, more biodegradable organics, for example, into acetic and oxalic acids. Sontheimer[75] has summarized the German findings to date which have led to the current theories of operation of BAC.

Although aerobic bacteria are necessary to obtain the benefits from BAC, so also is the adsorptive capacity of the GAC for the dissolved organic materials that will serve as food for these bacteria. This means that the surface area and pore volume of the activated carbon should be high. Stated another way, the organic materials present in solution should be adsorbable onto the activated carbon column, because the contact times of solutions with the activated carbon particles in the columns or beds are normally short (15-30 minutes). This does not necessarily give the bacteria sufficient time to degrade larger organic carbon molecules, ideally to carbon dioxide and water. Therefore, retaining the dissolved organic molecules in the activated carbon columns so that the bacteria then will have sufficient time to degrade them is important, even though the actual contact times involved are rather short.

Many organic materials are readily adsorbed onto GAC, but many others are not. For example, high molecular weight natural humic acids, so prevalent in drinking water supplies, are not readily adsorbed by activated carbon.[76] If solutions of these non-sorbable organic materials are ozonized before passage through the GAC columns, they are converted to more readily biodegradable organic materials.[76,77,78] At the same time, ozonation introduces a large quantity of oxygen into the water, which promotes aerobic bacterial growth.

3. Advantages of Biological Activated Carbon

In European pilot studies and in drinking water treatment plants by many workers[74,76,79-85] have shown that ozonation followed by granular activated carbon adsorption results in:

- More effective removal of dissolved organics from solution by the BAC,
- Increased operating life of the activated carbon columns before having to be reactivated especially if the GAC can be kept free of halogenated organics.
- Biological conversion of ammonia in the GAC columns,
- Use of less ozone for removing a given amount of organics than using ozonation alone. (BAC is more cost-effective over ozonation in removing Dissolved Organic Carbon - DOC),
- Filtrates from BAC columns in drinking water plants can be treated with small quantities (0.1-0.5 mg/ℓ) of chlorine or chlorine dioxide, which produces drinking water of acceptable bacterial quality (zero coliforms) and provides a residual disinfectant for distribution systems.

Independent studies on physical-chemical treated sewage at the Cleveland Regional Sewer District,[78] and in Israel[86] have confirmed these advantages with respect to removing organic materials.

4. European Background

Introduction of granular activated carbon into European drinking water treatment practices occurred after World War II. Its initial application was for dechlorination, then for tastes and odor removal.[87] Many surface waters containing ammonia undergo break-point chlorination at the beginning of the treatment process. This technique effectively removes ammonia, but produces considerable amounts of residual chlorine and chlorinated products in the water.[85] German water treatment objectives are to process surface waters to the same quality as that of natural groundwater (which does not have to be treated in many cases). Therefore, waters

treated by break-point chlorination have to be dechlorinated before they are treated further or distributed.[88] Schalekamp[80] points out that in Switzerland a residual chlorine concentration of only 0.05 mg/ℓ is permitted in finished drinking water. Therefore, the raw water chlorine dose is removed by granular activated carbon prior to the addition of 0.05 mg/ℓ of chlorine dioxide for final disinfection.

Combinations of ozone and granular activated carbon first were installed in the Dusseldorf area in the early 1960's[87] but nearly ten years passed until the biological activity in the activated carbon columns was recognized as being beneficial. By the early 1960's, the lower Rhine River water quality had declined, and advantage was taken of filtration of organic materials from the river water through the sand banks of the Rhine. Wells were dug into the river banks and water is drawn from these wells as the treatment plant raw water.

In the intervening years since the introduction of ozone/activated carbon at Dusseldorf, the beneficial effects of biological activity in the activated carbon columns have been recognized, characterized and optimized. After ozonation, the water is allowed to stand for 20-30 minutes to allow the more refractory organic compounds sufficient time to react with residual ozone. This retention time also allows residual ozone to be utilized, rather than simply to be destroyed when passed through the activated carbon column.

On the other hand, the Rhine River also contains considerable amounts of chlorinated organic materials that are not removed during river bank filtration. These halogenated materials also are more resistant to oxidation by ozone than are non-halogenated organics and thus are less likely to be converted into easily biodegradable materials. In addition, halogenated organics are variably adsorbed onto activated carbon.[19,89]

Combining the variable adsorptivity of halogenated organics compounds on granular activated carbon with their lesser reactivity upon ozonation and their lower biodegradability means that breakthrough of halogenated organic compounds occurs sooner than does breakthrough of non-halogenated organic compounds, even if the granular activated carbon columns are biologically activated. Thus German water works along the Rhine in the Dusseldorf area monitor their activated carbon column capacities for Total Organic Chlorine (TOCl)[90-92] as well as by DOC[93] and/or UV absorption. Activated carbon columns at three Dusseldorf plants along the Rhein (Flehe, Am Staad, Holthausen) are backwashed every 4-6 weeks and reactivated every 6 months.

When Dusseldorf activated carbons are thermally reactived, however, only some 80 percent of the activated carbon charge is taken out of the columns. This leaves a portion of biologically active activated carbon in the column so that the level of bioactivity will not drop significantly when fresh or reactivated activated carbon is added. With fresh activated carbon columns, about 15 days of operation usually are required for biological activity to build up to an effective "steady state", particularly for ammonia removal.[94]

WSRD Pilot Plant Results

In late 1976, WSRD began a pilot plant study on the use of ozone to extend the life of a granular activated carbon adsorber used as a sand replacement system as measured by Total Organic Carbon - and Trihalomethane Formation Potential (2 day, 25°C) concentrations. This study was prompted by the successful results from pilot- and full-scale BAC tests conducted in Europe (principally West Germany) cited above.

In this test a granular activated carbon adsorber receiving settled ozonated water and a granular activated carbon adsorber receiving settled unozonated water were operated for a 10 month study period. Both units had about a 9 minute empty bed contact time. Ozone dosages applied to the settled water (20 minute plug flow contact time) and dissolved ozone concentrations prior to filtration or adsorption are shown in Figure 30. Because of an increase in ozone demand within the system and the resultant loss of ozone residual, the applied ozone dose was increased following ozone contactor cleaning early in the 9th month of operation.

Figure 31 compares the TOC concentrations in both effluents. Figure 31 illustrates the extension in bed life afforded by the combination of ozone followed by granular activated carbon. Operating time was extended from about 3-3/4 months to about 7-1/2 months according to Criterion 2, increase of 0.5 mg/ℓ of TOC concentration.

Figure 32 shows a similar trend for the removal of trihalomethane formation potential, although the MCL requirement was never exceeded in either effluent during this study. The results of this study are encouraging enough to prompt additional in-house and extramural research on biological activated carbon during FY78, particularly to determine whether or not the use of ozonation prior to adsorption improves granular activated carbon performance with respect to Criterion 1, the control of low molecular weight halogenated organic compounds.

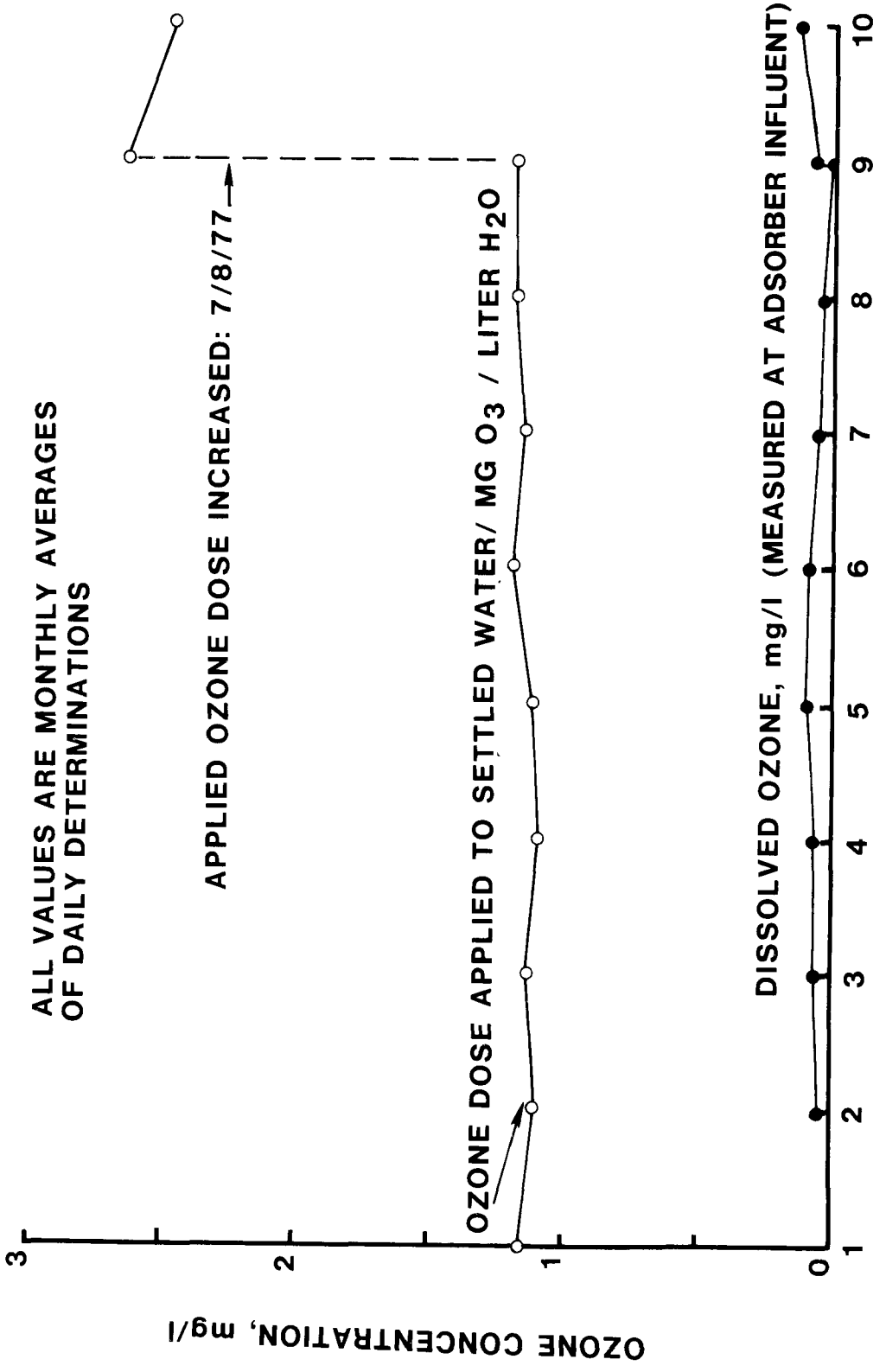

FIGURE 30. OZONE CONCENTRATIONS

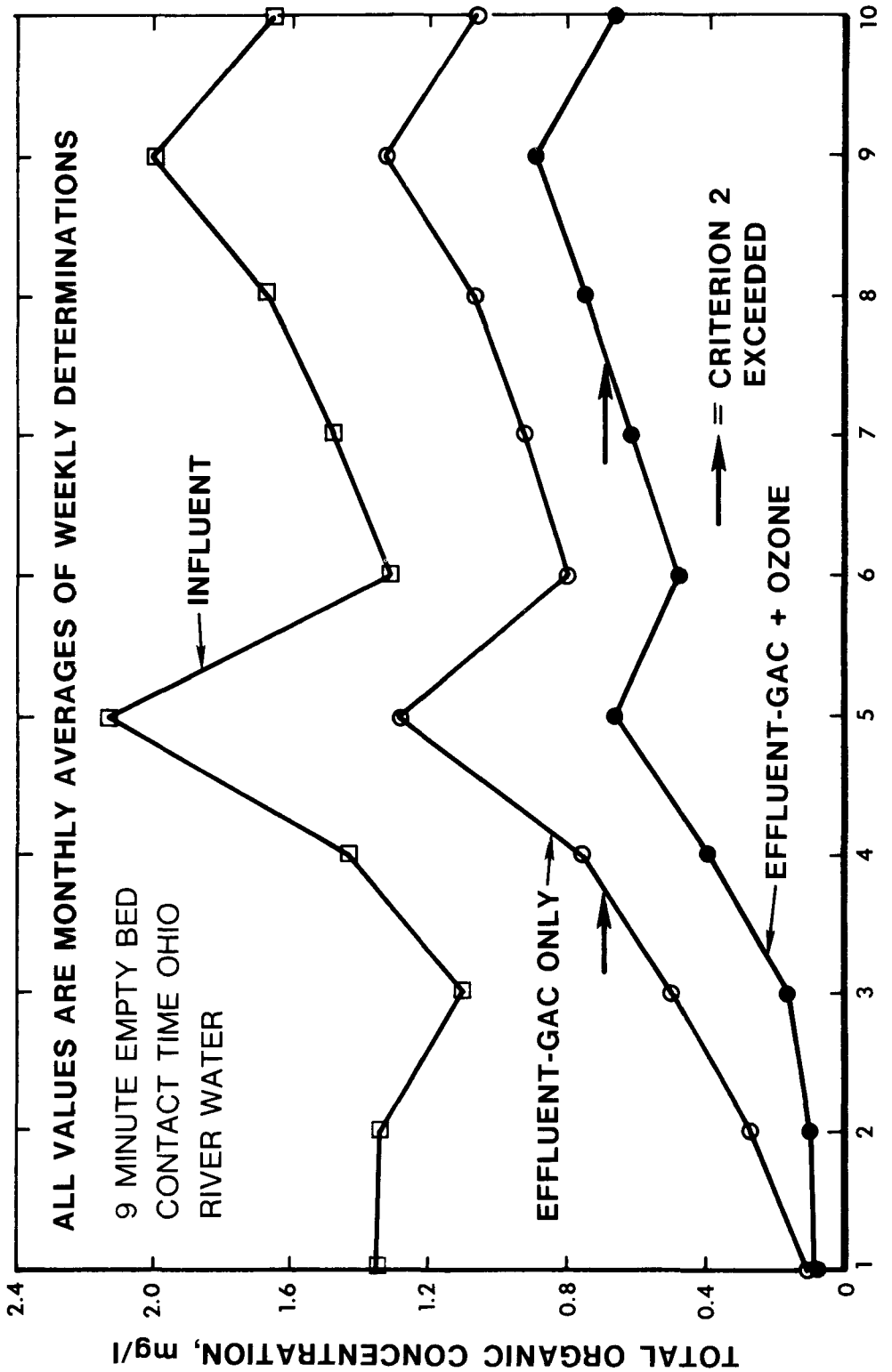

FIGURE 31. INFLUENCE OF OZONATION PRIOR TO ADSORPTION ON ORGANIC CARBON REMOVAL

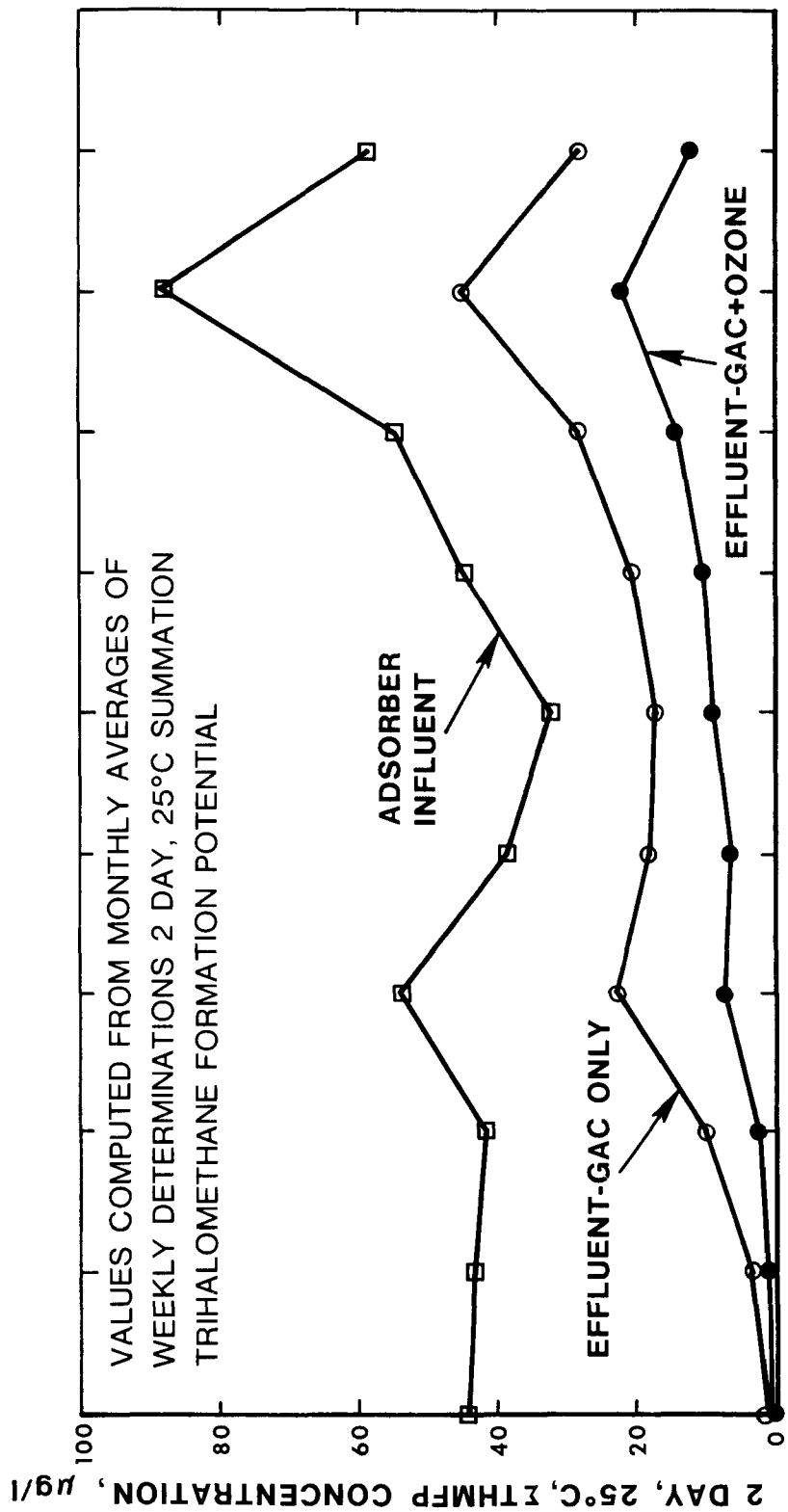

FIGURE 32. INFLUENCE OF OZONATION PRIOR TO ADSORPTION ON TRIHALOMETHANE FORMATION POTENTIAL REMOVAL

Economic Analysis Data

This text supplements the economic analysis information presented in the Interim Guide on pages 36 to 54, and is divided into five sections. The first section contains basic cost information that can be used to present a generalized framework for considering the cost impact of using granular activated carbon adsorption. In the next two sections, specific operational configurations and their influence on system costs are considered. For example, the tradeoffs that exist between Empty Bed Contact Time (EBCT) and Reactivation Frequency (RF) are examined in one section, and the effect of activated carbon cost and reactivation frequency is considered in the other. In the fourth section the impact of inflation on the choice of systems is evaluated. Because reactivation is a significant portion of the cost of a granular activated carbon treatment system, it is considered separately in the final section. Another source of supplementary economic analysis information is the Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes.[65]

Basic Costs

The data utilized in this section are the same as used to develop costs in the Interim Guide. Tables XI, XII, and XIII, and Figure 13 in the Interim Guide pages 37, 38, 40, and 42, respectively provide examples of the use of this baseline information.

Influence of Empty Bed Contact Time

As discussed in the Interim Guide examining the cost tradeoffs that exist between bed depth (EBCT) and reactivation frequency (RF) for a given quality of water is important. This relationship is examined using an "R" ratio. The "R" ratio allows the changing of two variables at one time (EBCT and RF). For example, in a sand replacement system, if the removal efficiency of granular activated carbon is proportional to EBCT and RF, then a system with an EBCT of 10 minutes and an RP of one month (R = 0.1) might be assumed to be equivalent in cost to one with an EBCT of 20 minutes and an RF of two months (R = 0.1). As shown on page 44 in the Interim Guide, however, although the R's are the same, the costs are not. Table XXI duplicates the data in Table XIV (page 41 of the Interim Guide) with the exception that values for "R" have been added.

Another way of examining the tradeoff between cost, RF, and EBCT is shown in Figures 33, 34, 35, and 36. In these figures the relationship that exists between the cost, EBCT, and RF for 10 and 100 mgd sand replacement systems and for 10 and 100 mgd postfilter adsorbers can be seen. The problems of non-proportionality between cost and performance can also be seen in these data. For example, in Figure 35 if the required EBCT was 10 minutes with a one month reactivation frequency, the unit cost would be 6.6 cents/1000 gal. If the EBCT were increased to 18 minutes, the period between reactivations would have to be increased to approximately 2.5 months or greater to achieve a favorable economic tradeoff. Therefore, to merit an 80 percent increase in empty bed contact time, the period between reactivations would have to increase by at least 150 percent. This important concept is examined more fully both in the Interim Guide (see pages 27, 34, and 35) and earlier in Appendix A, pages A69 to A76.

Table XXI. COST COMPARISON AMONG GRANULAR ACTIVATED CARBON SYSTEMS

System Type	Design Flow (mgd)	Peak Capacity (mgd)	Empty Bed Contact Time (minutes)	Reactivation Frequency in Months									
				0.1 mo.		0.25 mo.		0.5 mo.		0.75 mo.		1.0 mo.	
				¢/1000 gal	R *	¢/1000 gal	R	¢/1000 gal	R	¢/1000 gal	R	¢/1000 gal	R
Sand Replacement	70	100	14.3	62.4	0.007	27.9	0.017	15.8	0.035	11.5	0.052	9.3	0.070
	70	100	28.6	118.6	0.003	52.0	0.009	28.8	0.017	20.8	0.026	16.7	0.035
	70	100	42.9	173.6	0.002	75.4	0.006	41.4	0.012	29.7	0.017	23.7	0.023
Sand Replacement	70	70	10	45.1	0.010	20.4	0.025	11.7	0.050	8.6	0.075	7.0	0.100
	70	70	20	85.1	0.005	37.7	0.012	21.1	0.025	15.3	0.038	12.3	0.050
	70	70	30	124.1	0.003	54.3	0.008	30.1	0.017	21.7	0.025	17.4	0.033
Post-Filter Adsorber	70	70	10	32.7	0.010	17.4	0.025	11.8	0.050	9.8	0.075	8.7	0.100
	70	70	20	57.8	0.005	28.9	0.012	18.6	0.025	14.9	0.038	13.0	0.050
	70	70	30	82.0	0.003	39.8	0.008	24.9	0.017	19.6	0.025	16.9	0.033

* $R = \frac{\text{time between reactivations in months}}{\text{empty bed contact time in minutes}}$

Table XXI. COST COMPARISON AMONG GRANULAR ACTIVATED CARBON SYSTEMS (Contd.)

System Type	Design Flow (mgd)	Peak Capacity (mgd)	Empty Bed Contact Time (minutes)	Reactivation Frequency in Months									
				2.0 mo.		3.0 mo.		4.0 mo.		5.0 mo.		6.0 mo.	
				¢/1000 gal	R*	¢/1000 gal	R	¢/1000 gal	R	¢/1000 gal	R	¢/1000 gal	R
Sand Replacement	70	100	14.3	5.8	0.140	4.5	0.210	3.9	0.280	3.4	0.350	3.1	0.420
	70	100	28.6	10.2	0.070	7.9	0.105	6.7	0.140	5.9	0.175	5.4	0.210
	70	100	42.9	14.4	0.047	11.1	0.070	9.4	0.093	8.3	0.117	7.6	0.140
Sand Replacement	70	70	10	4.4	0.200	3.5	0.300	2.9	0.400	2.6	0.500	2.4	0.600
	70	70	20	7.6	0.100	5.9	0.150	5.0	0.200	4.5	0.250	4.1	0.300
	70	70	30	10.6	0.067	8.2	0.100	7.0	0.133	6.2	0.167	5.6	0.200
Post-Filter Adsorber	70	70	10	6.9	0.200	6.2	0.300	5.9	0.400	5.6	0.500	5.5	0.600
	70	70	20	9.9	0.100	8.7	0.150	8.1	0.200	7.7	0.250	7.5	0.300
	70	70	30	12.5	0.067	10.9	0.100	10.1	0.133	9.5	0.167	9.2	0.200

* $R = \frac{\text{time between reactivations in months}}{\text{empty bed contact time in minutes}}$

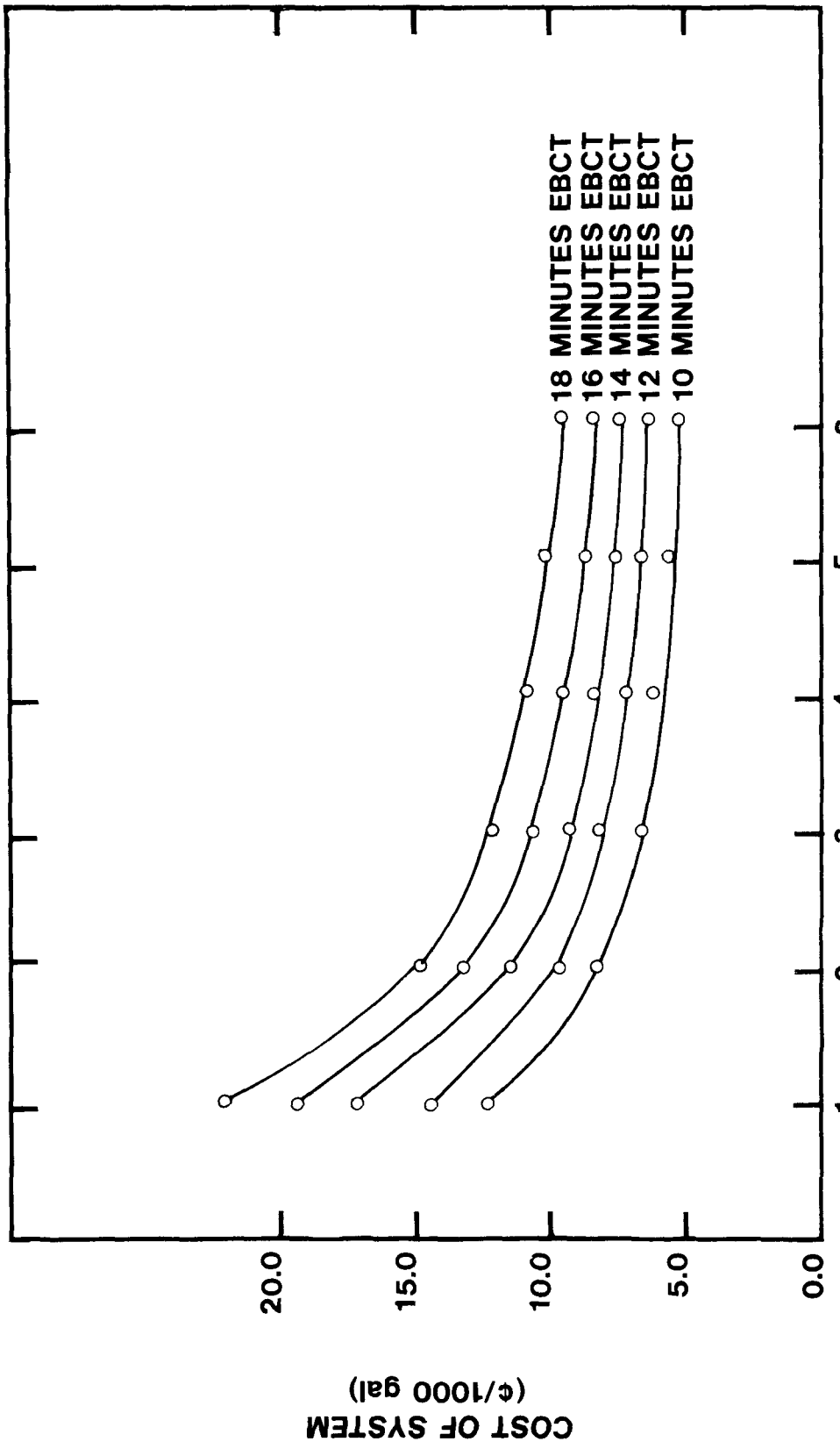

FIGURE 33 EFFECT OF EMPTY BED CONTACT TIME (EBCT) AND REACTIVATION PERIOD ON SYSTEM COST FOR 10 mgd SAND REPLACEMENT SYSTEM

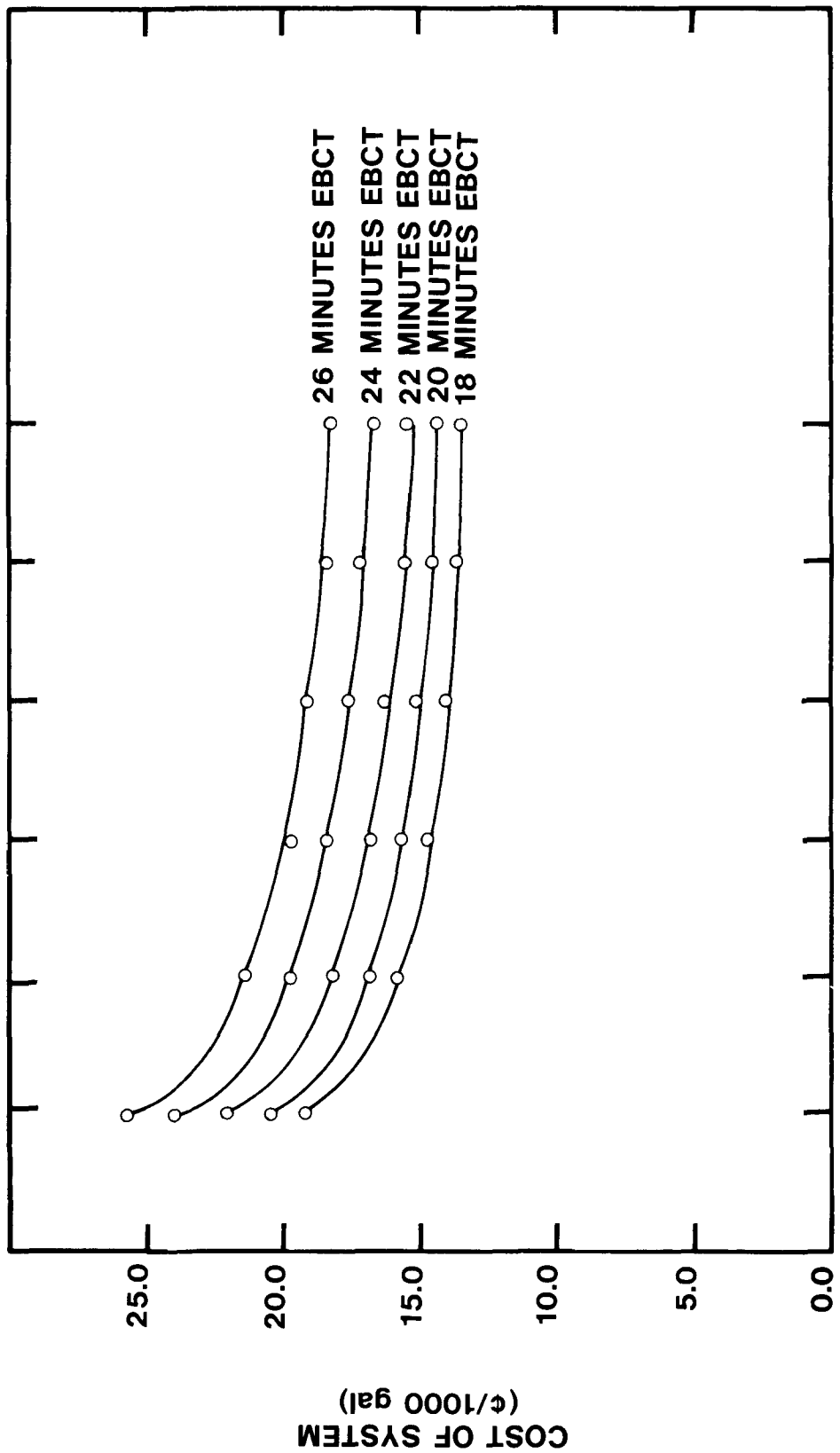

FIGURE 34 EFFECT OF EMPTY BED CONTACT TIME (EBCT) AND REACTIVATION PERIOD ON SYSTEM COST FOR 10 mgd POST-FILTER ADSORBER

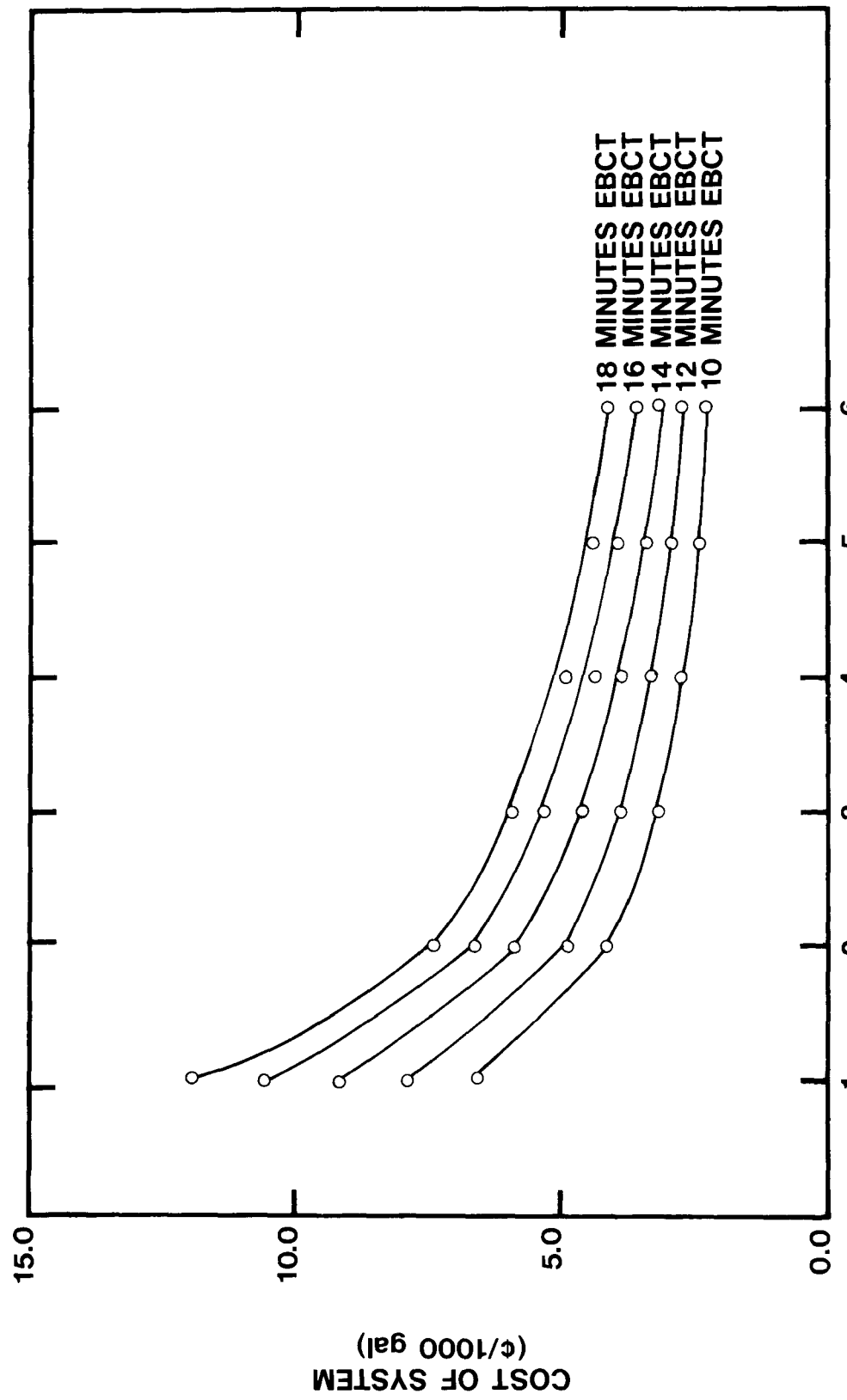

FIGURE 35 EFFECT OF EMPTY BED CONTACT TIME (EBCT) AND REACTIVATION PERIOD ON SYSTEM COST FOR 100 mgd SAND REPLACEMENT SYSTEM

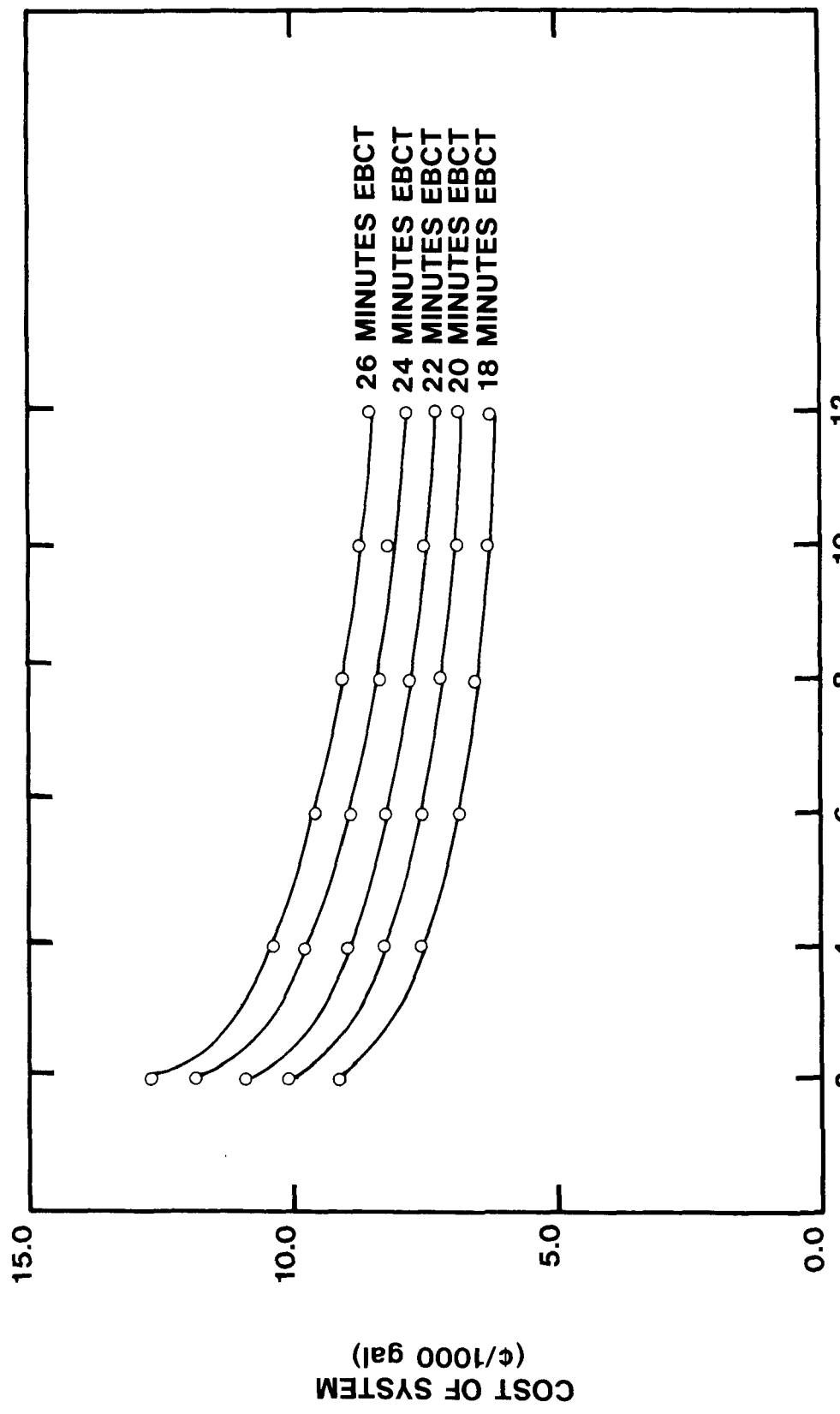

FIGURE 36 EFFECT OF EMPTY BED CONTACT TIME (EBCT) AND REACTIVATION PERIOD ON SYSTEM COST FOR 100 mgd POST-FILTER ADSORBER

Influence of Granular Activated Carbon Cost

Because of the wide variations in the types of activated carbon available and their prices and performances, a water purveyor must have some understanding of the relationship between activated carbon cost and performance. If a lower cost activated carbon also has lower performance, requiring more frequent reactivation, then its use may result in higher total system cost as opposed to using a higher cost carbon with better performance. Figures 37 through 39 show the effect of activated carbon cost and RF on the cost of 10 and 100 mgd sand replacement systems and for a 100 mgd post-filter adsorber system, see also page 48 of the Interim Guide.

Influence of Inflation

In the Interim Guide, Table XV (page 53) contains a summary of the "present value" of the expenditures for 10 and 100 mgd sand replacement and 10 and 100 mgd post-filter adsorber systems. These data have been calculated for two discount rates (6 percent and 8 percent) and three inflation rates (5 percent, 7 percent, and 9 percent). Capital expenditures were assumed to be amortized over 20 years at 7 percent interest, and reflect a continuous, constant expenditure pattern over the life of the facility.

Tables XXII, XXIII and XXIV show the costs over time for 10 and 100 mgd sand replacement systems and 10 and 100 mgd post-filter adsorption systems at assumed inflation rates of 5 percent, 7 percent, and 9 percent. Table XV (page 53) in the Interim Guide summarizes present value calculations for the given investment streams for each combination of system configuration and inflation rate.

Figures 40 and 41 supplement Figures 18 and 19 in the Interim Guide (pages 50 and 52) by showing the effect of 5 percent and 7 percent inflation rates for two 10 mgd systems (one of each type.) In contrast to the 100 mgd systems, the post-filter adsorbers never become less expensive than the sand

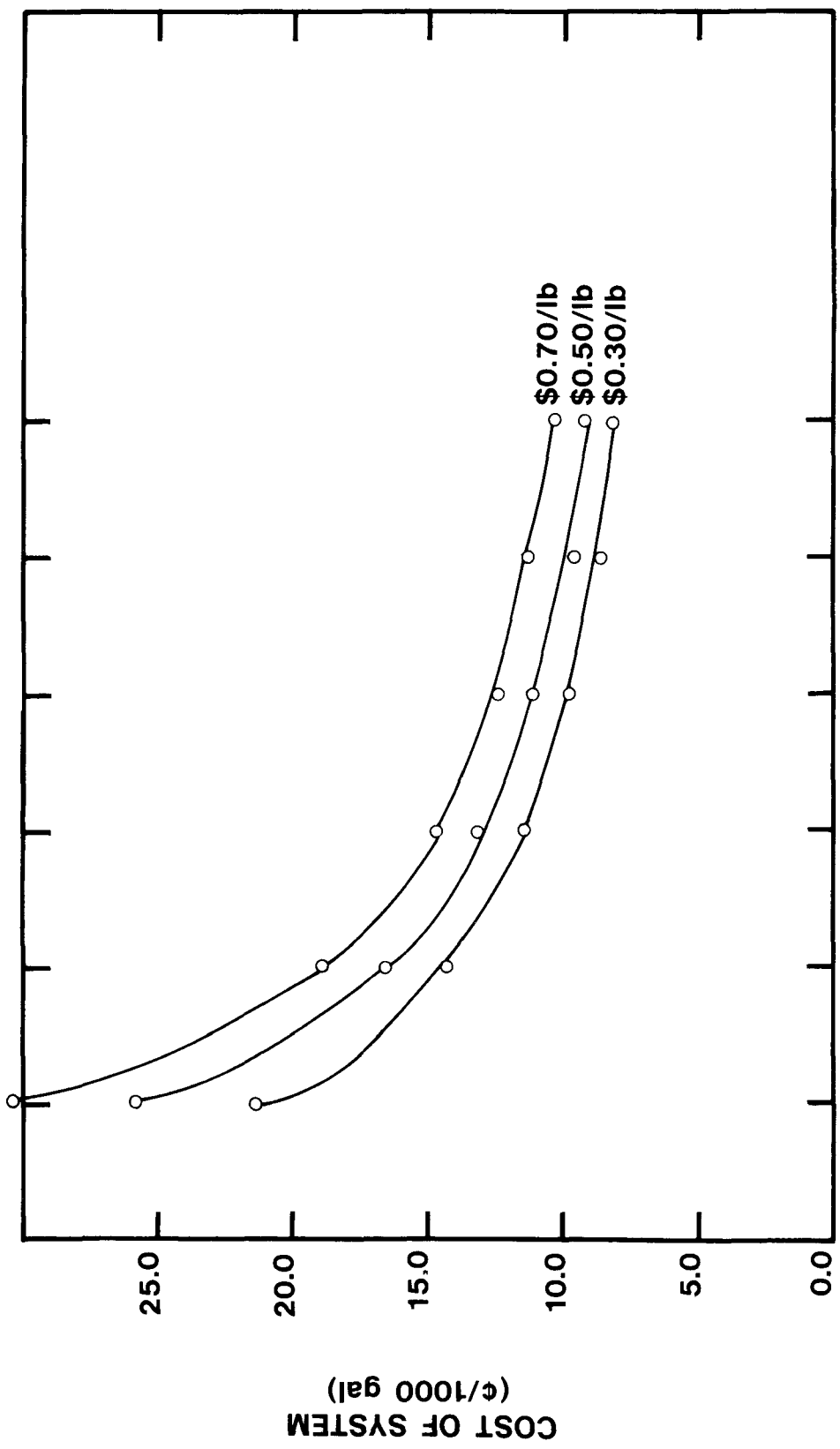

FIGURE 37 EFFECT OF ACTIVATED CARBON COST AND REACTIVATION PERIOD ON SYSTEM COST FOR 10 mgd SAND REPLACEMENT SYSTEM

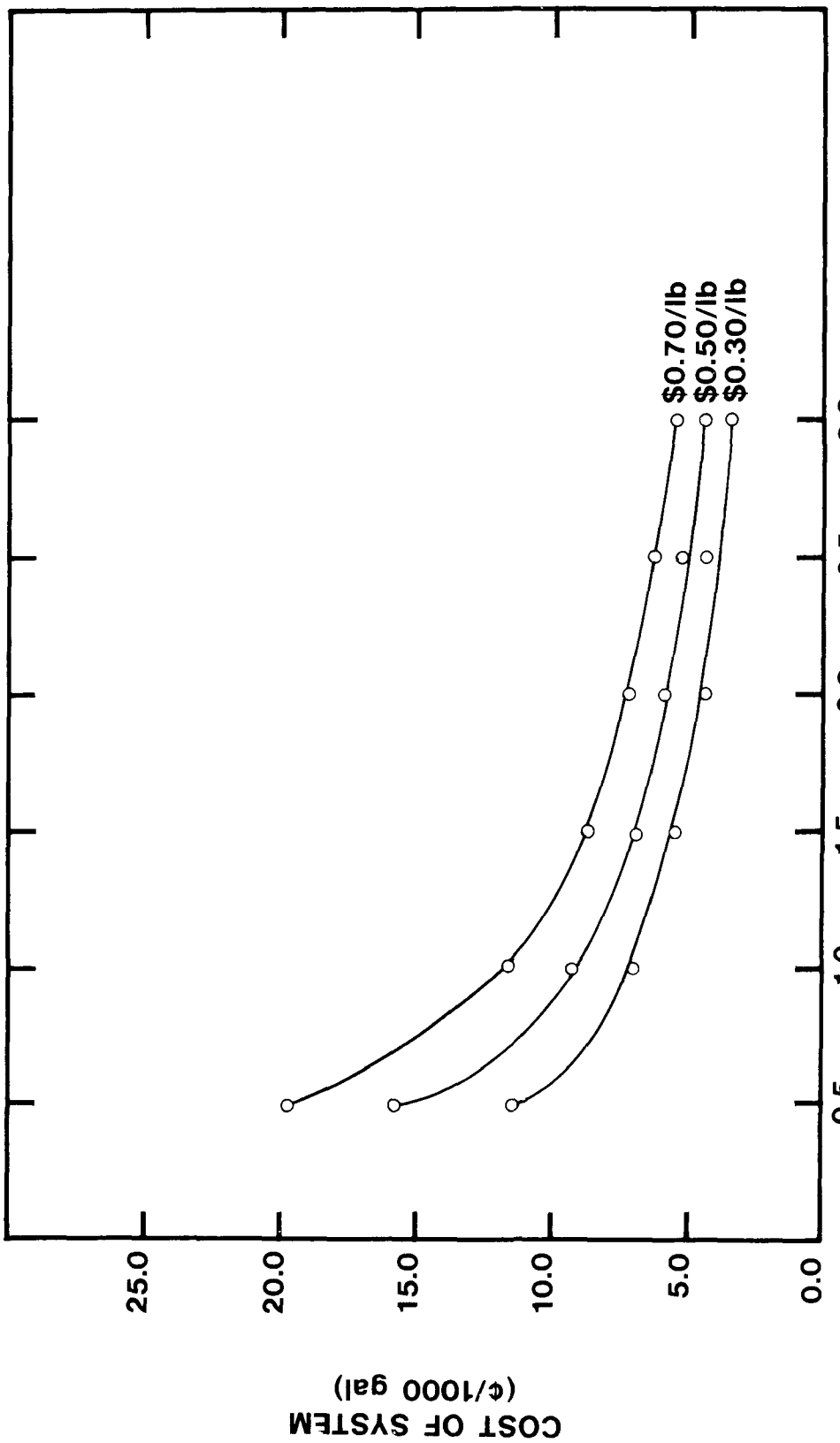

FIGURE 38 EFFECT OF ACTIVATED CARBON COST AND REACTIVATION PERIOD ON SYSTEM COST FOR 100 mgd SAND REPLACEMENT SYSTEM

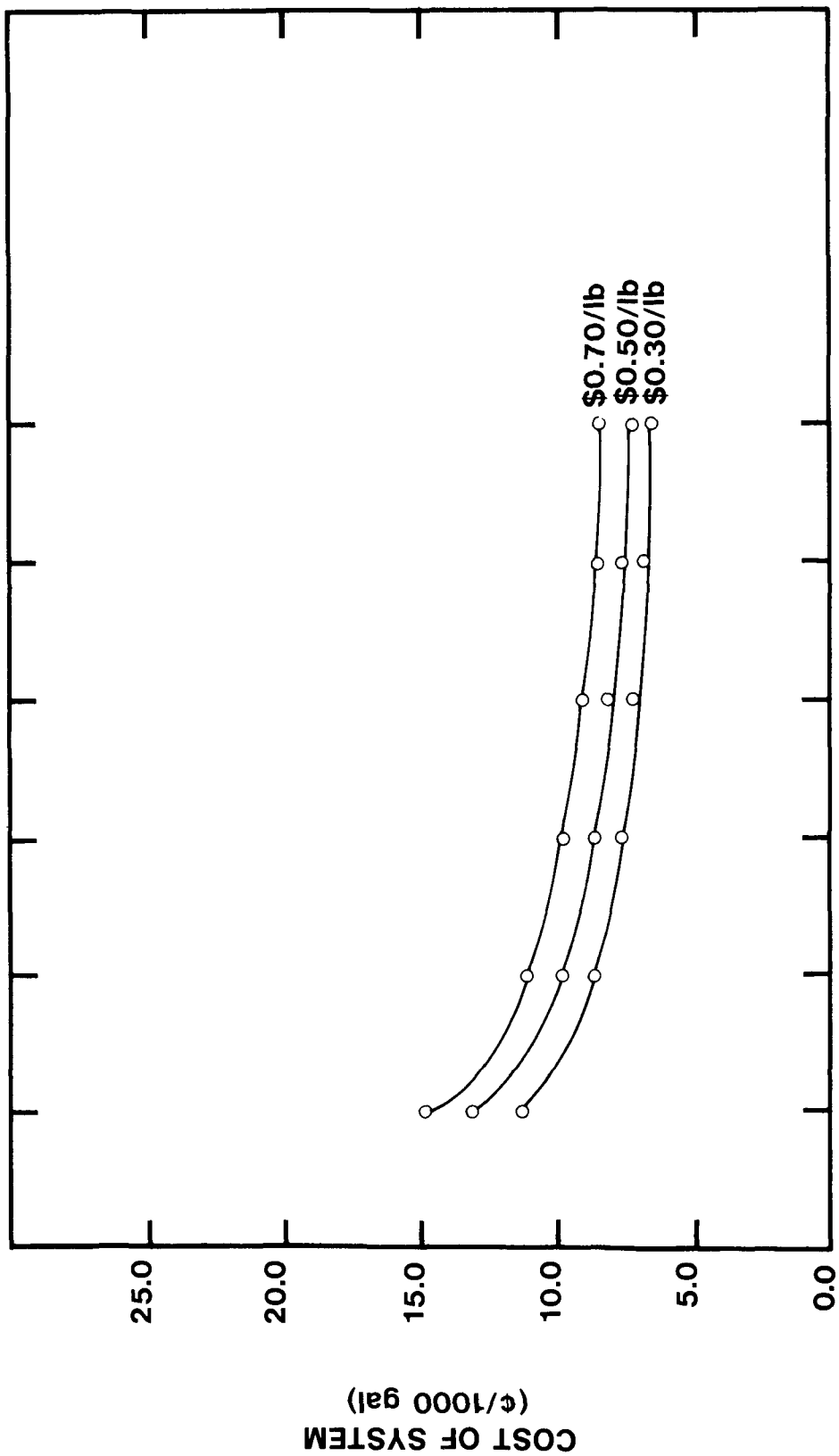

FIGURE 39 EFFECT OF ACTIVATED CARBON COST AND REACTIVATION PERIOD ON SYSTEM COST FOR 100 mgd POST-FILTER ADSORBER

Table XXII. INFLATIONARY IMPACT FOR INVESTMENTS IN POST FILTER ADSORPTION AND SAND REPLACEMENT (5%)

Costs in ¢/1000 gal

Years After Construction	10 mgd						100 mgd					
	Post-Filter Adsorption			Sand Replacement			Post-Filter Adsorption			Sand Replacement		
	Capital	O&M	Total	Capital	O&M	Total	Capital	O&M	Total	Capital	O&M	Total
0	9.14	7.59	16.73	3.93	9.24	13.17	4.65	4.01	8.66	1.70	5.18	6.88
1	"	7.99	17.13	"	9.70	13.63	"	4.21	8.86	"	5.44	7.14
2	"	8.39	17.53	"	10.18	14.11	"	4.42	9.07	"	5.71	7.41
3	"	8.81	17.95	"	10.70	14.63	"	4.64	9.29	"	6.00	7.70
4	"	9.25	18.39	"	11.22	15.15	"	4.87	9.52	"	6.30	8.00
5	"	9.71	18.85	"	11.78	15.71	"	5.12	9.77	"	6.61	8.31
6	"	10.20	19.34	"	12.37	16.30	"	5.37	10.02	"	6.94	8.64
7	"	10.71	19.85	"	12.99	16.92	"	5.64	10.29	"	7.29	8.99
8	"	11.24	20.38	"	13.64	17.57	"	5.92	10.57	"	7.65	9.35
9	"	11.81	20.95	"	14.32	18.25	"	6.22	10.87	"	8.04	9.74
10	"	12.40	21.54	"	15.04	18.97	"	6.53	11.18	"	8.44	10.14
11	"	13.02	22.16	"	15.79	19.72	"	6.86	11.51	"	8.86	10.56
12	"	13.67	22.81	"	16.58	20.51	"	7.20	11.85	"	9.30	11.00
13	"	14.35	23.49	"	17.41	21.34	"	7.56	12.21	"	9.77	11.47
14	"	15.07	24.21	"	18.28	22.21	"	7.94	12.59	"	10.26	11.96
15	"	15.82	24.96	"	19.20	23.13	"	8.34	12.99	"	10.77	12.47
16	"	16.61	25.75	"	20.16	24.09	"	8.75	13.40	"	11.31	13.01
17	"	17.44	26.58	"	21.16	25.09	"	9.19	13.84	"	11.87	13.57
18	"	18.32	27.46	"	22.22	26.15	"	9.65	14.30	"	12.46	14.16
19	"	19.20	28.37	"	23.33	27.26	"	10.13	14.78	"	13.09	14.79
20	"	20.20	29.34	"	24.50	28.43	"	10.64	15.29	"	13.74	15.44

Table XXIII. INFLATIONARY IMPACT FOR INVESTMENTS IN POST FILTER ADSORPTION AND SAND REPLACEMENT (7%)
Costs in ¢/1000 gal

Years After Construction	10 mgd						100 mgd					
	Post-Filter Adsorption			Sand Replacement			Post-Filter Adsorption			Sand Replacement		
	Capital	O&M	Total	Capital	O&M	Total	Capital	O&M	Total	Capital	O&M	Total
0	9.14	7.59	16.73	3.93	9.24	13.17	4.65	4.01	8.66	1.70	5.18	6.88
1	"	8.14	17.28	"	9.88	13.81	"	4.29	8.94	"	5.54	7.24
2	"	8.71	17.85	"	10.57	14.50	"	4.59	9.24	"	5.93	7.63
3	"	9.32	18.46	"	11.31	15.24	"	4.91	9.56	"	6.34	8.04
4	"	9.98	19.12	"	12.10	16.03	"	5.26	9.91	"	6.79	8.49
5	"	10.68	19.82	"	12.95	16.88	"	5.62	10.27	"	7.26	8.96
6	"	11.42	20.56	"	13.86	17.79	"	6.02	10.67	"	7.77	9.47
7	"	12.22	21.36	"	14.83	18.76	"	6.44	11.09	"	8.32	10.02
8	"	13.08	22.22	"	15.86	19.79	"	6.89	11.54	"	8.90	10.60
9	"	13.99	23.13	"	16.98	20.91	"	7.37	12.02	"	9.52	11.22
10	"	14.97	24.11	"	18.16	22.09	"	7.89	12.54	"	10.19	11.89
11	"	16.02	25.16	"	19.44	23.37	"	8.44	13.09	"	10.90	12.60
12	"	17.14	26.28	"	20.80	24.73	"	9.03	13.68	"	11.66	13.36
13	"	18.34	27.48	"	22.25	26.18	"	9.66	14.31	"	12.48	14.18
14	"	19.63	28.77	"	23.81	27.74	"	10.34	14.99	"	13.36	15.06
15	"	21.00	30.14	"	25.48	29.41	"	11.06	15.71	"	14.29	15.99
16	"	22.47	31.61	"	27.30	31.23	"	11.84	16.49	"	15.29	16.99
17	"	24.04	33.18	"	29.17	33.10	"	12.66	17.31	"	16.36	18.06
18	"	25.72	34.86	"	31.21	35.14	"	13.55	18.20	"	17.51	19.21
19	"	27.53	36.67	"	33.39	37.32	"	14.50	19.15	"	18.73	20.43
20	"	29.45	38.59	"	35.73	39.66	"	15.52	20.17	"	20.04	21.74

Table XXIV. INFLATIONARY IMPACT FOR INVESTMENTS IN POST FILTER ADSORPTION AND SAND REPLACEMENT (9%)

Costs in ¢/1000 gal

Years After Construction	10 mgd						100 mgd					
	Post-Filter Adsorption			Sand Replacement			Post-Filter Adsorption			Sand Replacement		
	Capital	O&M	Total	Capital	O&M	Total	Capital	O&M	Total	Capital	O&M	Total
0	9.14	7.59	16.73	3.93	9.24	13.17	4.65	4.01	8.66	1.70	5.18	6.88
1	"	8.27	17.14	"	10.04	13.97	"	4.36	9.01	"	5.64	7.34
2	"	8.99	18.13	"	10.93	14.86	"	4.74	9.39	"	6.14	7.84
3	"	9.77	18.91	"	11.89	15.82	"	5.16	9.81	"	6.69	8.39
4	"	10.62	19.76	"	12.94	16.87	"	5.61	10.26	"	7.29	8.99
5	"	11.55	20.69	"	14.08	18.01	"	6.11	10.76	"	7.94	9.64
6	"	12.56	21.70	"	15.32	19.25	"	6.65	11.30	"	8.65	10.35
7	"	13.67	22.81	"	16.68	20.61	"	7.24	11.89	"	9.42	11.12
8	"	14.87	24.01	"	18.16	22.09	"	7.88	12.53	"	10.26	11.96
9	"	16.18	25.32	"	19.78	23.71	"	8.58	13.23	"	11.18	12.88
10	"	17.61	26.75	"	21.54	25.47	"	9.34	13.99	"	12.18	13.88
11	"	19.17	28.31	"	23.45	27.38	"	10.17	14.82	"	13.27	14.97
12	"	20.87	30.01	"	25.54	29.47	"	11.07	15.72	"	14.46	16.16
13	"	22.72	31.86	"	27.82	31.75	"	12.06	16.71	"	15.76	17.46
14	"	24.74	33.88	"	30.30	34.23	"	13.13	17.78	"	17.17	18.87
15	"	26.94	36.08	"	33.01	36.94	"	14.31	18.96	"	18.71	20.41
16	"	29.33	38.47	"	35.96	39.89	"	15.58	20.23	"	20.39	22.09
17	"	31.95	41.09	"	39.17	43.10	"	16.98	21.63	"	22.22	23.92
18	"	34.80	43.94	"	42.67	46.60	"	18.49	23.14	"	24.21	25.91
19	"	37.90	47.04	"	46.49	50.42	"	20.15	24.80	"	26.39	28.09
20	"	41.28	50.42	"	50.66	54.59	"	21.95	26.60	"	28.76	30.46

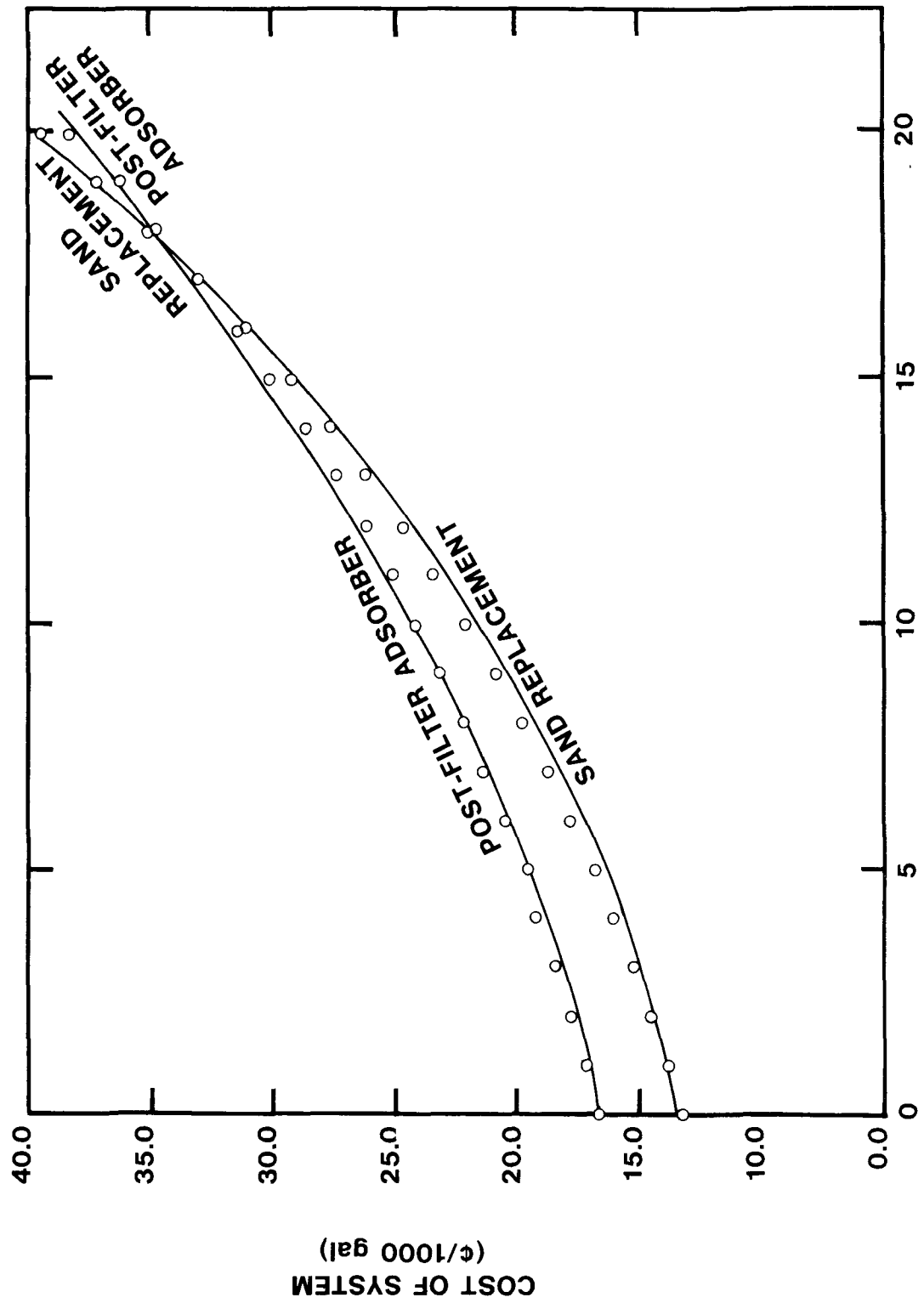

FIGURE 40 EFFECT OF 7% INFLATION RATE ON COST OF 10 mgd POST-FILTER ADSORPTION AND SAND REPLACEMENT SYSTEMS

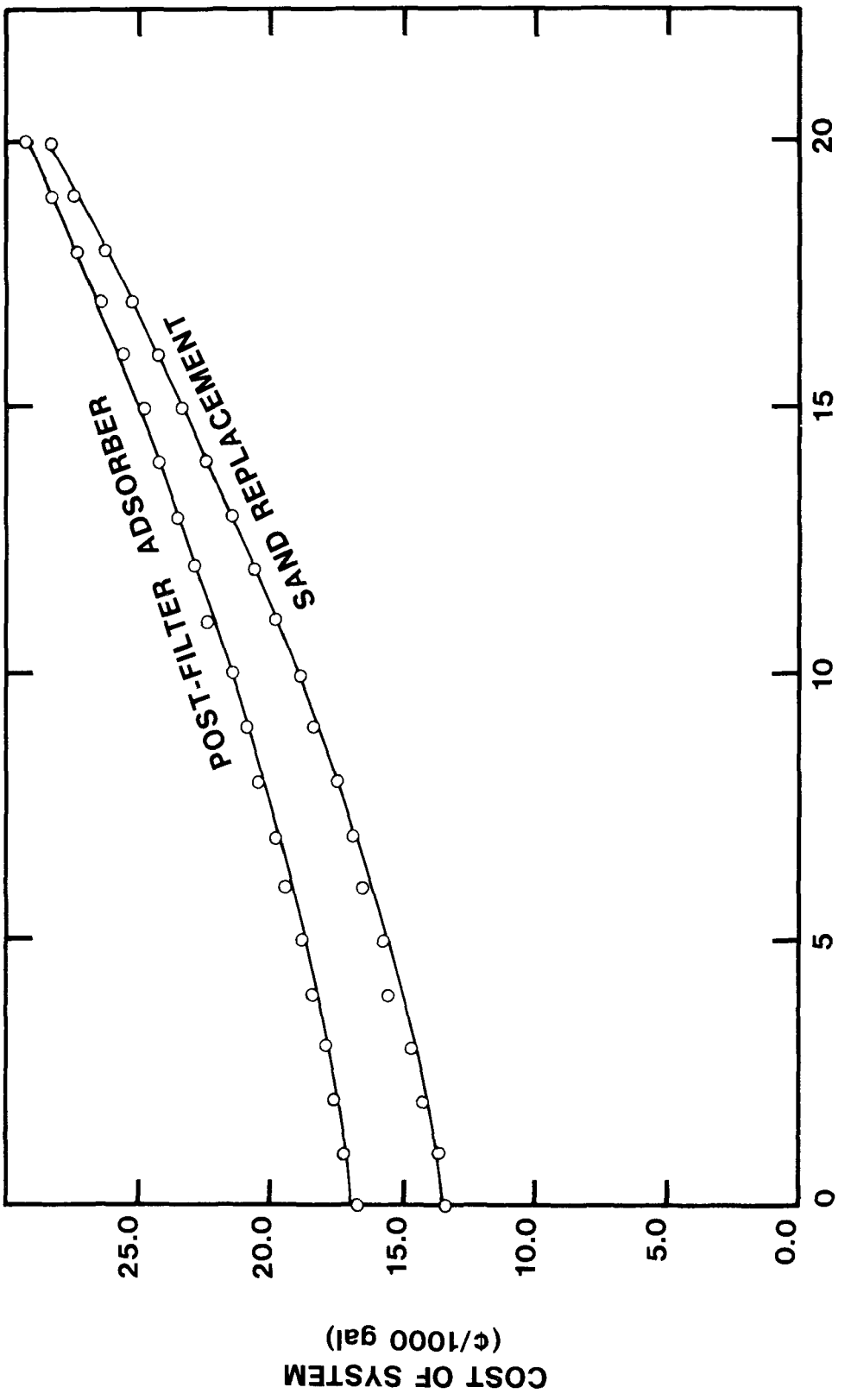

FIGURE 41 EFFECT OF 5% INFLATION RATE ON COST OF 10 mgd POST-FILTER ADSORPTION AND SAND REPLACEMENT SYSTEMS

replacement systems. For small systems, post-filter adsorbers are less desirable from an economic point of view than for larger systems. A possible alternative that minimizes the economic impact of using granular activated carbon adsorption in small systems would be to consider the use of truck transport and regional reactivation systems.[65]

Cost of Reactivation

The most common (but not the only) method of reactivating carbon is by the use of multi-hearth furnaces, and a significant portion of the cost of using granular activated adsorption treatment is associated with on-site reactivation. Figures 42 and 43 show the annual capital (amortized over 20 years at 7 percent interest) and annual operating and maintenance cost for reactivation based on reactivation rate in lbs/day and can be used to calculate this cost.

Using the data from Table X (page 34) in the Interim Guide, an example will be constructed to demonstrate a convenient method for estimating a unit cost based on the activated carbon use rate for reactivation. Assume a 100 mgd treatment plant with an activated carbon use rate as given in line 3, column 4 in Table X (page 34) (530 mg/ℓ). The use rate converted to pounds per day as follows:

Use Rate = 530 mg/ℓ x 8.34 lbs/gal =

4,420 lbs/mil gal

Multiplying by 100 mgd yields a reactivation rate of =

442,000 lbs/day

Entering Figures 42 and 43 at 442,000 lb/day yields an approximate annual capital cost of 430,000 $/yr and annual operating cost of 6,500,000 $/yr. The total annual cost, therefore, is 6,930,000 $/yr for this rather high adsorbent use rate. The total yearly cost is divided by the annual flow (100 mgd x 365 days/yr = 36,500 mgy) to yield:

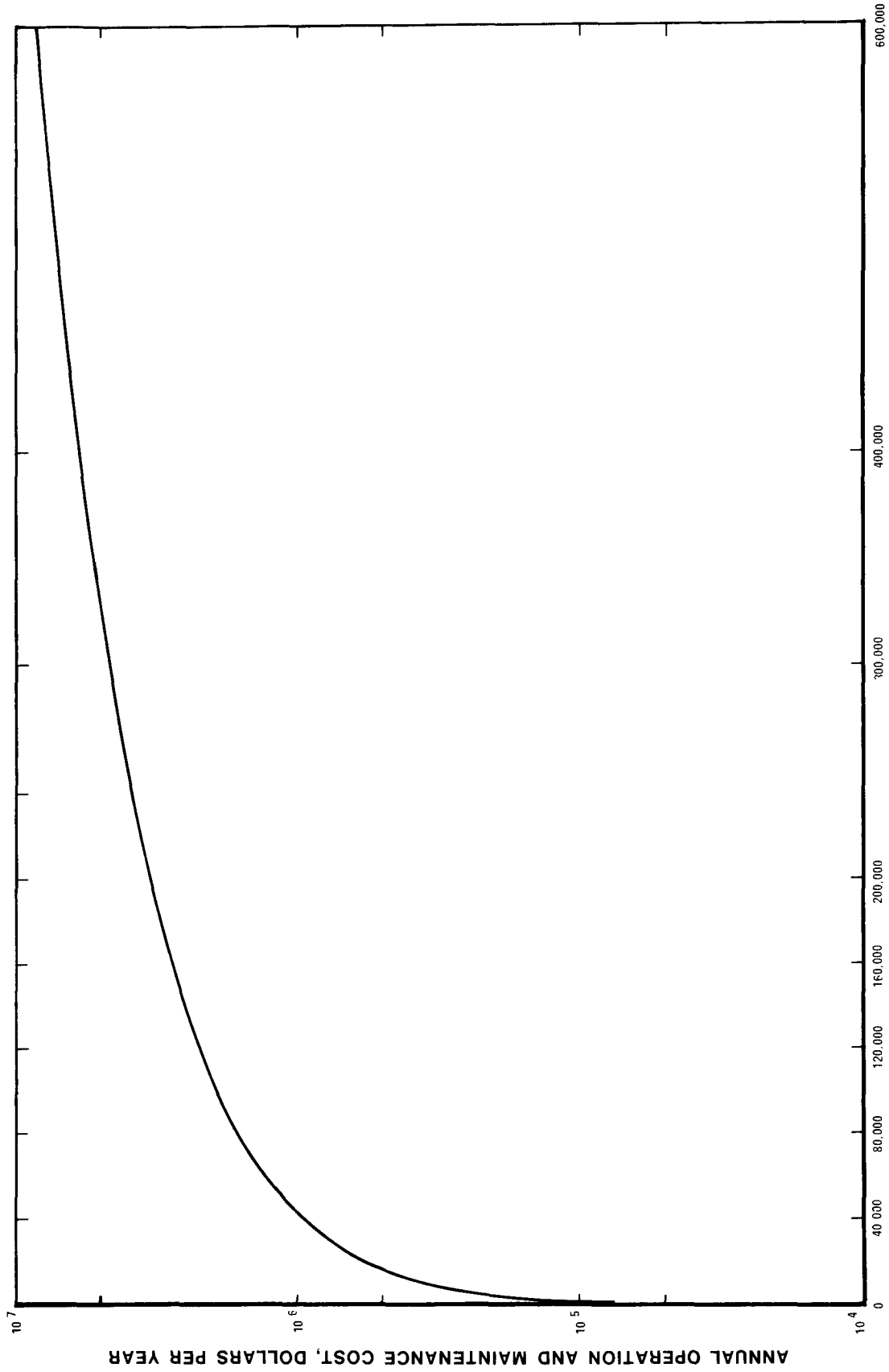

FIGURE 42. ANNUAL OPERATION AND MAINTENANCE COST FOR MULTI-HEARTH GRANULAR ACTIVATED CARBON REACTIVATION SYSTEMS

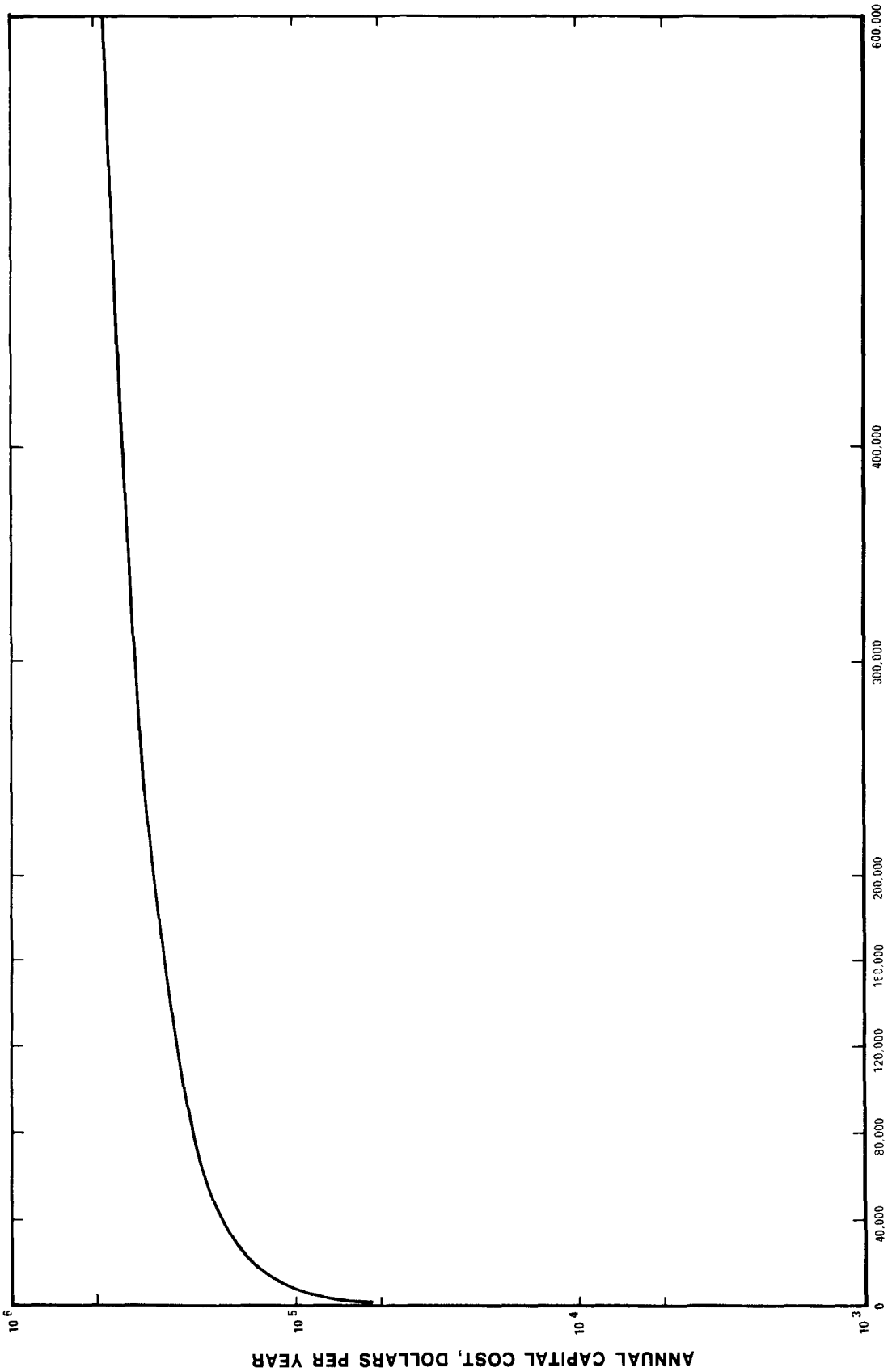

FIGURE 43. ANNUAL CAPITAL COST (20 YEARS AT 7 PER CENT) FOR MULTI-HEARTH GRANULAR ACTIVATED CARBON REACTIVATION SYSTEMS

$$\text{Unit Cost} = \frac{\$6.93 \times 10^6/\text{yr}}{36{,}500 \text{ mgy}} = \$190/\text{mg or 19 cents/1000 gal.}$$

The above unit cost is for buying and operating the reactivation furnace only.

Summary

This material is intended to supplement the material on pages 36 to 54 of the "Interim Treatment Guide for Controlling Organic Contaminants in Drinking Water Using Granular Activated Carbon." It presents data that can be used to provide additional understanding of the cost of using granular activated carbon adsorption treatment for controlling organic contaminants in drinking water.

ACKNOWLEDGMENTS

Because of the size and complexity of this report, its importance, and the short time that was available for its completion, the authors judge that this is one of the more difficult assignments given to them. It could not have been completed without help. The authors wish to acknowledge the contribution of many members of the Physical and Chemical Contaminant Removal Branch (listed at the end of the Interim Treatment Guide) who helped gather the data contained in Appendix A, as well as Dale W. Dietrich and his staff of artists, Nancy J. Quilhot, Stephen E. Wilson and Newell J. Maston who prepared all of the Figures in the Interim Treatment Guide and Appendix A. They also wish to acknowledge the efforts of the Principal Investigators of the extramural projects from which additional data were obtained. Finally, this difficult project could not have been successfully completed without the dedicated and skillful efforts of Ms. Maura M. Lilly who typed all of the drafts and the final manuscript so willingly and rapidly.

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APPENDIX B

ANALYTIC METHODOLOGY

FOR

MONITORING PILOT COLUMN TESTS

Written by

Alan A. Stevens

Reviewed by

Gordon G. Robeck

APPENDIX B

TABLE OF CONTENTS

ANALYTIC METHODOLOGY FOR MONITORING PILOT COLUMN TESTS

INTRODUCTION

The methods needed to monitor the granular activated carbon treatment pilot studies can be divided into three specific categories:

1. Low molecular weight halogenated organic compounds, excluding trihalomethanes
2. Organic Carbon
3. Terminal "Summation Trihalomethane"

Some inherent flexibility exists in each of these categories with regard to specific measurement methods, instruments selected, and so forth. This discussion will attempt to address some of the options available and relate them as closely as possible to present, proposed, or future U.S. EPA Standard Methods that are ultimately needed to meet compliance monitoring requirements.

LOW MOLECULAR WEIGHT HALOGENATED ORGANIC COMPOUNDS EXCLUDING TRIHALOMETHANES - PERFORMANCE CRITERION 1

This group of organic compounds has an operational definition. The intent is to include such low boiling (low molecular weight) halogenated organics as carbon tetrachloride, tri- and tetrachloroethylene, vinyl chloride, and others often found in contaminanted drinking waters. This group is selected because of: 1) relative ease of analyses, 2) they are common contaminants, 3) evidence suggests that they break through granular activated carbon adsorption systems earlier than higher molecular weight toxic materials and therefore as a monitor, place more stringent operating requirements on the process giving a higher level of protection to the consumer.

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*"Summation Trihalomethanes" is the arithmetic sum of the concentration of the individual species of trihalomethane found in a given sample. This parameter is called "Total Trihalomethane" in the proposed Regulation.

EPA researchers have determined that over 30 purgeable halogenated organic compounds can be detected and most resolved by use of the two gas chromatographic columns under the conditions listed for use in the approved purge and trap trihalomethane method[1] and when the "multi-purpose" trap containing silica gel is used. Table I lists these compounds in order of increasing retention time when a 0.2 percent Carbowax 1500 on Carbopak C column is used.

TABLE I

COMPOUNDS DETERMINABLE ON 0.2% CARBOWAX 1500 ON CARBOPAK C

In Order of Increasing Retention Time

chloromethane
bromomethane
vinyl chloride
chloroethane
methylene chloride
1,1-dichloroethylene
bromochloromethane
1,1-dichloroethane
trans-1,2-dichloroethylene
chloroform
1,2-dichloroethane
1,1,1- trichloroethane
carbon tetrachloride
bromodichloromethane
1,2- dichloropropane — unresolved
2,3-dichloro-1-propene — unresolved
trans-1,3-dichloropropene
trichloroethylene
1,1,2- trichloroethane — unresolved
dibromochloromethane — unresolved
cis-1,3-dichloro-1-propene — unresolved
1,2-dibromoethane
2-bromo-1--chloropropane
bromoform — unresolved
1,1,1,2-tetrachloroethane — unresolved
tetrachloroethylene
1,1,2,2-tetrachloroethane
1,4-dichlorobutane
chlorobenzene

A second column (N-octane on Porasil-c) changes the retention order (see Table II), gives different separations, and allows detection of some organic compounds with higher boiling points.

TABLE II

COMPOUNDS DETERMINABLE ON N-OCTANE ON PORASIL-C

In Order of Increasing Retention Time

vinyl chloride — unresolved
chloromethane — unresolved
bromomethane
1,1-dichloroethylene
chloroethane
trans-1,2 dichloroethylene
methylene chloride
carbon tetrachloride
chloroform — unresolved
cis-1,2-dichloroethylene — unresolved
1,1-dichloroethane — unresolved
bromochloromethane — unresolved
1,1,1-trichloroethane — unresolved
trichloroethylene — unresolved
bromodichloromethane
dibromomethane — unresolved
tetrachloroethylene — unresolved
1,2-dichloroethane
dibromochloromethane — unresolved
trans-1,3-dichloro-1-propene — unresolved
1,2-dichloropropane — unresolved
cis-1,3-dichloro-1-propene — unresolved
1,1,2-trichloroethane — unresolved
2-bromo-1-chloropropane
chlorobenzene
1,2-dibromoethane
bromoform
1-chloro-1-hexene
chlorohexane
1,1,2,2-tetrachloroethane — unresolved
pentachloroethane — unresolved
o-chlorotoluene
m-dichlorobenzene — unresolved
hexachloroethane — unresolved
p-dichlorobenzene — unresolved
1,4-dichlorobutane — unresolved
o-dichlorobenzene — unresolved
hexachlorobutadiene
1,2,4-trichlorobenzene

Therefore, the operational definition of those low molecular weight halogenated compounds excluding trihalomethanes related to performance Criterion 1 is; those compounds that can be detected by use of the U.S. EPA approved trihalomethane method - purge and trap version.[1] Note: Determining these compounds as part of the granular activated carbon adsorption system process control program should not be a large analytic burden when the water utility required to use granular activated carbon treatment has selected the proper approach for the required measurement of trihalomethane concentrations.

The purge and trap method is selected for this analysis mainly because gas chromatographic conditions have not been well defined for resolution of as many compounds by the liquid-liquid extraction method,[2] and because of the difficulty of solvent interference in the liquid-liquid extraction method with the detection of many compounds eluting sooner than chloroform. This is not to say, however, that these conditions could not be developed. Additionally, care must be taken in selecting a particular purge-and-trap apparatus for introduction of the sample into the gas chromatograph, as a well designed apparatus is needed to eventually accomplish resolutio of the same lower boiling compounds (vinyl chloride, bromomethane, and so forth). Details of this are to begin in a supplemental writeup extending the coverage of the EPA approved trihalomethane method to this larger group of compounds.

In spite of the resolving power of the two columns used for the purge and trap trihalomethane method,[1] all possible purgeable organohalides and isomers cannot be identified unambiguously. Identifications by dual column GC-specific halogen detection are still presumptive. In order to avoid escalating analytical costs (e.g. - mass spectrometric (MS) detection), these presumptive identifications are considered sufficiently accurate and granular activated carbon adsorption treatment should be adjusted to reduce any of these contaminants to less than 0.5 µg/ℓ based on a comparison with an analytical standard of the compound of presumed identity, "Performan Criterion 1." Except in the case of some isomer differentiations, MS confirmation of compound identity might be useful enough to warrant the effort and could ultimately lead to a better designed treatment strategy.

ORGANIC CARBON - PERFORMANCE CRITERIA 2 and 3

Analytic Method

A method for the determination of organic carbon must include a step to remove or adjust for the presence of inorganic carbonate. Instruments on the market today, using manufacturers recommended procedures, do this adequately and efficiently. Many procedures, however, effect the removal of carbonate by acidification with mineral acid followed by exhaustive purging of carbon dioxide to waste. In this process, a purgeable fraction of organic carbon (POC) is lost. Ideally, this purgeable fraction should be included in any total organic carbon (TOC) measurement. Research in WSRD laboratories, however, has shown that, in general, the POC concentration is only a small fraction of the TOC concentration and little organic carbon (< 10 µg/ℓ) would be lost by measuring only the non-purgeable organic fraction (NPOC). Only occasionally have POC concentrations been found in the range of 0.1 - 0.3 mg/ℓ. When the insignificance of POC can be demonstrated, only NPOC need be measured. Note: For these cases NPOC determinations can be used to satisfy the TOC requirements of "Performance Criteria 2 and 3." This can simplify the sampling requirements and analysis and expand the options for methods and instruments that can be used.

Because of the requirements of the Performance Criteria 2 (measure a change of 0.5 mg/ℓ) and the commonly found low concentrations of organic carbon in a granular activated carbon column effluent (< 0.1 mg/ℓ) the method used to measure organic carbon must be more precise and accurate when compared to methods and instruments used in the waste water treatment field, where concentrations of organic carbon are often in the hundreds of milligrams per liter. Required precision and accuracy for measurement of organic carbon in granular activated carbon column effluents therefore must be in the range of 0.1 mg/ℓ $\pm$ .05 mg/ℓ or better. Although no EPA standard procedures now exist for this purpose, instruments are available that can be operated

according to manufacturers instructions to achieve these goals. At least one of these is capable of measuring both POC and NPOC independently.

The instrument (and method) must also be capable of measuring TOC concentrations as high as those expected to occur in the granular activated carbon column influent (2-10 mg/ℓ). This is well within the range of instruments capable of the required low level analysis.

Sampling

Because of the variability with time of concentrations of organic carbon in actual treatment situations, determining what constitute a representative "baseline" (TOC_o) sample for all systems is difficult. Additionally, activated carbon fines emanating from new granular activated carbon adsorbers have been observed to influence organic carbon determinations. For these reasons, the first organic carbon measurements are recommended to be performed after one week of adsorber operation and be performed at least in triplicate twice during a 2-day period (six samples each on adsorber influent and effluent). The average of effluent values not influenced by activated carbon fines (activated carbon are not visible, or samples do not have a NPOC value considerably higher than others of the set) is then the "baseline" (TOC_o) effluent concentration against which future effluent samples are compared, Performance Criterion 2, and determines the initial organic carbon removal percentage, Performance Criterion 3, when compared with a "baseline" influent concentration.

Sample containers should be the same as those used for sampling for trihalomethane analysis when the POC fraction is to be measured. Headspace requirements are not as important when the POC fraction has previously been shown to be insignificant.

TERMINAL SUMMATION* TRIHALOMETHANES - MAXIMUM CONTAMINANT LEVEL REQUIREMENT

General

A detailed method for determining Terminal Trihalomethane (Term THM) concentrations has been described by Stevens and Symons.[3] The principle of Term THM measurement "Terminal Summation Trihalomethane" is the special case where the individual species Term THM concentrations in the units μg/ℓ are arithmetically summed.

Because their formation is not instantaneous, trihalomethane (THM) concentrations increase in the water as it flows through a water treatment plant (unless removed during treatment) to reach some value higher than that which would be observed if an analysis for THM species was performed immediately after sampling at the first point of chlorination. Further, the consumer is likely to receive water with THM concentrations higher than those leaving the plant because the reaction proceeds in the distribution system. Additionally, not only are the concentrations of THM time dependent, but the rate of the reaction is dependent on pH, precursor concentration, nature of precursors, temperature and to some degree free chlorine concentration early in the chlorination process. Finally, the ratio of chloroform to other trihalomethanes is highly dependent on the bromide content of the source water.

The Term THM concentration is defined as the concentration of THM that occurs at the termination of the measurement of this parameter. To measure Term THM concentration, chlorine-precursor reaction conditions are selected according to the treatment practiced at the particular plant being evaluated. In general, to determine Term THM a sample of water is chlorinated under these plant conditions, and chloroform and other THM species concentrations are determined after some preselected holding period or periods.

*As noted previously "Total" is used in the proposed Regulation, rather than "Summation" to mean the arithmetic sum of individual trihalomethane concentrations.

The Term THM concentration is an important parameter for evaluating drinking water quality because it is an estimate of the concentration of THM reaching the consumer at various points (residence times) in the distribution system. Therefore, determining the change with time in the Term THM concentration in the effluent of a granular activated carbon adsorption system is a good estimate of whether or not the effluent would meet the summation trihalomethane maximum contaminant level required by the Interim Primary Drinking Water Regulations.

The selected conditions for the Term THM measurement must be the same as those experienced at the water treatment plant or distribution system and must be reproducible from sample to sample. Critical conditions to consider are time of reaction (time elapsed before halting the halogenation reaction with a reducing agent) maintenance of a chlorine residual, temperature, pH, prevention of loss of the volatile products during the time of contamination and avoidance of contamination of reagents.

Effect of Time

Although a single measurement of THM concentrations after a storage period of several days in a bottle under appropriate conditions can give a useful determination of the Term THM concentration for that specified time, much more information can be gained from the reaction-rate curves obtained by plotting THM concentrations vs. time. The rate curves obtained by periodic measurement of THM concentrations in properly stored finished water can be used to estimate the future THM concentrations at any given time after water leaves the treatment plant, as required by the Interim Primary Drinking Water Regulations. This is particularly important when the goal is to estimate ultimate consumer exposure to THM at different points along the distribution system. The THM concentration-vs-time curve

is especially useful where the utility has a large variation in the time that water is in various parts of the distribution system.

When analyzing a granular activated carbon adsorption system effluent, simply measuring a single point on the THM growth curve such as one representing maximum residence time in the distribution system would place a requirement on adsorber performance more stringent than required under the Interim Primary Drinking Water Regulations. To be consistent with that part of the Regulation, generation and use of a complete THM growth rate curve is recommended to properly evaluate adsorber performance. Specifically, the effluent water from the granular activated carbon adsorption unit should be chlorinated in a manner consistent with treatment plant practice where free chlorination is used (see below). Aliquots of that water are then stored for various times from "0" (corresponding to clear well) to "T" (corresponding to maximum time in distribution system). The intermediate time samples ($\frac{T}{2}$, $\frac{T}{4}$, and so forth) determining the shape of the THM growth curve and, therefore, expected THM concentrations at intermediate distribution system residence times.

A minimum of five points on the curve (0, T, and 3 in between) are selected consistent with the sampling plan for THM MCL compliance monitoring. The average Term Summation THM concentration obtained from those five values (of Term Summation THM at respective times) is then used to judge adsorber performance.

Maintenance of Chlorine Residual

In conventional U.S. water treatment practice, maintenance of a free chlorine residual throughout the distribution system often is recommended or required. The continued reaction of precursor with chlorine to yield trihalomethanes depends on the maintenance of a free chlorine residual. Thus for evaluation of systems, where free chlorination is practiced, a chlorine-residual measurement always must be performed at the time of THM analysis to ensure that a free residual is present.

Effect of Temperature

Upon chlorination of a natural water, approximately twice as much chloroform can be formed in a given period of time at 25°C as is formed at 3°C. This range of temperature is not uncommon, summer to winter, in U.S. surface waters. A need for close temperature control during the determination of Term THM concentration, therefore, is indicated. Because temperature largely is controlled seasonally, this temperature effect must be taken into account, if extrapolations to summer operating conditions from winter pilot studies and vice versa are made.

Effect of pH

The trihalomethane formation rate has been shown to increase with an increase in pH. Because pH is a factor determining rate of THM formation and therefore Term THM values, the pH should be controlled near that found in the distribution system.

Loss of Volatile Species.

To prevent misleading losses of trihalomethanes produced during the reaction period, the reactions must be carried out in sealed, head-space-free containers. Container materials should be all glass or glass with PTFE-lined caps. Standard glass-stoppered reagent bottles filled to overflowing so as to wet the stopper surface or the PTFE-septum-sealed serum vials, used for sampling for Inst. THM determinations have been found suitable.

Effect of Bromide or Iodide Contamination

As mentioned earlier, bromide or iodide present in the water can cause formation of THM species other than chloroform, as a result of first reacting with chlorine. In the case of bromide, the relative amounts of THM species formed has been shown to be highly dependent on the bromide content of the water and the chlorine dose, presumably because these determine the ratio of bromine to chlorine available for completing reactions. This change of product ratio, because bromine-containing

species are heavier than chloroform, could cause a dramatic change in calculated Terminal Summation Trihalomethane values.

Preliminary work indicates that equal amounts of bromine and chlorine substitution as trihalomethanes would be expected if the original bromide concentration is as little as 2 percent of the chlorine dose. Clearly, any bromide or iodide contamination of reagents used will cause a different ratio of THM species to be formed than would occur normally on chlorination of that water under plant conditions and must be avoided.

Effect of Precursor Contamination

In the WSRD laboratory, distilled, deionized, activated carbon-filtered water has been used for "blank" water for reagent preparation. At pH 7, the contribution of precursor in reagents has been small. At higher pH, however, blank values tend to be higher. Care should be taken to minimize volumes of reagents used in Term THM measurements in order to avoid this contribution to the THM concentrations obtained.

Procedure for Terminal Trihalomethane Determination

A test for Term THM concentrations can be standardized in approach, but the conditions for sample treatment and storage will vary widely from system to system depending upon distribution-system residence time, total clorine demand of the sample, ambient temperature of the system, and pH of the finished water in the particular system under investigation. These variables must be chosen to match those in the system.

In work at the WSRD laboratory, a large (1-3 liter) sample of water is collected, and the pH adjusted to that selected with an appropriate inorganic (e.g. phosphate or borate) buffer. The final buffer strength is about 0.01 M, although the strength is not critical as long as the desired pH is maintained. The sample then is chlorinated, if needed, by the addition of a previously standardized chlorine or hypochlorite solution. Sufficient chlorine is added at this time to maintain a free residual for the duration of the test period.

Several sample bottles are filled and capped head-space-free, two bottles for each point to be determined on the THM growth rate curve. For example, ten bottles are needed for the five points on the curve to be determined. One of the zero-time sample bottles contains sodium thiosulfate to immediately reduce the chlorine so that the "0" time THM concentration is measured. The other zero-time sample has no reducing agent and is used for measurement of the chlorine residual. This entire sequence from sample collection to the capping of the bottles should be done as quickly as possible to avoid loss of THM during the manipulations.

The samples, except zero-times, are stored at the selected temperature. After the preselected times one sample bottle is opened and an aliquot is transferred by pouring into a smaller bottle containing sodium thiosulfate to prevent further reaction of precursor with chlorine. This smaller bottle is quickly sealed head-space-free to await THM analysis. This measurement determines a THM concentration for the respective time on the rate curve. A second bottle is opened at the same preselected time and the chlorine residual is measured.

The actual measurement of THM concentrations that are arithmetically summed to produce the "summation" or "total" value can be performed by use of either of the two U.S. EPA approved procedures for that determination (purge-and-trap or liquid-liquid extraction).[1,2] The calculated sum of the THM concentrations by the EPA approved procedure is the Terminal Summation Trihalomethane concentration for the respective time period.

Briefly, for the purge and trap[1] analysis, the sealed sample is brought to 25°C prior to opening in order to obtain reproducible purging efficiencies. A 5-mℓ aliquot then is removed and transferred to a glass purging apparatus, wherein the trihalomethanes are stripped from the aqueous phase by passage of a flow of helium upward through the sample. The trihalomethanes stripped in this manner are collected on a sorbant, porous polymer material contained in a stainless steel trap that is placed in series with the purging device. The trihalomethanes are desorbed thermally from the trapping material onto a gas chromatographic column. Finally, temperature-programmed gas chromatography is carried out, and the concentrations of trihalomethanes are measured by use of a halogen-specific detector. The liquid-liquid extraction method[2] involves the extraction of a small volume of water with an even smaller volume of organic solvent, followed by gas chromatographic analysis of the extract using an electron-capture detector.

Summary

Weekly analysis of the effluent from a granular activated carbon adsorption system by this procedure will provide a good estimate of whether or not the delivered drinking water will be in compliance with the trihalomethane maximum contaminant limits as specified in the Interim Primary Drinking Water Regulations.

ACKNOWLEDGMENTS

The author and compiler wish to express their sincere thanks to Ms. Maura M. Lilly, who typed this Appendix so quickly and accurately, such that the entire Interim Guide could be finished on time.

REFERENCES

1. "The Analysis of Trihalomethanes in Finished Waters by the Purge and Trap Method," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, Sept. 9, 1977.

2. "The Analysis of Trihalomethanes in Drinking Water by Liquid/Liquid Extraction," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

3. Stevens, A.A. and Symons, J.M., "Measurement of Trihalomethane and Precursor Concentration Changes," JAWWA, 69, No. 10, 546-554 (Oct. 1977).

APPENDIX C

DESIGN OF PILOT GRANULAR ACTIVATED CARBON COLUMNS

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and

Kenneth L. Kropp

Reviewed by

Gordon G. Robeck

APPENDIX C

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DESIGN OF PILOT GRANULAR ACTIVATED CARBON COLUMNS

Introduction

The "Interim Treatment Guide for Controlling Organic Contaminants in Drinking Water Using Granular Activated Carbon" describes two adsorption schemes. The first, is to retrofit an existing water treatment plant by replacing the filtration media with granular activated carbon, and the second, called post-filter adsorption, requires separate contactors following te filtration step. The ability of either adsorption scheme to reduce the concentration of trace organics should be investigated on-site using a small manageable system before expending large sums of money on a process design that may give marginal performance. Trial experimentation (i.e. pilot studies) permits selecting the appropriate concept through improved engineering judgement. This Appendix describes the design and operation of the EPA Water Supply Research Division's experimental adsorption systems used in organic removal studies. This material is presented for guidance as an example of one approach to gathering adsorption performance data.

Selection of Materials

One precaution taken by EPA in trace organic studies is to construct pilot scale equipment with stainless steel, Teflon, and glass whenever possible to minimize contamination from structural materials during experimentaiton. Whether or not materials such as rubber, acrylic resin, polyvinylchloride (PVC), polyethylene tubing, or similar products would compromise the experimental results is not known. To avoid this possibility, however, these materials should not be used if possible.

Adsorption Columns

Because of a limitation of available water, the WSRD pilot scale adsorbers consist of 3.8 cm (1.5 inches) diameter glass columns 153 cm (60 inches) in length. A schematic of the experimental system with details on fabrication are shown in Figures 1-4. The columns are arranged so that both modes, sand replacement and post-filtration adsorption, can be studied simutaneously if desired. Granular activated carbon is placed in column 1 (see Figure 1) to a depth allowable in the existing filter boxes at the water treatment plant. Settled water should be applied to this unit at an approach velocity similar to that in the existing plant. Approximately 15 cm (6 inches) of graded gravel should be placed in the bottom of the columns as an aid in distributing the backwash water. Some type of surface scrubbing (air or water scour) should be incorporated in the system because with granular activated carbon, like sand, most of the filtration occurs in the upper few centimeters of the bed and vigorous scouring insures adequate cleansing. The surface scrubber shown in Figure 1 (see also Figures 2 and 4) is intended to slide on a Teflon ferrule so that it can be located close to the granular activated carbon surface for effective agitation. If headloss monitoring is desired, a U-tube manometer or a sensitive pressure gage can be included in the design. If, however, headloss is not monitored, a backwashing schedule such as that used within the existing plant can be employed.

Establishing Test Conditions

Like disinfection, the process of adsorption is very dependent upon contact time (see Figure 24, Appendix A, page A72). The term "empty bed contact time" (EBCT) is commonly used to characterize this adsorption variable and is calculated by dividing the volume of media "V" by the hydraulic loading "Q" (i.e. $\frac{V}{Q}$ = EBCT). Assuming a filter box contains from 76 to 122 cm (30 to 48 inches) of media and the hydraulic loadings range from 4 to 8 m/hr (2 to 4 gal/min/ft^2) then the EBCT in a sand replacement

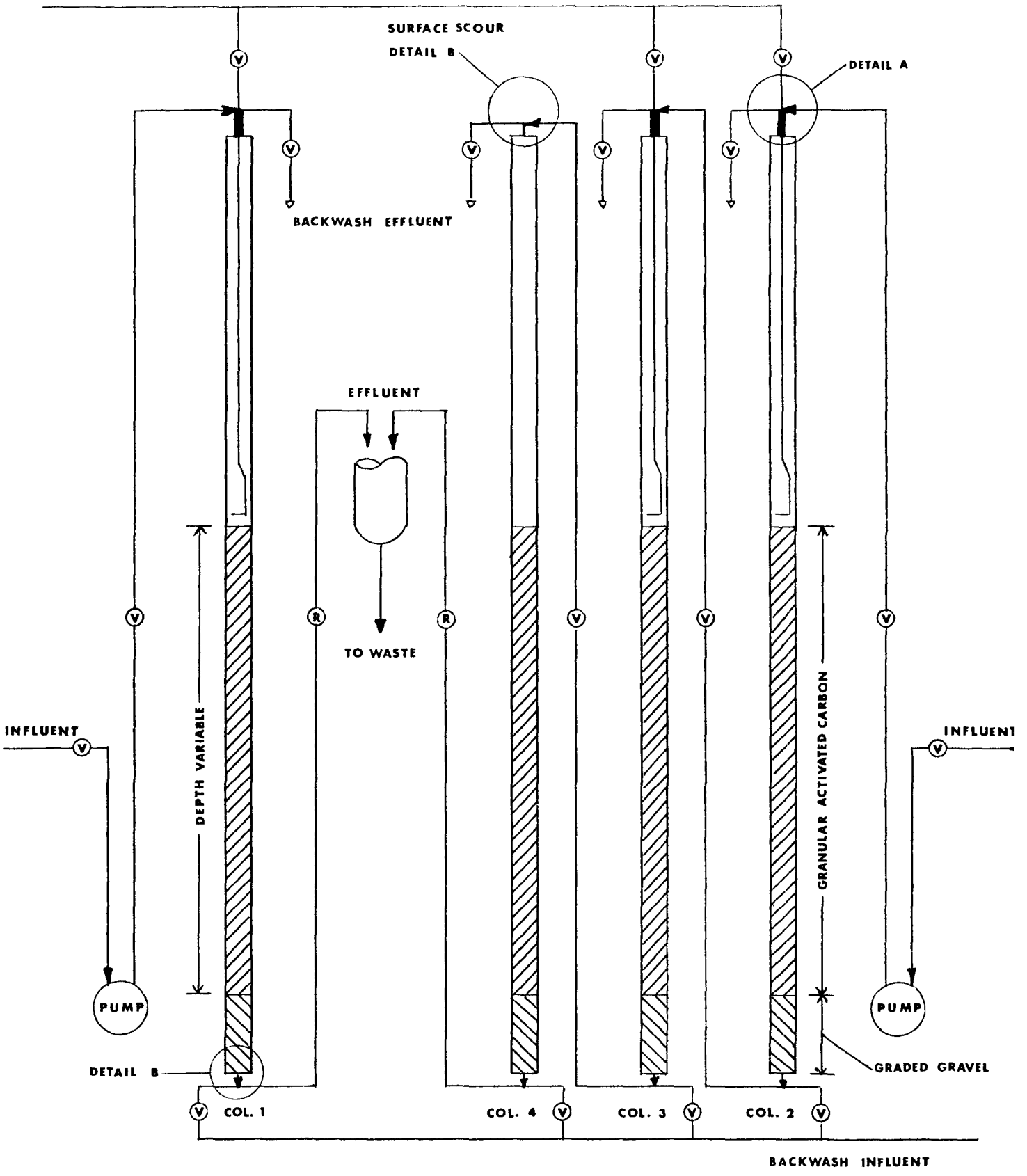

FIGURE 1 PILOT GRANULAR ACTIVATED CARBON COLUMNS

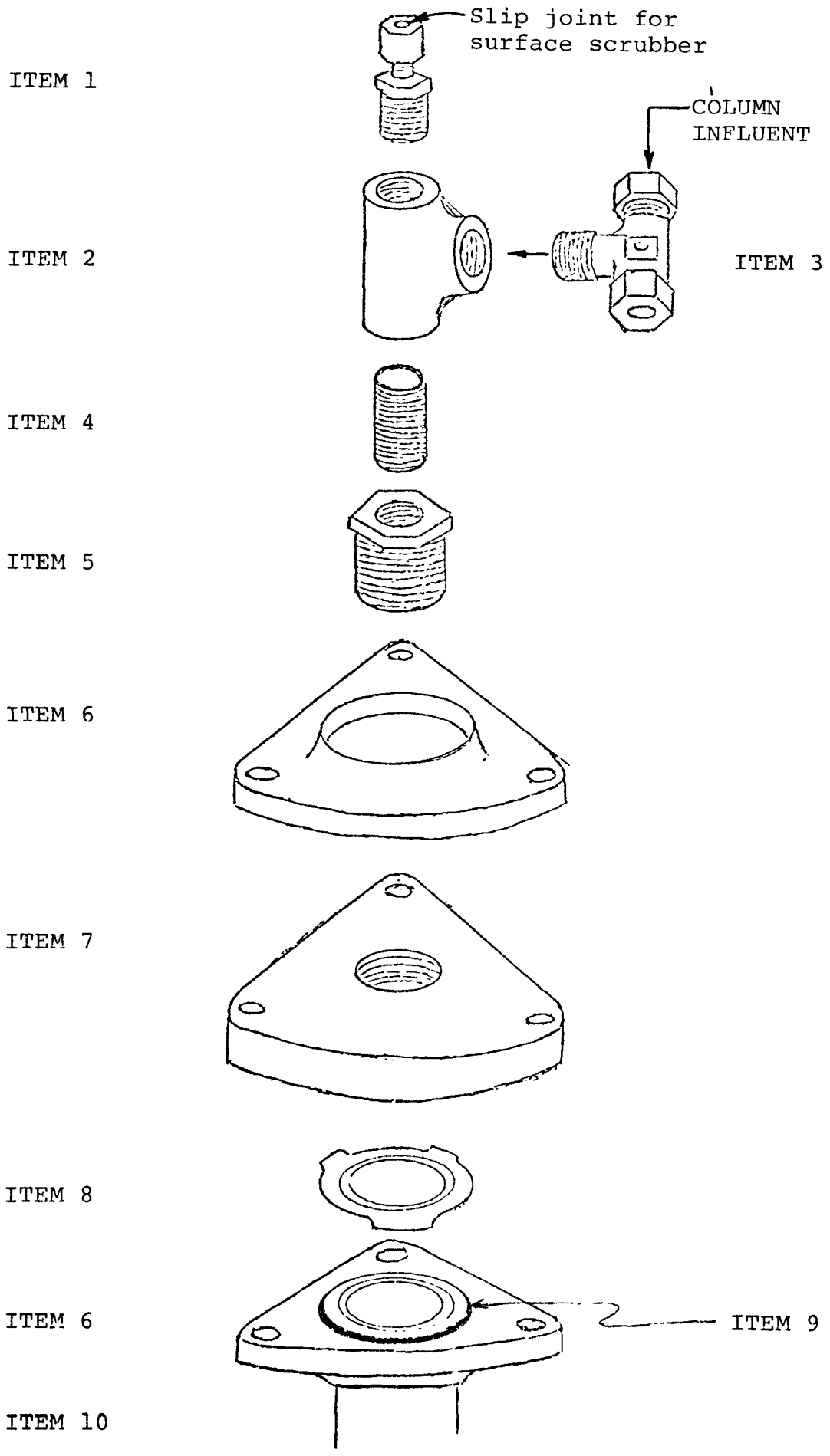

FIGURE 2 DETAIL A

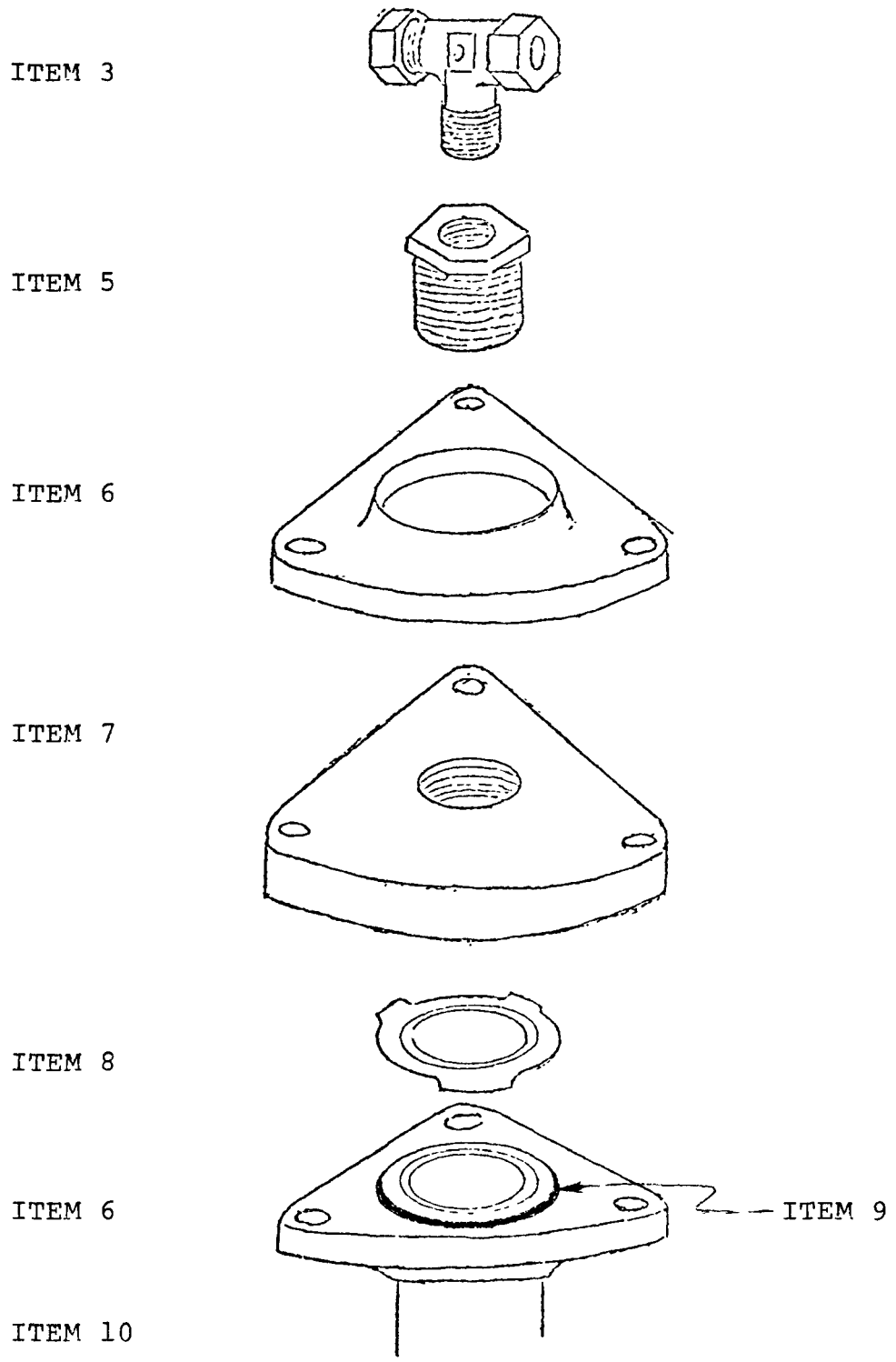

FIGURE 3 DETAIL B

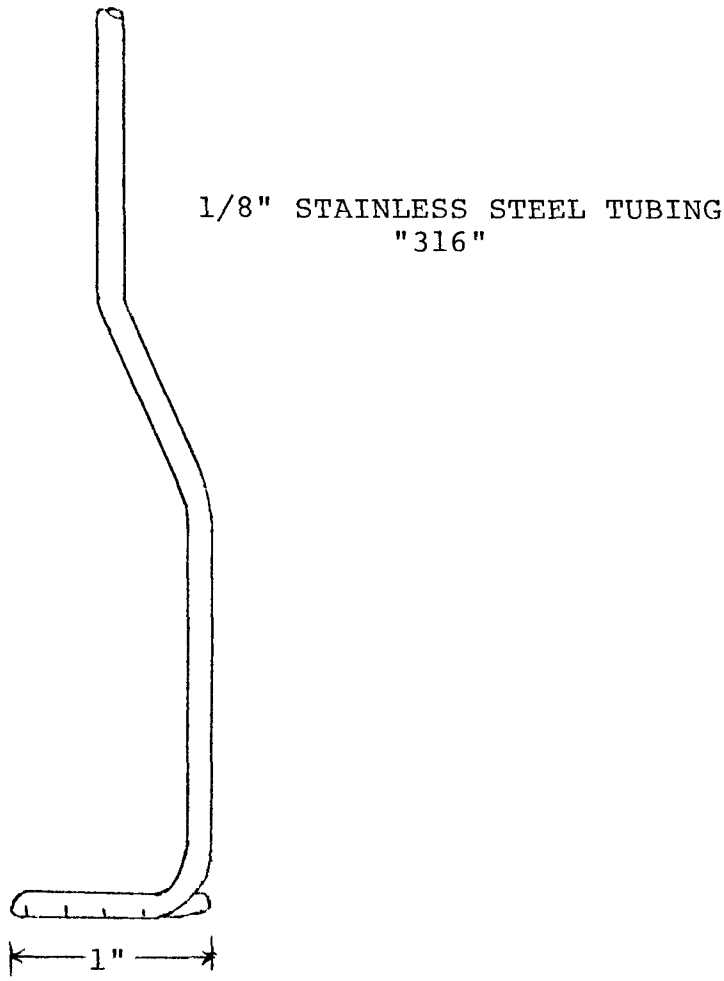

FIGURE 4 SURFACE SCOUR

mode could typically vary between 1.5 to 15 minutes, with an average of 7 to 8 minutes.

The additional columns shown on Figure 1 can be operated concurrently in a post-filter adsorption mode to examine the effects of longer empty bed contact times. For example, columns 2, 3, and 4 (Figure 1) can be charged with granular activated carbon, exposed to filtered rather than settled water, and sampled in series to monitor the breakthrough (wave front) of specific organics ("Performance Criterion 1") and the total organic carbon ("Performance Criterion 2 and 3"). On the other hand an investigator may desire to use column 2 as a sand filter receiving settled water and columns 3 and 4 as adsorbers. Another column in series would further increase the EBCT. Additional columns and the appropriate plumbing modifications would allow a utility to investigate in parallel, rather than in sequence, performance of different brands of commercially available granular activated carbon, should that be desirable. Finally, the choice as to whether or not to apply disinfected water to the adsorber will depend on how the final treatment scheme will be arranged. The engineer should have some experimental "breadth" to select the most satisfactory adsorption design.

Operation

The granular activated carbon must be wetted before it is put into service. This is accomplished by backwashing the material similar to the initial steps in using any granular media. Gently tapping or bumping the columns might be necessary to insure that the media is wetted. Sufficient freeboard should exist to permit 50 percent bed expansion during backwash. The frequency of backwashing during the experimental study will vary, depending upon the same factors influencing full-scale filtration (e.g., headloss, turbidity, carryover floc from settling, etc.) Details on monitoring the system are given in Appendix B, however, a routine operation schedule would include the following:

Parameter	Frequency
Flow Adjustment, Q	Daily
Temperature, pH, Turbidity	Investigator's discretion -- Based on variability of applied water
Low Molecular weight halogenated organic compounds	Weekly
Organic Carbon	Weekly
Terminal Summation THM	Weekly

At most field installations no restriction in available water volume would exist as it does in the WSRD pilot plant. Therefore larger, at least 10 cm (4 inch) diameter columns are recommended for use in the treatability studies proposed in the Interim Treatment Guide (see pages 23-26.)

The EPA Water Supply Research Division is currently designing an experimental adsorption system using 10 cm (4 inch) diameter glass columns. The system will be installed in at least one existing water treatment plant, and the experimental results along with the problems encountered with pumps, maintenance, and operation will be reported on when available. Details may be obtained by writing to the Director, Water Supply Research Division, Municipal Environmental Research Laboratory, 26 West St. Clair Street, Cincinnati, Ohio 45268.

PARTS LIST

ITEM NUMBER	DESCRIPTION*	QUANTITY
1	STAINLESS STEEL MALE CONNECTOR 1/8" TUBE x 1/4" PIPE THREAD BORED THRU WITH TEFLON FERRULES (EXAMPLE - SWAGELOK FITTING # SS-200-1-4-BT WITH TEFLON FERRULES)	3 EACH
2	1/4" STAINLESS STEEL PIPE TEE	3 EACH
3	STAINLESS STEEL MALE BRANCH TEE 1/4" TUBE x 1/4" PIPE THREAD (EXAMPLE - SWAGELOK FITTING # SS-400-3-4TTM)	8 EACH
4	1/4" STAINLESS STEEL CLOSE NIPPLE	3 EACH
5	1/2" x 1/4" STAINLESS STEEL REDUCING BUSHING	8 EACH
6	1-1/2" CORNING CONICAL FLANGE STYLE 1, ALUMINUM, # 72-9061	16 EACH
7	1/2" TEFLON SHEET SHAPED LIKE THE FLANGE IN ITEM 6, BOLT HOLES CLEARENCE DRILLED FOR 5/16 x 18 BOLTS, CENTER DRILLED AND TAPPED FOR 1/2" PIPE THREAD	8 EACH
8	1-1/2" GASKET, STYLE 1-2, SOLID TFE, TYPE T, CORNING NUMBER 72-9255	8 EACH
9	1-1/2" CORNING CONICAL MOLDED INSERT (HARD), # 72-9057	8 EACH
10	1-1/2" x 72" CORNING PYREX CONICAL PROCESS GLASS PIPE # 72-7501	4 EACH
	ALUMINUM 5/16 x 18 x 2" BOLTS W/NUTS	24 EACH
V	STAINLESS STEEL FORGED BODY SHUT-OFF VALVE WITH VEE TYPE STEM AND 1/4" TUBE FITTINGS (EXAMPLE - WHITEY VALVE # SS-1VS4)	17 EACH
R	STAINLESS STEEL FORGED BODY REGULATING VALVE WITH 1/4" TUBE FITTINGS (EXAMPLE - WHITEY VALVE # SS-1RS4)	2 EACH
PUMP	STAINLESS STEEL AND TEFLON GEAR PUMP WITH MAGNETIC COUPLING AND INTERNAL BY-PASS (EXAMPLE - MICROPUMP # 12-50-316)	2 EACH

* MENTION OF COMMERCIAL PRODUCTS DOES NOT CONSTITUTE ENDORSEMENT BY USEPA.

PARTS LIST (CONT.)

ITEM NUMBER	DESCRIPTION*	QUANTITY
	STAINLESS STEEL MALE CONNECTOR 1/4" TUBE x 1/8" PIPE THREAD FOR USE WITH MICROPUMPS (EXAMPLE - SWAGELOK FITTING # SS-400-1-2)	4 EACH
	STAINLESS STEEL 1/4" UNION TEE (EXAMPLE - SWAGELOK FITTING # SS-400-3)	8 EACH
	STAINLESS STEEL TUBE REDUCER 1/8" x 1/4" WITH 1/8" TEFLON FERRULES (EXAMPLE - SWAGELOK FITTING # SS-200-R-4 WITH TEFLON FERRULES) TO BE USED WITH THE SHUT-OFF VALVES ON THE SURFACE SCOUR LINE.	3 EACH
	1/8" STAINLESS STEEL TUBING "316" FOR SURFACE SCOUR. SHAPED AS IN FIGURE 4 AND PLACED THRU ITEM 1 (DETAIL A) AND CONNECTED TO THE SURFACE SCOUR VALVE USING THE STAINLESS STEEL TUBE REDUCER.	20 FEET
	1/4" STAINLESS STEEL TUBING "316" FOR ALL CONNECTIONS OTHER THAN SURFACE SCOUR.	60 FEET
	1/2" TEFLON TAPE USED FOR SEALING ALL PIPE THREAD CONNECTIONS	2 SPOOLS

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Acknowledgments

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