

OPERATIONAL ASPECTS OF GRANULAR ACTIVATED CARBON ADSORPTION TREATMENT

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Much has been written about the effectiveness of adsorption using granular activated carbon as a drinking water treatment process for the removal of organic contaminants.<sup>1</sup> Although the effectiveness of this process is generally recognized for organic control, questions have arisen concerning possible disadvantages that might occur during the use of granular activated carbon. The purpose of this report is to critically review these questions and summarize what is currently (June, 1978) known concerning each. Seven questions will be covered:

- 1) Do excessive bacterial growths occur on granular activated carbon?
- 2) Are endotoxins created when granular activated carbon is used?
- 3) Is turbidity effectively removed by granular activated carbon beds?
- 4) Do heavy metals leach from virgin granular activated carbon?
- 5) Do polynuclear aromatic hydrocarbons leach from virgin granular activated carbon?
- 6) Do materials desorb or "slough" in a slug from granular activated carbon?
- 7) Does thermal reactivation of granular activated carbon cause air pollution?

1) Do excessive bacterial growths occur on granular activated carbon?

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. Activated carbon removes residual disinfectant while concentrating bacteriological nutrients. Both factors could contribute to biological growth. This section of the report summarizes some of the bacteriological data from full scale and pilot plant studies where granular activated carbon was or is being used continuously. The intermittent use of activated carbon such as in home treatment units or the use of an oxidant to stimulate biological activity in activated carbon, are separate topics and not addressed in this report.

#### European Experience

Ford<sup>2</sup> in pilot plant studies at Foxcote (United Kingdom), frequently found higher plate counts (22°C) in the granular activated carbon filtrate than the sand filtrate. Table I, the summary of a 5-year comparison, shows 60 percent of the samples from the adsorption beds exceeded a bacterial count of 10/ml while the sand filter effluent only contained greater than 10 colonies/ml 20 percent of the time. The predominant organism in the effluent from the activated carbon filter was tentatively identified as "chlorine-damaged Flavo bacteria". Ford felt 3 days was insufficient for the development of easily visible colonies at 22°C so he suggested an incubation period of 7 days for future studies.

Table I

Frequency of Occurrence of Agar Plate Counts

3-Days, 22°C <sup>2</sup>

Plate Count, <u>Colonies/ml</u>	Sand <u>Effluent</u>	Activated Carbon <u>Effluent</u>
0-10	80%	40%
11-100	14%	25%
101-500	3%	10%
>500	3%	25%
No. of Samples	455	446

Melbourne and Miller<sup>3</sup> reported an interesting finding at Colwick (United Kingdom). Bacterial growths did not always occur on the activated carbon beds. For example, when appreciable numbers of bacteria were applied to the activated carbon, bacterial concentrations were reduced. At times when prechlorination or caustic soda softening was used, however, few bacteria remained in the influent to the activated carbon, yet growth of organisms within the bed was significant.

Knoppert and Rook<sup>4</sup> (Rotterdam) studied the effects of frequent backwashing for controlling bacteriological activity in pilot activated carbon adsorbers receiving filtered water. One adsorber was backwashed daily and the other twice a month. The bacterial count (22°C) increased from 10<sup>2</sup>/ml to 10<sup>4</sup>/ml within the first two months service then steadily declined. The authors concluded the bacterial quality from the adsorber backwashed daily was slightly better than the effluent from the less frequently washed bed. The plate count incubated at 37°C never exceeded 10/ml from either adsorber.

In the full scale water treatment plant at Vigneux-sur-seine (France), Richard<sup>5</sup> sampled the effluent from several types of granular activated carbons and found the agar plate count (24 hrs. at 37°C) slightly higher from the activated carbon as compared to a sand filter control. Tests for total and fecal coliforms were always negative.

Schalekamp<sup>6</sup> studied the bacterial content of granular activated carbon effluents at the Lengg Waterworks in Zurich, Switzerland. He found rather high bacterial counts after three days at 20°C, between  $10^2$  to  $10^4$ /ml, in effluents from pilot activated carbon columns. Similar data from the operating waterworks, however, showed bacterial counts between 10 and 40/ml. These operating filters were backwashed twice per week. Van Lier and co-workers<sup>7</sup> studied the bacterial count after three days at 22°C in the effluent from activated carbon filters in Amsterdam. In this study, bacterial counts declined from approximately  $10^4$ /ml in the applied water to  $10^3$ /ml in the effluent from the activated carbon filters.

In the Federal Republic of Germany the drinking water requirement for general bacterial populations as measured by plate count is 20/ml for systems employing treatment with disinfection. Engels<sup>8</sup> reports that at Düsseldorf, employing granular activated carbon adsorption following filtration, the effluent consistently meets this requirement even prior to final disinfection. At the Dohne plant in Mülheim ozonation is employed preceding granular activated carbon adsorption in an effort to increase the biological populations within the adsorber thereby enhancing organic removal. Even in this case, the general bacterial population in the effluent from the granular activated carbon adsorbers was only 3,700/ml.<sup>9</sup>

## United States Experience

During the summer of 1975, Sylvia and coworkers<sup>10</sup> investigated the extent of bacteriological regrowth in granular activated carbon filters. Bacterial concentrations (Standard Plate Count at 35°C for 48 hours) were routinely monitored in the applied water (coagulated, settled, and chlorinated Merrimack River water in Lawrence, Mass.) and in the effluent from both a 30-inch and 48-inch deep pilot granular activated carbon filter (9 min. and 14 min. empty bed contact time, respectively).

Table II summarizes the mean plate count results for the summer and fall test period.

Table II

Mean ( $G_m$ ) Standard Plate Count/ml

(Pilot Plant, Lawrence, MA)

Period	Influent	Effluent	
		9 min. EBCT	14 min. EBCT
June - Sept.	60	2800	4000
Sept. - Nov.	15	2000	55

Coliform analysis were also performed and out of 667 determinations, coliforms were detected in the granular activated carbon filter effluents on 22 occasions. The highest concentrations of coliforms occurred during a period when the settling basin was not performing adequately and coliforms were similarly detected in the effluent from the control (sand) filter.

The columns were backwashed approximately every 48 hours and bacterial concentrations were examined with respect to time in service. The samples

collected 1 hour after backwash consistently had higher standard plate counts than either the 24 or 48 hour samples, but no attempt was made to pinpoint exactly when the peak occurred.

Sylvia attempted to identify some of the gram negative bacterial species. Using the Minitek<sup>tm</sup> system (a produce of BBL<sup>\*</sup>) the following organisms were identified:

Salmonella arizona

Providencia alcalifaciens

Citrobacter freundii

Yersinia enterocolitica

Enterobacter cloacae

Enterobacter agglomerans

Proteus rettgeri

Hansen<sup>11</sup> reported bacteriological regrowth in his activated carbon filters but felt they could be controlled through an improved backwashing schedule along with increased chlorination to the applied water. Mr. Hansen, a water treatment plant superintendent, has several years operational experience with granular activated carbon and recommends never allowing a filter or adsorber to stand idle for over an hour. If a granular activated carbon filter must be out of service for a longer period, it should be diligently backwashed before resuming operation.

The bacterial quality of untreated and treated Ohio River water from the EPA Water Supply Research Division's (WSRD) organics removal pilot plant was routinely monitored over a four-month period by the staff of the WSRD

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\*Mention of commercial products does not constitute endorsement by EPA

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 III), in general, show 99 percent reduction in the bacterial count through the treatment plant. Note 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.

Table III

MONTHLY MEAN ( $G_m$ ) STANDARD PLATE COUNT

(Pilot Plant Studies - Ohio River Water)

All bacterial counts are No./ml

Time in Operation Months	Raw	Settled	Effluent from Dual Media Filter	Effluent from Granular Activated Carbon Adsorber (EBCT = 10 min)
1	19,600	1650	137	63
2	12,000	1000	270	72
3	7,170	790	80	29
4	6,680	700	100	37



No attempt was made to measure attached growths. An attempt was made, however, to isolate and identify the predominant populations in the pilot plant. In the effluent from the granular activated carbon, five or six different types of colonies could be recognized and two genera, Flavobacterium and Xanthomonas were identified from smear plates.

Currently (1978), several ongoing studies include monitoring bacteriological development within granular activated carbon beds. For example, at Little Falls, New Jersey<sup>12</sup> standard plate counts (2-day, 35°C) and coliform analyses are being made daily on the effluent from three full-scale adsorbers. The applied water has a mean ( $G_m$ ) plate count less than 10/ml and after one month in service, the mean SPC of the granular activated carbon effluent is approximately  $10^2$ /ml.

In the pilot GAC column study at Kansas City, Missouri<sup>13</sup> O'Connor is examining attached bacterial growth and the effects of hot-water (co-current flow) washing. Also, studies are under way in Miami, Florida examining microbial flora in granular activated carbon columns. Parsons<sup>14</sup> examined the effluent from a pilot granular activated carbon by several bacterial isolation methods and concluded most bacterial growth went undetected by Standard Methods. Her work is continuing in the tepid climate of southern Florida and some of the organisms thus far identified include:

Pseudomonas - like bacteria

Enterobacter agglomerans

Acinetobacter

Alcaligenes faecalis

Moraxella

Flavobacterium

In summary, the purpose of water treatment is to produce a safe (potable) and palatable product. Bacteria can multiply within granular activated carbon beds, however, studies have shown the concentration of bacteria depends on:

- o length of time the granular activated carbon sits idle
- o the concentration (and possibly type) bacteria in the applied water
- o the procedure used to enumerate the bacteria (22°C versus 35°C or 37°C)
- o the length of times after backwashing and total time in service
- o applied total organic carbon
- o depth of bed
- o temperature

None of the investigators cited expressed any real concern for the bacteriological activity observed and several commented on how easily the populations were controlled by a small amount of post disinfectant. Other studies have shown a reduced disinfectant demand in granular activated carbon effluents, further simplifying the task of final disinfection. Finally, indicator organisms (coliforms) or pathogens have not been shown to increase through granular activated carbon beds.

2) Are endotoxins created when granular activated carbon is used?

Endotoxins are lipopolysaccharide-protein complexes produced in the cell walls of Gram-negative bacteria. 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 in Table III. Using the Limulus lysate bioassay,<sup>15</sup> 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 (Table IV). The encouraging finding was that no increase in pyrogenic activity occurred in the effluent from the granular activated carbon bed.

Table IV.

MONTHLY MEAN ( $G_m$ ) ENDOTOXIN CONCENTRATIONS,  $\mu g/l$

(Pilot Plant Studies - Ohio River Water)

Time in Operation, Months	Raw	Coagulated/Settled	Dual Media Effl.	Granular Activated Carbon Adsorbent Effluent (EBCT = 10 min.)
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

An extramural project entitled "Pyrogenic Activity of Carbon-Filtered Waters"<sup>16</sup> is underway at Texas A&M University. Samples for endotoxin concentrations are being collected from about a dozen full-scale water treatment plants utilizing granular activated carbon adsorption. The empty bed contact time for these adsorption systems range from 4 to 13 minutes and the time in service ranges from slightly over 1 month to 9 years. This study is near completion and thus far no instances have been found where endotoxin levels increased through the granular activated carbon. In all cases, the concentrations were either unchanged or reduced through the activated carbon. The companion standard plate counts have also been low in this study.

In summary, studies to date (1978) have not shown increased endotoxin concentration in effluent from granular activated carbon filters, some of which have been in service for several years.

3) Is turbidity effectively removed by granular activated carbon beds?

One decision facing a state regulatory agency when a water utility requests permission to replace the sand in their filters with granular activated carbon is whether or not some sand should remain in the filter as a guard against floc penetration. This section of the report summarizes some of the performance data available from both a full-scale water treatment plant and pilot plant studies. The question of whether granular activated carbon should be used alone (sand replacement) or only following filtration (post-filter adsorption) is a separate topic and is not addressed here.

Specifications for Filter Media

The manner in which particulates are removed during filtration has been examined and reported by numerous investigators, and traditional design criteria cover hydraulic loading rates, media size, and filter depth. For example, until recently in the United States probably 90 to 95 percent of all gravity filters were designed based on a hydraulic rate of 2 to 2.5 gallons per square foot per minute ( $\text{gpm/ft}^2$ ) through 24 to 28 inches of granular medium having an effective size of 0.4 to 0.5 mm. That these criteria have been proven effective should not preclude modifications or changes that can be demonstrated to provide equal performance. Evidence of changes can be seen in some newer water treatment plants designed within the past 10 years that have a variety of loading rates and multiple-type media in their filters.

In the AWWA Standard for Filtering Material<sup>17</sup> the effective size for filter sand is reported as ranging between 0.38 and 0.65 mm and for filter

anthracite, between 0.45 and 1.60 mm. The only physical constraints other than cleanliness are:

"Filter sand shall consist of hard, durable grains of siliceous material less than 2.4 mm in greatest dimension ...."

"Filter anthracite shall consist of hard, durable anthracite coal particles of various sizes; the hardness shall be not less than 2.7 on the Moh scale; the specific gravity shall not be less than 1.4 ...."

Granular activated carbon "shall be composed of hard durable grains; specific gravity shall be between 1.3 and 1.6." (This is given in Appendix A of Reference 17 as "information only".)

Table V compares some of the properties of materials used in granular filters

Table V

PHYSICAL PROPERTIES OF GRANULAR FILTERING MEDIA

Medium Description	<u>Granular Activated Carbon</u>		Sand	Anthracite
	Coal Base	Lignite Base		
Effective size(s) mm	0.55 to 0.65	0.80 to 0.90	0.38 to 0.65	0.45 to 1.6
Uniformity coefficient (UC)	$\leq 1.9$	$\leq 1.7$	1.2 to 1.7	$\leq 1.8$
Density (gm/cc)	1.4	1.4	2.65	1.57

### Sand With Granular Activated Carbon in the United States

In 1975, Symons<sup>18</sup> attempted to contact all the U. S. water utilities using granular activated carbon and sent a questionnaire concerning adsorption practices. One of the questions asked was, "Was sand required to be left under the granular activated carbon?" Twenty-eight of the 37 facilities that responded to the question said "Yes", and the amount of sand required averaged 8 inches. Survey results included those from utilities in 22 states.

### Comparison of Sand to Granular Activated Carbon as a Filtering Media

#### Field Study

Studies conducted in 1970 by the Lawrence Experiment Station examined the parallel operation of a 30-inch deep sand filter (es = 0.46 mm; UC = 1.9 resting on 18 inches of graded gravel) and a 33-inch deep granular activated carbon (Filtrisorb 200)<sup>\*</sup> filter (resting on 15 inches of graded gravel with no sand) within the municipal water treatment plant at Lawrence, Massachusetts. The hydraulic loading was 2.5 gpm/ft<sup>2</sup> and Figure 1 shows the results for turbidity removal. The turbidity in the effluent from the granular activated carbon filter was as low or lower than the turbidity in the sand filter effluent in all samples. Thus, granular activated carbon was concluded to be as effective as sand for use as a filtration medium (under the conditions of the experiment), and the State of Massachusetts allows the use of granular activated carbon (without any sand) as both a filtration and an adsorption medium.

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\* Calgon Corp., Pittsburgh, Pa. See the Table (coal base) for physical properties.

### Pilot Plant Studies

Further studies by personnel at the Lawrence Experiment Station on a small scale showed that the greatest floc buildup in a granular activated carbon filter adsorber occurs (as one would expect with a sand filter) within the top six inches.<sup>19</sup> Pilot scale studies by the WSRD showed that granular activated carbon (Filtrisorb 200 and 400) was comparable to dual media (anthracite/sand) for turbidity removal (see Figures 2 and 3). Floc penetration, as indicated by headloss at various depths, is much greater in a dual media filter, see Figure 4. Because it is a single medium, granular activated carbon provides more surface than depth filtration see Figure 4, and, consequently, filter runs may be shorter than those for a dual medial filter, but comparable to those for sand filters.

Head loss and effluent turbidity data were also collected for a 30-inch pilot column containing lignite base granular activated carbon treating settled water, (larger effective size, see Table V). These data are compared to similar data collected from a dual-media filter in Figure 5. Note that along the "Total Headloss" curve for the lignite-base granular activated carbon the effluent turbidity was 0.1 NTU after 40 hours and only 0.2 NTU after nearly 90 hours. Turbidity breakthrough up to 0.7 NTU occurred after almost 40 hours with the dual-media system. Also some depth filtration occurred in the lignite-base granular activated carbon system.

In summary, studies in both the laboratory and the field demonstrate granular activated carbon with an effective size of 0.90 mm or less and an uniformity coefficient of 1.9 or less is as effective a filtering media as sand or as an anthracite/sand (dual media) mixture. The experiences in



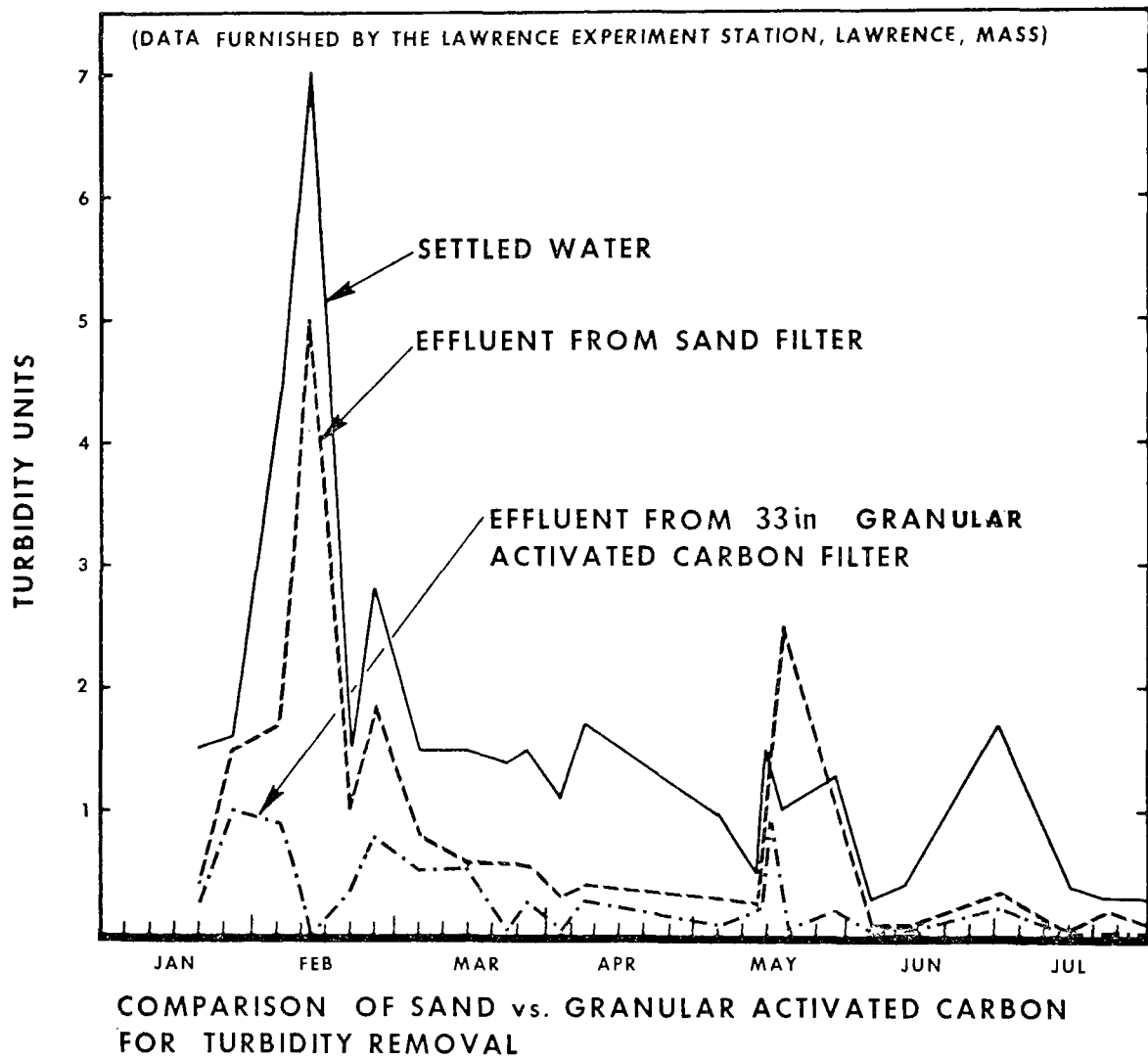
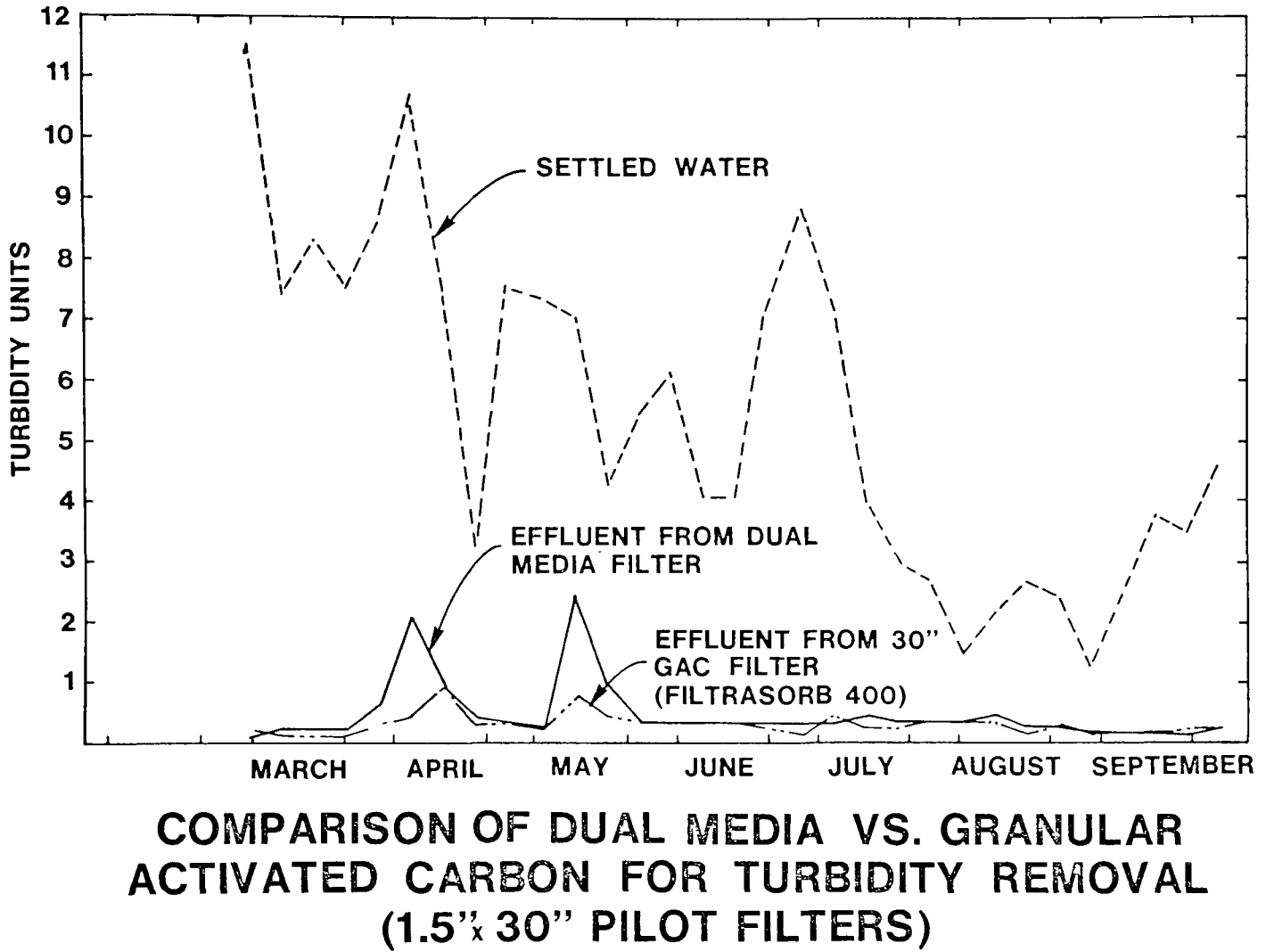
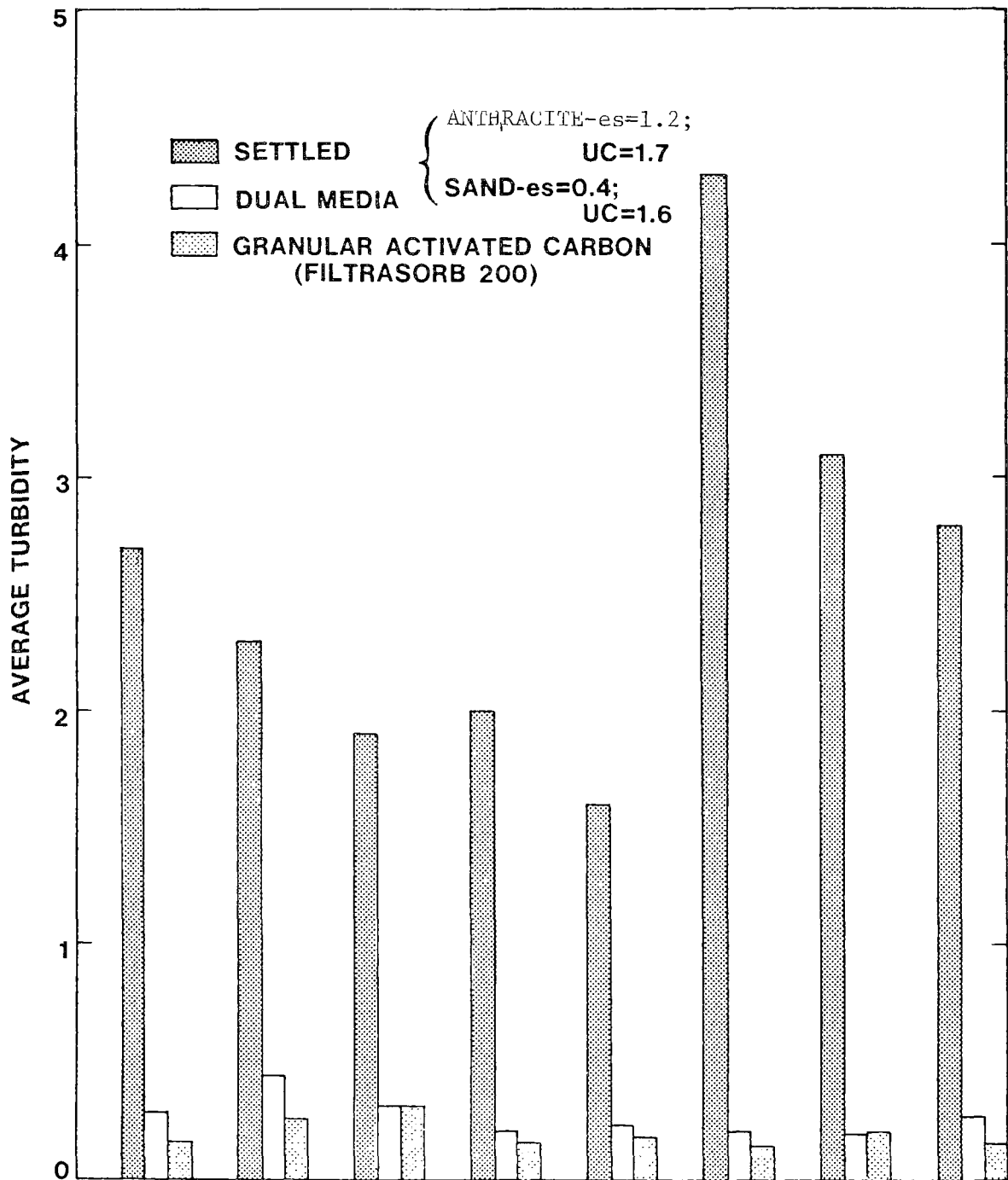


FIG 1

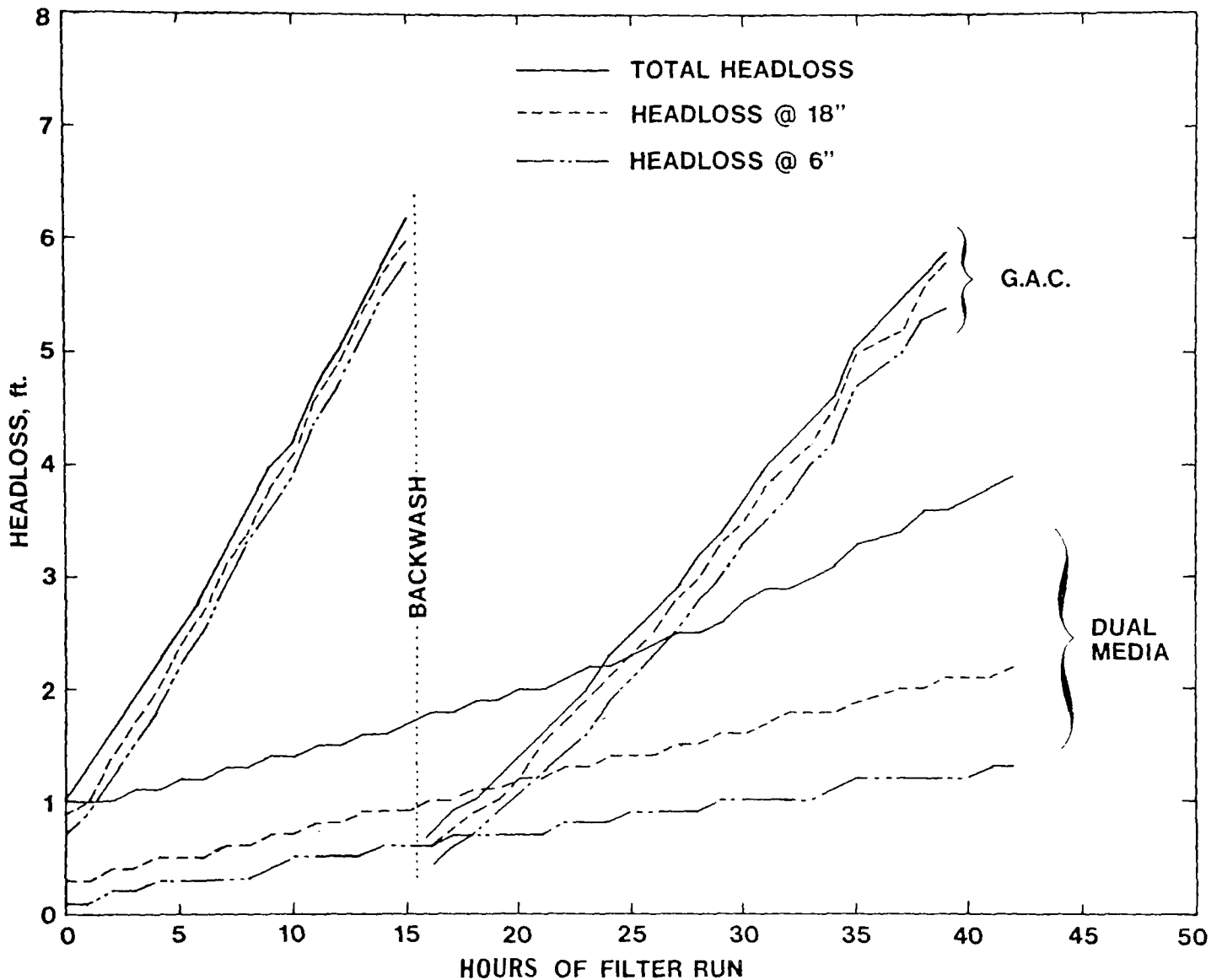


**FIG 2**



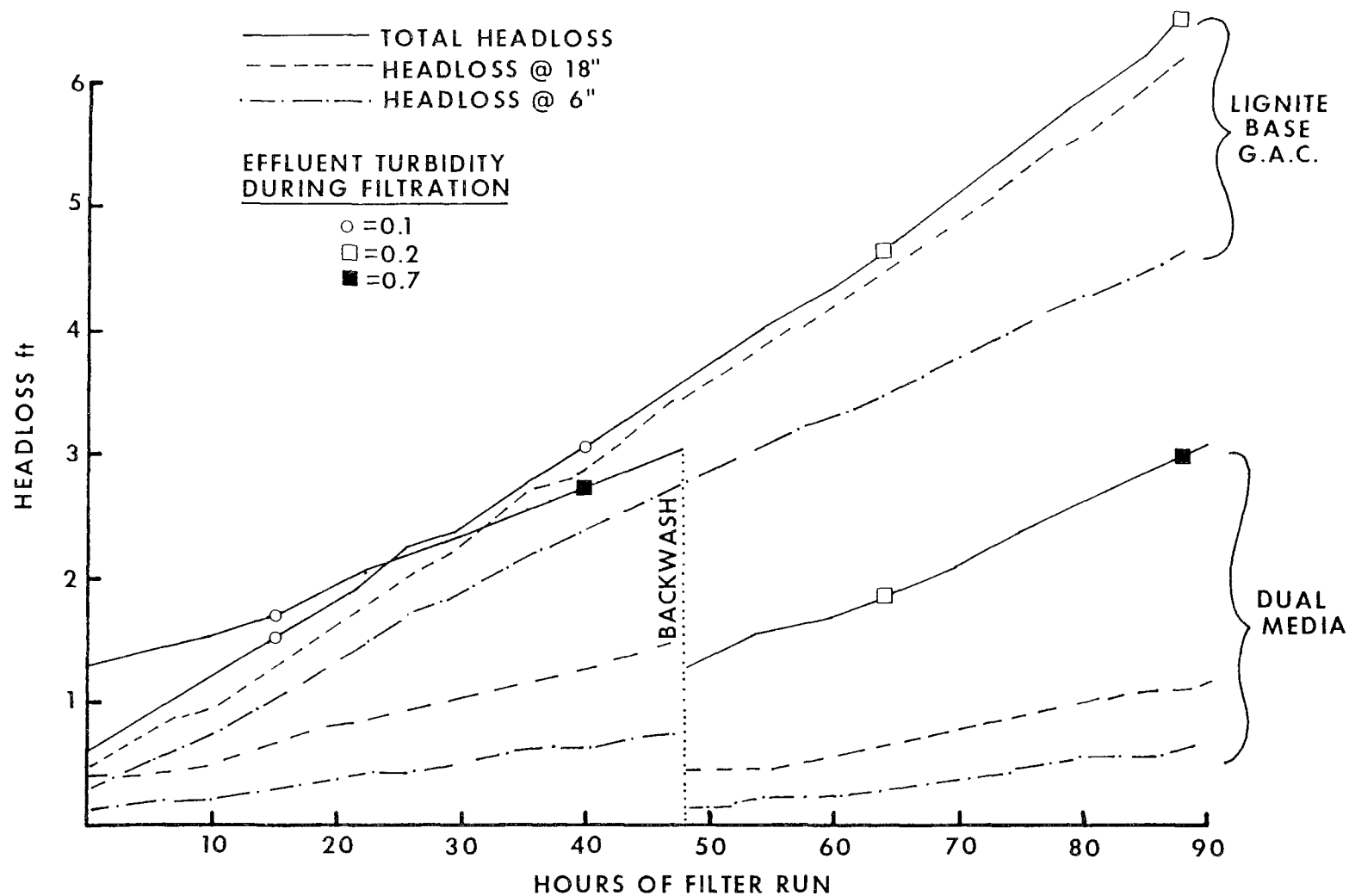
WEEKLY COMPARISON OF DUALMEDIA VS.  
GRANULAR ACTIVATED CARBON FOR TURBIDITY  
REMOVAL ( 4in x 30in PILOT FILTER )

FIG 3



**HEADLOSS WITHIN VARIOUS DEPTHS FOR GRANULAR ACTIVATED CARBON & DUAL MEDIA (PILOT PLANT)**

**FIG 4**



COMPARISON OF GRANULAR ACTIVATED CARBON  
AND DUAL MEDIA FILTER PERFORMANCE  
(PILOT PLANT)

FIGURE 5

the Lawrence, Massachusetts water works and the EPA pilot plants in Cincinnati, Ohio have also shown that a graded gravel base (or an equivalent means of providing an uniformly distributed backwash flow) is necessary for proper filter cleansing; however, any sand layer below 24 or more inches of granular activated carbon ( $d_{10} = 0.90$  mm or less;  $UC = 1.9$  or less) is redundant as a safeguard to floc penetration, and space could better be utilized with additional granular activated carbon.

Because adsorption is directly related to contact time, the depth of the granular activated carbon is directly related to its effectiveness and longevity of performance. Therefore, every inch of sand left in a filter is one inch less adsorption medium that could be effectively adsorbing organics. Another consideration is the handling of the granular activated carbon if frequent reactivations are necessary. The sand-activated carbon interface might make educting only activated carbon difficult, as some mixing of media within the filter bed is likely. This would require an additional sand separation step to avoid the formation of fused siliceous material in the reactivation furnace.

4) Do heavy metals leach from virgin granular activated carbon?

Directo, Chen, and Miele<sup>20</sup> sampled virgin granular activated carbon for metal content as part of a study for treating municipal wastes. Twenty-five grams of Calgon Filtrasorb 300 (a bituminous coal base granular activated carbon) were refluxed 24 hours with acid (6N HCl), then rinsed with distilled water. Table VI shows the concentrations of metals found in that washing.

Recently, (1978) approximately 2500 gm of Calgon Filtrasorb 400 were flushed repeatedly with distilled water within the EPA Water Supply Research Division laboratories. Table VII shows the concentration of several parameters expressed both as mg/l (in the recycled water) and mg/kg in the activated carbon. This also demonstrated under very anomalous and stressed conditions, some materials can be leached from granular activated carbon. More importantly, however, are the results obtained when an actual drinking water was used to flush the adsorbent. Following the distilled water refluxing, the granular activated carbon was exposed to approximately 1000 gallons of Cincinnati tap water (four days of continuous flow) then the influent and effluent were resampled. No discernible increases (but some decreases) in the same parameters were observed (Table VII).

Table VI.

Heavy Metals in Granular Activated Carbon -- Acid Refluxing<sup>20</sup>  
(mg/kg carbon)

Metal	Virgin Filtrasorb 300
Hg	1.92
Se	<0.96
Sb	<7.20
Sn	<48.00
Co	<4.80
Tl	<24.00
Mo	<12.00
Ti	240.00
V	24.00
Be	2.40
Bi	<24.00
Zn	1.20
Cr	7.20
Pb	16.80
Ni	12.00
Mn	26.40
Cu	<1.20
Ba	50.40
Cd	1.20
As	108.00
Fe	617.00
Al	1536.00
Sr	72.00
Ca	391.00



Table VII

Leaching of Materials from Granular Activated Carbon

Parameter	Distilled Water Reflux <sup>a</sup>			Tap Water Flush <sup>b</sup>	
	Before <sup>*</sup>	After <sup>*</sup>	mg/kg carbon	Influent <sup>*</sup>	Effluent <sup>*</sup>
Hardness	<1	38	851	130	130
Turbidity	0.04	0.1	-	0.08	0.10
Color	1	3	-	3	3
TDS	<0.1	48	1075	210	209
Cl	<10	<10	<224	20	19
SO <sub>4</sub>	<15	<15	<336	70	67
NO <sub>3</sub> (N)	<0.3	<0.3	<6.2	1.3	1.4
Na	<1	1.3	29.1	12.6	12.5
Ba	<0.2	<0.2	<4.5	<0.2	<0.2
As	<0.005	0.015	0.3	<0.005	<0.005
Se	<0.005	<0.005	<0.1	<0.005	<0.005
F	<0.1	<0.1	<2.2	0.1	0.1
Ca	<0.1	10.3	231	34.0	32.4
Mg	<0.01	0.73	16.3	8.28	8.91
pH	5.4	8.8	-	7.5	7.4
Ag	<0.03	<0.03	<0.7	<0.03	<0.03
Cu	0.03	<0.02	<0.4	0.03	<0.02
Mn	<0.03	0.04	0.9	<0.03	<0.03
Pb	<0.005	<0.005	<0.1	<0.005	<0.005
Fe	<0.1	<0.1	<2.2	<0.1	<0.1
Zn	<0.02	<0.02	<0.4	<0.02	<0.02
Hg	<0.0005	<0.0005	<0.01	<0.0005	<0.0005
TOC	0.12	0.33	4.7	1.44	0.28
ΣTHM	0.007	<0.0001	<0.01	0.027	<0.0001

<sup>a</sup> 56ℓ distilled water cycled approximately 100 times through approximately 2500 gm F-400 granular activated carbon

<sup>b</sup> Approximately 1000 gallons of Cincinnati tap water flushed through activated carbon column following step a.

\* Except for turbidity, pH, and color concentrations are mg/ℓ

In summary, inorganic compounds are associated with fresh granular activated carbon and under stressed conditions (i.e., acid refluxing or continuously recycling distilled water) quantifiable amounts of inorganics can be leached out of the adsorbent. From the available data, however, the likelihood of this being a problem with natural water is remote.

- 5) Do polycyclic aromatic hydrocarbons leach from virgin granular activated carbon?

Most of the granular activated carbon commercially available for water treatment is made from bituminous coal or lignite. These base products may contain polycyclic aromatic hydrocarbons\* (PAH) and the question is do these contaminants survive thermal activation (or are they possibly created during the activation step) only to be released when exposed to water?

Andelman and Suess<sup>21</sup> present a good overview of the literature concerning PAH's in water. In 1961, Borneff and Fischer<sup>22</sup> extracted 50 kg of activated carbon with benzene and were unable to find typical PAH adsorption bands using paper chromatography. More recently (1978) Zoldak<sup>23</sup> used a high pressure liquid chromatography procedure developed by Sorrell, et al.<sup>24</sup> and analyzed the influent and effluent of an activated carbon column that had been refluxed with distilled water then exposed to Cincinnati tap water for four days (see previous section on inorganics). Three of 14 PAHs were detected in quantifiable concentrations (i.e., greater than 1 ng/l), however these contaminants were in the influent as well as the effluent. For example, the total PAH's in the distilled water before refluxing were 24 ng/l (parts per trillion) and 22 ng/l afterwards. For perspective, the World Health Organization<sup>25</sup> (WHO) has a recommended limit of 200 ng/l for six readily detectable PAH's (see Table VIII).

In summary, few analytical studies have specifically addressed the question of PAH's leaching from granular activated carbon, however, from the available information this is not considered a problem.

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\* Also called polynuclear aromatic hydrocarbons, (PNA)

Table VIII  
PAH Concentrations (ng/ℓ) Leached from Fresh

PAH	Granular Activated Carbon <sup>a</sup>		Tap Water <sup>b</sup> Influent	Tap Water Effluent
	Before Reflux	After Reflux		
phenanthrene	6	10	2	2
anthracene	NF	<1	NF	NF
fluoranthene <sup>c</sup>	4	7	<1	<1
pyrene	14	5	<1	<1
1-methyl pyrene	<1	<1	NF	NF
chrysene	NF	NF	NF	NF
benzo(a)anthracene	NF	NF	NF	NF
perylene	NF	NF	NF	NF
benzo(a)pyrene <sup>c</sup>	NF	NF	NF	NF
benzo(b)fluoranthene <sup>c</sup>	NF	NF	NF	NF
benzo(k)fluoranthene <sup>c</sup>	NF	NF	NF	NF
dibenz(ah)anthracene	NF	NF	NF	NF
benzo(ghi)perylene <sup>c</sup>	NF	NF	NF	NF
indeno(1,2,3-cd)pyrene <sup>c</sup>	NF	NF	NF	NF
ΣPAH	24	22	2	2

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<sup>a</sup> F-400 granular activated carbon

<sup>b</sup> Cincinnati, Ohio tap water

<sup>c</sup> World Health Organization (WHO) indicator PAHs (ΣPAH < 200 ng/ℓ)

NF - not found

6) Do materials desorb or "slough" in a slug from granular activated carbon?

The effectiveness of adsorption is influenced by the temperature and pH of the water, but to a greater degree adsorption depends on:

- o concentration of adsorbent and adsorbate
- o contact or residence time
- o competition for available adsorption sites

Concern, therefore, has been expressed about having contaminants concentrated on the granular activated carbon and then subsequently released in a "slug" because of changing conditions.

Crittenden,<sup>26</sup> in a bisolute adsorption study, showed that during a column test, periods occurred when the effluent concentration of a weakly adsorbed material exceeded its influent values in the presence of a more strongly adsorbed compound. The "over shoots", as they were termed, were explained by an adsorption equilibrium theory, however, they seldom exceeded the influent by 20 percent. Some of this difference could be the result of analytical variability.

A good example of adsorption equilibrium phenomenon is shown in Figure 6 (Symons et al.)<sup>1</sup> Carbon tetrachloride in the tap water at Cincinnati was removed effectively during periods of high influent concentrations. As the influent concentration of carbon tetrachloride declined, the contaminant began to desorb. Although the influent concentrations exceeded 50 µg/l, desorption concentrations were generally less than 10 µg/l. These high concentrations of carbon tetrachloride in the tap water had no discernible effects on the trihalomethane concentrations in the effluent from granular activated carbon columns that had been in service

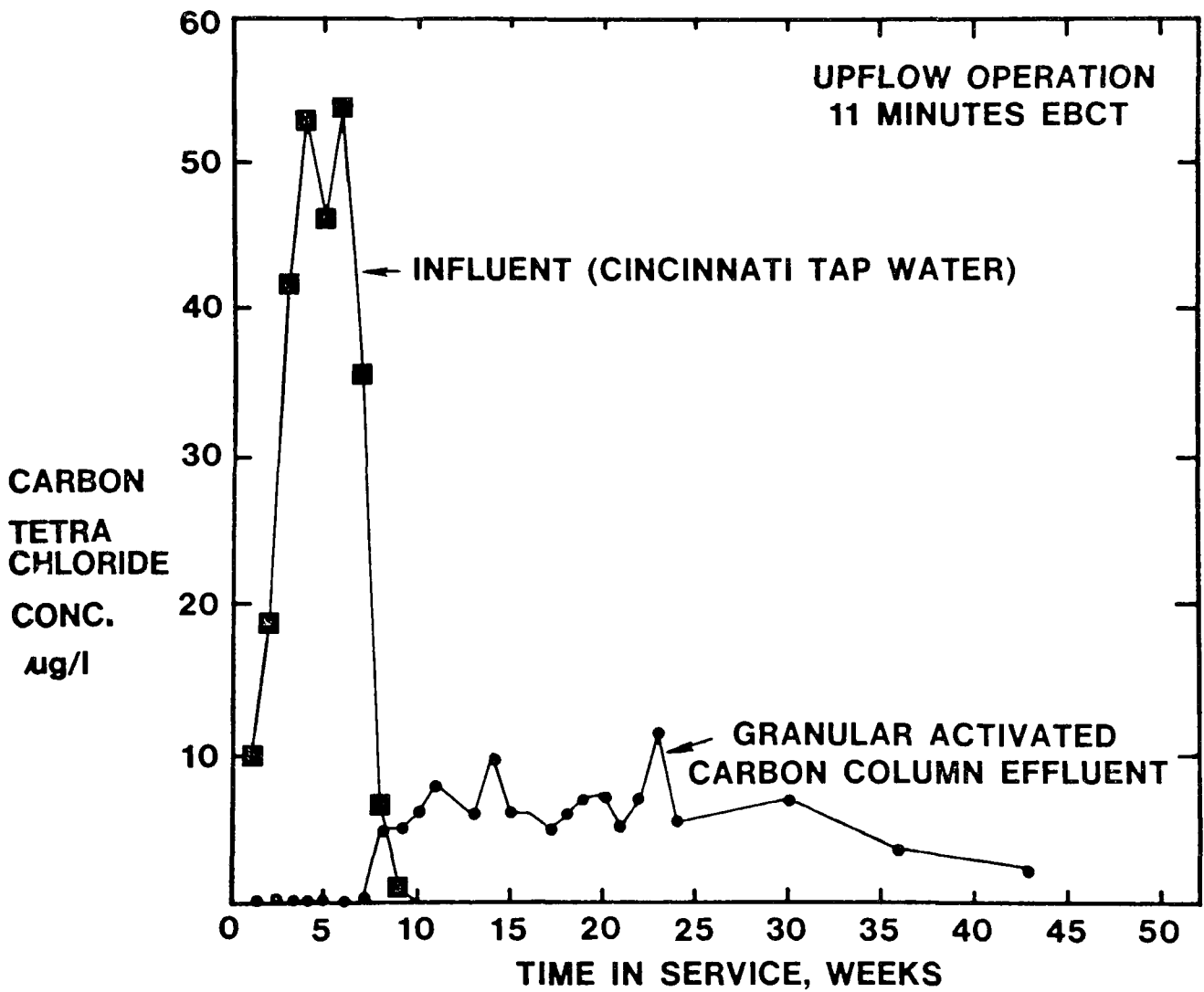


FIGURE 6. PERFORMANCE OF GRANULAR ACTIVATED CARBON BED FOR CARBON TETRACHLORIDE REMOVAL (Ref. 1)

for several weeks (see Figure 7). This at least demonstrates that trihalomethanes are not desorbed abruptly because of high carbon tetrachloride concentrations.

In a laboratory study on competitive adsorption, Snoeyink<sup>27</sup> noted little difference in the adsorptive characteristics of anthracene (a polynuclear aromatic hydrocarbon) both with and without humic acid. He concluded, therefore, that PAH will probably not associate with poorly adsorbable humic substances and result in "leakage of PAH from [activated] carbon beds".

A recent (1978) study at EPA shows the effects of varying water quality on inorganic desorption. Over a 2-1/2 month period, a lignite base granular activated carbon (ICI-1030) was intermittently exposed (58 to 90 hours/wk) to arsenic<sup>+3</sup> (0.11 mg/l to 0.23 mg/l), chromium<sup>+3</sup> (0.03 mg/l to 0.05 mg/l) and methyl mercury (0.004 mg/l). These contaminants were "spiked" in a good quality ground water. Cadmium (0.015 mg/l) and selenium (0.042 mg/l) were then selected as candidate contaminants in the influent to the activated carbon. Samples of the effluent analyzed twice daily for one week showed undetectable concentrations of methyl mercury and chromium. Some arsenic was detected in the effluent, however, it was also in the influent for some unexplainable reason (perhaps leaching from the sedimentation tanks).

In summary, adsorption and desorption occurs within granular activated carbon..... The differential migration of contaminants is presently (1978) unpredictable without on-site pilot scale adsorption studies; however, from the available data no evidence exists to support the belief that organic or inorganic materials are concentrated, only to be released in dangerous "slugs". The data show desorption, if any, is gradual and not abrupt.

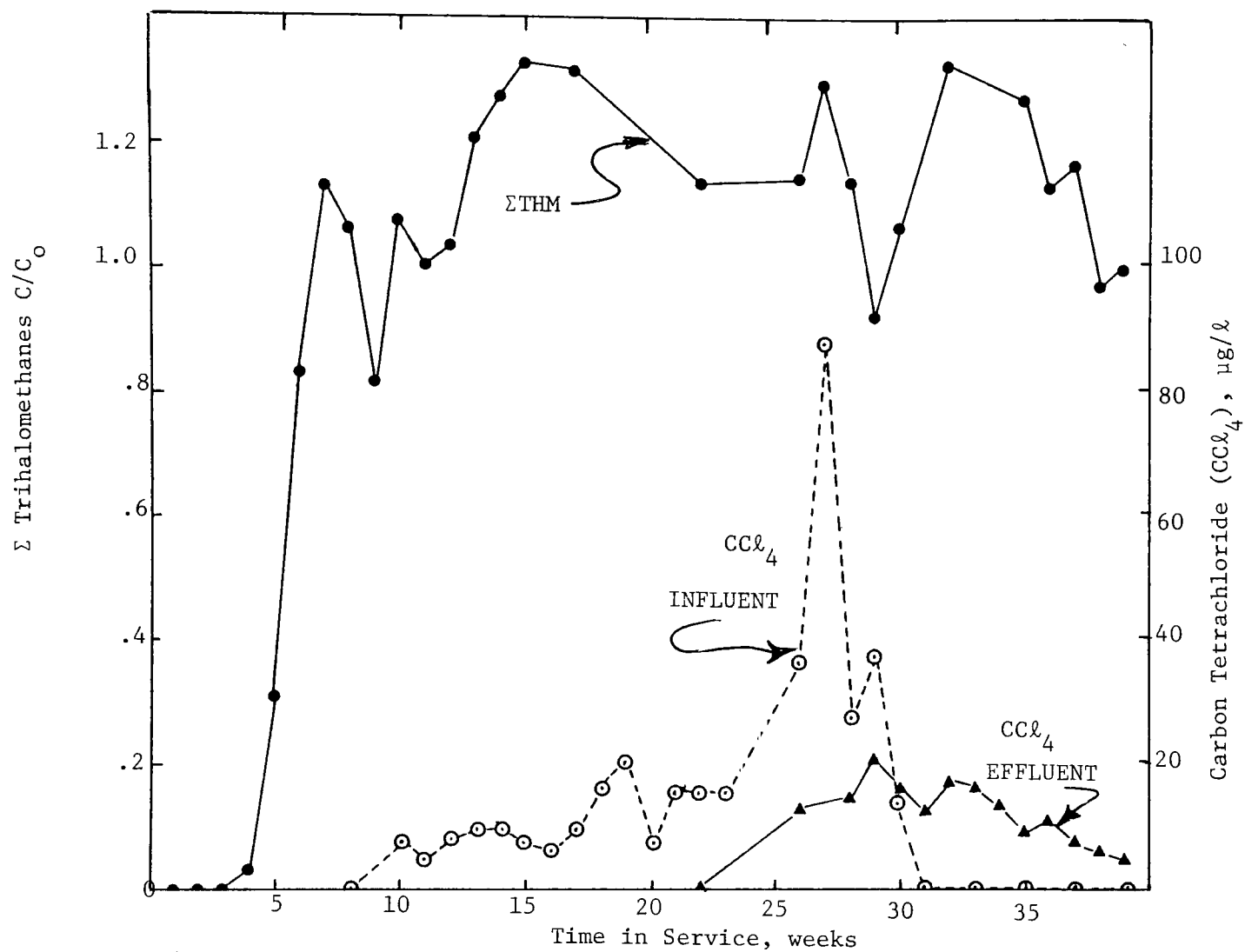


Figure 7. Influence of Carbon Tetrachloride Adsorption on Previously Adsorbed Summation Trihalomethanes



7) Does thermal reactivation of granular activated carbon cause air pollution?

Two studies were found that discussed the quality of exhaust gases from the air pollution control equipment associated with thermal reactivation of granular activated carbon used for treating sewage. From the first from Kyoto, Japan<sup>28</sup>, the properties and components of exhaust gas from the reactivation furnace itself, the after-burner and the scrubber during the reactivation of activated carbon are shown in Table IX. From these data, the dust and odor strength are shown to be reduced by after-burning, but sulfurous acid gas and NO<sub>x</sub> increase some. The scrubber is also effective for removing dust and sulfurous acid gas, but did not contribute to the removal of NO<sub>x</sub>. The increase of odor at the scrubber was caused by the use of secondary effluent for scrubbing. In the second and third reactivation, the concentrations of odorous substances and other chemicals contained in the exhaust gas from the reactivation furnace and after-burner were measured.

These results in Table X show the concentration of odorous substances at the outlet of reactivation furnace is high, but after after-burning, the concentration was considerably reduced.

At Pomona, California<sup>20</sup> flue gases discharged from the top hearth of the multi-hearth furnace contained both particulate and obnoxious-smelling substances. These air pollutants were controlled through an air pollution control system consisting of a baghouse for particulate removal and an afterburner, operated in series with the baghouse for odor control. The afterburner was operated at a temperature range of 719°C (1326°F) to 741°C (1368°F). The baghouse was operated at a temperature ranging from 149°C (300°F) to 163°C (325°F). Although maintaining a high temperature in

Table IX. Exhaust Gas Component <sup>28</sup>

Items	Method of Analysis	Outlet of Re-generation Furnace			Outlet of After Burning			Outlet of Scrubber		
		1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
Gas Temperature    °C		240	240	266	620	650	643	40	50	25
Dry Gas Volume Nm <sup>3</sup> /H	JIS Z8808	69	83	88	675	272	185	373	294	229
Moisture            V/V %	JIS Z8808	42.4	42.8	39.4	22.5	21.6	35.9	2.4	12.2*	13.1
Dust                g/Nm <sup>3</sup>	JIS Z8808 Dust Tube Method	1.31	3.14	3.84	0.16	0.27	0.26	0.05	0.05	0.06
SO <sub>2</sub> ppm	JIS K0103 Solution Conductivity Method	3	<5	<5	235 ~240	140 ~170	350 ~400	6~9	<5	<5
NO                 ppm	JIS K0104 Chemical Radiation Method	62 ~74	66 ~70	-	100 ~110	85 ~89	-	113 ~123	107 ~111	-
NO <sub>x</sub> ppm	JIS K0104	65 ~76	66 ~70	40 ~60	105 ~115	88 ~94	125 ~135	118 ~128	107 ~115	125 ~130
Power of Odor    (PO)	Equilibrium Method in Salt Water	11.9	11.9	10.4	2.6	1.0	0	5.3	2.3	5.1
CO <sub>2</sub> V/V %	Orsat Method	10.9	10.4	9.6	11.4	7.6	10.2	8.3	5.8	9.9
O <sub>2</sub> V/V %	Orsat Method	3.3	3.3	0.9	4.0	9.3	6.1	8.6	12.4	6.2
CO                 V/V %	Orsat Method	-	3.3	2.9	-	0	0	-	0	0.2

Table X. Concentration of Odorous and Other Substances in Exhaust Gas (ppm)

Items		Measuring Method	Threshold Value	Outlet of Furnace		Outlet of After Burning	
Name	Chemical Formula			2nd	3rd	2nd	3rd
Hydrogen Cyanide	HCN	JIS K0109 Pyridine Pyrazolon Method		4.2	5.2	<0.08	<0.006
Carbon Disulfide	CS <sub>2</sub>	E.A. Notification No.9 FPD-GC Method		120	90	<0.1	<0.02
Acetic Acid	CH <sub>3</sub> COOH	FID-GC Method		280	370	40	<0.2
Formaldehyde	HCHO	JIS K0102 Acetylacetone Method	1.0	<0.7	0.19	<0.5	<0.01
Acetaldehyde	CH <sub>3</sub> ·CHO	FID-GC Method	0.21	<30	19	<30	<0.3
Methane	CH <sub>4</sub>	FID-GC Method		1100	1.360	<10	35
Ethane	C <sub>2</sub> H <sub>6</sub>	FID-GC Method		54	3.5	<10	<0.3
Ammonia	NH <sub>3</sub>	JIS K0099 Indo Phenol Test		990	680	0.49	0.25
Tri-methyl Amine	(CH <sub>3</sub> ) <sub>3</sub> ·N	E.A. Notification No.9	0.0021	<0.05	<0.08	<0.05	<0.008
Hydrogen Sulfide	H <sub>2</sub> S	E.A. Notification No.9	0.005	<3	780	<0.03	0.15
Methyl Mercaptan	CH <sub>3</sub> ·SH	E.A. Notification No.9	0.041	<1	<2	0.002	<0.05
Dimethyl Sulfide	(CH <sub>3</sub> ) <sub>2</sub> ·S	E.A. Notification No.9		<0.5	<0.1	<0.001	<0.03

the baghouse to prevent condensation problems is advantageous, precaution had to be exercised to prevent the temperature from rising to within  $10^{\circ}\text{C}$  ( $50^{\circ}\text{F}$ ) to  $38^{\circ}\text{C}$  ( $100^{\circ}\text{F}$ ) of the critical temperature of the fabric filter. Thus, to minimize the danger of burning the filter bags, the baghouse inlet was equipped with a valved side connection for dilution air addition. Under normal furnace operating conditions, the dilution air inlet valve was maintained in a closed position. When the baghouse temperature increased beyond  $163^{\circ}\text{C}$  ( $325^{\circ}\text{F}$ ), however, which could have been triggered by a disruption of the activated carbon feed rate or plugging of the quench tank screen or both, the dilution air valve was manually opened for such a duration as needed to restore the temperature to about  $163^{\circ}\text{C}$  ( $325^{\circ}\text{F}$ ).

During reactivation, odors were detected and this was confirmed by the relatively high odor number of 3 odor units/l (90 odor units/SCF). Particulate emission was also high and averaged 0.30 kg/hr (0.64 lb/hr). Based on the particulate emission rate data, the baghouse removed only about 25 percent of the incoming dust load, which was significantly below the design removal efficiency of 99 percent. The emission data only represented samples collected over a 45 to 60 minute sampling period, however. The total actual weight of dust collected from the baghouse over the 53-hour reactivation period was only 14.7 kg (32.5 lbs.), which represented about 56 percent of the calculated dust removed.

In Table XI a summary of the emission data from the various components of the air pollution control system is presented. For purposes of comparison, the emission data obtained during the third regeneration of the lead contactor of the tertiary two-stage carbon adsorption system is also included

TABLE 11. SUMMARY OF AIR POLLUTION CONTROL SYSTEM PERFORMANCE

Parameters	APCD Emission Limit	1st Regeneration of IPC Carbon Column			3rd Regeneration of Two- Stage Carbon Column (III 3A)		
		Baghouse Inlet	Baghouse Outlet	Afterburner Outlet	Baghouse Inlet	Baghouse Outlet	Afterburner Outlet
1. <u>Particulate Matter</u>							
Concentration, mg/l	0.46	7.82	3.57	0.48	4.16	1.08	0.017
Emission Rate, kg/hr	0.45	2.11	1.44	0.30	0.98	0.36	0.11
2. <u>Oxides of Nitrogen, (NO<sub>x</sub>)</u>							
Concentration, mg/l dry	225.00	49.00	120.00	423.00	40.00	--	180.00
Emission Rate, kg/hr		0.016	0.068	0.49	0.012	--	0.18
3. <u>Oxides of Sulfur (SO<sub>2</sub>)</u>							
Concentration, mg/l SO <sub>2</sub>	2000.00	--	Nil	729.00	Nil	Nil	149.00
Emission Rate, kg/hr		--	Nil	1.17	--	--	0.26
4. <u>Hydrocarbons</u>							
Concentration, mg/l C		5530.00	2800.00	221.00	740.00	561.00	Nil
Emission Rate, kg/hr		0.74	0.56	0.066	0.09	0.095	--
5. <u>Carbon Monoxide (CO)</u>							
Concentration, % vol. dry		5.00	1.7	0.47	1.36	0.86	0.11
6. <u>Odor</u>							
Odor Units/l		777.00		3.00	706.00		0.70
7. <u>Gas Flow</u>							
Temp., ° C		271.00	121.00	665.60	177.80	70.60	620
Rate, l/sec		75.00	112.00	167.00	66.00	93.00	177.4

in this table. The emission parameters evaluated were significantly higher in the IPC activated carbon reactivation than in the activated carbon column III 3A. This observation was expected, considering that the ICP activated carbon column was subjected to a much heavier load of organic matter than column III 3A. Because both of these studies related to sewage treatment the air polluting is more difficult than would be the case by drinking water.

The following is a quotation from an April 27, 1978 letter from Dr. McGinnis III of the SHIRCO, Co. concerning this subject:

"As you know, the exhaust emissions which are of concern, fall into two general catagories: (1) particulate emissions, and (2) gaseous pollutant emissions, e.g. oxides of sulphur in nitrogen, hydrocarbons, and certain specific organic compounds. I will address these two catagories of emissions individually.

With regard to particulate emissions, we have made a number of measurements during pilot regeneration studies of granular carbon from industrial waste water treatment applications. These measurements have indicated typical uncontrolled particle loadings of 0.10 grains per dry standard cubic foot, or equivalently 0.001 pounds per hour of particulates per pound per hour of carbon regenerated. These uncontrolled emission levels approach compliance with existing codes. However, to assure a considerable margin on actual particulate emissions versus allowable, we typically supply a venturi scrubber which reduces the particulate emissions from the stack to 0.02 grains per dry standard cubic foot or equivalently 0.0002 pounds per hour of particulates per pound per hour

carbon regenerated. The fundamental reason for these low particulate emissions lies in the process which we employ. Since there is no stirring of the carbon, entrainment of fines is minimized and particulate emissions are quite low.

As to the emissions of gaseous pollutants, we have thus far made specific measurements only during regenerations of granular carbons used in industrial waste water treatment. In these cases, the carbon loadings are much heavier than one would expect in a municipal potable water application. However, following afterburning and scrubbing, concentrations of gaseous pollutants have been reduced to acceptable levels.

During our pilot tests of potable water carbons which have been used for taste and odor removal, we have made no specific measurements. However, I can say that qualitatively there are no obvious odors emitted from the stack after water scrubbing and without afterburning. This would tend to indicate that the small quantities of organic compounds present on the potable water carbons are being incinerated within the furnace itself. Although the atmosphere in the furnace is tightly controlled to minimize oxygen concentration, there are small leaks which provide sufficient oxygen to combust the compounds volatilized from the carbon."

Although data were not available in the literature, personal communications with the water utilities of Zürich, Switzerland and Düsseldorf, Fed. Rep. of Germany revealed that their reactivation furnaces had been operating for about 2 years on granular activated carbon used for drinking water treatment and that the air pollution control devices (after-burners and dust collectors) were effective. Therefore, air pollution should not be a problem from thermal reactivation of granular activated carbon.

## SUMMARY

Several questions have frequently been raised over the possible operational problems that might occur should granular activated carbon adsorption become wide-spread as an organic control unit process in the United States. This paper has examined seven of these possible problems and summarized the data available (much unpublished) on them. These data show that these potential problems are either non-existent or minor and should not be cause for preventing the use of this unit process in water treatment.

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