THM PRECURSOR REMOVAL EFFICIENCY OF REGENERATED AND VIRGIN CARBON*

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ABSTRACT

Aqueous chlorine reacts with certain precursors in water to form trihalomethanes (THMS)—suspected carcinogens/mutagens. It is necessary to minimize the concentration of THMs in finished water, either by removing the precursor before chlorination or by removing the THMs by advanced treatment. Granulated activated carbon (GAC) is an accepted procedure for removing the precursor from water. This article evaluates the different methods of regeneration in restoring the quality of the spent carbon and compares the removal efficiency of precursors by virgin and regenerated carbon.

Parallel pilot plant investigations were made using virgin and regenerated carbon. The size of each column was 4" individual diameter and 6' long, with glass reducers at both ends. The carbon depth was 36"—the flow maintained at 2.75 gal/min/sq. ft. Trihalomethane formation potential (THMFP) was measured at the end of 72 hours. The results show that all the three processes restored the carbon through regeneration to near virgin state. Statistical modeling indicates that all regenerated carbons performed alike, however, TOC removal failed to show any distinct correlation with precursor removal.

Aqueous chlorine reacts with certain precursors in water to form trihalomethanes (THMs); prominent among these are: $CHCl_3$, $CHBr_2Cl$, $CHCl_2Br$, and $CHBr_3$. It has been postulated that precursors responsible for formation of trihalomethanes

are ubiquitous in surface waters. Rook [1] and Bellar [2] were perhaps the first investigators to report the formation of micro-quantities of THM in water. Chloroform and other volatile organics are suspected carcinogens/mutagens. The presence of trihalomethanes in drinking water has raised the concern of public health safety. It is therefore necessary to minimize the concentration of trihalomethanes in the finished water. This can be achieved by various methods, such as, removal of trihalomethanes after formation, removal of trihalomethane precursors (THMFP), and the use of alternative disinfectants.

The main advantage of removal of THMs is that the municipalities will not have to change the disinfectant—chlorine. However, the interaction of aqueous chlorine with the precursors in water in addition to THMs produces other halogenated and non-halogenated byproducts. Most of these byproducts at this time cannot be measured individually by gas chromatographic techniques, but they can be measured as a group, as "organic halogen" (OX). But this test needs perfection [3], before it can be used as a routine test. Stevens, *et al.* appear to believe that chlorine dioxide in water may produce quinones, ketones, chloroquinones, and epoxides in varying quantities depending upon the dose and organic matter [4]. It is possible that some of these byproducts may pose greater health risks than THMs. THM precursors may be removed by chemical treatment [5, 6] or by adsorption.

Stevens, *et al.* reported the removal of precursors by a granular activated carbon (GAC) column [7]. Other studies (West Virginia [8], Jefferson Parish, LA [9]) showed that THM precursors could be removed by GAC treatment. The empty bed contact time (EBCT) were 7.1 and 23 minutes respectively.

The effectiveness of GAC for removing THM precursor on a continuous basis depends upon many factors including the cost of treatment because it is cheaper in most instances to regenerate the spent carbon rather than replacing it. Hence the performance of regenerated carbon, in removing precursors, is also of interest.

The objectives of this research were 1) To evaluate the different methods of regeneration in restoring the quality of the spent carbon. 2) To compare the removing efficiency of precursors by virgin and regenerated GAC.

This was accomplished by first using the GAC as filter media until GAC approached the limit of its absorption capacity. Then, the GAC was thermally regenerated. To provide comparison, three different regenerative processes were used. Following regeneration, the GAC was again tested for twelve weeks in parallel with virgin GAC and comparative measurements made in terms of TOC and precursor removal. The parameters measured daily were pH, alkalinity, carbon dioxide and dissolved oxygen. Weekly analyses were performed for THM and total organic carbon (TOC).

METHODOLOGY

The schematic flow diagram of the Potomac Treatment Plant[1] is shown in Figure 1. Water for this study was obtained after filtration but prior to chlorination.

The set up of the columns is illustrated in Figure 2. It consisted of four glass columns, (4″ internal diameter and 6′ long) with glass reducers at both ends. Fisher-Porter low flow rotameters were used to control flow rates and Meriam manometers to monitor the headloss through the carbon bed. The system used interconnecting teflon tubing. Calgon Filterasorb 400 was soaked in Super "Q" water before loading into the columns. Each column was backwashed with filtered water to remove the additional carbon fines.

The carbon depth in each column was 36″. The columns were then placed in service and operated at 2.75 gal/min/sq. ft. with an empty bed residence time of eight minutes. The influent water and effluent from the four columns were monitored until the adsorptive capacity of GAC was exhausted. Backwashing was done with filtered water, once or twice a week depending on the head loss. At the end of the test the carbon was removed from the columns and shipped for regeneration to three different firms. The processes used were fluidized bed, multi-hearth furnace, and infra-red. The fluidized bed bench-scale regeneration equipment consisted of a batch, fluidized bed reactor designed and instrumented for precise control of fluidizing gas flows, temperatures, and composition. The product gases from the reactor pass through a high efficiency cyclone to collect any entrained dust. The carbon was regenerated for a residence time of 5 minutes at $1650°F$.

The laboratory multi-hearth furnace unit, used an indirectly fired rotary kiln 8″ I.D. × 5′ long and the maximum temperature was $1750°F$ with an atmosphere of air and steam. The reactivation time was ≤ 20 minutes and volume yield ≥ 98 percent.

In infra-red regeneration process unit the residence time was 25 minutes at $1700°F$, 0.75″ carbon bed thickness and 0.66 lb/hr steam atmosphere purge. Filtrasorb 400 was placed in parallel with the columns containing the regenerated carbon. Thus during this phase of study it was possible to compare the effectiveness of regenerated carbon with virgin carbon.

Dissolved oxygen was analyzed with an oxygen meter[2]. Alkalinity was calculated utilizing the relationships between pH, alkalinity and temperature. All analyses were conducted according to Standard Methods for the Examination of Water and Wastewater [10].

All glassware for trihalomethane analysis was cleaned and oven baked at $200°C$ for at least two hours. For trihalomethane analysis samples were collected

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[1] Managed by Washington Suburban Sanitary Commission (WSSC)
[2] YSA Model 54.
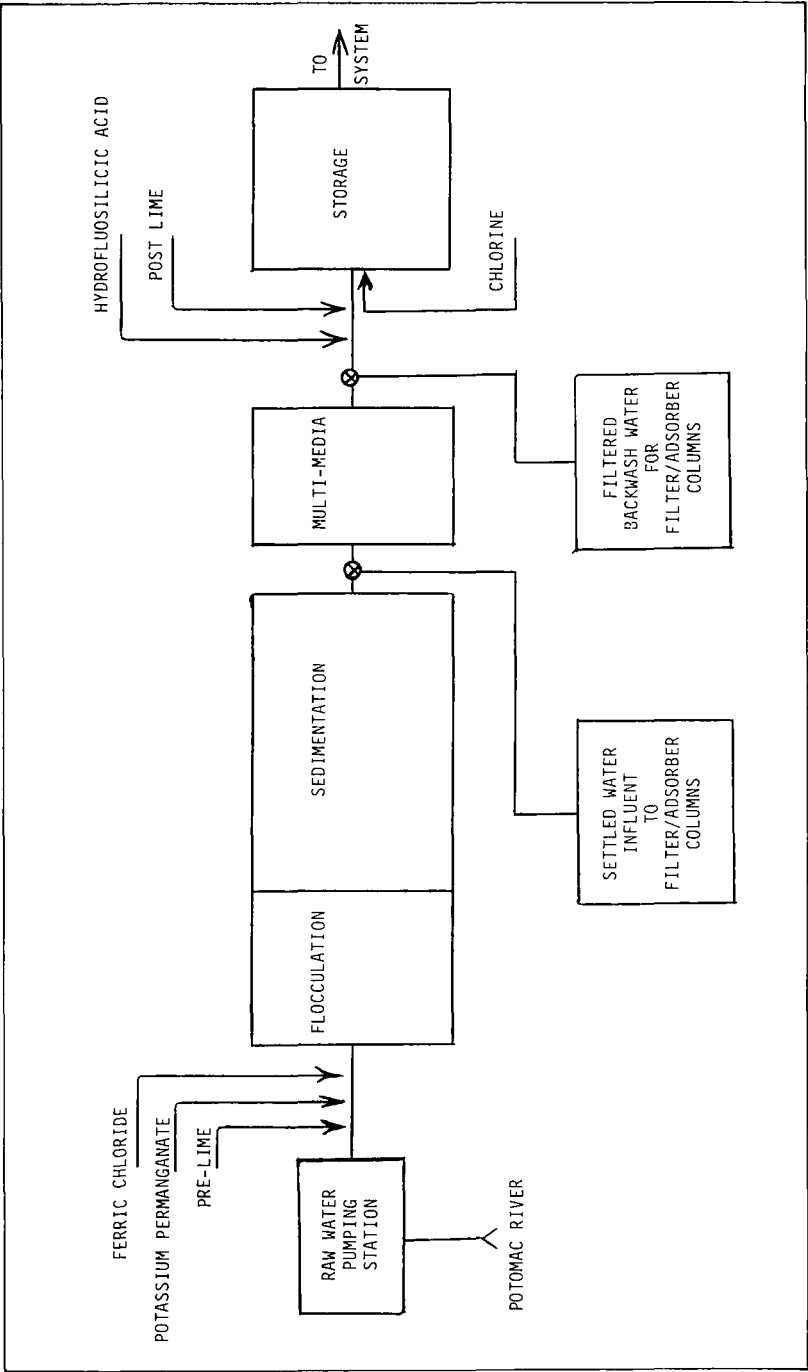[3] Dohrmann/Envirotech DC 54 Ultralow.

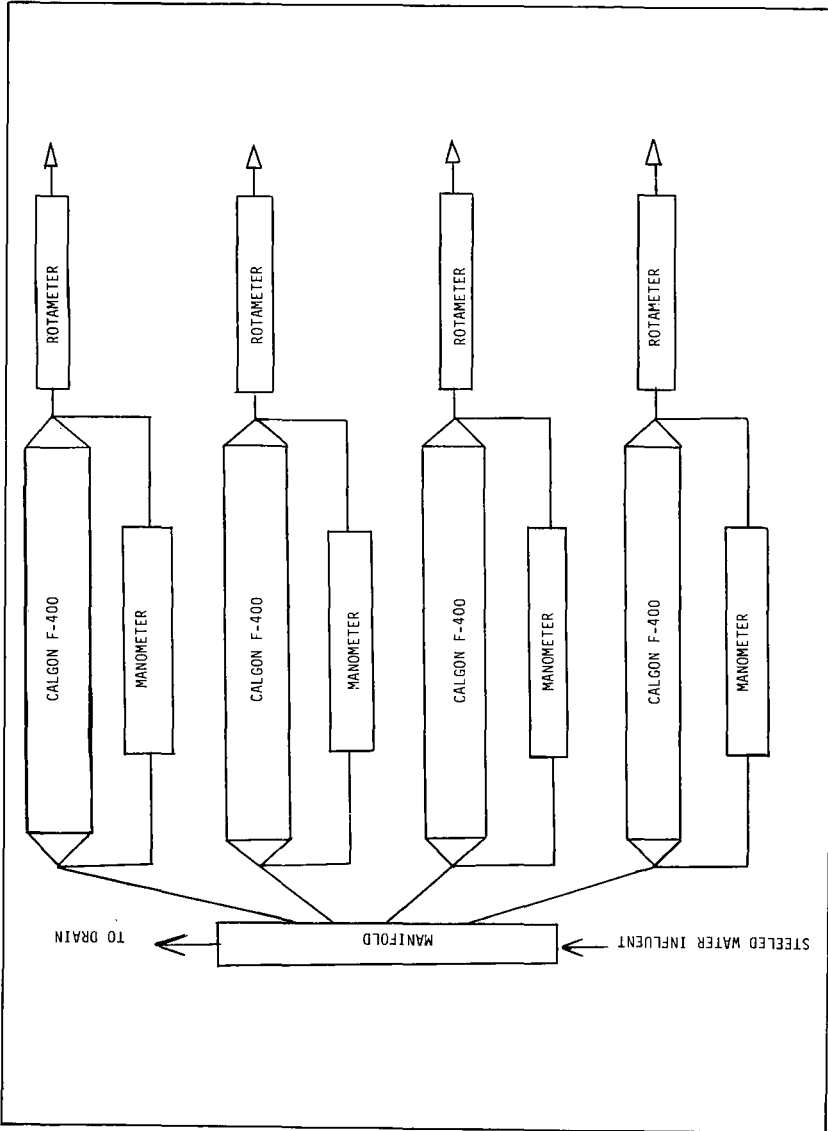Figure 1. Potomac River Water Filtration Flow Sheet

Figure 2. Schematic of Filtration/Adsorption Columns for use with Virgin and Regenerated GAC

in 750 ml amber storage bottles with teflon line screw caps. A portion of each sample was then used to fill 22 ml test tubes. To the remaining samples, chlorine solution was added so that the samples had 5 ml/l chlorine. Stevens and Symons have stressed the importance of measuring trihalomethane formation potential (THMFP), because the THM formation is not instantaneous [11]. The concentration of THMs continues to increase in the distribution system until the precursors or chlorine is exhausted. It was estimated that the flow through time in the distribution system is about seventy-two hours. Consequently, THMFP was studied at the end of seventy-two hours. The chlorine was quenched by adding sodium thiosulfate.

The analysis for THMs was performed by the liquid-liquid extraction technique. Ten ml of the sample were taken in a screw capped test tube to which 1 ml of pentane was added. The tube was capped tightly, and shaken vigorously for one minute. It was allowed to stand until the separation of phases was clearly visible. A liquid of the upper organic phase was removed carefully with disposable pipette and transferred to micro vials before it was sealed. These micro vials were arranged in sequence on the rack for the GC analysis. The instrument automatically injects one sample after another, and the results are printed. The area on the graph was integrated for determination of the concentration of the sample in micrograms per liter (μg/l).

The quantitative measurements for all the samples were carried out with a Hewlett-Packard Model 5830 Gas Chromatograph fitted with a Ni^{63} electron capture detector. The glass column was $\frac{1}{4}'' \times 4'$, packed with 10 percent FFAP on gas-chrom Q. The operating data of the GC is provided below:

Column: 6.4mm $\times$ 1.2m ($\frac{1}{4}'' \times 4'$) Glass
Packing: 10% FFAP on Gas-Chrom Q
Carrier Gas: Argon-Methane 95%/5%
Carrier Gas Flow Rate: 50 ml/min
Open Temperature: 90°C
Injection Temperature: 250°C
Detector: Ni^{63} Electron Capture
Detector Temperature: 300°C

Liquid-liquid extraction method using pentane has been investigated in detail by many researchers [12-14]. These researchers found that pentane has the advantages of low solubility in water, good distribution coefficients and favorable polarity and volatility for effective separation from the THMs.

This technique has the advantages of being fast (about 5 minutes per sample), has minimal interferences from other commonly occurring organics in water and requires very little equipment besides an electron capture GC detector.

Samples for total organic carbon (TOC) analysis were collected in 125 ml amber storage bottles and filtered through membrane filter 47 mm (0.45 μm pore size). Analyses were made using a total organic carbon analyzer.

In the first twelve weeks, the influent TOC ranged from 2.1 mg/l to about 4.6 mg/l. The percent TOC removed indicated that initially a period of adjustment occurred during the first week of operation. The TOC removed during this week was approximately 52 percent, however, in the next week the removed rate jumped to 81 percent. This was the peak efficiency period. The decline period commenced approximately from the sixth week, and in the twelfth week the TOC removal efficiency approached about 5 percent.

The various parameters describing the properties of spent carbon as measured by the different companies is presented in Table 1.

The iodine number for virgin carbon as prescribed by the manufacturer is 1000 (min). This index in the spent carbon ranged from 653 to 804. Also, the molasses numbers recorded by each firm was lower than that of the low level of virgin carbon (Table 2). All three companies restored the carbon through regeneration to near virgin state.

Table 3 summarizes the TOC removal efficiencies in the second phase of the study. In this phase the three regenerated carbons were compared under parallel conditions with virgin carbon. In this phase the peak removal efficiency occurred in the third week. During the weeks that followed, there was a steady and gradual decline in the performance of the carbon, with the exception that during the twelfth week the removal efficiency varied from 28 to 34 percent, as compared to the first phase where the range was 1 to 7 percent. There is no

Table 1. Properties of Spent Carbon

Parameter	Firm A Fluidized Bed	Firm B Multi-hearth Furnace	Firm C Infra-Red
Apparent Density (g/cc)	0.535	0.695	0.527
Iodine Number (mg/g)	804	653	693
Molasses Number	175	—	182
Ash Content (%)	7.1	8.8	8.03
Effective Size (mm)	0.6	0.6	0.6

Table 2. Properties of Regenerated Carbon

Parameter	Firm A	Firm B	Firm C	Virgin Carbon
Apparent Density (g/cc)	0.502	0.505	0.493	0.465-0.497
Iodine Number (mg/g)	1004	969	896	1000 (min)[a]
Molasses Number	235	259	292	200-400[b]
Ash Content (%)	7.7	7.3	8.32	6-8[b]
Effective Size (mm)	0.74	0.6	0.590	0.55-0.65[a]

[a]Product specifications for Filtrasorb 400 according to Calgon Product Data Bulletin 27-33 dated 1978.

[b]Typical properties.

Table 3. Total Organic Carbon (mg/l) Using Regenerated and Virgin Carbon

Week	Influent	Effluent			
		Firm A	Firm B	Firm C	Virgin Carbon
1	3.98	2.56	1.69	2.76	1.64
2	4.16	2.74	2.81	2.90	2.81
3	6.11	1.47	1.59	1.53	1.28
4	4.99	1.39	1.50	1.54	1.34
5	3.88	1.58	1.74	1.69	1.41
6	4.44	1.99	2.17	2.11	1.86
7	3.42	1.64	1.77	1.84	1.60
8	2.97	1.49	1.68	1.70	1.47
9	2.78	1.53	1.67	1.68	1.52
10	2.62	1.50	1.62	1.71	1.59
11	2.76	1.65	1.82	1.79	1.62
12	2.57	1.77	1.84	1.83	1.70

apparent explanation for this variation that occurred equally in all four columns starting week five. This should be verified by increasing or decreasing the bed depths.

Figure 3 is the graphical representation of the percentage of TOC removal data that occurred in the second twelve week period. From this graph it appears that virgin carbon provides the best results.

TOC removal is one of the important factors used in evaluating the effectiveness of carbon. Data for this parameter was statistically analyzed (Tables 4 and 5) to determine if there were any significant differences between the different reactivation processes. The F value was 2.8, and the expected value at the 0.05 tolerance level was 3.47. Hence, the three different regeneration processes resulted in no significant differences in the organic carbon absorption properties of the carbon.

Table 6 summarizes the dissolved oxygen (DO) and carbon dioxide (CO_2) and various other parameters recorded in this study. These DO and CO_2 are thought to provide some basis for evaluating the presence of biological activity within the carbon bed. CO_2 may be absorbed from and/or released to the atmosphere, at the same time it can be produced by bacterial assimilation of the organic matter. The results of both phases appear to show the lack of any pattern by either of the two parameters. In the absence of any bacteriological measurement, the only conclusion that can be drawn is that the micro-organisms, if present, were small in number.

The THM precursor(s) removal was also investigated. Total trihalomethane formation potential was measured in the influent and effluent (Table 7). The instantaneous TTHMs in unchlorinated influent varied; it ranged from 1.2 to 4.6 μg/l. The TTHMFP in the chlorinated influent at the end of seventy-two
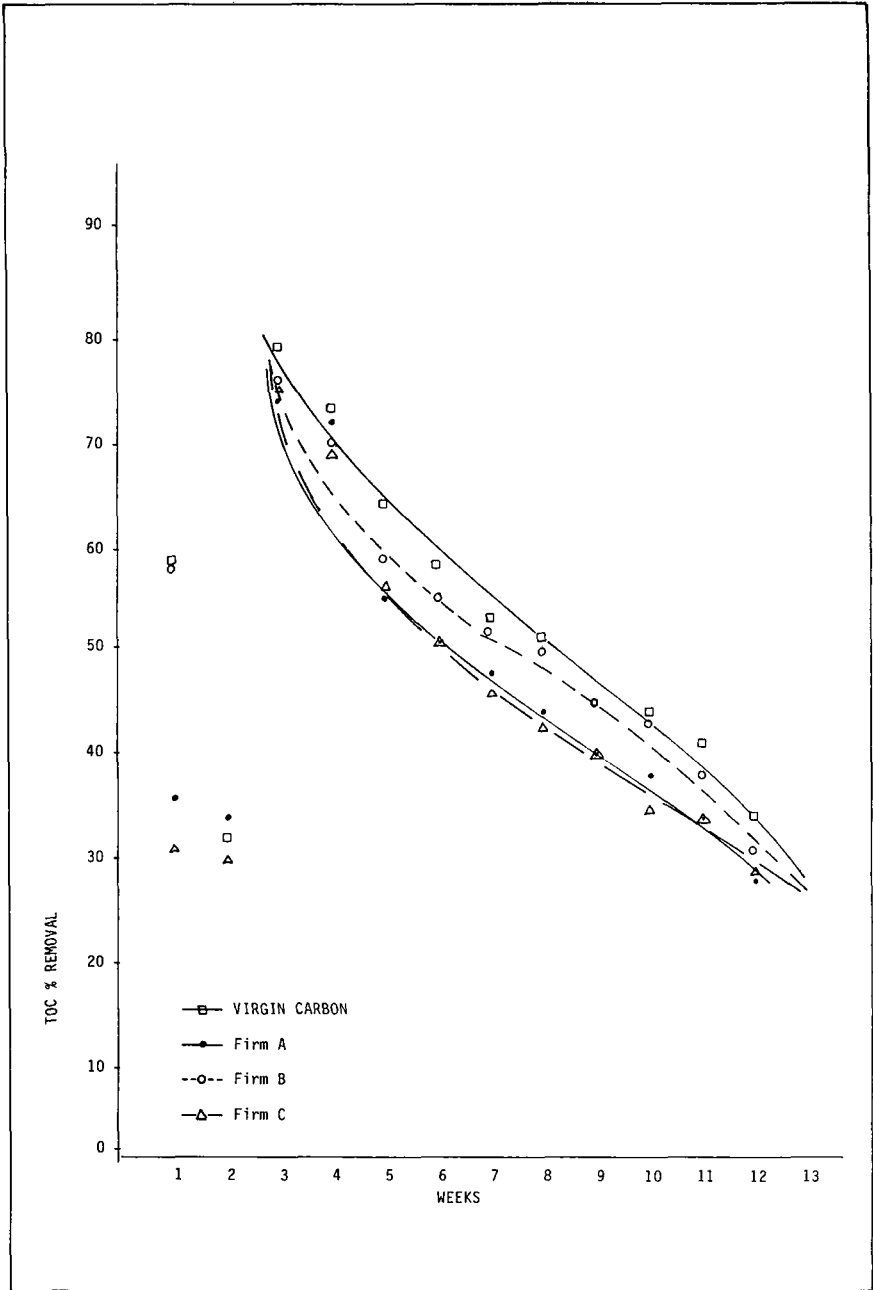
Figure 3. Percent TOC Removal

Table 4. Test to Find Significant Difference Among
Three or More Quantities (TOC Removal)

Source:
Between weeks
Between companies
Error

Company	Mean	Standard Deviation
Firm A	49.25	14.44
Firm B	47.67	14.61
Firm C	45.00	15.30

Table 5. Analysis of Variance and the F Test

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F
Weeks	11	6,771	616	
Companies	2	111	56	2.8
Error	22	446	20	$p > 0.05$
Total	35	7,328		

hours also varied weekly; the minimum was 94.96 μg/l in the fifth week, and the maximum concentration occurred in the twelfth week, the value was 167.85 μg/l. It is interesting to note that with the possible exception of two weeks (third and fifth), the influent TTHMFP exceeded the limit of 100 μg/l promulgated by U.S. EPA for the finished water [15]. The maximum THM removal rate occurred in the first two weeks; it varied from 81 to 89 percent. The TTHMFP percentage removal for virgin carbon during these two weeks was 87 and 84. The removal rate in the tenth week was approximately 50 percent. However, in the next two weeks, the precursor removal decreased drastically.

The effluent concentration during this period was in excess of 100 μg/l [15]. In the parallel test the effluent from virgin carbon had 91.81 μg/l of TTHMFPs.

Statistical analysis (ANOVA) for THM precursor removal are presented in Tables 8 and 9. The F value was 5.38, which is significant at $p < 0.05$. However, a student t-test yielded a value of 0.68 indicating that there was no significant difference between any two of these processes. Since t-test is performed on means, it does not take into consideration the weekly differences, hence the two tests provided different results. It is therefore necessary to perform an extensive study on the kinetics of THM precursor removal.

Figure 4 shows the percent THMFP removal in the effluent from each of four columns. Comparing it with Figure 3, one finds that the breakthrough for TTHMFP for the regenerated carbon was sharper than the breakthrough for TOC. The TOC failed to show any distinct correlation with precursor removal.

Table 6. Daily Analysis Summary
Column Effluents

Parameter	Week	Influent	Firm A	Firm B	Firm C	Virgin Carbon
Alkalinity	1-4	58	46	57	58	58
	5-8	65	65	65	65	65
	9-12	76	76	76	76	76
pH	1-4	9	8.9	8.9	9	9
	5-8	8	8.1	8.1	8.1	8.1
	9-12	7.8	7.7	7.7	7.7	7.7
Temperature °C	1-4	22	22	22	22	22
	5-8	25	25	25	25	25
	9-12	27	27	27	27	27
D.O. (mg/1)*	1-4	9.3	7.7	7.6	7.6	7.6
	5-8	6.4	5.0	5.0	4.9	5.0
	9-12	5.9	4.1	4.1	4.0	4.1
CO_2 (mg/l)**	1-4	0.1	0.2	0.2	0.2	0.2
	5-8	1.7	2.0	2.0	2.0	2.0
	9-12	2.9	3.6	3.6	3.6	3.6

*Δ DO mg/l = (Influent-Effluent)
**Δ CO_2 mg/l = (Effluent-Influent)

Table 7. Total Trihalomethane Formation Potential
(μg/l) Chlorinated Samples

		Column			
Week	Influent	Firm A	Firm B	Firm C	Virgin Carbon
1	100.42	10.56	13.41	14.22	13.04
2	96.79	14.89	15.20	18.07	15.76
3	93.64	23.12	19.93	26.49	24.01
4	118.69	30.65	26.15	29.67	36.18
5	94.96	44.52	39.95	47.01	43.91
6	117.27	47.96	50.54	57.30	53.81
7	125.45	46.61	67.20	62.79	52.92
8	147.51	64.53	64.18	69.43	63.71
9	142.99	65.66	70.33	69.93	65.31
10	130.23	61.97	63.64	65.75	60.94
11	154.41	97.08	124.89	129.34	80.35
12	167.85	126.51	119.33	135.73	91.81
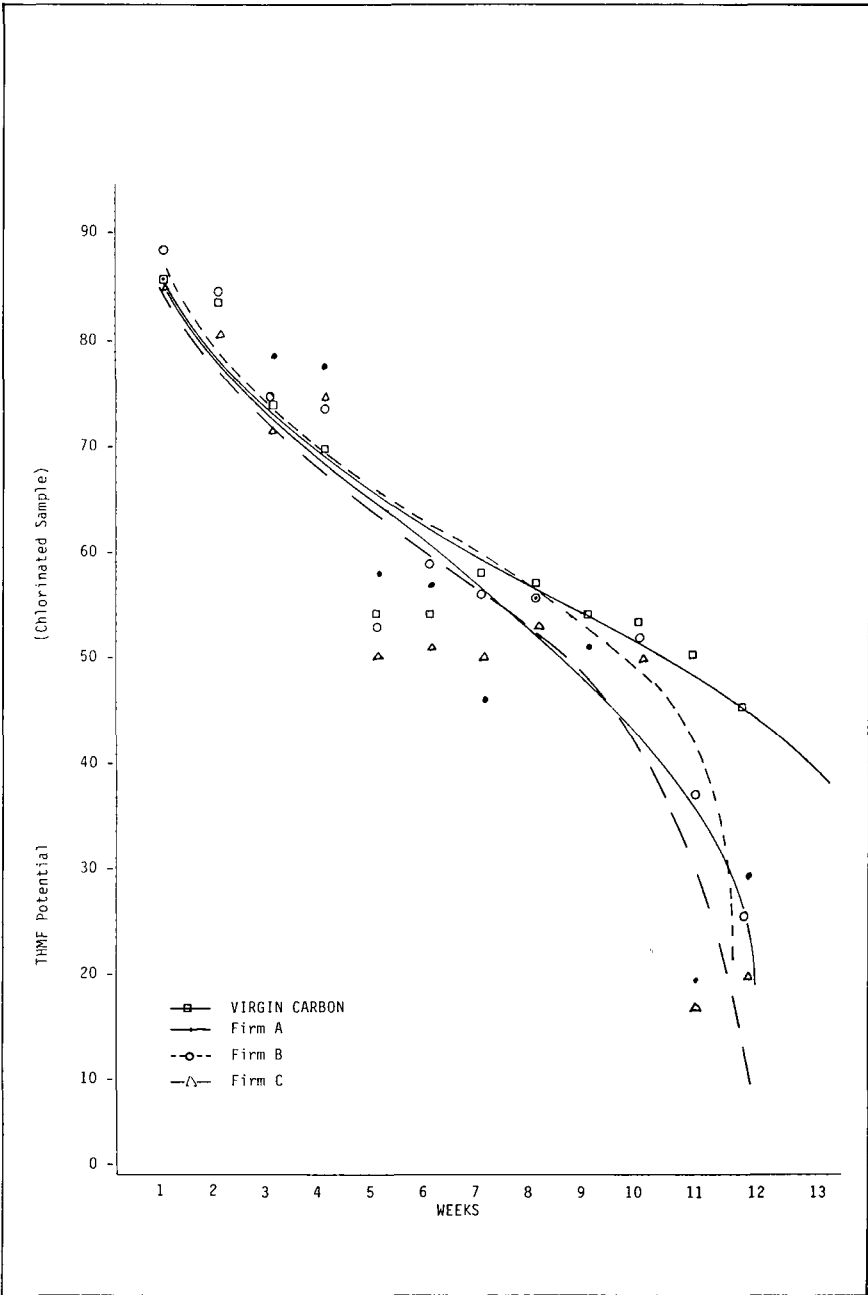
Figure 4. Percent Trihalomethane Removal

Table 8. Significant Difference Test (for TTHMFP)

Source:		
Between weeks		
Between companies		
Error		

Company	Means	Standard Deviation
Firm A	60.17	18.62
Firm B	57.92	21.25
Firm C	5.45	21.84

Table 9. Analysis of Variance TTHMFP

Source of Variation	Degree of Freedom	Sum of Squares	Mean Square	F
Week	11	13,634.30	1239.49	
Comparison	2	195.39	97.69	5.38
Error	22	399.28	18.15	
Total	35	14,228.97		

This shows that TOC may be measuring some substances that are not trihalomethane precursors, which means TOC data may not provide a useful surrogate indicator for precursors.

Regardless of the actual performance of the filters collectively, one very important aspect of the study was that under given identical conditions all the columns provided almost identical results, i.e., replication from one column to the next is possible, and virgin carbon under parallel conditions provides results similar to the regenerated carbons.

In summary, the regeneration processes used in this study were capable of returning spent carbon to near virgin state. All the regenerated carbons performed alike, however, more research is needed to study the economics of using GAC for TTHM precursor removal.

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