This study investigated removal of five haloacetic acids (HAA5) (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid) in biologically active carbon (BAC) columns. An acclimated granular activated carbon (GAC), or BAC, column effectively removed four of the HAA5 that had been spiked in the influent at 50 µg/L each. Only trichloroacetic acid, detected at 10 µg/L in the effluents, was not completely removed. After the biological activity on acclimated GAC was eliminated by autoclaving, the HAA removal efficiency was significantly reduced. In another experiment, the removal of HAAs in a new GAC column was continuously monitored for 76 days. The new GAC effectively removed HAAs. HAA removal at the beginning of this experiment was from carbon adsorption, whereas biodegradation was the HAA removal mechanism later in the experiment. The results of this study are significant to the water industry—removal of HAAs using BAC may provide a new technology for control of disinfection by-products.

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Use of BAC for HAA removal—
PART 2, COLUMN STUDY

Haloacetic acids (HAAs) are a group of organic disinfection by-products (DBPs) newly regulated under the Stage 1 Disinfectants/DBP Rule (D/DBPR) (USEPA, 1998). The maximum contaminant level for the sum of five haloacetic acids (HAA5) under the D/DBPR is 60 µg/L. These five HAAs are monochloroacetic acid (ClAA), monobromoacetic acid (BrAA), dichloroacetic acid (Cl₂AA), dibromoacetic acid (Br₂AA), and trichloroacetic acid (Cl₃AA). Enhanced coagulation/softening for precursor removal and alternative disinfectants are common methods of controlling HAAs and other DBPs in finished water (Krasner & Amy, 1995; Singer, 1994).

It is well-documented that biological filtration effectively removes ozonation by-products (Wang et al, 1995; Krasner et al, 1992; Reckhow et al, 1992; Xie & Reckhow, 1992) and some natural organic matter (NOM) (Hozalski et al, 1999; Huck, 1999); however, limited information is available on the use of biofiltration for HAA removal. In 1993, Singer et al (1993) reported rapid elimination of HAAs in treated water during aquifer storage and suggested that biological
degradation was the mechanism. In 1994, Williams et al (1994) reported extremely low levels of HAAs at the maximum residence time locations in three water distribution systems and suggested biological degradation was responsible. Further studies were conducted by the same research group to isolate the bacteria in their distribution systems and to investigate HAA biodegradation pathways (Williams et al, 1998; Williams et al, 1997; Williams et al, 1995). Singer et al (1999) reported HAA removal by granular activated carbon (GAC) filtration and suggested that biological degradation of the HAAs had occurred.

Although GAC adsorption can remove trihalomethanes, it is generally considered impractical for drinking water treatment because GAC requires frequent regeneration (Graese et al, 1987). It was also commonly assumed that GAC does not effectively remove HAAs because HAAs are hydrophilic and ionized organic compounds in drinking water. Speth and Miltner’s (1998) report suggested that activated carbon adsorption could be an efficient process for HAA removal, because the Freundlich values \( q_e \) for \( \text{Cl}_2\text{AA} \) and \( \text{Cl}_3\text{AA} \) (1,630 and 11,700 µg/g[L/µg] \( ^n \), respectively) are much higher than those of chloroform and bromodichloromethane (93 and 241 µg/g[L/µg] \( ^n \), respectively). A similar study by Zhang et al (1998) gave the Freundlich \( q_e \) values of 1,600 µg/g for \( \text{Cl}_2\text{AA} \) and 3,900 µg/g for \( \text{Cl}_3\text{AA} \) at \( C_e = 0.08 \) µM. There is, however, little information
about batch-, pilot-, and full-scale studies of HAA removal by GAC adsorption.

This article provides the results of experiments conducted to remove five HAAs in biologically active carbon (BAC) and new GAC columns. The effects of autoclaving on HAA elution and removal in GAC columns were investigated, as well as the results of carbon adsorption, biofilm development, and biodegradation in a new GAC column during a 76-day study.

EXPERIMENTAL METHODS

GAC columns. GAC columns were packed using glass burettes with an internal diameter of 11 mm (0.43 in.) and 40 mL of GAC in the environmental engineering laboratory at Pennsylvania State University–Harrisburg. Acclimated GAC (also referred to as BAC) samples were collected from two GAC filters at a local water treatment plant. The GAC in the filters had been online for 4 and 26 months, respectively. Additional carbon columns were packed with new GAC or GAC that had been autoclaved at 121°C for 30 min. All columns were operated with an empty bed contact time (EBCT) of 20 min and run to the end of the study without backwash.

Synthetic water samples. Synthetic water was prepared using finished water from the same water treatment plant. During the course of this study, the typical HAA concentrations in the finished water were 4 µg/L for ClAA, 11 µg/L for Cl2AA, and 8 µg/L for Cl3AA. The finished water samples were spiked with 50 µg/L each of five HAAs: ClAA, BrAA, Cl2AA, Br2AA, and Cl3AA. The water also contained 1–2 mg/L of total chlorine residual. The chlorine residual was not quenched in any of the column studies.

HAA analysis. HAA concentrations were analyzed using US Environmental Protection Agency method 552.2 with a few modifications (Xie et al., 1998; USEPA, 1995). The procedure involves water sample extrac-
tion with methyl tertiary butyl ether, HAA derivatization with acidic methanol, separation, and analysis with gas chromatography–electron capture detection. Before sample extraction, HAA samples were preserved with sulfuric acid (pH < 2.0) and kept at 4°C.

RESULTS AND DISCUSSION
HAA removal in BAC columns. Four GAC columns were used in this experiment: two BAC columns packed with acclimated GAC samples (4 and 26 months, respectively) and two columns packed with autoclaved GAC (4 and 26 months, respectively). In both BAC columns, CIAA, CI₂AA, Br₂AA, and Br₂AA were completely removed during a 7-h run (Figures 1–4). CI₁AA, however, was detected in the effluents at 10 µg/L (Figure 5). The removal efficiency for HAAs was significantly reduced in the columns with autoclaved GAC (Figures 1–5). Both Br₂AA and Cl₃AA were removed to a moderate degree in the column with autoclaved four-month GAC. The removal was lower in the column with autoclaved 26-month GAC (Figures 4 and 5). This indicates that carbon adsorption was also involved in removing these two HAAs. The removal efficiency of autoclaved four-month GAC was better than BAC for Cl₃AA (Figure 5). This may be because of the decarboxylation degradation that Cl₃AA undergoes at high temperatures. In the column with

The results . . . indicate that all five haloacetic acids (HAAs) are biologically degradable, and biological degradation is the primary mechanism for HAA removal using biologically active carbon.
autoclaved four-month GAC, the Cl$_3$AA decarboxylation degradation regenerated more adsorption sites on GAC for Cl$_3$AA removal. Little BrAA removal was obtained using either autoclaved 4- or 26-month GAC (Figure 2). The concentrations of CIAA and Cl$_2$AA were significantly increased in the effluents of autoclaved GAC columns, especially in the first 3 h (Figures 1 and 3). This indicates that the elution of CIAA and Cl$_2$AA occurred on autoclaved GAC.

The results of this 7-h run study indicate that all five HAAs are biologically degradable and that biological degradation is the primary mechanism for HAA removal using BAC. The results also indicate that biological degradation of Cl$_3$AA is a slow process. This agrees with the results reported in several studies—a batch-scale study (Zhou & Xie, 2000), in water distribution systems (Williams et al, 1997), and in GAC filters (Singer et al, 1999). The authors suggest that the main HAA removal mechanism using autoclaved GAC was carbon adsorption, which is supported by data reported by others (Speth & Miltner, 1998; Zhang et al, 1998).

To further study the elution of HAAs from autoclaved GAC, the authors conducted experiments using new and 26-month GAC, with and without autoclaving. When HAA-free reagent water was used as the influent, no HAA was detected in the effluent from the new GAC, autoclaved new GAC, or 26-month GAC. High concentrations of ClAA and Cl$_2$AA were detected in the autoclaved 26-month GAC effluent, especially in the first 30 min (Figure 6). At 30 min, the effluent concentrations were 110 and 380 µg/L for CIAA and Cl$_2$AA, respectively. Br$_2$AA was also detected, but at a much lower level (1.7 µg/L at 30 min). The concentrations of Cl$_3$AA were < 1 µg/L, and no BrAA was detected. The authors suggest that the elution of CIAA and Cl$_2$AA may be because of the reaction between adsorbed NOM and chlorine at the elevated temperature or desorption of HAAs on autoclaved GAC. Absence of Cl$_3$AA in the effluent may be from decarboxylation of Cl$_3$AA at the elevated temperature. A study of the mechanism eluting HAA from GAC is currently under way at Pennsylvania State University–Harrisburg.
HAA removal in a new GAC column. The removal of HAAs by carbon adsorption was further studied using a new GAC column. The influent was a synthetic water sample spiked with five HAAs at 50 µg/L each. All five HAAs were completely removed in the 7-h run (Figure 7). Again, this result agrees with those reported by others (Speth & Miltner, 1998; Zhang et al, 1998). It had been commonly assumed that GAC does not adsorb HAAs well because of their hydrophilic nature and the ionized forms present in the pH conditions of natural water. Additional studies are needed to investigate GAC adsorption capacity for HAAs during a longer GAC column operation time.

Biofilm development in a new GAC column. A 76-day experiment was conducted to investigate the removal of HAAs in a new GAC column using the synthetic water samples. This long-term study allowed the authors to better understand GAC adsorption capacity and bioactivity development. CIAA was almost completely removed in the first 31 h and after 35 days of the column run (Figure 8). No CIAA was removed between days 3 and 8. BrAA was almost completely removed within the first 41 h and after 45 days of the column run (Figure 9). Little BrAA was removed between days 6 and 8. The removal patterns for CIAA and BrAA were similar.

Cl₂AA was nearly removed in the first 9 days and after 66 days of the column run (Figure 10). No removal was observed between days 25 and 50. Br₂AA was almost completely removed within the first 24 days and after 66 days (Figure 11). The lowest removal efficiency for Br₂AA was approximately 40%, which occurred between days 58 and 63. The highest effluent concentrations of Cl₂AA and Br₂AA occurred much later than the highest effluent concentrations of CIAA and BrAA. Cl₃AA was completely removed during the experiment (1–76 days; Figure 12). Within the first 30 h, or after 68 days of the column run, the HAA₅ were nearly removed (< 5 µg/L in effluents; Figure 13). Between 30 h and 67 days, the effluent concentrations for HAA₅ ranged from 10 to 110 µg/L with an influent level of approximately 275 µg/L.

The results of this 76-day column study indicate that both carbon adsorption and biological degradation are involved in haloacetic acid removal.
involved in HAA removal. The HAA removal at the beginning of the run was from carbon adsorption. After GAC adsorption capacity for a HAA was exhausted and before the bioactivity for the HAA was developed, no HAA removal was observed. Once the bioactivity was fully developed, the HAA was completely removed by biological degradation. This mechanism is illustrated by the removal patterns of ClAA, BrAA, and Cl2AA (Figures 8–10). For Br2AA, the bioactivity was developed before the GAC adsorption capacity was completely exhausted. The nearly complete removal of Cl3AA during the column run also indicates that the adsorption capacity of Cl3AA was not exhausted. On the basis of the reported Freundlich values for Cl2AA and Cl3AA (1,630 and 11,700 µg/L/µg)n, respectively; Speth & Miltner, 1998), the estimated breakthrough time for Cl3AA is 63 days, 7.2 times that of Cl2AA (9 days). The bioactivity for degradation of Cl3AA may have been developed during the 76 days of operation, and biodegradation of Cl3AA may have prolonged the breakthrough time for Cl3AA. As discussed earlier, biodegradation alone would not result in a complete removal of Cl3AA at an EBCT of 20 min.

The differences in the GAC exhaustion time for each HAA indicates that the adsorption capacity of GAC for each HAA is different—the adsorption capacity of GAC is higher for dihaloacetic acids (e.g., Cl2AA) than for monohaloacetic acids (e.g., CIAA). GAC has the highest adsorption capacity for Cl3AA. These results agree with those reported in other batch tests (Zhou, 2000; Speth & Miltner, 1998; Zhang et al, 1998) and column tests (Zhang et al, 1998).

The time required for the development of bioactivity to degrade each HAA also varied, with the bioactivity for degradation of dihaloacetic acids lagging behind that of monohaloacetic acids. The residual chlorine may have limited impact on the bioactivity in GAC filters because the chlorine could be removed by the top layer of GAC. Further study is necessary to quantify the effect of residual chlorine in the influent and backwash water and the time and temperature required to develop bioactivity for HAA removal.

Significance to the water industry. The study results are significant to the water industry—GAC filters are used in many water treatment plants; therefore, removal of HAAs using BAC could provide a new treatment process for DBP control. To effectively remove HAAs, bioactivity should be developed before the GAC is exhausted. Bioactivity development may be a slow process at low temperatures; thus, GAC should not be replaced during cold weather (e.g., late fall through spring). Complete GAC replacement should also be avoided. Replacing GAC dur-
ing warm weather (summer or early fall) or seeding a new GAC bed with acclimated GAC would speed up bioactivity development. The installation of residential point-of-use and point-of-entry GAC filters has increased in recent years; thus, GAC filtration may provide a final barrier to HAAs in drinking water.

**CONCLUSIONS**

BAC effectively removed five HAAs (50 µg/L each of ClAA, Cl₂AA, Cl₃AA, BrAA, and Br₂AA) from water in a 7-h run. The removal efficiency for Cl₃AA was slightly lower than for the other four HAAs. The HAA removal efficiency was significantly less when autoclaved GAC was used. The primary HAA removal mechanism of the BAC was biological degradation. In another experiment, biological activity for HAA degradation was developed inside a new GAC column, and the results showed that the time required for the bioactivity to develop was different for each HAA. HAAs in the column were removed by carbon adsorption before the bioactivity was developed. After the bioactivity was fully developed, four HAAs (ClAA, Cl₂AA, BrAA, and Br₂AA) were almost completely removed. Cl₃AA was completely removed; this may be because of both carbon adsorption and biodegradation.

In the experiment using autoclaved acclimated GAC and HAA-free reagent water, ClAA and Cl₂AA were detected in the effluent at several hundred micrograms per litre. This may be from formation or desorption of these two HAAs. The elution of BrAA, Br₂AA, and Cl₃AA was insignificant, which may be because of the low bromide level in water and the decarboxylation of Cl₃AA during autoclaving.

The results of this study indicate that BAC could be an effective process for HAA removal. To speed up the bioactivity development process, water utilities could replace their GAC during warm weather and/or seed the new GAC bed with acclimated GAC.
mated GAC. Additional studies are required to further investigate the effect of residual chlorine in the influent and backwash water on HAA removal in BAC filters and the time and temperature requirements for the development of bioactivity in GAC filters.

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REFERENCE


