Effects of EBCT and Water Temperature on HAA Removal using BAC

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Halocetic acids (HAAs) are a group of disinfection by-products (DBPs) regulated under the Stage 1 Disinfectants/Disinfection Byproducts Rule (D/DBPR). The maximum contaminant level for five HAAs is 60 µg/L. These five regulated HAAs are monochloroacetic acid (ClAA), dichloroacetic acid (Cl₂AA), trichloroacetic acid (Cl₃AA), monobromoacetic acid (BrAA), and dibromoacetic acid (Br₂AA). The upcoming Stage 2 D/DBPR may require water utilities to comply with this maximum contaminant level by using locational running annual averages instead of running annual averages. This will require water utilities to better control peak DBP levels in their distribution systems. As a result of this requirement, many water utilities are interested in identifying and adopting cost-effective HAA control technologies. Currently, the best available technologies for HAA control include enhanced coagulation/softening and granular activated carbon (GAC) adsorption for precursor removal and the use of alternative disinfectants.

BACKGROUND

Singer et al (1993) first reported that HAAs were rapidly degraded in chlorinated finished drinking water during underground storage and suggested that HAAs were removed through aerobic biodegradation. Williams et al (1994)
found that HAA concentrations were reduced to non-detectable levels at maximum residence time locations in three distribution systems during warm seasons. Williams et al (1995) suggested that the presence of active biofilm or high heterotrophic bacteria counts was correlated with the HAA degradation. An enzymatic degradation involving a haloacid dehalogenase was also suggested for the biological removal of HAAs (Williams et al, 1996). Singer et al (1999) reported HAA removal by GAC filtration and suggested that biological degradation of HAAs had occurred in GAC filters. Thomas et al (2000) evaluated the fate of HAAs during aquifer storage and recovery in southern Nevada. A rapid decline of HAA concentrations during aquifer storage and recovery indicated in situ microbial oxidation of HAAs. Wobma et al (2000) also reported that HAAs were easily removed in GAC filters through biodegradation. The GAC filters were operated with empty bed contact times (EBCT) ranging from 3.6 to 8.4 min. Greater removal was observed in June and July versus March, April, and May, pointing to potential effects of temperature. Studies by Wobma et al indicated that the removal of HAAs, presumably by biodegradation processes within the GAC filter bed, was more effective when water temperatures were high. Xie and Zhou (2002) also found that HAAs were effectively removed in a biologically active carbon (BAC) column operated with an EBCT of 20 min at room temperature.

All of these studies indicated that biodegradation played a major role for HAA removal.

McRae et al (2004) reported HAA biological degradation by bacterial enrichment cultures. This research indicated that biodegradation is a potential mechanism for HAA reduction in surface waters and drinking water distribution systems. The degradation rates for a pseudo-first-order kinetic model were determined for ClAA, BrAA, and Cl3AA at 21–25°C. The mechanism of HAA degradation in GAC filters was also investigated in the authors’ group (Tung, 2004). With bacterial enrichment cultures, HAA degradation occurred in both anoxic and aerobic conditions. HAA removal in a GAC filter was also simulated with a biofilm model. The results from an HAA degradation mechanism study will be published elsewhere.

EBCT is a critical consideration in the design and operational criteria for GAC filters. Average EBCTs for GAC filters range from 5 to 20 min. The question is whether HAAs can be effectively removed at these EBCTs after the GAC adsorption capacity is exhausted. Further, as water temperature changes in various seasons, HAA removal at low water temperatures needs to be investigated.

**OBJECTIVES**

The objectives of this study were to investigate the effects of EBCT and water temperature on HAA
removal in BAC columns and to conduct a kinetic analysis for HAA removal at various EBCTs and temperatures. The information on the effect of EBCT and water temperature will be used for the design and operation of BAC filters for HAA removal.

MATERIALS AND METHODS
Carbon and water samples were collected from a local surface water treatment plant. The plant uses rapid mixing, flocculation, clarification, GAC/sand filtration, and chlorine disinfection. Before GAC/sand filtration, prechlorination or intermediate chlorination was used for iron and manganese removal. The chlorination point was changed in various seasons to minimize DBP formation in the finished water. The depth of GAC medium in the filter is about 107 cm; the average EBCT for the GAC filter is approximately 16 min. BAC samples were obtained from one of this plant’s GAC filters that had been online for 2.5–3.0 years. The BAC sample was collected when the raw water temperature in the plant was near the study temperatures (e.g., 4, 10, 20, and 30°C). This was done to minimize the time required to equilibrate BAC columns at the temperature in the laboratory study.

Four BAC columns were packed using 50-mL glass burettes with a 1.05 cm internal diameter. Each burette contained 40 mL of BAC collected at the plant described earlier. BAC bed height was approximately 46 cm. Column influent was fed into the column by gravity. For each BAC column, a peristaltic pump with silicone tubing connected to the column outlet was used to regulate the flow rate. The flow rates at 8.0, 4.0, 2.7, and 2.0 mL/min gave EBCTs of 5, 10, 15, and 20 min, respectively. These BAC columns and pumps were placed in a temperature-controlled incubator. Experiments were conducted at four temperatures (4, 10, 20, and 30°C) and four EBCTs (5,
Finished water with 1–2 mg/L of free chlorine residual from the local water treatment plant was spiked with six HAAs at 50 µg/L each and used as the BAC influent. These six HAAs are ClAA, BrAA, C2AA, Cl3AA, bromochloroacetic acid (BrClIAA), and Br2AA. BAC influent and effluent samples were collected hourly through an 8-h study period which started after a 12-h equilibration. The equilibration of BAC columns was achieved by running the synthetic influent at the study temperature and EBCT for 12 h.

HAA concentrations in BAC influents and effluents were determined using US Environmental Protection Agency method 552.2 (USEPA, 1995) with a few modifications (Xie et al, 1998, 2002). The analytical procedure involves methyl tertiary butyl ether extraction, acidic methanol derivatization, and gas chromatography analysis. The gas chromatograph used in this study was equipped with a split/splitless injector; a liquid autosampler; an electron capture detector; and a 30-m long, 0.25-mm internal diameter, 0.25-µm film thickness capillary column. Before extraction, HAA water samples were preserved with sulfuric acid (pH < 2.0) and kept at 4°C to minimize HAA biodegradation.

RESULTS AND DISCUSSION

Effects of EBCT and temperature on HAA removal. A typical set of steady-state influent and effluent ClIAA concentrations at 4°C and four EBCTs are shown in Figure 1. The average influent concentration for ClIAA over the 8-h run (nine data points) was 58.7 ± 0.6 µg/L. Increasing the EBCT decreased the ClIAA levels in the BAC effluents. Average effluent concentrations (nine data points) with EBCTs at 5, 10, 15, and 20 min were 35.9 ± 0.8 µg/L, 19.5 ± 1.3 µg/L, 9.2 ± 1.1, and 1.8 ± 0.2 µg/L, respectively.

Removal efficiencies of two monohaloacetic acids at four EBCTs (5, 10, 15, and 20 min) and four
Temperatures (4, 10, 20, and 30°C) are shown in Figures 2 and 3, respectively. Increasing EBCT or temperature increased C1AA removal efficiencies, as shown in Figure 2. At 4°C, the average C1AA removal efficiency increased from 39% at an EBCT of 5 min to 67% at 10 min, 84% at 15 min, and 97% at 20 min. At an EBCT of 5 min, the average C1AA removal efficiency increased from 39% at 4°C to 79% at 10°C, 99% at 20°C, and 99.6% at 30°C. Regardless of the EBCT (from 5 to 20 min), a nearly complete removal of C1AA is achieved at 20°C or higher. At an EBCT of 5 min, a temperature at 5°C resulted in the lowest C1AA removal. However, this lowest C1AA removal could be improved by using a longer EBCT. For many water systems, EBCT is longer in cold months because of a lower water demand, resulting in a lower water production rate. A similar trend was observed for BrAA removal. Increasing EBCT or temperature increased BrAA removal efficiencies (Figure 3).

Removal efficiencies of three dihaloacetic acids—Cl2AA, BrClAA, and Br2AA—at four EBCTs and four temperatures are shown in Figures 4, 5, and 6, respectively. Increasing EBCT or temperature also increased Cl2AA removal efficiencies (Figure 4). At 4°C, Cl2AA removal increased from 27% at an EBCT of 5 min, to 55% at 10 min, 69% at 15 min, and 89% at 20 min. With an EBCT of 5 min, the average Cl2AA removal efficiency increased from 27% at 4°C to 56% at 10°C, 96% at 20°C, and 98% at 30°C. A nearly complete removal of Cl2AA is achieved at 20°C or higher with all four EBCTs. A similar trend was observed for the removal of BrClAA and Br2AA (Figures 5 and 6, respectively). In comparison with monohaloacetic acids, dihaloacetic acids had slightly lower removal efficiencies. This is in agreement with results from bench-scale studies (Tung, 2004; Zhou & Xie, 2002) that indicate that C1AA is more readily biodegradable than Cl2AA.
Removal efficiencies of Cl₃AA at four EBCTs and four temperatures are shown in Figure 7. Increasing EBCT or temperature also increased Cl₃AA removal efficiencies (Figure 7). At 4°C, Cl₃AA removal rates increased from 7% at an EBCT of 5 min to 9% at 10 min, 35% at 15 min, and 65% at 20 min. At 10°C the Cl₃AA removal rate was 23% at an EBCT of 5 min, 50% at 10 min, 67% at 15 min, and 79% at 20 min. At 20°C or higher, Cl₃AA removal was 80% or higher with three EBCTs (10, 15, and 20 min). At an EBCT of 5 min, the average Cl₃AA removal efficiency increased from 7% at 4°C to 23% at 10°C, 56% at 20°C, and 88% at 30°C. The removal of bromodichloroacetic acid (BrCl₂AA), chlorodibromoacetic acid (ClBr₂AA), and tribromoacetic acid (Br₃AA) was not investigated in this study because they are not regulated under the D/DBPR. The instability of Br₃AA and the cost of BrCl₂AA and ClBr₂AA neat compounds are additional reasons for not including them in the study. However, the trend of their removal should be similar to that of Cl₃AA. At the same EBCT and water temperature the removal efficiency of Cl₃AA is much lower than for monohaloacetic acids. This agrees with the fact that Cl₃AA is more resistant to biological degradation than monohaloacetic acids and dihaloacetic acids, as reported in several studies (McRae et al, 2004; Tung, 2004; Zhou & Xie, 2002).

Average removals for HAA6 are shown in Figure 8. At 10°C, a 5-min EBCT resulted in a 57.8% average removal of HAA6. At 5°C, however, a 10-min EBCT is required for a 52.1% average removal of HAA6. In a real water sample, the relative level of six HAAs varies based on water quality parameters (e.g., bromide and natural organic matter), chlorination conditions (e.g., chlorine dose and pH), and chemical and biological degradation. The evenly weighted arithmetic mean for HAA6 mentioned here may not reflect the overall removal of HAA6 in real water samples. However, this simplified average removal can guide water professionals in design and operation of a BAC filter.

Both EBCT and water temperature affected the removal of HAAs using BAC filtration. A longer EBCT can be used to compensate for the effect of a lower water temperature. For many water systems, however, the removal of HAAs in cold months is not critical because of the reduced formation of trihalomethanes and HAAs. In addition, the reduced water demand in cold months also reduces water production and increases the EBCT.

Similar results regarding the effects of temperature and EBCT on HAA removal in BAC filters were also observed in a field study. This column study and the field study also indicated that residual free chlorine (1–2 mg/L) had little effect on the character of BAC filtration. Free chlorine can be removed in the top few inches of a GAC bed. However, residuals from chloramines, especially at high levels, could substantially impair the ability of a BAC filter to reduce HAAs, as reported by Tung (2004).

**Kinetic analysis.** A variable-order kinetic model (Logan, 2001), \( R = kC^n \), is used to describe the HAA removal in BAC filters. In this model, \( R \) is the removal rate, \( k \) is the reaction rate constant, \( C \) is the concentration of a specific reactant species, and \( n \) is the reaction order.

The influent concentrations \( C_{in} \) and the effluent concentrations \( C_{eff} \) of the BAC columns obtained at various EBCTs were used to calculate the HAA removal rates, \( R \), as shown in Eq 1

\[
R = (C_{in}-C_{eff})/EBCT
\]  

Because of concentration changes in the BAC columns, log mean concentration in each BAC column, \( C_{lm} \), was calculated (Eq 2) and used in the variable order kinetic model.

\[
C_{lm} = (C_{in}-C_{eff})/\ln(C_{in}/C_{eff})
\]  

By plotting \( \log R \) versus \( \log C_{lm} \) a linear regression line was obtained (Figure 9). The reaction order can be determined by the slope of the regression line as shown in Eq 3

\[
\log R = n \log C_{lm} + \log k
\]  

Most HAA effluent concentrations at 20 and 30°C were near their method detection limits (<1 µg/L). Those data could not accurately describe HAA removal rates.
and were not used for modeling. HAA concentrations obtained at two lower temperatures (4 and 10°C) were used to calculate $R$ and $C_{lm}$. Because of its higher effluent concentration, $Cl_3AA$ concentrations at 20°C were also used. Three plots on $Cl_3AA$ removal rates versus $Cl_3AA$ concentrations at 4, 10, and 20°C are shown in Figure 9.

As shown in Table 1, the reaction orders of HAA removal at 4°C were below 0.5. This suggests that the HAA removals in the BAC columns at 4°C were likely independent of HAA concentrations and tended to follow the zero-order model. This indicates that HAA removal was limited by the biological activities in BAC columns at 4°C. This zero-order reaction model is apparently in contrast with the first-order reaction model reported by McRae et al (2004) and Tung (2004). For biological degradation, a zero-order reaction is generally observed at a high substrate (e.g., HAA) level. In this study, the HAA level (µg/L) is low. However, the relative HAA concentration could be high because of a very low biological activity at 4°C. This will result in a zero-order reaction.

At 10°C, the reaction orders of mono- and dihaloacetic acid removal were close to one, as shown in Table 2. This suggests that their removals at 10°C in the BAC columns were dependent on HAA concentrations and tended to follow the first-order reaction model. This indicates sufficient biological activities were established in BAC columns and HAA removals were limited by their concentrations. This result is supported by those reported by McRae et al (2004) and Tung (2004) that HAA degradation observed at 20°C can be modeled using a pseudo-first-order reaction.

However, the reaction order for $Cl_3AA$ removal at 10°C was 0.29. This suggests that $Cl_3AA$ removal at 10°C was likely independent of its concentration and tended to follow the zero-order model, indicating that there were limited biological activities for $Cl_3AA$ degradation at 10°C. This is in agreement with the possibility that a different bacterium or bacteria may be responsible for $Cl_3AA$ degradation as reported by McRae et al (2004) and Tung (2004). At 20°C the $Cl_3AA$ removal model followed the first-order model (Figure 9). This indicates that sufficient biological activities had been developed for $Cl_3AA$ and its removal was only dependent on its concentration. The model for $Cl_3AA$ removal at 30°C was not calculated because its effluent concentration was near the detection limits and not reliable for modeling.

In order to evaluate the HAA removal rate, the pseudo-first-order reaction rates at 10°C water temperature were
determined for all HAAs, including Cl$_3$AA. The reaction rate constants and half-lives are listed in Table 3. For a 50% removal of mono- and dihaloacetic acids at 10°C, the required EBCT ranges from 6 to 8 min. However, for a 50% removal of Cl$_3$AA at 10°C, a 17.3-min EBCT is required. As shown in Table 3, the model did not fit Cl$_3$AA removal well, as indicated by the low correlation coefficient value ($R^2$) 0.889.

**CONCLUSIONS**

Results of this study indicate that both EBCT and water temperature greatly affected the HAA removal in BAC columns. Increasing water temperature or EBCT increased the removal of HAAs. At a temperature of 20°C or higher, HAA removal did not increase greatly for different EBCTs. At 4°C, HAA removal was the lowest of all temperatures. At temperatures greater than 20°C, HAA removal increased with increasing EBCT for waters at 10°C or higher.

HAA removal in BAC columns had different kinetic models at different temperatures. At 4°C, HAA removal tended to follow a zero-order reaction model. This indicates that HAA removal may be limited by biological activities on its surface. At 10°C, the mono- and dihaloacetic acid removal tended to follow the first-order reaction model. This indicates that biological activities were fully developed at 10°C and HAA removal was limited by their concentrations. For Cl$_3$AA removal, a first-order reaction model was obtained at 20°C but not at 10°C. The kinetic study indicates that a 6- to 8-min EBCT is required for a 50% removal of mono- and dihaloacetic acids at 10°C. However, a 17.3-min EBCT is required for a 50% removal of Cl$_3$AA. The kinetic results are comparable to those observed for HAA6 at various EBCTs and temperatures.

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**FOOTNOTES**

1Hewlett Packard 6890, Wilmington, Del.