

## filtration

Biofilters seeded with mixed-culture nitrifiers from Lake Austin, Texas, and fed nutrient and Lake Austin water biodegraded the four trihalomethanes (THMs) commonly found in treated drinking water—bromoform, chloroform, dibromochloromethane, and dichlorobromomethane. THMs were degraded by cometabolism, and degradation increased with increased THM bromine substitution and increased total ammonia-nitrogen biodegradation. Overall, these experiments resulted in sustained THM removals ranging from 10 to 60% for varying operating conditions. Three operational issues were also studied: THM product toxicity, nutrient limitations, and monochloramine inhibition of ammonia and THM degradation. The cometabolism stability index represents a simple and useful parameter for evaluating the likelihood of product toxicity problems in biofilter operation. Nutrient limitations (e.g., iron and copper) may exist for natural water sources, and supplemental nutrients may be needed to achieve maximum THM degradation rates. Influent monochloramine concentrations of 1 mg/L (or less) as Cl<sub>2</sub> appear to be a good target for stable operation of developed biofilms.

# Trihalomethane cometabolism by a mixed-culture nitrifying biofilter

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**D**uring drinking water disinfection, natural organic matter combines with the disinfectant to produce disinfection by-products (DBPs), including haloacetic acids (HAAs) and trihalomethanes (THMs). Chlorine disinfection remains popular in the United States (Connell et al, 2000a; 2000b), although many utilities now use combinations of chlorine and chloramines to avoid excessive THM and HAA formation. A typical treatment scheme consists of an initial period of chlorination to help achieve disinfection goals followed by quenching with ammonia at some point in the treatment train to meet DBP goals through the lower DBP formation rates associated with chloramines. Significant formation of THMs and HAAs can occur within treatment plants, even during relatively short periods of chlorination (Singer et al, 1999b; Symons et al, 1982). Therefore, approaches for minimizing DBP formation or for removing DBPs within treatment plants are of great value.

Biodegradation offers a new approach for removing DBPs. Evidence of HAA biodegradation in drinking water environments continues to mount (McRae et al, 2004; Xie & Zhou, 2002, 2000; Baribeau et al, 2000; Singer et al, 1999a; Williams et al, 1998, 1997). HAA biodegradation is not at all surprising because the ability of mono- and dichloroacetic acid to support microbial growth is well



The published report, *Cometabolism of Trihalomethanes in Nitrifying Biofilters (91100F)*, is available from IWA Publishing at [www.iwap.co.uk](http://www.iwap.co.uk) or is free to AwwaRF subscribers by calling 303-347-6121 or logging on to [www.awwarf.org](http://www.awwarf.org).

documented in the microbiology and hazardous waste literature (Janssen et al, 1985; Motosugi & Soda, 1983).

THMs and HAAs tend to form together, so biological DBP removal processes must be able to deal with both classes of DBPs to be of any practical value in regulatory compliance. Unfortunately, THM biodegradation is a

ments were conducted using biofilters seeded with mixed-culture nitrifiers from Lake Austin, Texas, to develop a new biological treatment process for THM destruction in drinking water treatment plants based on THM cometabolism by nitrifying bacteria growing on ammonia in multimedia filters.

**For statistically similar total ammonia-nitrogen degradation, no significant change in trichloromethane degradation occurred whether dibromochloromethane was present or not.**

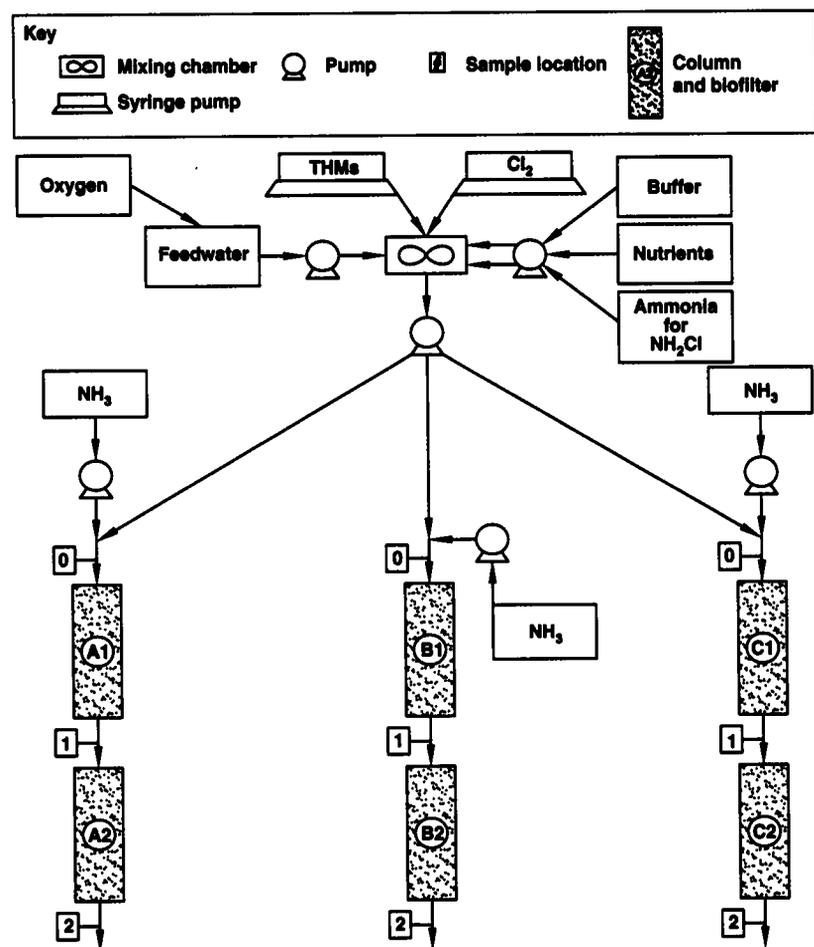
much more difficult proposition than HAA biodegradation. No evidence indicates that THMs can support microbial growth. Considerable evidence is available, however, for cometabolism of chloroform by bacteria growing on other chemicals, including ammonia (Aziz et al, 1999; Ely et al, 1997; Alvarez-Cohen & McCarty, 1991b). Cometabolism can be defined as the fortuitous biodegradation of a target chemical (i.e., the cometabolite, THMs) through reactions catalyzed by one or more nonspecific microbial enzymes. Because of the greater difficulty in biodegrading THMs, the development of a THM biotreatment process is the limiting factor in implementing biological treatment for DBP control.

Previous batch kinetic experiments demonstrated that all four THMs—bromoform, chloroform, dibromochloromethane, and dichlorobromomethane—could be degraded by both a pure culture, *Nitrosomonas europaea*, and mixed-culture nitrifiers at rates reasonable for process implementation (Wahman et al, 2006; 2005). In addition, these experiments determined the product toxicity (represented by transformation capacity) associated with degrading each THM. Transformation capacity ( $T_c$ ) represents the maximum mass of cometabolite that can be degraded per unit mass cells or the mass of cometabolite degradation required to completely inactivate the cells (Alvarez-Cohen & McCarty, 1991a). On the basis of these results, experi-

**MATERIALS AND METHODS**

**Biofilter setup.** The biofilter system (Figure 1) consisted of a filtered distilled–deionized water feed supplemented with nutrients (calcium, magnesium, copper, and iron) based on batch *N. europaea* growth (Wahman

**FIGURE 1** Biofilter system schematic



Cl<sub>2</sub>—chlorine, NH<sub>2</sub>Cl—monochloramine, NH<sub>3</sub>—ammonia, THM—trihalomethane

et al, 2005) and a carbonate/phosphate buffer to simulate natural waters (approximately 200 mg/L as CaCO<sub>3</sub>). THMs were added via a syringe pump, and oxygen was added to the feedwater when required, raising the biofilter influent dissolved oxygen to nonlimiting levels (approximately 16–20 mg/L). The biofilters were packed wet and seeded during the packing process with a mixed-culture inoculum isolated from Lake Austin (Wahman et al, 2006). Before initiating flow, the biofilters were operated in batch mode for approximately 1 h to promote nitrifier attachment to the media.

Experiments were conducted in three parallel trains (A, B, and C). Each train consisted of two biofilters in series. The nominal influent ammonia concentrations for trains A, B, and C were different (4, 2, and 1 mg/L total ammonia-nitrogen [TOTNH<sub>3</sub>], respectively). In this research, TOTNH<sub>3</sub> represents the sum of ammonia-nitrogen (NH<sub>3</sub>-N) and ammonium-nitrogen (NH<sub>4</sub><sup>+</sup>-N). Sampling points were at the first biofilter's influent (sample location 0), between the two biofilters in a train corresponding to the first biofilter's effluent and second biofilter's influent (sample location 1), and at the second biofilter's effluent (sample location 2).

The nominal empty bed contact time (EBCT) was 4 min after the first biofilter and 8 min after the second. The biofilters were packed with 30 × 40-mesh anthracite and had a nominal surface loading rate (SLR) of 0.63 gpm/sq ft (37 m/d). With the use of the biofilm-scaling procedure proposed by Manem and Rittmann (1990), the experimental biofilters simulate full-scale filters operating

with 8-min EBCTs and an SLR of 2.5 gpm/sq ft (147 m/d), if biofilm shear loss is chosen as the scaling parameter or 3.5 gpm/sq ft (205 m/d) if external mass transport is chosen as the scaling parameter. Both of these operating conditions fall into typical values reported for rapid filtration (MWH Inc., 2005).

For some experiments, the feedwater was changed from distilled–deionized water to Lake Austin water. As required when feeding Lake Austin water, the system was modified to form chloramines or add micronutrients such as iron and copper. Lake Austin water is a typical surface water with an alkaline pH (8.26–8.43), moderate alkalinity (169–190 mg/L as CaCO<sub>3</sub>), and dissolved organic carbon (3.4–4.6 mg/L as C; Roalson et al, 2003).

**Trihalomethane analysis.** THM concentrations were measured using US Environmental Protection Agency method 551.1 with modifications (USEPA, 1995). Concentrations of individual THM species were analyzed on a gas chromatograph<sup>1</sup> with a liquid autosampler and a column<sup>2</sup> with constant pressure and splitless injection. The initial oven temperature was set to 32°C for 3.5 min. The temperature was ramped at 20°C/min to 72°C and remained at 72°C for 3.5 min for a total analysis time of 9 min.

**Ammonia and monochloramine analysis.** Ammonia was measured with an ammonia electrode<sup>3</sup> connected to a pH/ion selective electrode meter<sup>4</sup> calibrated with standards. Monochloramine was measured<sup>5</sup> on an ultraviolet (UV)-visible spectrophotometer<sup>6</sup> at 655 nm calibrated with standards.

**TABLE 1** Product toxicity evaluation parameters

Variable	Definition	Value*	Units
$\alpha_1$	[NH <sub>3</sub> -N]/[TOTNH <sub>3</sub> ] at 23.5°C and pH 8.0	0.049†	Dimensionless
Y	Bacterial cell yield	0.33‡	mg TSS/mg TOTNH <sub>3</sub>
$K_{S\text{NH}_3\text{-N}}$	Ammonia-nitrogen half-saturation coefficient	0.16	mg/L NH <sub>3</sub> -N
$k_{\text{TOTNH}_3}$	TOTNH <sub>3</sub> maximum substrate utilization rate constant	2.9	mg TOTNH <sub>3</sub> /mg TSS/d
$k_d$	Endogenous decay coefficient	0.020§	1/d
$k_{\text{TCM}}$	TCM pseudo-first-order rate constant	0.10	L/mg TSS/d
$k_{\text{BDCM}}$	BDCM pseudo-first-order rate constant	0.15	L/mg TSS/d
$k_{\text{DBCM}}$	DBCM pseudo-first-order rate constant	0.20	L/mg TSS/d
$k_{\text{TBM}}$	TBM pseudo-first-order rate constant	0.23	L/mg TSS/d
$T_{\text{cTCM}}$	TCM transformation capacity	9.2	µg TCM/mg TSS
$T_{\text{cBDCM}}$	BDCM transformation capacity	7.3	µg BDCM/mg TSS
$T_{\text{cDBCM}}$	DBCM transformation capacity	6.5	µg DBCM/mg TSS
$T_{\text{cTBM}}$	TBM transformation capacity	5.6	µg TBM/mg TSS

BDCM—bromodichloromethane, DBCM—dibromochloromethane, NH<sub>3</sub>-N—ammonia-nitrogen, TBM—tribromomethane, TCM—trichloromethane, TOTNH<sub>3</sub>—total ammonia-nitrogen, TSS—total suspended solids

\*Wahman et al, 2005; unless otherwise noted

†Spittel et al, 2005

‡Rittmann et al, 2001; value also assumes volatile suspended solids equals TSS in cells.

§Wahman, unpublished

**TABLE 2**  $C_{si}$  values for biofilter runs

Run (Period)	Nominal Trihalomethane Concentrations— $\mu\text{g/L}$										
	1 (2)	1 (4)	1 (5, 6)	3 (6-10) 4 (1-4)	2 (1)	2 (2)	2 (3) 3 (4)	2 (4)	2 (5)	2 (6) 3 (2)	2 (7)
TCM	40	20	30	40	50	75	100	0	0	100	100
BDCM	20	0	0	0	0	0	0	0	0	0	0
DBCM	20	0	0	0	0	0	0	10	25	10	25
TBM	20	0	0	0	0	0	0	0	0	0	0
$C_{si}$											
Train A	0.40	4.2	2.8	2.1	1.7	1.1	0.84	3.0	1.2	0.65	0.49
Train B	0.39	4.1	2.7	2.1	1.7	1.1	0.82	2.9	1.2	0.64	0.48
Train C	0.38	4.0	2.6	2.0	1.6	1.1	0.79	2.8	1.1	0.62	0.46

$C_{si}$ —cometabolism stability index, BDCM—bromodichloromethane, DBCM—dibromochloromethane, TBM—tribromomethane, TCM—trichloromethane

**Dissolved oxygen and pH analyses.** Dissolved oxygen was measured with an oxygen probe<sup>7</sup> connected to a dissolved oxygen meter<sup>8</sup> calibrated per the manufacturer's recommendations. pH was measured using a combination pH electrode<sup>9</sup> on a pH/ion selective electrode meter<sup>4</sup> calibrated with pH standards of 4, 7, and 10.

**Product toxicity.** Product toxicity was observed when THMs were cometabolized by nitrifiers in batch kinetic experiments (Wahman et al, 2005) and in the initial biofilter experiments presented in this article. A simple formula was derived to quantify the expected product toxicity of THMs fed during biofilter experiments to guide the design and interpretation of subsequent experiments. For bacteria to provide sustained degradation of THMs, the net growth rate on ammonia (based on Monod kinetics) must be greater than the inactivation rate from THM degradation. Inactivation results from the toxicity of THM degradation products and is characterized by  $T_c$ . To help quantify the balance between net growth and inactivation rates, a new term, the cometabolism stability index ( $C_{si}$ ), was developed.  $C_{si}$  is the ratio of the net growth rate ( $r'_g$ ) to the sum of the inactivation rates for the four THMs ( $r_i$ ) and is shown in Eq 1:

$$C_{si} = \frac{r'_g}{r_i} = \frac{Yk_{TRIN} - k_d \left( \frac{K_{SNH_3-N} + \alpha_1 S_{TOTNH_3}}{\alpha_1 S_{TOTNH_3}} \right)}{\dots} \quad (1)$$

$$\frac{k_{1TCM} S_{TCM}}{T_{cTCM}} + \frac{k_{1BDCM} S_{BDCM}}{T_{cBDCM}} + \frac{k_{1DBCM} S_{DBCM}}{T_{cDBCM}} + \frac{k_{1TBM} S_{TBM}}{T_{cTBM}}$$

in which  $r'_g$  indicates the net rate of bacterial cell growth (mg/d total suspended solids [TSS]);  $r_i$  is the rate of THM bacterial inactivation (mg/d TSS);  $S_{TOTNH_3}$  is the  $TOTNH_3$  concentration (mg/L  $TOTNH_3$  as N); and  $S_{THM}$  is the THM concentration ( $\mu\text{g/L}$  THM). Other terms are defined in Table 1.

Eq 1 indicates that for stable biofilter operation,  $C_{si}$  must be  $\geq 1$ . All of the terms in the  $C_{si}$  except THM and  $TOTNH_3$  concentrations are bacteria-specific and were previously determined from batch kinetics experiments for the pure culture, *N. europaea* (Wahman et al, 2005). Because the mixed cultures showed kinetic values similar to *N. europaea* and individual THM transformation capacity values were determined for *N. europaea* and verified for a mixed culture, the information for *N. europaea* was used in these calculations (Wahman et al, 2006; 2005).

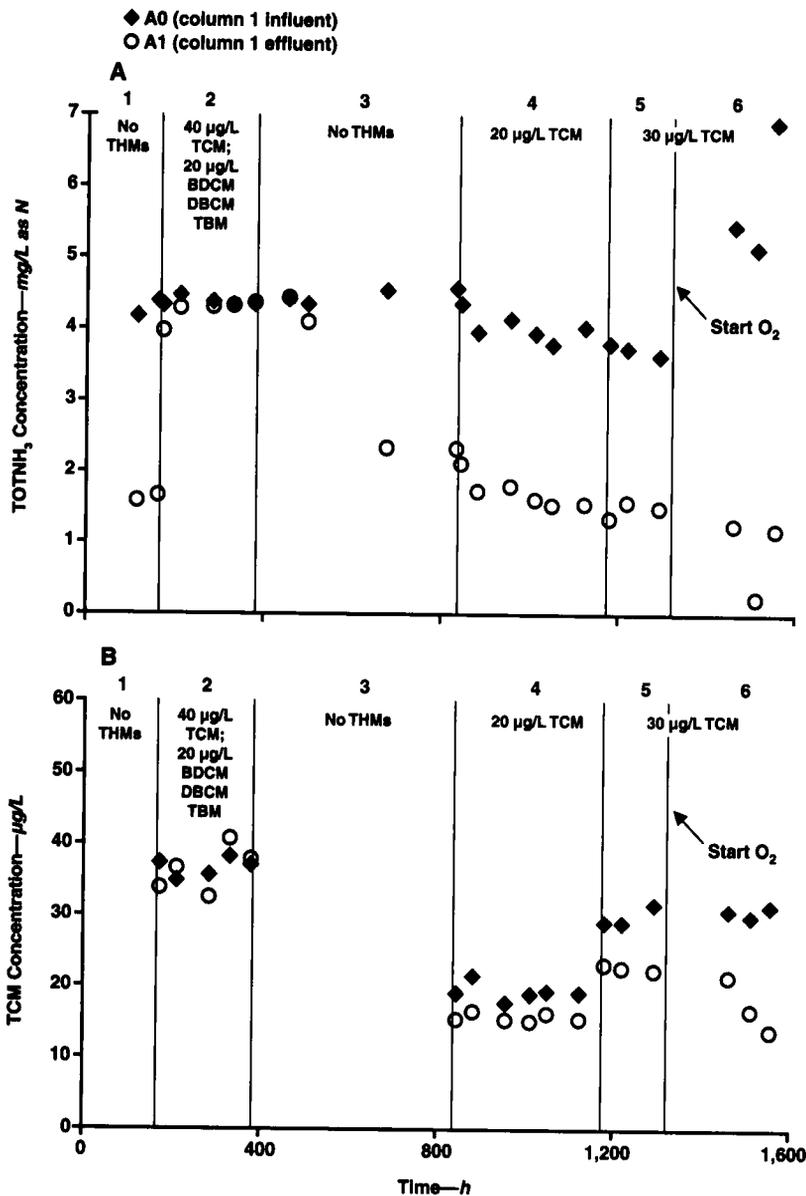
To simplify the analysis, the influent  $TOTNH_3$  and THM concentrations were used to evaluate possible product toxicity. Rigorously, these concentrations only define the  $C_{si}$  at the influent to the first biofilter in the absence of mass transfer resistances into the biofilm. The parameter values used to calculate  $C_{si}$  are summarized in Table 1. Table 2 lists  $C_{si}$  values for combinations of THM concentration and speciation tested in the biofilter experiments shown in this article.

**Simplified THM cometabolism model.** A simplified model of THM cometabolism in a biofilter can be obtained by ignoring mass transport resistances and assuming an ideal plug flow reactor with a residence time equal to the contact time in the biofilter. By using the rate equations for  $TOTNH_3$  and THM detailed previously by Wahman et al (2005), a closed-form solution for the removal of a given THM can be obtained and is shown in Eq 2:

$$\frac{S_{THM_n}}{S_{THM_0}} = e^{-\Delta TOTNH_3 \frac{k_{1THM}}{k_{TOTNH_3}}} \quad (2)$$

in which  $S_{THM_0}$  is the THM influent concentration ( $\mu\text{g/L}$  THM);  $S_{THM_n}$  is the THM effluent concentration from the  $n$ th (1 or 2) biofilter in the series ( $\mu\text{g/L}$  THM); and  $\Delta TOTNH_3$  is the influent  $TOTNH_3$  minus the effluent  $TOTNH_3$ . Other terms are defined in Table 1.

**FIGURE 2** TOTNH<sub>3</sub> and TCM concentrations for train A (run 1) fed nutrient water



BDCM—bromodichloromethane, DBCM—dibromochloromethane, N—nitrogen, O<sub>2</sub>—oxygen, TBM—tribromomethane, TCM—trichloromethane, THM—trihalomethane, TOTNH<sub>3</sub>—total ammonia-nitrogen

Numbers at the top of the columns indicate operating periods during each run.

On the basis of Eq 2, the THM normalized effluent concentration ( $S_{THM_n}/S_{THM_0}$ ), and therefore THM fractional removal, will be independent of the influent THM and TOTNH<sub>3</sub> concentrations and for a given  $\Delta$ TOTNH<sub>3</sub> removal, dependent on the THM rate constant ( $k_{1,THM}$ ). Thus, Eq 2 can be used to approximate the maximum expected removal of each THM species as a function of ammonia removal.

established (period 1). The initial THM addition of 40 µg/L TCM and 20 µg/L each of bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM) resulted in an immediate loss of TOTNH<sub>3</sub> degradation (period 2) as subsequently predicted from  $C_{si}$  for these THM influent concentrations (Table 2). The first sample after THM addition showed that all four THMs were degraded in all three trains as

**Statistical analyses.** Tukey's paired comparison method was used to compare the performance of different operating periods of the biofilters (Berthouex & Brown, 2002). A two-sided 95% confidence interval of the studentized range statistic was used for all paired comparisons (Harter, 1960). Graphing software<sup>10</sup> was used for a nonlinear fit of data and to generate 95% confidence intervals for Eq 2.

## RESULTS AND DISCUSSION

Biofilters seeded with a Lake Austin mixed culture were operated under varying conditions that were broken into four runs. In runs 1 and 2, the biofilters were fed nutrient water. In runs 3 and 4, the feedwater was switched to Lake Austin water. In run 4, monochloramine was added. During each run, three trains were operated under different influent TOTNH<sub>3</sub> concentrations (4, 2, and 1 mg/L as N, respectively). To illustrate the trends seen during biofilter operation, only the data from train A (TOTNH<sub>3</sub> nominal influent of 4 mg/L as N), which are representative of the trends seen in trains B and C, are shown.

**Run 1.** Run 1 consisted of an initial operating period to establish nitrification, explored THM product toxicity, and resolved dissolved oxygen limitations for train A. Figure 2, parts A and B, detail the TOTNH<sub>3</sub> and trichloromethane (TCM) concentrations for train A during run 1. Initially, only TOTNH<sub>3</sub> was added to the biofilters until nitrification was

shown in Table 3, with this degradation leading to the decrease in TOTNH<sub>3</sub> removal because of product toxicity. Essentially no TOTNH<sub>3</sub> or THM degradation occurred after approximately 48 h of operation during period 2.

Once the THMs were removed from the influent (period 3), all three trains recovered their previous TOTNH<sub>3</sub> degradation as nitrification was reestablished. On the basis of C<sub>si</sub> and to avoid THM product toxicity, the influent THM concentration was set to approximately 20 µg/L TCM after the biofilters recovered from the process upset (period 4) with a subsequent increase to 30 µg/L TCM without (period 5) and with (period 6) the addition of oxygen. TCM removal for train A during periods 4 and 5 averaged 4 and 7 µg/L, respectively. Once oxygen was added in period 6, TOTNH<sub>3</sub> and TCM removal increased, with TCM removal reaching 15 µg/L at the end of period 6 for train A. Oxygen addition continued throughout the remaining biofilter experiments to ensure that oxygen was not limiting in the biofilters.

As shown in Table 2, the initial speciation and concentration of THMs fed in run 1 was too high, because the calculated C<sub>si</sub> value of 0.40 was well below the value of 1 expected for stable operation. Thus, the low value of C<sub>si</sub> proved to be a good predictor for the loss of TOTNH<sub>3</sub> removal and the absence of THM removal under this feed condition. The subsequent lower TCM concentrations (20 and 30 µg/L) resulted in a C<sub>si</sub> > 1 and stable biofilter operation with TCM removal. Overall for run 1, the experimental findings were consistent with the C<sub>si</sub>

**TABLE 3** Run 1 (period 2) performance at 172 h

Train	ΔTOTNH <sub>3</sub> mg/L N	S <sub>THM2</sub> /S <sub>THM0</sub>				
		TCM	BDCM	DBC	TBM	Total THMs
A	0.86	0.87	0.82	0.80	0.81	0.83
B	1.2	0.84	0.79	0.75	0.75	0.80
C	0.62	0.89	0.86	0.84	0.84	0.87

BDCM—bromodichloromethane, DBCM—dibromochloromethane, S<sub>THM0</sub>—influent TCM, BDCM, DBCM, TBM, or total THM concentration (µg/L), S<sub>THM2</sub>—effluent concentration from second biofilter in series (µg/L), S<sub>TCM0</sub>—37 µg/L, S<sub>BDCM0</sub>—19 µg/L, S<sub>DBC0</sub>—18 µg/L, S<sub>TBM0</sub>—18 µg/L, S<sub>THM0</sub>—92 µg/L, TBM—tribromomethane, TCM—trichloromethane, THM—trihalomethane, TOTNH<sub>3</sub>—the sum of ammonia-nitrogen (NH<sub>3</sub>-N) and ammonium-nitrogen (NH<sub>4</sub><sup>+</sup>-N), ΔTOTNH<sub>3</sub>—influent TOTNH<sub>3</sub> minus the effluent TOTNH<sub>3</sub>

predictions and demonstrated sustained cometabolism of TCM in the biofilters.

**Run 2.** During run 2 (Figure 3, parts A–C), the influent TCM concentration was increased from 50 µg/L (period 1) to a maximum nominal influent concentration of 100 µg/L (period 3). After period 3, the influent THM was changed from TCM to DBCM to provide information on a bromine-substituted THM. The influent DBCM concentration ranged from 10 to 25 µg/L (periods 4 and 5, respectively). Finally, both TCM and DBCM were fed simultaneously (periods 6 and 7) to provide a comparison with biofilter performance when they were fed individually.

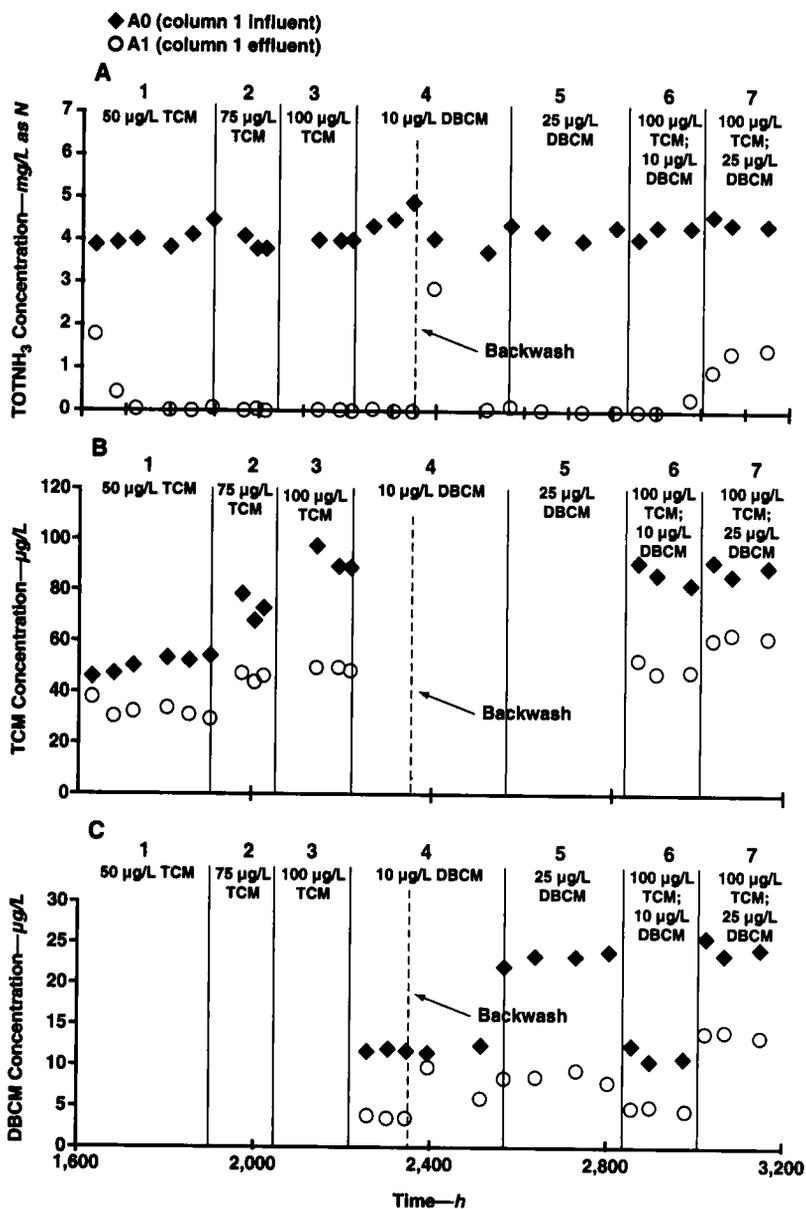
During run 2, both TCM and DBCM were degraded in all three trains, with train A achieving maximum removals of 46 and 73%, respectively. No apparent THM product toxicity (based on TOTNH<sub>3</sub> removal) occurred during run 2 except when both TCM and DBCM were fed simultaneously, and then only in train A, as demonstrated by the increased effluent TOTNH<sub>3</sub> concentration in Fig-

**TABLE 4** Run 1 and 2 performance summary for train A (first biofilter in series)

Run	Period	Sample Size	ΔTOTNH <sub>3</sub> mg/L N	TCM Influent µg/L	S <sub>TCM1</sub> /S <sub>TCM0</sub>	DBC Influent µg/L	DBC <sub>1</sub> /DBC <sub>0</sub>
1	4	6	2.3 ± 0.094	19 ± 1.2	0.81 ± 0.034		
1	5	3	2.3 ± 0.18	30 ± 1.5	0.76 ± 0.049		
2	1	4	4.1 ± 0.25	53 ± 1.7	0.60 ± 0.045		
2	2	3	3.9 ± 0.18	73 ± 5.3	0.63 ± 0.022		
2	3	3	4.0 ± 0.021	92 ± 4.8	0.54 ± 0.024		
2	4	3	4.6 ± 0.31			12 ± 0.16	0.27 ± 0.019
2	5	4	4.2 ± 0.14			23 ± 0.8	0.36 ± 0.029
2	6	3	4.1 ± 0.17	87 ± 4.3	0.57 ± 0.018	11 ± 1.0	0.39 ± 0.029
2	7	3	3.2 ± 0.39	88 ± 2.8	0.70 ± 0.034	24 ± 1.1	0.57 ± 0.032

DBC—dibromochloromethane, S<sub>TCM0</sub>, S<sub>DBC0</sub>—influent TCM and DBCM concentrations (µg/L), S<sub>TCM1</sub>, S<sub>DBC1</sub>—effluent TCM and DBCM concentrations from first biofilter in series (µg/L), TCM—trichloromethane, TOTNH<sub>3</sub>—the sum of ammonia-nitrogen (NH<sub>3</sub>-N) and ammonium-nitrogen (NH<sub>4</sub><sup>+</sup>-N), ΔTOTNH<sub>3</sub>—influent TOTNH<sub>3</sub> minus the effluent TOTNH<sub>3</sub>

**FIGURE 3** TOTNH<sub>3</sub>, TCM, and DBCM concentrations for train A (run 2) fed nutrient water



DBCM—dibromochloromethane, N—nitrogen, TCM—trichloromethane, TOTNH<sub>3</sub>—total ammonia-nitrogen

Numbers at the top of the columns indicate operating periods during each run.

ure 3, part A, for periods 6 and 7. The general absence of product toxicity was expected on the basis of the calculated  $C_{si}$  values (Table 2) for periods 1, 2, 4, and 5.

The  $C_{si}$  for periods 3, 6, and 7 during run 2 was <1, predicting process failure. Although these predictions proved to be too conservative, the lowest  $C_{si}$  values prevailed during periods 6 and 7 when train A showed a partial loss of nitrification, indicating the usefulness of the

$C_{si}$  concept. Even though the  $C_{si}$  concept did not necessarily predict performance in all cases, it offers a good framework for evaluating product toxicity. Some refinement of the parameter values in Eq 1 in combination with further experience in operating the process may be needed to better define the minimum feasible  $C_{si}$  value for successful operation.

Biofilter performance during periods 6 and 7 was surprising for two reasons. First, based on the  $C_{si}$  values in Table 2, difficulties with product toxicity would have been expected for all three trains but did not occur in trains B and C. Second, the biofilter in train A appeared to restabilize at a higher TOTNH<sub>3</sub> effluent concentration, rather than proceeding to complete loss of nitrification as observed in run 1.

Nutrient limitations offer a possible explanation for these observations. The enzyme responsible for ammonia oxidation, ammonia monooxygenase, is proposed to contain iron and copper (Arp & Stein, 2003). If the product toxicity associated with THM degradation results in the inactivation of ammonia monooxygenase in a way that does not allow the recovery of the iron or copper associated with the enzyme, these nutrients could become limiting as the mass of degraded THMs increases. Because train A degraded the greatest mass of THMs and TOTNH<sub>3</sub>, nutrient limitations could explain the observation.

Likewise, nutrient limitations could explain the restabilization of process performance in that the process stabilized to a THM and TOTNH<sub>3</sub> degradation level that the available nutrient supply in the

feedwater could support. Additional research is needed to confirm this hypothesis.

**Comparison of runs 1 and 2.** A summary of average measurements taken for different operating conditions in train A during runs 1 and 2 is provided in Table 4. Because TOTNH<sub>3</sub> removal was complete after the first biofilter in the series and THM removal did not occur without TOTNH<sub>3</sub> removal, only values for the first biofilter were

used in calculations for both TOTNH<sub>3</sub> and THM concentrations.

From Eq 2, two trends observed in the biofilter data are expected: as  $\Delta\text{TOTNH}_3$  increases,  $S_{\text{THM}_n}/S_{\text{THM}_0}$  decreases; and for a given  $\Delta\text{TOTNH}_3$ , the THM with the larger rate constant will produce a lower  $S_{\text{THM}_n}/S_{\text{THM}_0}$ . Both trends are highlighted in Table 4 for train A.

Similarly, Figure 4 shows that the two trends held for all three trains during runs 1 and 2. Eq 2 was fit to the TCM and DBCM data for all three trains to determine the kinetic rate constant ratio ( $k_{1\text{THM}}/k_{\text{TOTNH}_3}$ ) and its 95% confidence limit for each THM. Because  $k_{\text{TOTNH}_3}$  should be the same for each operating condition, the higher value for this ratio with DBCM compared to that with TCM implies that  $k_{1\text{DBCM}}$  is significantly  $> k_{1\text{TCM}}$ . Therefore, the trend in degradation rates found in the batch kinetic studies (Wahman et al, 2006; 2005) continued in the biofilter experiments because DBCM (the more bromine-substituted THM) has a larger rate constant than TCM.

In addition, for statistically similar TOTNH<sub>3</sub> degradation, no significant change in TCM degradation occurred whether DBCM was present or not. This result matched observations from the batch kinetic studies that showed no enzyme competition among THMs at the concentrations typical of drinking water treatment.

The results from runs 1 and 2 suggest that for a  $\Delta\text{TOTNH}_3$  of 2 mg/L as N, TCM and DBCM removal of 25 and 35%, respectively, can be achieved, which is a level of performance potentially attractive for drinking water treatment practice. The ratio of THM cometabolism to ammonia degradation is higher for the bromine-substituted THMs, but greater attention to product toxicity is required when bromine-substituted THMs are present at increasing concentrations.

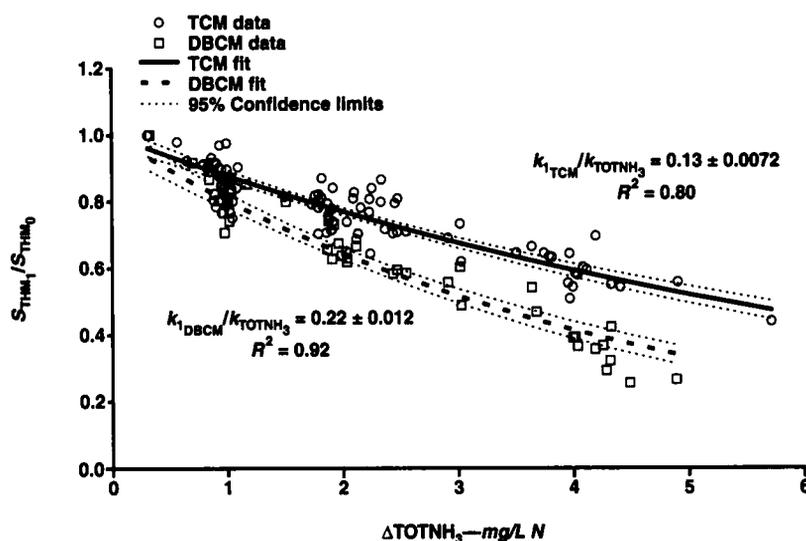
**Run 3.** After completing the biofilter experiments on nutrient water, the feedwater was changed to Lake Austin water to provide a more realistic test of THM cometabolism under drinking water treatment conditions. This operating phase, run 3, consisted of periods during which issues of apparent nutrient deficiency and THM product toxicity were investigated and resolved. Parts A and B of

**TABLE 5** Run 3 (period 10) summary (first biofilter in series)

Train	Sample Size	$\Delta\text{TOTNH}_3$ mg/L N	TCM Influent μg/L	$S_{\text{TCM}_1}/S_{\text{TCM}_0}$
A	5	4.0 ± 0.11	44 ± 3.0	0.79 ± 0.067
B	6	2.0 ± 0.034	44 ± 2.7	0.89 ± 0.070
C	6	1.0 ± 0.032	44 ± 2.7	0.95 ± 0.049

$S_{\text{TCM}_0}$ —influent TCM concentration (μg/L),  $S_{\text{TCM}_1}$ —effluent TCM concentration from first biofilter in series (μg/L), TCM—trichloromethane, TOTNH<sub>3</sub>—the sum of ammonia-nitrogen (NH<sub>3</sub>-N) and ammonium-nitrogen (NH<sub>4</sub><sup>+</sup>-N),  $\Delta\text{TOTNH}_3$ —influent TOTNH<sub>3</sub> minus the effluent TOTNH<sub>3</sub>

**FIGURE 4** THM cometabolism performance curves for runs 1 and 2



DBCM—dibromochloromethane,  $k_{1\text{DBCM}}/k_{\text{TOTNH}_3}$ —ratio of the DBCM pseudo-first-order rate constant to TOTNH<sub>3</sub> maximum substrate utilization rate constant (mg/L TOTNH<sub>3</sub>),  $k_{1\text{TCM}}/k_{\text{TOTNH}_3}$ —ratio of the TCM pseudo-first-order rate constant to TOTNH<sub>3</sub> maximum substrate utilization rate constant (mg/L TOTNH<sub>3</sub>),  $R^2$ —coefficient of determination,  $S_{\text{THM}_0}$ —influent THM concentration (μg/L),  $S_{\text{THM}_1}$ —effluent THM concentration from first biofilter in series (μg/L), TCM—trichloromethane, TOTNH<sub>3</sub>—total ammonia-nitrogen,  $\Delta\text{TOTNH}_3$ —influent TOTNH<sub>3</sub> minus the effluent TOTNH<sub>3</sub> from first biofilter in series

Figure 5 detail the TOTNH<sub>3</sub> and TCM concentrations during run 3 for train A.

Before starting THM addition, an initial period (period 1) was given for the trains to reestablish nitrification after backwashing. The initial THM addition of 100 μg/L TCM and 10 μg/L DBCM resulted in a decrease in TOTNH<sub>3</sub> degradation for all three trains (period 2). Therefore, THM addition was stopped, the trains were allowed to reestablish TOTNH<sub>3</sub> degradation (period 3), and only 100 μg/L TCM addition was attempted (period 4). Again, TOTNH<sub>3</sub> degradation declined, and THM addition was stopped (period 5) until TOTNH<sub>3</sub> degradation was reestablished.

**TABLE 6** Run 4 performance summary for train A

Period	Sample Size	TOTNH <sub>3</sub>		NH <sub>2</sub> Cl		TCM	
		Influent mg/L N	$\Delta_{Total}$ mg/L N	Influent mg/L Cl <sub>2</sub>	$\Delta_{Total}$ mg/L Cl <sub>2</sub>	Influent $\mu$ g/L	$S_{TCM_2}/S_{TCM_0}$
1	4	4.0 ± 0.11	2.9 ± 0.21			48 ± 3.3	0.81 ± 0.081
2	3	4.0 ± 0.14	2.9 ± 0.29	0.49 ± 0.046	0.47 ± 0.031	42 ± 4.9	0.89 ± 0.051
3	3	4.1 ± 0.10	2.9 ± 0.092	0.97 ± 0.030	0.96 ± 0.025	42 ± 2.9	0.81 ± 0.015
4	3	3.9 ± 0.10	1.7 ± 0.053	2.6 ± 0.17	2.6 ± 0.14	38 ± 2.0	0.89 ± 0.052

$\Delta_{Total}$ —total change across both biofilters in series, NH<sub>2</sub>Cl—monochloramine,  $S_{TCM_0}$ —influent TCM concentration ( $\mu$ g/L),  $S_{TCM_2}$ —effluent TCM concentration from second biofilter in series ( $\mu$ g/L), TCM—trichloromethane, TOTNH<sub>3</sub>—the sum of ammonia-nitrogen (NH<sub>3</sub>-N) and ammonium-nitrogen (NH<sub>4</sub><sup>+</sup>-N)

On the basis of successful operation during run 2 (periods 3 and 6) for similar influent concentrations and TOTNH<sub>3</sub> removal (Table 4), it was surprising that the biofilters continued to process failure (i.e., loss of nitrification) during periods 2 and 4, even though the  $C_{si}$  (Table 2) predicted problems with product toxicity for these influent THM concentrations. After recovery of TOTNH<sub>3</sub> degradation and the subsequent addition of 40  $\mu$ g/L TCM (period 6), only train C achieved total TOTNH<sub>3</sub> removal through the first biofilter in the series. This performance differed from run 2, during which, for the same TCM concentration, total TOTNH<sub>3</sub> removal occurred in the first biofilter in the series for all trains.

In addition, the removal of TCM was significantly lower than that of the comparable operation for run 2 for all three trains. Trains A and B appeared to stabilize at a lower TOTNH<sub>3</sub> degradation rather than continuing to show a decrease in TOTNH<sub>3</sub> degradation over time, similar to run 2 (period 7) for train A. In contrast to run 2 (period 7), the  $C_{si}$  values during run 3 (period 6) were > 1, indicating that process failure was not the cause of the decreased removals.

A hypothesis to account for the lower TOTNH<sub>3</sub> degradation was that one or more micronutrients were limiting compared with the nutrient water. Because the enzyme responsible for ammonia oxidation (ammonia monooxygenase) is proposed to contain iron and copper (Arp & Stein, 2003) and calcium and magnesium are present at higher concentrations in Lake Austin water than in nutrient water, iron and copper were investigated. To test this hypothesis, the addition of iron was started initially (period 7) at the concentration used in the nutrient water (6  $\mu$ g/L) and was later increased (200  $\mu$ g/L) to ensure that adequate iron was available (period 8).

When iron was added, TOTNH<sub>3</sub> degradation improved in trains A and B. Train A obtained nearly complete TOTNH<sub>3</sub> degradation through the first biofilter in the series by the end of period 8. To provide evidence that iron was limiting, the iron feed was stopped (period 9). As a result, TOTNH<sub>3</sub> degradation for train A decreased, but no change was seen for trains B and C.

Because the previous iron addition did not result in complete TOTNH<sub>3</sub> degradation for train A, copper was added (15  $\mu$ g/L; period 10) as well. With the addition of iron and copper, all three trains completely degraded TOTNH<sub>3</sub> through the first biofilter in the series, as they had when fed nutrient water, thus providing a strong indication that the hypothesis was correct.

TCM degradation was variable during run 3 until iron and copper were added during period 10. As with runs 1 and 2, once TOTNH<sub>3</sub> removal was complete, essentially no further TCM removal occurred; therefore, only values for the first biofilter were used in calculations for both TOTNH<sub>3</sub> and TCM removals. The general trends observed in runs 1 and 2 are shown in Table 5. The  $S_{THM_n}/S_{THM_0}$  values for TCM again showed that increased TOTNH<sub>3</sub> degradation corresponded to increased THM degradation, because train A had a significantly higher THM removal than train C. Thus, the close association between TOTNH<sub>3</sub> degradation and THM cometabolism observed in the batch kinetic and previous biofilter runs held in run 3.

Comparing  $S_{THM_n}/S_{THM_0}$  values with comparable influent TCM concentrations during run 2 (period 1, Table 4), shows that performance during run 3 was significantly less for all three trains, with TCM removal only 30 to 50% of that observed during run 2. The lower TCM removal suggests that another condition, possibly other micronutrients, was limiting in addition to iron and copper.

**Run 4.** In run 4, the feed setup was modified to allow monochloramine (NH<sub>2</sub>Cl) addition to the Lake Austin water feed. Figure 6, parts A–C, shows the TOTNH<sub>3</sub>, NH<sub>2</sub>Cl, and TCM concentrations during run 4 for train A. A series of stepped increases in the influent monochloramine concentration was introduced to evaluate the effect of monochloramine on TOTNH<sub>3</sub> and TCM degradation. For the period of no monochloramine addition (period 1), train A did not achieve complete TOTNH<sub>3</sub> removal through the first biofilter in the series; therefore, analyses for all three trains were conducted on the basis of performance through both biofilters in the series.

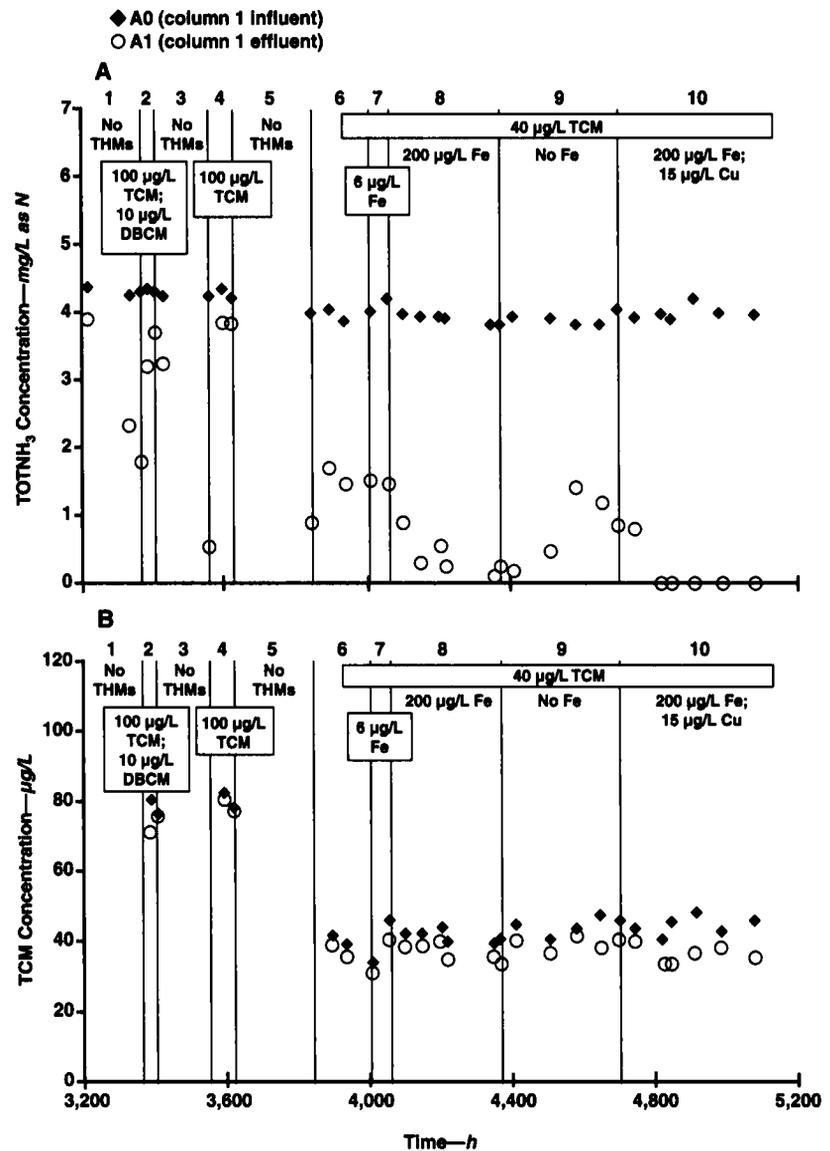
In run 4, TCM degradation was not significantly different from run 3 for each train during period 1 (Tables 5 and 6). For  $\text{NH}_2\text{Cl}$  additions of 0.5 and 1.0 mg/L as  $\text{Cl}_2$  (periods 2 and 3, respectively), the  $\text{TOTNH}_3$  degradation for each train was not significantly different from that in period 1. Once  $\text{NH}_2\text{Cl}$  addition began at 0.5 mg/L as  $\text{Cl}_2$  (period 2), TCM degradation decreased in all three trains, but not significantly. During period 3, TCM degradation returned to its previous level from period 1 even though the influent  $\text{NH}_2\text{Cl}$  concentration was increased to approximately 1.0 mg/L as  $\text{Cl}_2$  (Table 6).

Once the  $\text{NH}_2\text{Cl}$  influent was raised to 2.5 mg/L as  $\text{Cl}_2$  (period 4),  $\text{TOTNH}_3$  degradation decreased significantly in all three trains, reaching essentially zero for trains B and C at the end of the sampling period. The TCM degradation likewise decreased in accordance with the decrease in  $\text{TOTNH}_3$  degradation. During period 4, train A maintained a small amount of  $\text{TOTNH}_3$  degradation, but it steadily decreased over time. As a result,  $\text{NH}_2\text{Cl}$  addition was stopped, and one data point was taken to see if the trains showed signs of reestablishing  $\text{TOTNH}_3$  degradation (period 5). Train A showed an increased  $\text{TOTNH}_3$  degradation, whereas trains B and C showed only a small, yet measurable, improvement in  $\text{TOTNH}_3$  degradation.

The results from run 4 showed that monochloramine concentrations will impair stable process operation with respect to TCM or  $\text{TOTNH}_3$  removal at an influent concentration between 1 and 2.5 mg/L as  $\text{Cl}_2$ . Nitrification in drinking water systems has been reported at these monochloramine concentrations (Cunliffe, 1991). The precise monochloramine concentration is likely to be site-specific and perhaps dependent on operating conditions (e.g., the allowable monochloramine concentration may increase as the influent  $\text{TOTNH}_3$  concentration increases).

A possible confounding factor in run 4 was the formation of other DBPs once monochloramine was added

**FIGURE 5**  $\text{TOTNH}_3$  and TCM concentrations for train A (run 3) fed Lake Austin water

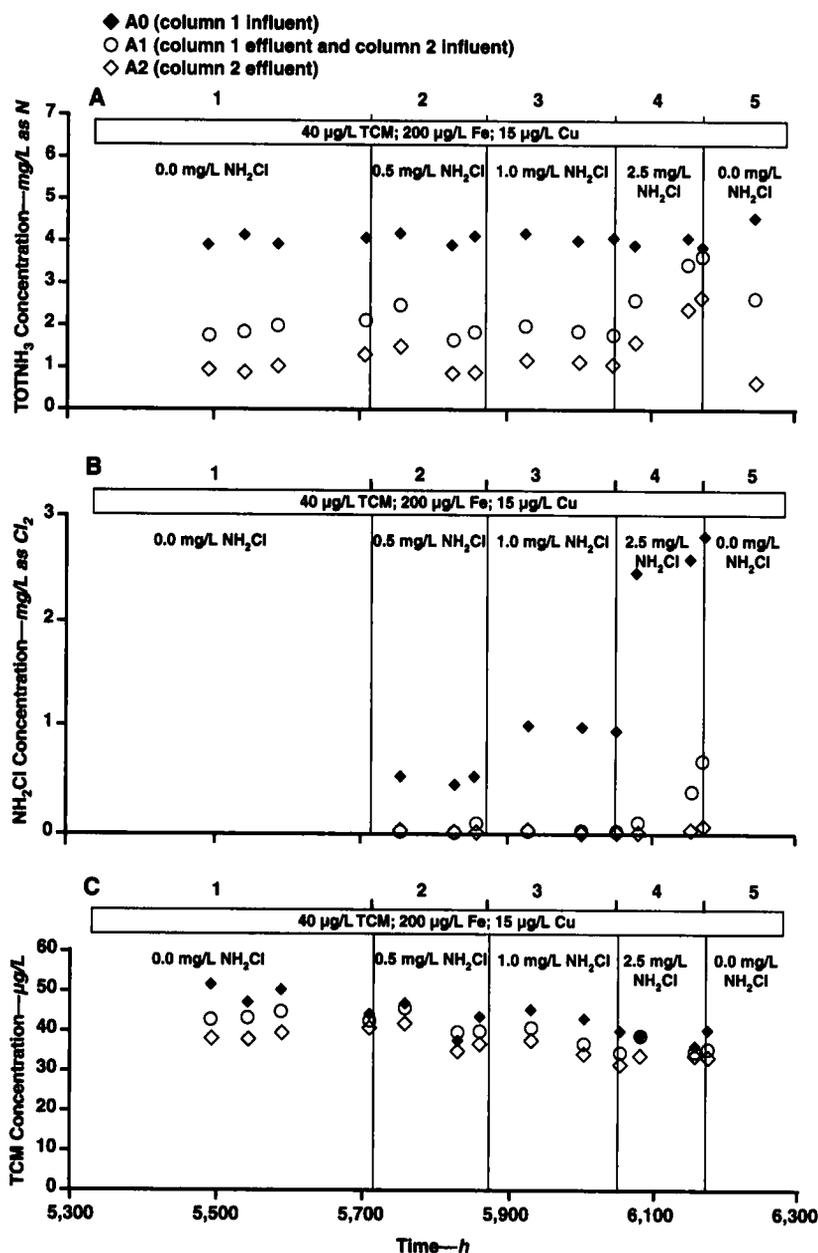


*Cu—copper, DBCM—dibromochloromethane, Fe—iron, N—nitrogen, TCM—trichloromethane, THM—trihalomethane,  $\text{TOTNH}_3$ —total ammonia-nitrogen*

*Numbers at the top of the columns indicate operating periods during each run.*

and the likelihood that the biofilm required time to adjust to these new DBPs. The influent and effluent chromatograms for the first biofilter in train A showed additional peaks at the 2.5 mg/L as  $\text{Cl}_2$  influent monochloramine condition (data not shown). The effluent chromatogram from this biofilter clearly showed a decrease in the number of additional peaks, indicating removal of these compounds in the biofilter (data not shown). For lower influent monochloramine values (0.5

**FIGURE 6** TOTNH<sub>3</sub>, NH<sub>2</sub>Cl, and TCM concentrations for train A (run 4) fed Lake Austin water



Cl<sub>2</sub>—chlorine, Cu—copper, Fe—iron, N—nitrogen, NH<sub>2</sub>Cl—monochloramine, TCM—trichloromethane, TOTNH<sub>3</sub>—total ammonia—nitrogen

Numbers at top of columns indicate operating periods during each run.

and 1 mg/L as Cl<sub>2</sub>), the influent to the trains did not show additional peaks whereas the effluent from both biofilters in the series for all trains showed additional peaks. Thus, low levels of DBPs appeared to have formed from the addition of monochloramine, with subsequent removal in the biofilm. The possibility that the biofilm required time to adjust to these new DBPs offers one

explanation for the following experimental results seen in run 4:

- an initial removal of TCM in period 1,
- the lack of TCM removal during period 2, and
- the subsequent reestablishment of TCM removal during period 3 to a similar level to period 1.

The monochloramine removal observed through the biofilters resulted from some combination of the natural monochloramine demand of the Lake Austin water, the reaction of monochloramine with the biomass present in the biofilter, and the cometabolism of monochloramine in a manner similar to that for THM cometabolism (Woolschlager et al, 2001; 2000). The natural demand of the water would be similar for all biofilters. The reaction with biomass would be expected to increase with TOTNH<sub>3</sub> removal because a larger removal implies a larger biomass population.

Similarly, if cometabolism of monochloramine was occurring, increased TOTNH<sub>3</sub> removal would be expected to correspond with increased monochloramine removal in a manner analogous to Eq 2 for THM cometabolism. The results for all three trains showed that an increase in TOTNH<sub>3</sub> removal corresponded with an increase in monochloramine removal. Therefore, reaction of monochloramine with biomass, cometabolism of monochloramine, or both, was most likely occurring.

## CONCLUSIONS

THM and TOTNH<sub>3</sub> removal occurred in nitrifying biofilters seeded with mixed-culture nitrifiers from Lake Austin. All four THMs were degraded, and the THM degra-

Increased TOTNH<sub>3</sub> degradation corresponded to increased THM degradation; thus, the close association between ammonia degradation and THM cometabolism observed in previous batch kinetic studies also held in the biofilter experiments. Overall, these experiments resulted in sustained THM removals ranging from 10 to 60% for varying operating conditions.

THM speciation is important because each THM exhibits a different product toxicity. The cometabolism stability index ( $C_{si}$ ) represents a simple and useful tool for judging the likelihood of product toxicity problems in biofilter operation. Because both THM cometabolism rate constants and THM product toxicities increase with increasing THM bromine substitution, a water's THM speciation is an important consideration for process implementation. Even though a given water may be kinetically

cal activity. Implementation of this process should involve relatively minor retrofitting of existing plants. The cometabolism would occur in granular media filters consisting of an upper layer of granular activated carbon. Utilities could carry out prechlorination followed by ammonia addition at a relatively low concentration (1–4 mg/L as N) sometime before the filters. A mixture of monochloramine and ammonia will result at the typical free chlorine concentrations (e.g., 2 mg/L as Cl<sub>2</sub>) used in treatment plants.

When the water is applied to the upper granular activated carbon layer in the filter, monochloramine will be destroyed, releasing ammonia (Fairey et al, 2004; Komorita & Snoeyink, 1985). At this point, an appropriate environment for microbial growth is established (i.e., an environment devoid of a disinfectant residual).

## Trihalomethanes and haloacetic acids tend to form together, so biological disinfection by-product removal processes must be able to deal with both classes of DBPs to be of any practical value in regulatory compliance.

avored on the basis of THM speciation, the resulting THM product toxicity may not allow stable treatment process performance.

Nutrient limitations may exist when using natural waters. To improve both TOTNH<sub>3</sub> and THM degradation, both iron and copper were added to the Lake Austin water. Other, unknown nutrients may have also been lacking, because overall performance was poorer than that observed when nutrient water was fed to the same biofilters.

An influent monochloramine concentration of 1 mg/L as Cl<sub>2</sub> (or less) appears to be a good target for stable operation of a developed biofilm. Because monochloramine addition was initiated after biofilm development, startup considerations could not be evaluated from these data and require further investigation. During the experiment, a relatively large increase in the influent monochloramine concentration was made from approximately 1 to 2.5 mg/L as Cl<sub>2</sub>. The influent monochloramine concentration of 2.5 mg/L as Cl<sub>2</sub> led to unstable operation; thus, further examination of concentrations between 1 and 2.5 mg/L as Cl<sub>2</sub> is needed. As a result, the actual allowable influent monochloramine concentration lies between 1 and 2.5 mg/L as Cl<sub>2</sub>, with 1 mg/L as Cl<sub>2</sub> being conservative.

This research demonstrated the feasibility of THM cometabolism in nitrifying biofilters. The experimental biofilters scale to full-scale filters operating at SLRs and EBCTs typical of practice. It is expected that the process can be implemented in filters now used in practice, using mixed cultures from source waters to establish biologi-

cal activity. Implementation of this process should involve relatively minor retrofitting of existing plants. The cometabolism would occur in granular media filters consisting of an upper layer of granular activated carbon. Utilities could carry out prechlorination followed by ammonia addition at a relatively low concentration (1–4 mg/L as N) sometime before the filters. A mixture of monochloramine and ammonia will result at the typical free chlorine concentrations (e.g., 2 mg/L as Cl<sub>2</sub>) used in treatment plants.

### ACKNOWLEDGMENT

This research was funded by the Awwa Research Foundation (AwwaRF) and the Texas Advanced Technology Research Program, whom the authors thank for their financial, technical, and administrative assistance. The comments and views detailed in this article may not necessarily reflect the views of AwwaRF, its officers, directors, affiliates, or agents.

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## FOOTNOTES

- <sup>1</sup>Hewlett Packard 5890A, Avondale, Pa.  
<sup>2</sup>J&W DB-5, Agilent Technologies, Santa Clara, Calif.  
<sup>3</sup>Thermo Orion 9512, Thermo Electron Corp., Waltham, Mass.  
<sup>4</sup>Orion Model 920A, Thermo Electron Corp., Waltham, Mass.  
<sup>5</sup>HACH method 10171 (0.04–4.5 mg/L Cl<sub>2</sub>), Hach Co., Loveland, Colo.  
<sup>6</sup>Agilent 8453, Agilent Technologies, Santa Clara, Calif.

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## **Trihalomethane cometabolism by a mixed-culture nitrifying biofilter**

*David G. Wahman, Lynn E. Katz, and Gerald E. Speitel Jr.*

Many utilities use a combination of chlorine and chloramines to avoid excessive trihalomethane (THM) and haloacetic acid (HAA) formation, but significant formation of THMs and HAAs can occur even during relatively short periods of chlorination. Biodegradation offers a new approach to removing THMs and HAAs, and evidence of HAA biodegradation in drinking water environments continues to build.

Experiments were conducted using biofilters seeded with mixed-culture nitrifiers from Lake Austin to develop a new biological treatment process for the

destruction of the four THMs commonly found in treated drinking water—bromoform, chloroform, dibromochloromethane, and dichlorobromomethane. The analysis was based on THM cometabolism by nitrifying bacteria growing on ammonia in multimedia filters. The experiments resulted in sustained THM removals ranging from 10 to 60% for various operating conditions. Reduction in THM concentrations may provide utilities with another option to help comply with the Stage 2 Disinfectants/Disinfection Byproducts Rule.—KD

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## **Effects of media, backwash, and temperature on full-scale biological filtration**

*Monica B. Emelko, Peter M. Huck, Bradley M. Coffey, and E. Franklyn Smith*

During ozonation, the amount of biodegradable organic matter (BOM) in natural waters increases. The presence of BOM is undesirable because it may result in biological instability of the drinking water and bacterial regrowth in the distribution system. This research investigated the sensitivity of BOM removal to operational parameters such as temperature, media type, and backwash conditions.

Full-scale biofiltration experiments demonstrated that good removal of BOM following ozonation can be achieved without compromising particle removal. At warm water temperatures, media type did not

influence BOM removal, but at cold water temperatures, granular activated carbon provided substantially better BOM removal than did anthracite. In contrast to particle removal, BOM removal was more resilient to changes in backwash protocol. Biomass was estimated by measuring the organically bound phosphorous (phospholipids); phospholipid biomass concentration was not directly related to BOM removal by filters. Although collapse pulsing is an optimized strategy for backwashing conventional filters, backwashing strategies for biofilters must be further optimized.—MPM