

Posttreatment aeration inside water tanks or in chlorine contact basins to strip trihalomethanes (THMs) after formation is an underused and cost-effective treatment option to reduce disinfection by-products. In this study, diffused aeration achieved removal rates of 9 to > 99.5%, depending on air-to-water ratio, water temperature, and THM species. Spray aeration—a more efficient process—achieved THM reductions of 20 to > 99.5%, depending on droplet diameter, droplet travel distance, water temperature, and THM species. Droplet diameter is an important design variable and is controlled by operating pressure and nozzle characteristics. Droplet travel distance, however, exerted a greater influence on THM removals. The average droplet diameter and travel distance variables can be developed into a unit air-to-water volumetric ratio that can be used to reasonably predict total THM removals. Free chlorine does not appear to be reduced by aeration because only a small fraction of it will be amenable to removal in a closed-system environment.

Posttreatment aeration to reduce THMs

Meeting the new maximum contaminant levels (MCLs) for trihalomethanes (THMs) established under Stage 1 of the Disinfectants/Disinfection Byproduct Rule (D/DBPR) is a challenge for many drinking water providers, both large and small. The Stage 1 and 2 D/DBPRs regulate the amount of total THMs (TTHMs), the amount of total haloacetic acids, and the amount of free disinfectant that can be present in finished drinking water by setting MCLs for each of these groups of compounds. The MCLs established in the Stage 1 D/DBPR remain the same in the Stage 2 D/DBPR and are summarized in Table 1 (USEPA, 2006, 1998).

Three general strategies have been adopted to deal with THM violations: switch from chlorination to an alternative disinfectant or disinfection regime, reduce THM precursors in the raw water by enhanced treatment processes, or remove THMs after they have formed (USEPA, 1981). Although aeration is a DBP control strategy for THMs, it is not effective for treatment of haloacetic acids. Although posttreatment aeration has not received as much attention as the other two control strategies, i.e., switching from chlorination and reducing organic precursors before the disinfection process, it has the potential to be the most cost-effective treatment option.

The most common form of air-stripping is via counter-current packed columns; this process is highly effective for THM reduction but requires additional infrastructure. The significant advantages offered by diffused and spray aeration are their simplicity and suitability for addition to existing treatment processes or water storage tanks; thus, both diffused and spray aeration are considered suitable for small and large water supply systems.

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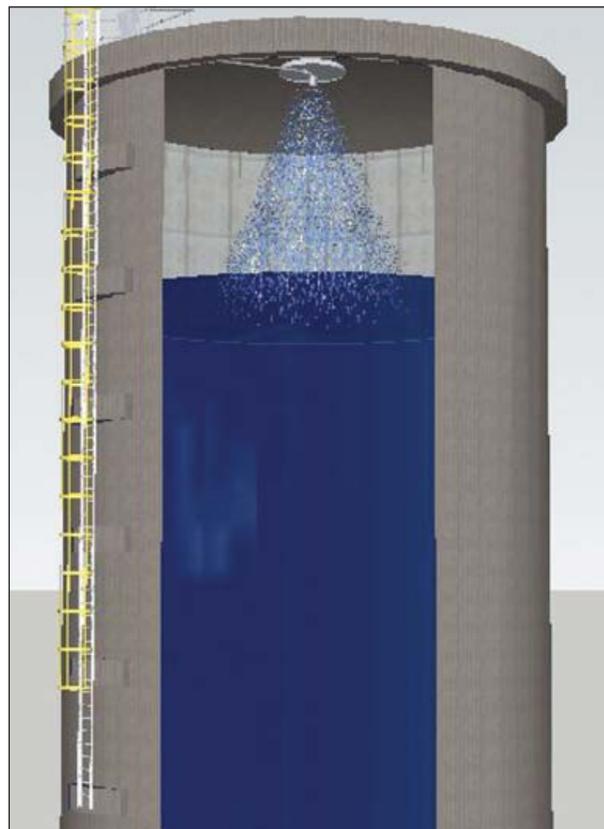
Diffused and spray aeration can both be described by an air-to-water ratio that is a dimensionless volumetric ratio of the volume of air that comes in contact with a volume of water (AWWA, 1999). Diffused aeration is the process of introducing air into the bottom of a vessel of water and allowing the air to bubble up through the water column, creating air-to-water contact. A diffused aeration device consists of an air compressor to provide the required air pressure, a matrix of pipes to distribute the air, and a set of diffusion devices to break up the air into bubbles. Diffused aeration has long been a recognized means to remove THMs (USEPA, 1981). Recent research has shown diffused aeration to be an inexpensive approach to THM reduction in water storage tanks (Sherant et al, 2007). In contrast, spray aeration facilitates the creation of an air-water interface by spraying water through the air. The interfacial surface area is the combined surface area of the individual droplets that are formed by the nozzle(s). A spray aeration device consists of a pump or some means of creating water pressure, piping to distribute the water, and a nozzle(s) to break the water up into droplets. In this research, a bench-scale diffused-aeration assessment using a factorial design and statistical analysis of variance (ANOVA) was conducted to determine the importance and interaction of variables known to affect air-stripping of THMs. On the basis of variable assessments from the bench-scale experiments, a fractional-factorial spray aeration study was designed to identify the critical design variables of THM reduction by spray aeration.

THM stripping by spray aeration is a relatively unexplored treatment option. After examination and quantification of the role of all significant variables (including water temperatures, THM speciation, droplet travel distance, and droplet interfacial surface areas), a modeling foundation was proposed to predict potential THM reductions under various spray-aeration operating and design conditions. The developed model suggests that design and installation of spray-aeration systems can be considered a feasible and effective THM reduction technique for both large and small water systems.

Because the US Environmental Protection Agency (USEPA) requires maintenance of a free chlorine residual > 0.2 mg/L in finished drinking water (USEPA, 2004), assessing the influence of aeration on free chlorine residual was an important component of this research. Bench-scale diffused-aeration tests were performed at high air-to-water ratios in order to assess potential changes in free chlorine levels during aeration.

EXPERIMENTAL APPROACH

General methodology. The research was conducted in three major phases: a diffused-aeration bench-scale study, a spray-aeration pilot-scale optimization study, and an assessment of chlorine-stripping potential during diffused aeration. Results of each phase of experimentation con-



In this research, spray aeration achieved trihalomethane (THM) reductions of 20 to > 99.5%, depending on droplet Sauter mean diameter, droplet travel distance, water temperature, and THM species. Some storage systems may require nothing more than a redesign of water tank influent piping and addition of a spray nozzle, similar to what is shown in this illustration, system in order to realize significant THM reductions.

tributed to the experimental direction of the succeeding phase. The influence of experimental factors on overall performance of diffused and spray aeration was determined by ANOVA statistical analysis. Data were analyzed using statistical analysis software.¹ Because the software does not determine the percent contribution of individual variables in overall experimental analysis, Taguchi methods were used to establish the percent contributions of each variable to overall THM removal (Ross, 1988).

Assessment of diffused aeration. Bench-scale experimentation focused on identifying key operational and design variables that affect air-stripping performance. Temperature, airflow rate, contact time, mixing intensity, and THM concentration were selected on the basis of published literature (Bilello & Edward, 1986; Bishop & Dwarkanath, 1985; Roberts & Levy, 1985, 1983; Chrostowski et al, 1982; Dykson & Hildebrand, 1982; Symons et al, 1981). Variable values evaluated in this study are summarized in Table 2. A fractional-factorial experimental design was used to quantify the influence of each variable and all two-variable interactions. Therefore, this design achieved a level

three experimental resolution, meaning that all main factors and two-factor interactions can be evaluated through ANOVA (Ross, 1988).

A stock solution was used to spike all challenge water used in bench- and pilot-scale experiments. Chloroform (CHCl₃) was the constituent that was emphasized in respect to the other THM species, with the final concentration of CHCl₃ accounting for 40% of TTHMs, and dichlorobromomethane (CHBrCl₂), chlorodibromomethane (CHBr₂Cl), and bromoform (CHBr₃) each accounting for 20% of TTHMs. The final target concentration of the stock solution was 600 mg/L TTHM. Initial source water TTHM concentrations for the bench-scale experiments were set at two levels—100 and 400 µg/L. Average concentrations were within 2% of the target for both concentrations, and the standard deviation for both initial concentrations for both levels was < 10% of the target concentration.

All bench-scale tests were performed using an in-house fabricated diffused aeration apparatus. As shown in Figure

1, four individual aeration vessels—each containing 3 L of water—were built from glass, stainless steel, and PTFE parts and were housed in a cooler. Air was supplied to each aeration vessel via a single air compressor, and airflow rates to each aerator were controlled by a 1- to 10-L/min flowmeter. All supplied air was run through a hydrocarbon trap² to ensure that the air was not contaminated with oil droplets from the compressor. Temperature probes were

placed inside each aeration vessel to monitor water temperature. An additional thermometer was placed in the air tube to monitor air temperature. Fine-bubble diffuser stones³ were plumbed in place by custom-fabricated PTFE fittings. A four-diffuser-stone air-tube configuration and

a single-stone air-tube configuration were fabricated from PTFE tubing. All tubing in contact with the THM-spiked water was PTFE or stainless steel. Water temperature was controlled at the low temperature level by immersion of the aeration vessel in an ice bath and at high temperature by immersion of the aeration vessel in a hot water bath.

Because of analytical and physical constraints, complete randomization of the experiments was not possible. Instead, all experiments conducted at air temperature of 20°C were conducted first, and all experiments at air temperature of 4°C were conducted second. Mixing of the challenge solution in one vessel allowed for reduction in sample analysis cost and resulted in four trial blocks of equal initial THM concentrations.

Challenge solutions were prepared by adding 20 L of reverse osmosis (RO)-filtered and distilled water with a measured free chlorine residual below detection limits (measured by a colorimeter⁴ with a resolution of 0.012 mg/L) to a glass carboy. For water temperatures of 1°C, it was necessary to chill the 20 L of RO water in an ice bath overnight before addition of stock solution. Stock solution was used to bring the TTHM concentration to either 100 or 400 µg/L. A stainless-steel paddle mixer was then lowered into the center of the carboy and run at a low speed for 5 min. Care was taken not to entrain air in the challenge solution. Initial THM concentrations were then measured directly from the carboy via motorized pipette as described subsequently. Next each individual aeration vessel was filled via a tube exiting from a valve in the bottom of the carboy. Care was taken not to introduce air, and turbulence was minimized during this process.

After each aeration vessel was filled, the device was allowed to aerate for 60 min. Samples from selected aeration vessels were taken after 45 min, and others were taken after 60 min to achieve a desired air-to-water ratio of 22.5:1 to 60:1 (as shown in Table 3). Samples were taken by motorized 25-mL pipette, which was

Bench-scale experimentation focused on identifying key operational and design variables that affect air-stripping performance.

TABLE 1 MCLs for disinfection by-products and disinfectants under the Stage 1 and 2 D/DBPRs

| Regulated Contaminants | MCL mg/L | Regulated Disinfectant | MRDL mg/L |
|--|----------|------------------------|------------------------|
| TTHM | 0.08 | Chlorine | 4.0 as Cl ₂ |
| HAA5 | 0.06 | Chloramines | 4.0 as Cl ₂ |
| Bromate (plants that use ozone) | 0.01 | ClO ₂ | 0.8 |
| Chlorite (plants that use ClO ₂) | 1.0 | | |

Source: USEPA, 2000; 1998

Cl₂—free chlorine, ClO₂—chlorine dioxide, D/DBPR—Disinfectants/Disinfection Byproducts Rule, HAA—haloacetic acid, MCL—maximum contaminant level, MRDL—maximum residual disinfectant level, TTHM—total trihalomethane

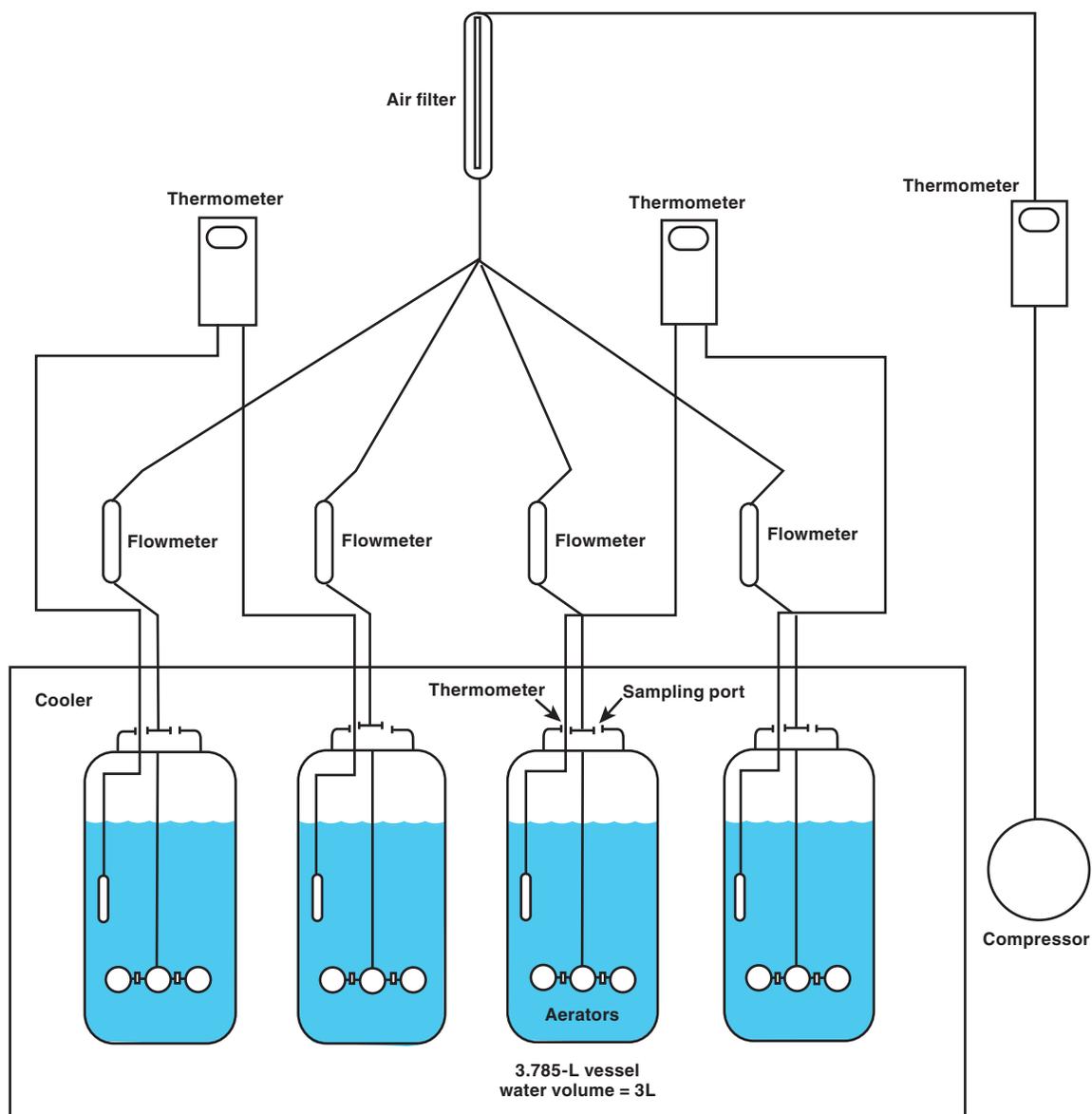
TABLE 2 Bench-scale experimental variables for diffused aeration study

| Variable | Level 1 | Level 2 |
|---|---------|---------|
| Water temperature—°C | 1 | 20 |
| Air temperature—°C | 4 | 20 |
| Airflow rate—L/min | 1.5 | 3 |
| Contact time—min | 45 | 60 |
| Concentration—µg/L | 100 | 400 |
| Number of diffusers (i.e., bubble size) | 1 | 4 |

lowered into the center of the vessel, filled, and then emptied into a 40-mL glass sample vial with PTFE septa. Again, care was taken not to introduce additional air-to-water contact by poor sample handling. Samples were inverted and inspected for air bubbles to ensure that they were headspace-free. All samples were taken in duplicate. Because the free chlorine residual of the stock solution was below the detection limit as measured by the colorimeter, a buffering agent was not used to prevent additional THM formation during sample storage time. Samples were stored in a refrigerator, shipped in coolers, and analyzed within 14 days according to method 551.1 for determination of organic compounds in drinking water (USEPA, 1995).

Assessment of spray aeration. After diffused aeration had been studied, the decision was made to investigate spray aeration. Spray aeration has the advantage of increased interfacial area and avoids the problem of individual gas bubbles reaching equilibrium (Munz & Roberts, 1989). Pilot testing of spray aeration to remove THMs was conducted in order to examine the role of Henry's constant (as a function of water temperature and THM species), droplet travel distance (or air-water contact time), and droplet Sauter mean diameter (SMD). The droplet travel distance and size reflect enough variation to statistically evaluate their overall contribution to THM removal. Operating conditions and design variables for each phase of pilot experimentation are summarized in Table 4. The

FIGURE 1 Schematic of bench-scale diffused-aeration apparatus



temperature range was chosen to encompass the changes that can be experienced throughout the calendar year. The design for the initial and final spray-aeration pilot-scale experiments was performed using the experimental design function of the statistical analysis software.¹

As shown in Figure 2, the pilot-scale experimental apparatus consisted of a 208-L drum connected to a 1.5-hp centrifugal pump⁵ with the spray aerator located at various heights over a collection container. An initial concentration sample port was located immediately after the influent pump with water flowing continually through the sampling tube. A large ball valve located down line from the sampling tube served to control the flow rate, which was monitored by a digital flowmeter.⁶ The average initial TTHM concentration before aeration was 99 µg/L with a standard deviation of 12.6 µg/L over 12 samples. Samples were collected using a funnel that channeled the spray directly into 40-mL sample vials. Additional experimental details associated with the pilot apparatus may be found elsewhere (Brooke, 2009).

Assessment of diffused-aeration influence on chlorine residual. The same diffused aeration used in the bench-scale experiments apparatus with the four-diffuser-stone configuration was also used for the free chlorine-stripping evaluation. To ensure that the experimental apparatus was chlorine demand-free, the apparatus was allowed to soak overnight in a strong bleach solution and then rinsed with RO water until it no longer produced a free chlorine residual before

each experiment. The challenge solution was made from 20-L batches of RO water mixed with sodium bicarbonate to add alkalinity, hydrochloric acid and/or sodium hydroxide to control pH, and sodium hypochlorite to add free chlorine. For the chlorine residual assessment, air-to-water ratios varied from 33:1 to 200:1, with pH conditions ranging from initial values of 9.3 to 6.1 in water containing an original free chlorine residual of ~1.0 mg/L and an alkalinity of 80 to 100 mg/L as calcium carbonate.

The pH was monitored by a probe with an accuracy of ±0.05. Free chlorine residual was monitored by a colorimeter⁴ with a resolution of 0.012 mg/L. Water temperature was allowed to equilibrate to room temperature, which averaged 22°C. The aeration vessel was filled with 3 L of challenge solution. The airflow rate through the diffuser stones was held constant at 10 L/min. Samples were analyzed every 10 min for 1 h, resulting in air-to-water volumetric ratios of 33:1, 67:1, 100:1, 133:1, 167:1, and 200:1. The first two experiments were run in duplicate with two aeration vessels operating independently. The pH was not controlled over the course of the initial two experiments. The final experiment was run in a single aeration vessel with the pH levels held constant by titration with hydrochloric acid.

THM analytical procedure. All THM concentration analyses were conducted by the Environmental Engineering Department at the Pennsylvania State University at Harrisburg. A modified version of method 551.1 was used for all analyses (USEPA, 1995). The electron capture gas chromatograph⁷ used in analysis was fitted with an auto sampler⁸ and auto injector. Each batch of samples included a lab-created spiked sample for calibration. The squared correlation coefficient (R^2) for spiked samples (provided by the lab) was > 0.99 for all four species of THMs, indicating satisfactory analytical accuracy.

RESULTS AND DISCUSSION

Diffused aeration assessment. Diffused aeration was an effective approach to removing THMs from water. Figure 3 shows experimentally derived percent removals of each THM species versus air-to-water ratio (AWWA, 1999) at 1 and 20°C. As expected, the air-to-water ratio had a significant effect on THM concentration, with TTHM removal rates increasing proportionally with an increasing air-to-water ratio. For example, CHCl₃ removals were consistently > 90% when air-to-water ratios were > 45:1. The influence of the Henry's constant on removals was also significant (Staudinger & Roberts, 1996). CHCl₃, having the highest Henry's constant, was the species most amenable to removal by diffused aeration followed by (in order of descending Henry's constants) CHBrCl₂, CHBr₂Cl, and CHBr₃. As expected, warmer temperatures resulted in higher THM removals as can be seen by comparing removals of each species at 20 and 1°C, shown in Figure 3, parts A and B, respectively.

TABLE 3 Calculated air-to-water ratios for a 3-L fixed-volume diffused-aeration reactor

| Airflow Rate—L/min | Time—min | Air-to-Water Volumetric Ratio (Dimensionless) |
|--------------------|----------|---|
| 1.5 | 45 | 22.5:1 |
| 1.5 | 60 | 30:1 |
| 3 | 45 | 45:1 |
| 3 | 60 | 60:1 |

TABLE 4 Operating and design variables evaluated during spray-aeration assessment

| Parameter | Experimental Conditions | | | |
|---------------------------|-------------------------|------|------|-------|
| | 1 | 2 | 3 | 4 |
| Operating Conditions | | | | |
| Water temperature—°C | 1 | 22 | 36 | NT |
| Design Variables | | | | |
| Droplet travel distance—m | 0.74 | 2.13 | 4.27 | NT |
| Droplet SMD—µm | 140 | 350 | 690 | 1,100 |

NT—not tested, SMD—Sauter mean diameter

Bubble size did not significantly influence or affect overall removal rates as was also observed by other researchers (Bilello & Edward, 1986). The lack of bubble-size influence for the range of bubble sizes created in these experiments may be attributable to the bubbles reaching THM saturation before they breached the surface of the water, thereby reducing the concentration gradient driving force (Roberts & Levy, 1983).

Several diffused aeration models based on a minimum air-to-water ratio were evaluated. The model that best matched experimental results in this study was initially proposed by other researchers (Sherant et al, 2007) and is derived from a mass balance approach to a fixed-volume water reactor as outlined in Eq 1:

$$\ln C_e = - \left(\frac{H_{cc} Q_a}{V_w} t \right) + \ln C_0 \quad (1)$$

in which C_0 is the initial concentration ($\mu\text{g/L}$), C_e is the effluent concentration ($\mu\text{g/L}$), H_{cc} is Henry's constant (dimensionless), V_w is the water volume (L), Q_a is the airflow rate (L/s), and t is time (s).

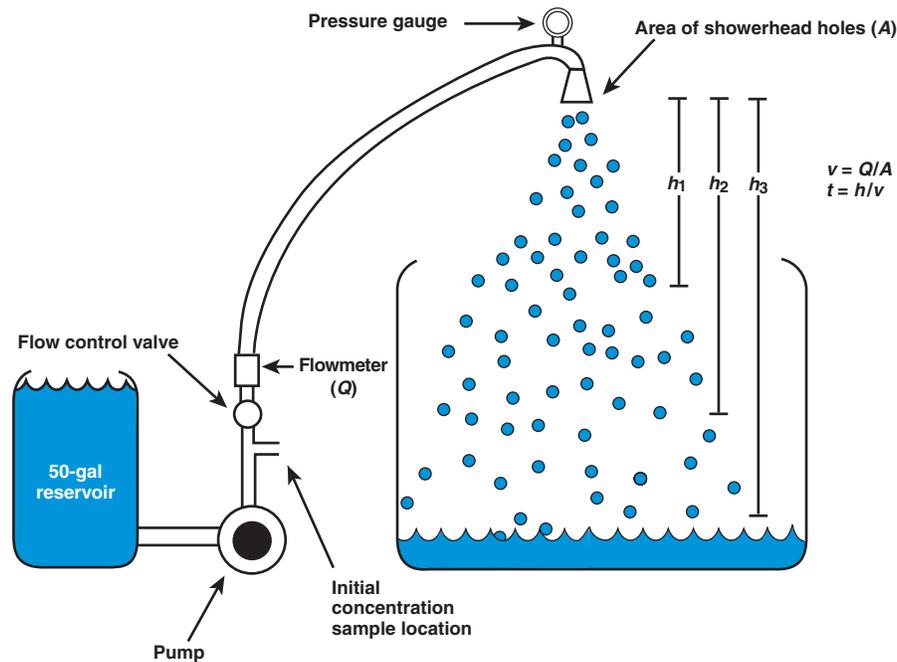
Figure 4 shows comparisons between the air-to-water ratios and percent removal predictions from Eq 1 and

the experimental results. Overall the mass balance model was a satisfactory predictor of the empirical results. Removals for the various THM species varied; CHCl_3 removals were consistently $> 90\%$ whereas CHBr_3 was the most problematic species, with removals ranging between 30 and 60%. This model is applicable only to batch-mode diffused aeration.

The operational variables that had the overall greatest influence on THM removals by diffused aeration were quantified from the ANOVA (Ross, 1988) and are summarized in Table 5. Overall water temperature had a significant effect on THM removal rates, with warmer temperatures resulting in higher removals, especially for the CHBr_3 species. The airflow rate (which when associated with a fixed volume of water resulted in varying air-to-water ratios) also exhibited a significant influence with higher airflow rates, resulting in higher removals, especially for CHCl_3 .

The overall percent error rate for the diffused aeration bench-scale experiments was $< 15\%$ for all four THM species, which implies that all major factors were considered, all major factors were reasonably controlled, and overall analytical error was acceptable (Ross, 1988). Interactions between these variables also were examined and accounted for. All factors and factor interactions

FIGURE 2 Schematic of final pilot-scale experimental apparatus



A = area of showerhead holes, Q = volumetric flow rate (m^3), v = exit flow velocity (m/s), h = distance from showerhead to water surface (m), and t = time (s).

contributing < 3% to overall percent removal rates were dropped from this analysis, and their contribution was pooled into the error term.

Spray aeration assessment. Diffused and spray aeration rely on the same basic mechanism for mass transport; a concentration gradient drives the THMs through an interfacial surface area, thus moving the THMs from liquid phase to gas phase. The key difference between diffused and spray aeration is that the bubbles created in diffused aeration have a finite volume and can reach saturation rapidly, meaning that the maximum THM removal may occur only for the first half metre of bubble contact (Roberts & Levy, 1983). Because bubbles have a small volume, the gas concentration of THMs inside the bubbles increases over time, thereby lessening the concentration gradient that provides the driving force for mass transfer. Diffused aeration is not recommended for depths greater than 5 m, which adds a design challenge for deep tanks (AWWA, 1999).

Spray aeration, in contrast, offers exposure to a larger air volume that greatly diminishes the effect of a decreasing

concentration gradient, thereby offering the potential for a more efficient aeration strategy. Some storage systems may require nothing more than a redesign of water tank influent piping and the addition of a spray nozzle system in order to realize significant THM reductions. As with a diffused-aeration apparatus, a spray aerator could be placed in either

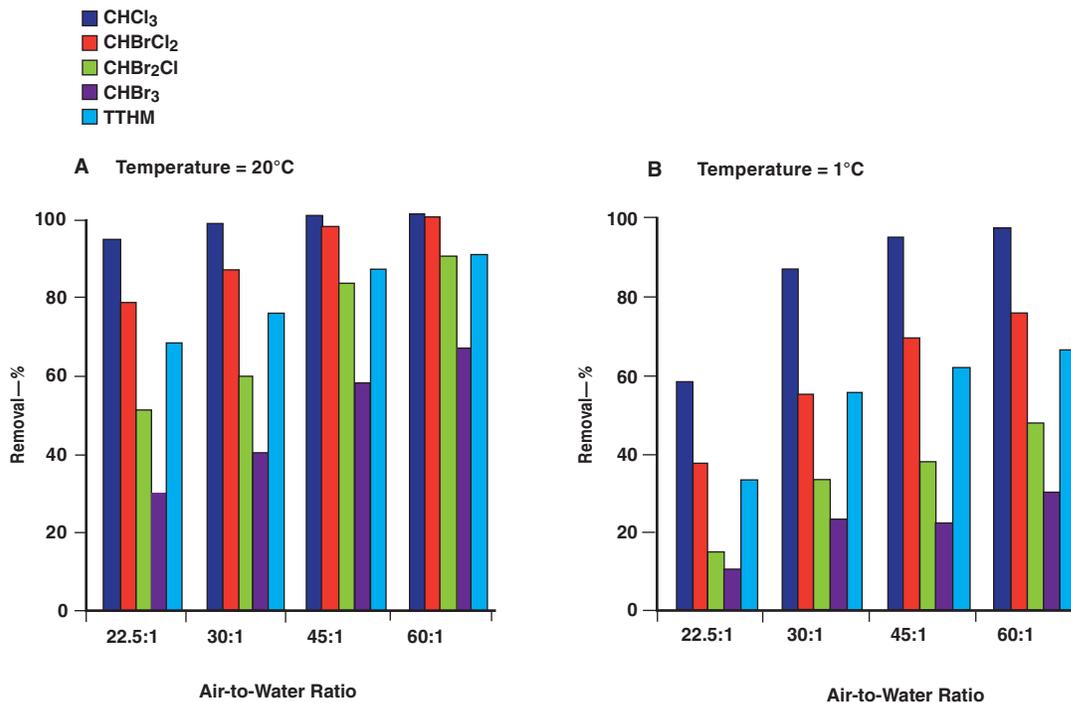
a water tower or at the ends of a clearwell chlorine contact chamber.

The spray aeration pilot-scale experiments focused on an assessment of operating and design variables affecting THM removal rates, with an emphasis on

gathering enough information to create a qualitative model that could be used to design, build, and operate a spray aeration apparatus in the field. Operating experimental variables were chosen to reflect likely worst-case operating conditions. Operating variables likely to influence THM removals, as indicated from the previous diffused aeration study, were selected for additional assessment. The operating and design variable levels used in the spray aeration experiment are summarized in Table 4.

Air-stripping of trihalomethanes
is a viable posttreatment strategy
for finished drinking water.

FIGURE 3 Bench-scale diffused-aeration removal of four THM species as a function of air-to-water ratio at 20°C (A) and 1°C (B)



CHBr₃—bromoform, *CHBrCl₂*—dichlorobromomethane, *CHBr₂Cl*—chlorodibromomethane, *CHCl₃*—chloroform, *THM*—trihalomethane, *TTHM*—total trihalomethane

Droplet travel distance and droplet SMD were selected as the primary design variables. Because the air–water interface is where mass transfer of THMs occurs during spray aeration, analysis of the droplet-size distribution and average droplet size—given by the SMD of the droplet created by a given nozzle—was necessary (AWWA, 1999). SMD analysis is performed using still photography or laser analysis, usually by the nozzle manufacturer, and is considered a nominal assessment of droplet size. The amount of pressure at the nozzle (or the resulting water flow rate) and the characteristics of the nozzle openings determine the SMD of droplets produced. When a nozzle vendor is contacted, it is important to know how much (if any) excess operating pressure is available or else have an estimate of the SMD required to meet treatment objectives. For this study, SMDs of 140, 350, 690, and 1,100 μm were selected.

Spray nozzles⁹ for the spray aeration pilot-scale optimization experimental trials were selected for their ability to produce a wide variety of droplet sizes (based on nozzle type and operating pressure) but have only one nozzle orifice. The large nozzle opening was considered a design advantage because it should help to prevent nozzle clogging. Nozzle clogging attributable to scaling is possible for water with elevated levels of calcium, especially at higher water temperatures, and should be considered during the design process.

The second design variable selected for this experiment was droplet travel distance, i.e., the distance a droplet travels after exiting the nozzle before contacting the water surface. Water droplet travel distance was considered an important variable because the opportunity for mass transfer increases with air–water contact time. An investigation was conducted to quantify droplet travel time on the basis of nozzle exit velocity, nozzle exit angle, drag, and droplet terminal velocity. Estimating and especially measuring or quantifying droplet travel time can be problematic, with numerous factors to consider. On the basis of observational comparisons of experimental results, it was estimated that droplet travel times were directly proportional to droplet travel distance. The simpler approach of using droplet travel distance rather than droplet travel time was used in this study and is recommended for practicable design purposes. Varying the droplet travel distance and keeping the nozzle exit velocity and droplet SMD constant also provided an overall assessment of the influence of air–water contact time.

Because appropriate mass transfer coefficients for volatile organic chemicals (VOCs) with relatively low Henry’s constants have not been adequately developed for spray aeration, the authors investigated the possibility of creating design graphs to predict THM removals on the basis of a proposed volumetric ratio of the air volume the droplet moves through to the average droplet volume. This ratio, referred to as a unit air-to-water volumetric ratio, is depicted in Figure 5. As a water droplet falls, the space it moves through has a volume that can be visualized as a long cylinder with a height (h_{avg}) equal to the average distance the droplet travels from nozzle exit to the water surface and a diameter (d_{SMD}) equal to the droplet SMD. The average droplet travel distance was assumed to be equal to a droplet travel path halfway between the maximum droplet travel distance at the exterior of the spray cone and the shortest vertical droplet travel distance at the center of the spray cone. This volumetric ratio, which is analogous to an air-to-water ratio used in counter-current packed towers or diffused aeration reactors, is derived in Eq 2:

$$\text{Unit air-to-water volumetric ratio} = \frac{\pi d_{SMD}^2 h_{avg}}{4} = \frac{1.5 h_{avg}}{d_{SMD}}, \text{ where } h_{avg} = \frac{h}{\cos^2 \theta} \quad (2)$$

in which h = nozzle height (m), θ = nozzle spray angle (degree), h_{avg} = average droplet travel distance (m), and

TABLE 5 ANOVA and percent contribution of experimental factors to bench-scale diffused-aeration removal of chloroform and bromoform

| Chloroform ANOVA | | | | | |
|------------------------------------|----|----------------|---------|-----------------|----------------------|
| Source | df | Sum of Squares | F Ratio | Probability > F | Percent Contribution |
| Water temperature | 1 | 1,243 | 141 | < 0.0001 | 28.0 |
| Airflow rate | 1 | 1,244 | 141 | < 0.0001 | 28.1 |
| Air temperature × concentration | 1 | 512 | 58 | < 0.0001 | 11.5 |
| Water temperature × airflow rate | 1 | 646 | 73 | < 0.0001 | 14.5 |
| Airflow rate × number of diffusers | 1 | 573 | 65 | < 0.0001 | 12.9 |
| Error | 23 | 203 | NA | NA | 5.0 |
| Bromoform ANOVA | | | | | |
| Source | df | Sum of Squares | F Ratio | Probability > F | Percent Contribution |
| Water temperature | 1 | 6,903 | 196 | < 0.0001 | 64.0 |
| Airflow rate | 1 | 2,844 | 81 | < 0.0001 | 26.5 |
| Error | 27 | 1,009 | NA | NA | 9.5 |

ANOVA—analysis of variance, df—degrees of freedom, NA—not applicable

d_{SMD} = droplet SMD (m). This model also assumes that the air concentration of THMs is maintained close to zero. In order to maximize concentration driving force in a relatively confined space (such as a water storage tank or chlorine contact basin), proper ventilation including the use of motorized fans may be required to enhance removals.

The unit air-to-water volumetric ratio can be used to successfully predict THM removals as shown in Figure 6 for various THM species and temperatures (2, 22, and 36°C). As depicted, spray aeration can achieve significant removals (> 80%) for all THM species with unit air-to-water volumetric ratios of 30,000:1, independent of temperature. As noted previously, increasing temperature will increase removals by spray aeration for all THM species (although the data associated with the lower temperature of 2°C were more variable).

Plots similar to Figure 6 are potentially useful to design engineers and utility personnel because they can facilitate reasonable estimates and control of both the droplet SMD of the spray aerators and average travel

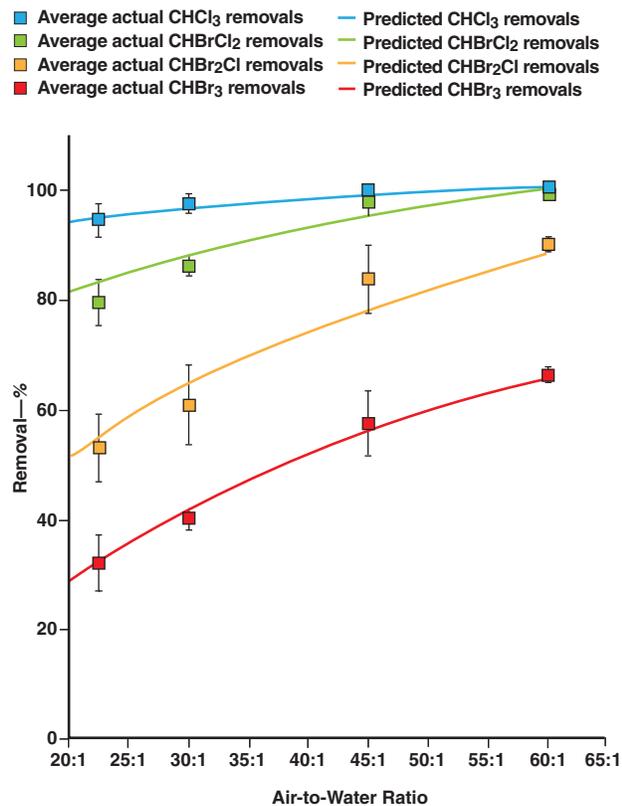
distance. As an example of the potential use of the design plots shown in Figure 6, in order to achieve an 80% reduction of $CHCl_3$ at 22°C, a dimensionless unit volumetric air-to-water ratio of roughly 9,000:1 will be required. Thus, using a spray nozzle that produces droplets with an SMD of 690 μm will require an average droplet travel distance of 4.14 m. The actual vertical travel distance (h) will be a function of the spray pattern angle as shown in Eq 2.

The influence of individual spray aeration pilot-scale experimental factors was quantified and is summarized in Table 6. The most important factors in THM removal by spray aeration were droplet travel distance, water temperature, and droplet SMD, with droplet travel distance being significantly more influential to THM removal than droplet SMD. From an engineering design perspective, optimizing water storage tank fill levels to allow for greater droplet travel distance easily outweighs the benefit of spending energy on creating smaller droplet SMDs by increasing spray pressure. If at all possible, greater emphasis should be applied to increasing average travel distance, given that its influence on THM removals is considerably greater than the effect of smaller droplet SMDs.

The 27% error rate for the final spray aeration experiment listed in Table 6 is between 15 and 50%, which typically indicates an incomplete but statistically valid model (Ross, 1988). Consequently, some variables were either imprecisely controlled or unaccounted for, analytical error may have been more than expected, or the initial concentration of THMs was not controlled with sufficient accuracy. Although initial concentration was not important in the bench-scale diffused aeration experiments, it is possible that in spray aeration in which the concentration of THMs in the air does not reach equilibrium with that in the water droplets, the difference in initial concentrations may have resulted in an unequal driving force for mass transfer between experimental runs. Another possible source of error was that all spray aeration experiments were conducted outside, where wind may have influenced droplet trajectory and therefore droplet travel distance as well as unequally influencing concentration gradient driving forces. Moreover, variations in droplet SMD because of a significant standard deviation in droplet distribution could also have influenced the outcome. Manufacturer evidence notes the variation in nominal droplet size may be significant from a given nozzle and flow rate.

One difference between diffused and spray aeration is that for spray aeration, removals of individual THM species at the same experimental conditions were significantly closer. The average difference between $CHCl_3$ and $CHBr_3$ removals in a given run for diffused aeration was 56%, but this difference was only 12% for spray aeration under similar operating conditions. This unexpected, relatively small difference between

FIGURE 4 Actual and predicted THM removals at 20°C for bench-scale diffused aeration



$CHBr_3$ —bromoform, $CHBrCl_2$ —dichlorobromomethane, $CHBr_2Cl$ —chlorodibromomethane, $CHCl_3$ —chloroform, THM—trihalomethane

Predicted removals are based on Eq 1.

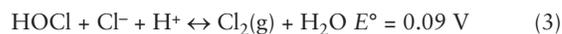
CHCl₃ and CHBr₃ removals may be attributable to the fact that VOCs with Henry's constants of < 0.55 are not controlled by the liquid-phase mass transfer coefficient but instead may be controlled by the gas-phase mass transfer coefficient (Roberts & Levy, 1983); the resulting removal differences between the THM species may be diminished when aeration regimes that maintain low THM concentrations in the bulk air phase are used.

Chlorine-stripping study. Spray and diffused aeration both demonstrated significant potential for THM removal, but an assessment of the effects of aeration on free chlorine residual was needed to satisfy concerns of water utilities that are required by USEPA to maintain a free chlorine residual of > 0.2 mg/L. Because of its ability to more precisely control operating conditions, the bench-scale diffused aeration system was used to assess the effect of various stripping conditions on free chlorine residual.

As shown in Figure 7, diffused aeration had minimal effect on free chlorine residuals even up to air-to-water ratios of 200:1, even when pH was controlled at 6.1 and where the majority of the chlorine would be in a nonionic form, i.e., hypochlorous acid (HOCl). Other researchers reported similar trends (Sherant et al, 2007).

An explanation for the apparent stability of free chlorine during aeration becomes clear upon examination of free chlorine water chemistry from a thermodynamic

perspective. The corresponding overall electrical potential is shown in Eq 3 (Benjamin, 2001):



in which E° is the cell potential at standard conditions.

The cell potential of a redox reaction is related to the equilibrium constant via Eq 4:

$$\ln K_{eq} = \frac{n F E^\circ_{\text{cell}}}{R t} \quad (4)$$

in which K_{eq} is the equilibrium constant, n is the number of electrons transferred, R is the universal gas law constant, t is temperature, and F is Faraday's constant. The equilibrium constant can be calculated from Eq 4, and the equilibrium expression can be developed as shown in Eqs 5 and 6:

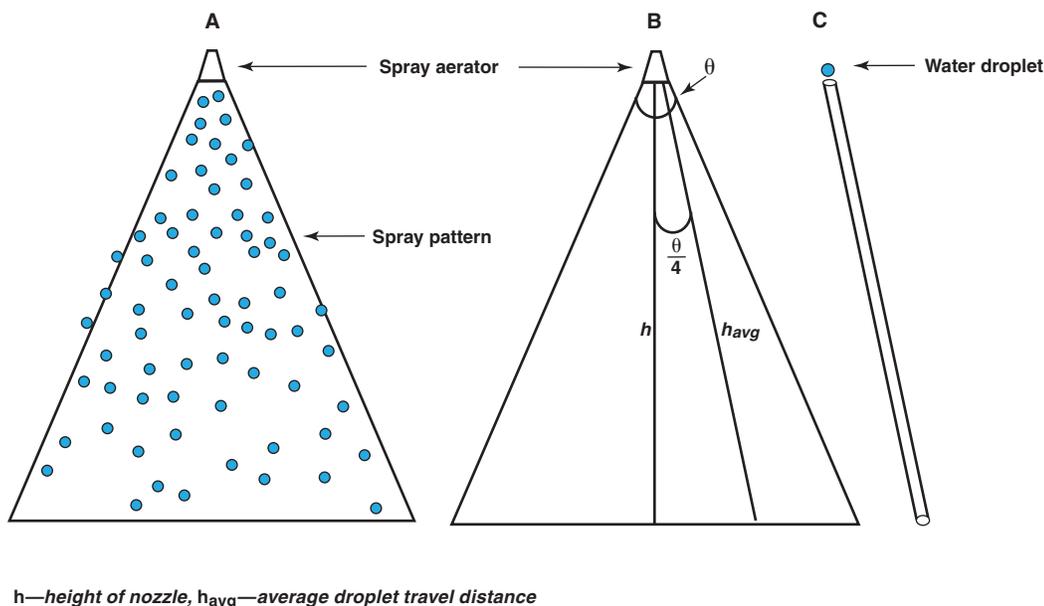
$$\ln K_{eq} = \frac{n F E^\circ_{\text{cell}}}{R t} = \frac{(2)(23,061)(0.09)}{(1.99)(298)} = 6.99 \quad (5)$$

or

$$K_{eq} = 1,096 = \frac{[\text{Cl}_2(\text{g})]}{(\text{HOCl})(\text{Cl}^-)(\text{H}^+)} \quad (6)$$

Assumptions of pH, chloride level, temperature, and free chlorine dose must be made for this example. Assuming a worst-case scenario (pH of 6, Cl⁻ of 250 mg/L, 20°C, and a total free chlorine residual of 1.0 mg/L as

FIGURE 5 Depiction of total air volume to total water-droplet volume in spray cone (A), average droplet travel distance (B), and volumetric ratio of cylindrical droplet path through the air to droplet volume of the water (C)

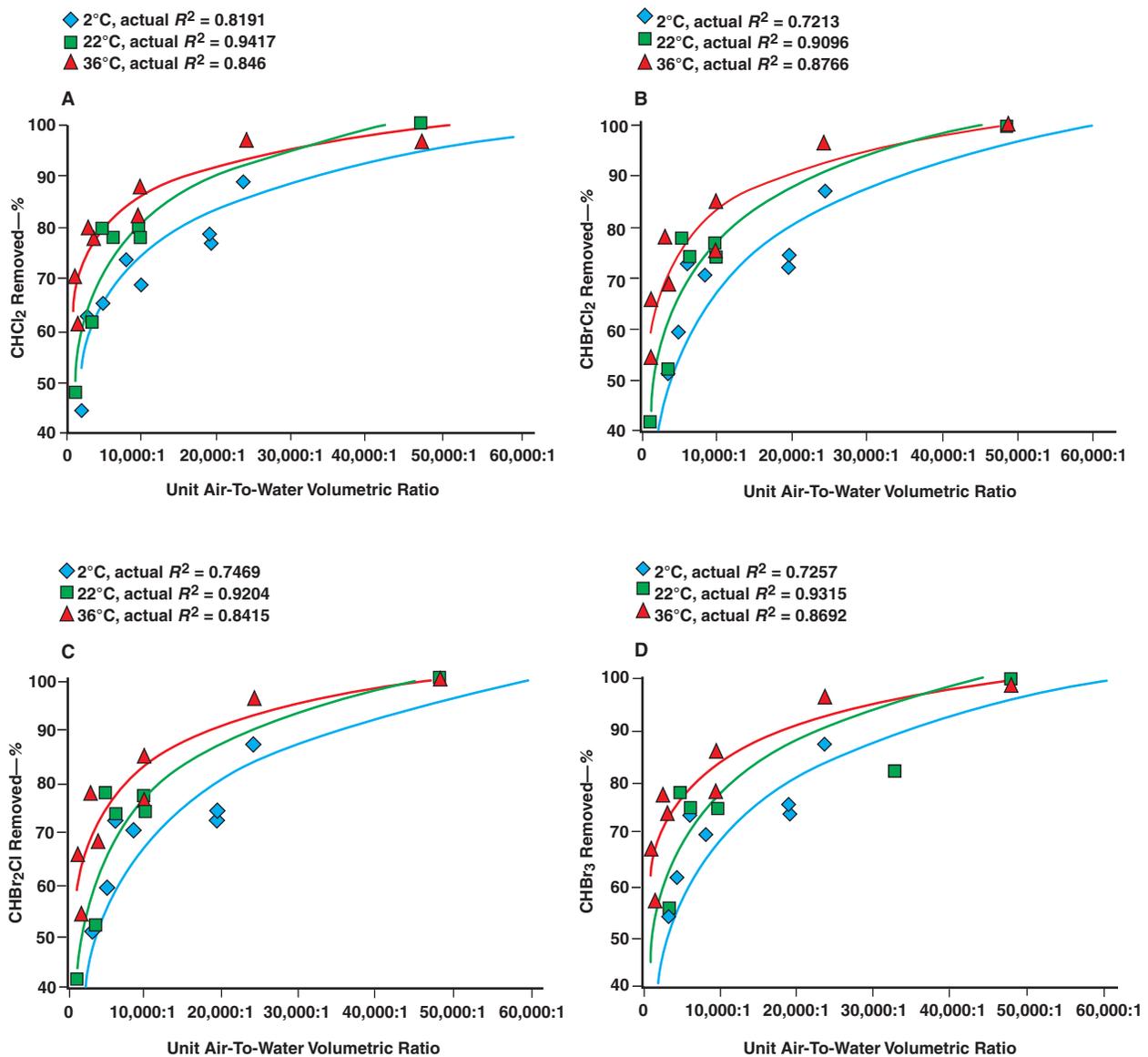


Cl₂) results in a total chlorine gas partial pressure of 1.1×10^{-10} atm and, on the basis of Henry's constant, would be in equilibrium with an aqueous free chlorine concentration orders of magnitude below typical chlorine detection limits. In short, free chlorine should not be significantly stripped by typical posttreatment aeration processes. The previous calculations are based more on a closed-system assessment, however, and the correlation between an enclosed storage tank vented to the atmo-

sphere and an enclosed diffused-aeration reactor vented to the atmosphere should be ascertained.

Despite this theoretical enclosed storage tank assessment, experience in the field working with a water utility in California did result in significant observed free chlorine residual reductions following implementation of spray aeration inside a storage tank. An investigation into the probable causes concluded that the change in influent flow pattern inside the storage tank exposed the

FIGURE 6 Percent removal of CHCl₃ (A), CHBrCl₂ (B), CHBr₂Cl (C), and CHBr₃ (D) versus unit air-to-water volumetric ratio for spray aeration



CHBr₃—bromoform, CHBrCl₂—dichlorobromomethane, CHBr₂Cl—chlorodibromomethane, CHCl₃—chloroform

influent water to chlorine-demanding surfaces that consumed the influent chlorine residual. After roughly 5 to 7 days of implementing this flow pattern change, the chlorine residual moved toward normal influent levels. Water utilities wanting to implement similar influent flow-pattern changes to storage tanks should be aware of this temporary reduction in chlorine residual, especially if the storage tanks have not been cleaned or serviced for an extended period of time.

CONCLUSION

Air-stripping of THMs is a viable posttreatment strategy for finished drinking water. In the current research, the THM species most amenable to removal by aeration was CHCl_3 , but significant reductions in all THM species are possible. Percent reduction of THMs during aeration was significantly influenced by water temperature, with warmer water having a greater stripping potential than colder water. In this study at the bench-scale level, diffused aeration achieved removal rates of 9 to > 99.5%, depending on air-to-water ratio, water temperature, and THM species. Because THMs have Henry's constants < 0.55, mass transfer may not be controlled exclusively by liquid film resistance but instead appears to be influenced by both gas and liquid film resistance. Consequently, spray aeration appears to be a more efficient approach to THM stripping, especially for THM species with lower Henry's constants.

In this study, spray aeration achieved THM reductions of 20 to > 99.5%, depending on droplet SMD, droplet travel distance, water temperature, and THM species. Droplet diameter is an important design variable and is controlled by operating pressure or nozzle flow rate and nozzle characteristics. Droplet travel distances, however, exerted a greater influence on THM removals. Thus, when a spray aeration system is designed for installation inside a water tank, variations in water levels inside the tank must be taken into account. Both the droplet SMD and travel distance variables can be developed into a unit air-to-water volumetric ratio that can be used to reasonably predict TTHM removals.

Free chlorine does not appear to be significantly reduced by aeration because only a small fraction of it will be amenable to removal. The assumption that spray aeration in an enclosed storage tank vented to the atmosphere is similar to an enclosed diffused-aeration reactor vented to the atmosphere must be verified. Water utili-

TABLE 6 ANOVA and percent contribution of experimental factors to spray aeration efficiency for removal of chloroform and bromoform

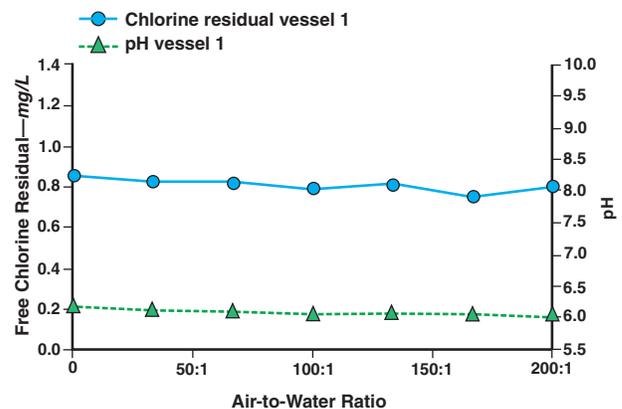
| Chloroform ANOVA | | | | | |
|----------------------|----|----------------|---------|-----------------|----------------|
| Source | df | Sum of Squares | F Ratio | Probability > F | Contribution % |
| Height | 2 | 3,114.3 | 106.6 | < 0.0001 | 34.4 |
| Temperature | 2 | 1,710.11 | 58.5 | < 0.0001 | 18.7 |
| SMD | 3 | 1,171.9 | 26.7 | < 0.0001 | 12.6 |
| Height × temperature | 4 | 738.3 | 12.6 | < 0.0001 | 7.6 |
| Error | 22 | 321.3 | NA | NA | 26.7 |
| Bromoform ANOVA | | | | | |
| Source | df | Sum of Squares | F Ratio | Probability > F | Contribution % |
| Height | 2 | 4,592.0 | 131.1 | < 0.0001 | 29.9 |
| Temperature | 2 | 2,803.8 | 80.1 | < 0.0001 | 18.2 |
| SMD | 3 | 2,851.0 | 54.3 | < 0.0001 | 18.6 |
| Height × temperature | 4 | 992.0 | 14.2 | < 0.0001 | 6.5 |
| Error | 22 | 385.3 | NA | NA | 26.8 |

ANOVA—analysis of variance, df—degrees of freedom, NA—not applicable, SMD—Sauter mean diameter

ties should be aware of temporary reductions of free chlorine residuals when initiating flow pattern changes in water storage tanks.

Recommendations. A study comparing the power costs of spray aeration and diffused aeration to determine a best available practice should be undertaken. In addition, a study to determine gas-phase and liquid-phase mass transfer coefficients for the THM species

FIGURE 7 Influence of diffused aeration on free chlorine residual as a function of air-to-water ratio and pH at pH 6.1



A computer-aided titrator was used to maintain the pH at 6.1.

would allow for a better theoretical understanding and optimization of THM stripping. A better mass transfer coefficient correlation model should be developed to take into account both liquid and gas film mass transfer resistances. The effects of increasing THM concentrations in the bulk air inside a water tank should be considered to allow for proper design of air ventilation systems. A more in-depth study of chlorine-stripping potential to confirm the results of these experiments would be appropriate. Additional spray-aeration assessments conducted indoors without the presence of atmospheric disturbances would likely result in lower experimental error.

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FOOTNOTES

¹JMP statistical analysis software, SAS, Cary, N.C.

²Hydrocarbon trap, Restek, Bellefonte, Pa.

³Fisher Scientific, Pittsburgh, Pa.

⁴Cat. 6700-00, Hach, Loveland, Colo.

⁵Sta-rite 1f98V, Sta-rite, Delavan, Wis.

⁶Great Plains Digital Instruments, Wichita, Kan.

⁷6890N GC-ECD, Agilent Technologies, Santa Clara, Calif.

⁸7683 Series, Agilent Technologies, Santa Clara, Calif.

⁹BETE, Greenfield, Mass.

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