

Control of Trihalomethanes in Wastewater Treatment

Guanghai Hua and Steven Yeats

Controlling trihalomethanes (THMs) discharged with wastewater treatment plant final effluent has become an important issue across the United States. Chlorination is by far the most widely used method for disinfecting treated wastewater. The reaction of free chlorine with certain organic compounds in the wastewater leads to the formation of disinfection byproducts, including THMs. Limited knowledge is available about the formation and control of THMs during wastewater disinfection.

Many utilities in Florida discharging to surface waters are having difficulty complying with limits for bromodichloromethane and dibromochloromethane, the two regulated THMs. This article presents a comprehensive evaluation of factors affecting THM formation during chlorination and details available technologies for controlling THMs in wastewater. The article also recommends ways for wastewater utilities to meet the effluent THM limitations.

Disinfection is a vital process to inactivate pathogenic microorganisms in drinking water and wastewater, but since the 1970s it has been recognized that disinfection can produce harmful byproducts and cause health concerns. Chlorine is by far the most widely used chemical disinfectant in water and wastewater treatment.

Chlorine readily reacts with certain organic compounds in water and wastewater to form disinfection byproducts (DBPs) that

cause health and regulatory concerns. DBPs have been linked to an increased risk of certain cancers and adverse reproductive effects. THMs and haloacetic acids (HAAs) are the two most abundant groups of known DBPs.

The U.S. Environmental Protection Agency (EPA) Stage 2 D/DBP rule sets the maximum contaminant level for four THMs and five HAAs at 80 g/L and 60 g/L, respectively, on a basis of a locational running annual average for drinking water. The four regulated THMs are chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform. Figure 1 shows the chemical structures of the THMs.

To protect surface water quality, the Florida Department of Environmental Protection (FDEP) sets regulatory limits for THMs for treated wastewater effluents discharged to surface waters. Unlike the Stage 2 D/DBP rule for drinking water, the FDEP sets a regulatory limit for each THM species. The annual average limits for chloroform, BDCM, DBCM, and bromoform are 470.8, 22, 34, and 360 µg/L, respectively, for a Class II or Class III surface water discharge (Table 1).

Because the limits for chloroform and bromoform are relatively high, it is not difficult for wastewater utilities to meet the chloroform and bromoform standards under typical wastewater chlorination conditions. Consequently, controlling BDCM and DBCM

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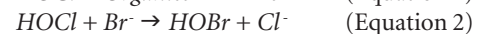
formation during chlorine disinfection is critical for wastewater utilities to meet the FDEP's THM surface water discharge standards.

Trihalomethane Formation During Chlorination

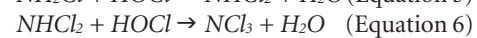
When chlorine is introduced into water, it reacts with DBP precursors to form byproducts. Natural organic matter (NOM) present in source water is the primary precursor for the formation of DBPs in drinking water (Reckhow et al, 1990). NOM is a complex mixture of organic compounds derived from the decay of vegetation and animal material.

The organic matter found in municipal wastewater is significantly different from drinking water supplies. The organic matter in wastewater typically consists of proteins, carbohydrates, and oils and fats (Metcalf & Eddy, 2002).

In addition to organic matter, bromide ions are important inorganic DBP precursors. Bromide ions are ubiquitous in water and wastewater and are quickly oxidized by chlorine to bromine during chlorination. Subsequent reactions between bromine and organic matter result in the formation of brominated THMs and HAAs. These reactions are summarized in Equations 1-3.



When ammonia is present in treated effluents, it reacts with chlorine to form chloramines. The formation of chloramines can be summarized in its simplest form by Equations 4-6.



The distribution of mono-, di-, and trichloramines primarily depends on the chlorine-to-ammonia ratio and the pH. Mono-

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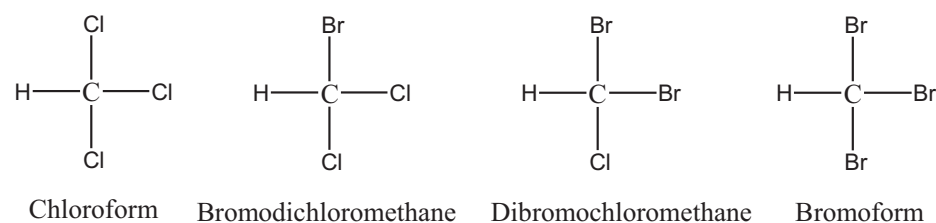


Figure 1: The THM Species

THMs	Class I: Potable Water Supply	Class II: Shellfish Propagation or Harvesting	Class III: Recreation, Propagation and Maintenance of a Healthy, Well-Balanced Population of Fish and Wildlife	
			Predominantly Fresh Water	Predominantly Marine Water
CHCl ₃	≤ 5.67 µg/L	≤ 470.8 µg/L	≤ 470.8 µg/L	≤ 470.8 µg/L
CHBrCl ₂	≤ 0.27 µg/L	≤ 22 µg/L	≤ 22 µg/L	≤ 22 µg/L
CHBr ₂ Cl	≤ 0.41 µg/L	≤ 34 µg/L	≤ 34 µg/L	≤ 34 µg/L
CHBr ₃	≤ 4.3 µg/L	≤ 360 µg/L	≤ 360 µg/L	≤ 360 µg/L

Table 1: Criteria for Surface Water Quality Classifications (FDEP, FAC 62-302.530)

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chloramine is predominant at low Cl_2 -N ratios (e.g. < 5 mg Cl_2 /mg N). Free chlorine residual appears when the chlorine-to-ammonia ratio exceeds a certain point (theoretical value at 7.6). This is often referred to as *break-point chlorination* (Figure 2).

In general, chloramines form fewer THMs and HAAs than free chlorine. Dihalogenated HAAs are the predominant known DBPs identified in chloraminated waters (Hua and Reckhow, 2008).

Figure 3 shows a conceptual model of the formation pathways of THMs and HAAs during chlorination and chloramination. Based on this model, formation of THMs, trichloroacetic acid (TCAA), and dichloroacetic acid (DCAA) proceeds through common dihalogenated intermediates.

Further halogenation of dihalogenated intermediates by chlorine leads to the formation of THMs and TCAA. THMs form through base-catalyzed hydrolysis, and the formation of THMs is favored at high pH values. Certain chemical factors prohibit chloramines from adding a third halogen to dihalogenated intermediates; therefore, chloramines are not active in the formation of THMs.

Numerous water quality and treatment factors affect THM formation. The formation and speciation of THMs primarily depends on source water characteristics and specific disinfection conditions. The type and abundance of organic precursors and bromide and iodide concentrations have been shown to significantly influence the concentration and speciation of THMs. Important disinfection variables affecting THM formation include contact time,

pH, chlorine dose, and temperature.

Several mechanistic and empirical models have been developed to describe the formation of THMs. For example, Equation 7 shows an empirical model to predict the formation of the four regulated THMs (Westerhoff, 2006).

$$\text{THMs} = 0.0412[\text{TOC}]^{1.098}[\text{Cl}_2]^{0.152}[\text{Br}^-]^{0.068}[\text{Temp}]^{1.069}[\text{pH}]^{0.263} \quad (\text{Equation 7})$$

This model predicts that the concentration of THM increases with increasing total organic carbon (TOC), chlorine dose, bromide, temperature, pH, and reaction time. Bromide ions affect the yield of THMs and greatly influence the speciation of THMs. Consequently, the presence of bromide is critical for controlling individual THM species.

The distribution of THM species depends primarily on the bromide-to-chlorine ratio. Figure 4 shows a qualitative profile of THM speciation as a function of the Br/ Cl_2 ratio. Chloroform predominates at low Br/ Cl_2 ratios.

More brominated THM species are formed with increasing bromide concentrations. The maximum levels of BDCM and DBCM appear at a medium range of bromide to chlorine ratios. Thus, the formation of BDCM and DBCM can be reduced or minimized either by reducing the bromide concentration to low levels or by increasing bromide concentration to high levels to shift the speciation toward the formation of chloroform or bromoform.

Figures 5-8 present examples of the effect of bromide concentration, pH, reaction time, dose, and temperature on THM formation. These results were obtained from laboratory bench-scale tests using natural waters.

As shown in Figure 5, Chloroform yield gradually decreased while bromoform yield gradually increased as bromide was increased. CHCl_2Br and CHClBr_2 yields passed through the maximum at 2-10 $\mu\text{mol/L}$ (160-800 $\mu\text{g/L}$) bromide concentration and decreased when bromide ions were increased. Bromoform was dominant when the bromide concentration was increased to 30 $\mu\text{mol/L}$ (2400 $\mu\text{g/L}$).

Figure 6 shows that THM concentration increased as reaction time and pH value increased. The formation of THMs exhibited an initial rapid phase within a few hours, followed by a more steadily increasing phase.

Varying pH also strongly influenced the formation of THMs. THM concentration increased by a factor of 2.8 and 1.6, respectively, when increasing pH from 5 to 7 and 10 for a 24-h contact time.

The chlorine dose and reaction temperature also have a significant impact on THM formation. The concentrations of THM increased nearly linearly with an increasing chlorine dose (Figure 7). A more than 100-percent increase in THMs was observed when increasing the reaction temperature from 5°C to 30°C (Figure 8); therefore, wastewater utilities may experience increased THMs in the chlorine contact basin during warm-weather operation compared to cold-weather operation.

Figure 9 shows the influence of ammonia on the formation of DBPs during chlorination. The ratio of chlorine to ammonia had a great impact on the THM yield. THM concentrations decreased rapidly as the ammonia-to-chlorine ratio increased. THM concentrations were below 8 $\mu\text{g/L}$ when the Cl_2/N (mg/mg)

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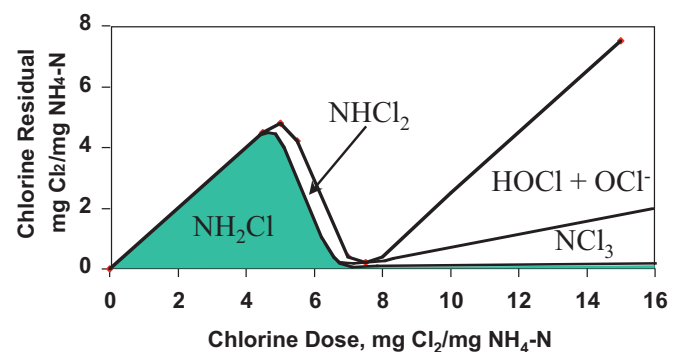
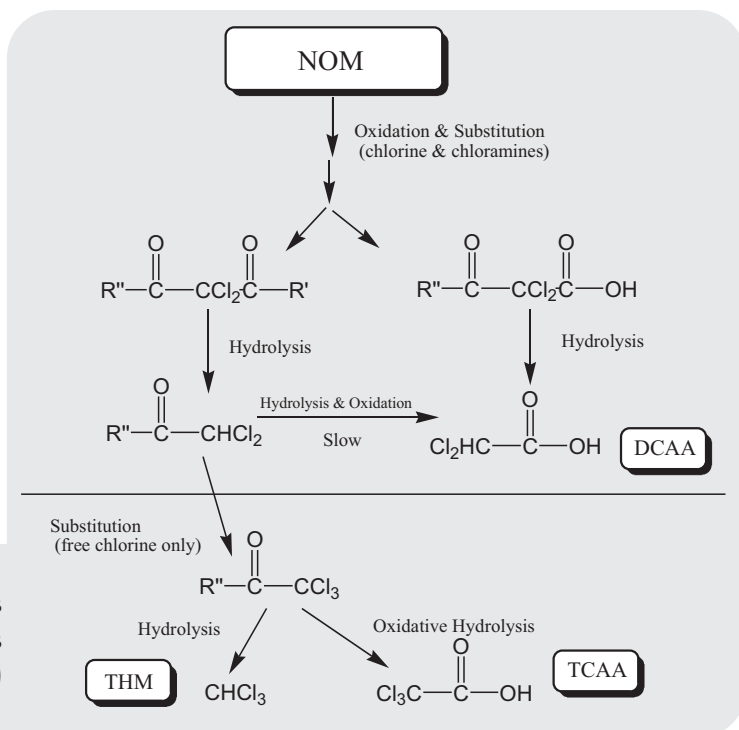


Figure 2: Theoretical Break-point Chlorination Curve

Figure 3: Conceptual model of the formation pathways of THMs and HAAs from chlorine and chloramines (Adapted from Hua and Reckhow 2008)



mass ratio was lower than 5. Adjusting the addition of ammonia is a practical way to control effluent THM levels for wastewater utilities using chloramines for disinfection.

Control of Trihalomethanes in Wastewater Treatment

THM Precursor Control

As part of the EPA's D/DBP rule, removal of NOM was defined as the best available technology to lower the concentration of DBPs in finished drinking water. Typical methods of controlling DBP precursors during drinking water treatment include enhanced coagulation, granular activated carbon (GAC) adsorption, ion exchange, and membrane filtration, but these precursor-control technologies may not be effective or practical for wastewater DBP control because of the significant difference in water quality.

For example, enhanced coagulation has been shown to be effective in removing high molecular weight and highly humic organic matter, such as humic acid and fulvic acid from drinking water (Chadik and Amy, 1985), but the occurrence of humic substances in treated wastewater may not be significant.

One study showed that coagulation is not effective in removing dissolved organic carbon (DOC) from a treated wastewater (Silva and Milligan, 2006). For this study, the DOC removal rate was only 20 percent at the highest alum coagulant dose (150 mg/L).

Other precursor-control technologies, such as GAC adsorption, ion exchange, and membrane filtration, usually have very high operation and maintenance (O&M) costs when applied to treated wastewater for DOC removal due to wastewater characteristics (e.g., high total organic carbon and total dissolved solids); therefore, the application of these technologies for THM precursor control would

likely present a significant financial burden for many wastewater utilities.

Optimizing the Chlorination Process

(1) Optimizing chlorine contact time and chlorine dose

Wastewater utilities in Florida with surface water discharge are required to meet the minimum microorganism disinfection standards and then dechlorinate the effluent before discharge. A typical chlorine contact basin design requires a minimum 15-minute contact time at design peak hour flow. The actual chlorine contact time could be much longer when the plant flow rate is well below the peak flow. Wastewater treatment plants can use multiple chlorine injection points based on plant flow to reduce the contact time and chlorine consumption.

(2) Reducing Sunlight Irradiation

Wastewater treatment plants typically use uncovered chlorine contact basins for disinfection, allowing the wastewater to be exposed

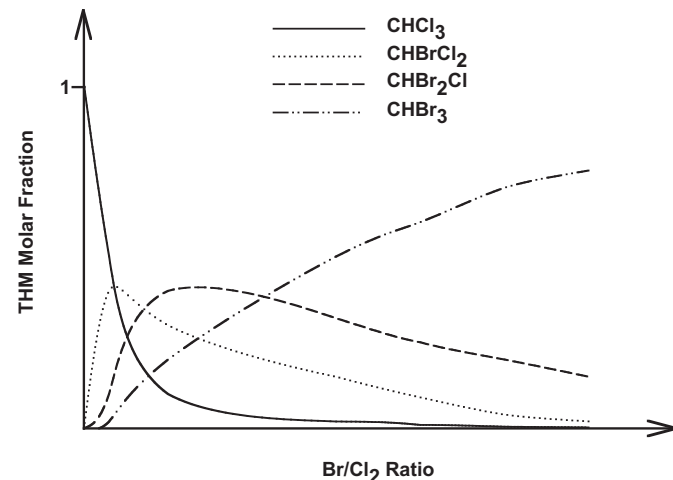


Figure 4: Qualitative profile of THM Speciation as a function of Br/Cl₂ Ratio

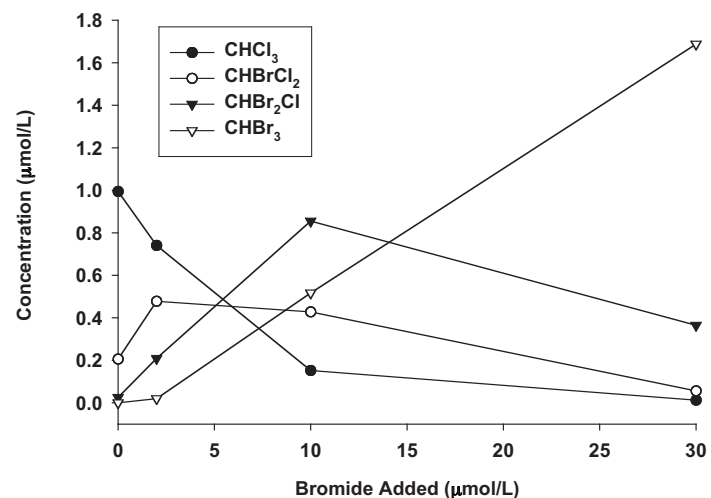


Figure 5: Effect of Bromide Concentration on THM Speciation (Reaction conditions: TOC=8.5 mg/L, pH=7, time=48h, temp=20°C, Cl₂=5.0 mg/L)

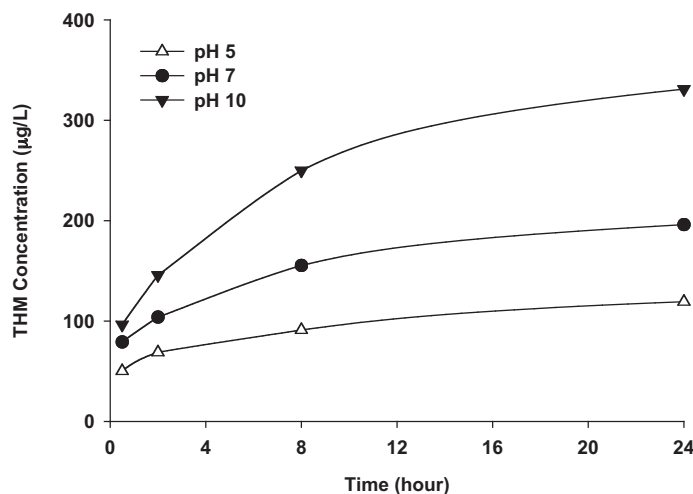


Figure 6: Effect of Reaction Time and pH on THM Formation (Reaction conditions: TOC=5.0 mg/L, temp=20°C, Cl₂=8.1 mg/L)

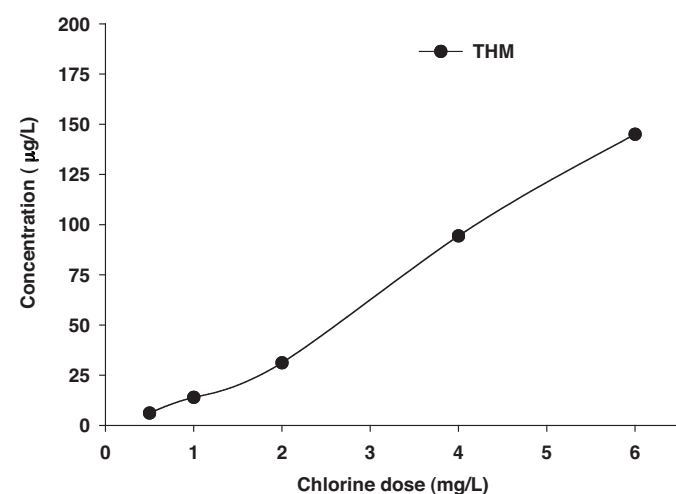


Figure 7: Effect of Chlorine Dose on THM Formation (Reaction conditions: TOC=5.0 mg/L, temp=20°C, time=48h, pH=7)

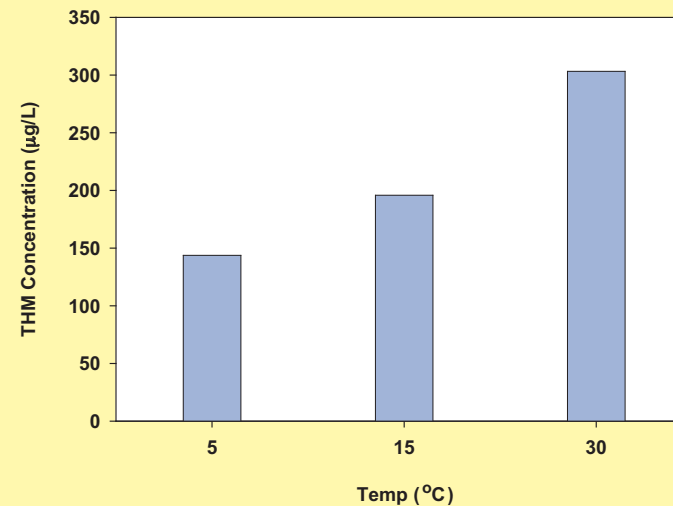


Figure 8: Effect of Temperature on THM Formation (Reaction Conditions: TOC=5.0 mg/L, time=48h, pH=7, Cl₂=6.0 mg/L)

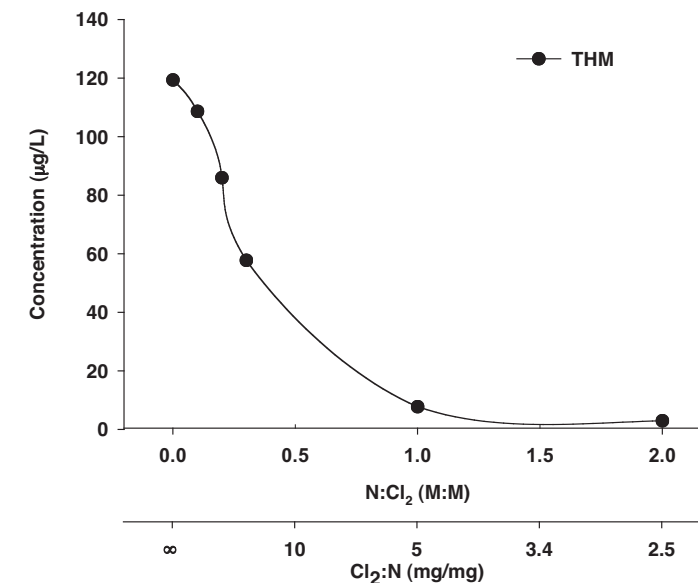
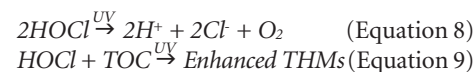


Figure 9: Effect of Chlorine-to-Ammonia Ratio on THM Formation (Reaction Conditions: TOC=2.6 mg/L, pH=7, time=48h, temp =20°C)

to UV irradiation from sunlight. Sunlight irradiation can cause dissociation of chlorine (Equation 8) and lead to chlorine loss in contact basins. Consequently, higher chlorine doses are needed to maintain chlorine residuals at the end of the contact basin.

At the same time, UV irradiation may act as a catalyst for THM formation, which results in increased THM concentrations. This hypothesis is shown in Equation 9. Fitzpatrick (2005) investigated the effect of sunlight irradiation on THM formation during wastewater disinfection. The results showed that free chlorine residual was significantly higher and the THM concentration was significantly lower in the covered chlorine contact basins compared with those in uncovered basins.

This study suggests that covered chlorine contact basins effectively reduced chlorine loss and THM formation. Wastewater utilities should take measures to reduce the sunlight irradiation to the chlorine contact basin to lower chlorine consumption and THM formation.



(3) Controlling chlorination pH

Many wastewater utilities have converted their chlorine gas disinfection system to the use of a sodium hypochlorite solution for chlorination primarily for safety and regulatory concerns. Unlike chlorine gas, the addition of sodium hypochlorite increases the wastewater pH due to the hydrolysis of hypochlorite solution.

As shown in Figure 6, THM formation is favored at high pH values. Controlling pH in

chlorine contact basins is an effective way to lower the THM levels during chlorination. Automated acid injection/mixing at the beginning of the basin and base injection/mixing at the end of the basin may be necessary for effective THM control and pH compliance.

(4) Adding Ammonia

Chloramine has been an increasingly popular secondary disinfectant for drinking water because of the stricter regulations on DBPs, but there has been some controversy over the application of chloramines in drinking water. Nitrification in the distribution system, degradation of elastomers in piping and plumber systems, increased lead concentrations, and formation of nitrogenous DBPs (e.g., N-Nitrosodimethylamine (NDMA)) and iodinated DBPs have caused significant concern (Singer, 2006).

Nonetheless, chloramination has been shown to be a practical, highly effective method of controlling DBPs in drinking water. Chloramination also has been used in wastewater disinfection for THM control (Erdal et al, 2008).

In general, chloramines are weaker disinfectants than free chlorine, but chloramines are more stable and last longer than free chlorine because of their lower oxidation potential. Adding ammonia can help maintain a lasting residual during wastewater disinfection, so adding ammonia to wastewater does not necessarily deteriorate the efficacy of the disinfection in the chlorine contact basin.

Another potential benefit of adding ammonia in THM control is the formation of bromoamines from the reaction of ammonia and bromine. Bromoamines are not active in the formation of brominated THMs. Equations 10-13 summarize the formation of bro-

moamines from ammonia and bromine.



The most critical parameter for the application of chloramination in wastewater is the chlorine-to-ammonia ratio. The dosage of chlorine and ammonia must meet the requirements of disinfection, chlorine residual compliance, and THM compliance. The optimum chlorine-to-ammonia ratio is site specific and can vary depending on the water quality and environmental conditions.

Although chloramination is an easy-to-practice and effective method of controlling THMs in wastewater, it has some significant disadvantages. Adding ammonia to treated wastewater increases the effluent total nitrogen (TN) concentration. Many wastewater treatment plants are required to reduce the nitrogen and phosphorus loads to receiving waters to control eutrophication and protect surface water quality.

Adding ammonia for THM control may not be feasible for those plants with a stringent effluent TN limit. Also, chloramination can form several highly toxic emerging DBPs, such as NDMA and iodo-acids, so using chloramination for wastewater THM control must be carefully studied.

(5) Bromide addition

Similar to chlorine, bromine is a highly effective disinfectant. The application of bromine in wastewater can be achieved by

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using either commercial bromine solution or by in-situ generation by adding chlorine and bromide ions simultaneously to the contact basin. The latter may be a more robust method for wastewater disinfection and CHBrCl₂ and CHBr₂Cl control.

As shown in Figures 4-5, the formation of THM shifts to more brominated species as bromide concentration increases. The addition of bromide does not control the formation total THMs; in fact, it can actually increase total THM concentrations due to the higher mass weight of bromide than chloride. Because of concerns over the formation of other brominated DBPs, the bromide dose should be limited to the level that can effectively control effluent CHBrCl₂ and CHBr₂Cl concentrations.

Post Treatment

Surface water discharge usually requires the wastewater effluent dissolved oxygen (DO) concentration to be elevated prior to discharge. A re-aeration tank is often used to increase the DO levels in the effluent. The re-aeration tank can be used for THM reduction because of the volatility of THMs.

THM removal by aeration is a function of initial THM concentration, water flow rate, and air flow rate (Tarquin, 2005). The removal of the individual species varies depending on the chemical properties of the THMs. Table 2 presents some chemical characteristics of the four THMs.

Henry's law constant (K_H) is an indicator of the solubility of a gas at a certain pressure. The higher the K_H , the lower the solubility of a gas. The order of the solubility of the four THMs is CHBr₃>CHBr₂Cl>CHBrCl₂>CHCl₃. The reverse order is true for the volatility of the THMs; therefore, the removal efficiency of THMs by aeration is expected to be in the order of CHCl₃>CHBrCl₂>CHBr₂Cl>CHBr₃.

Aerated chlorine contact basins have been used for disinfection and increasing effluent DO levels, but aeration may reduce disinfection efficiency by altering the basin from a plug flow reactor to segments of completely mixed reactor basins, which may promote short-circuiting.

Also, an aerated chlorine contact basin may not be effective in THM removal because THM removal by aeration is a function of the initial THM concentration. Aeration does not remove THM efficiently when the THM concentration is low. The re-aeration step can be placed after the chlorination and dechlorination process to optimize THM removal by aeration and maintain disinfection efficiency.

Alternative Disinfectants

The use of alternative disinfectants such as ozone, chlorine dioxide, and UV for waste-

THMs	CHCl ₃	CHBrCl ₂	CHBr ₂ Cl	CHBr ₃
MW (g/mol)	119.4	163.8	208.3	252.7
Boiling Point (°C)	62	90	117	149
Henry's Law Constant K_H @ 20 °C (Atm·m ³ /mol)	2.95×10 ⁻³	1.24×10 ⁻³	0.642×10 ⁻³	0.385×10 ⁻³

Table 2: Chemical Characteristics of THMs

water disinfection has been studied extensively and evaluated. These alternative disinfectants do not form THMs to any significant levels. Each has advantages and disadvantages.

Ozone and chlorine dioxide are less popular in the U.S. for wastewater disinfection. Ozone can oxidize bromide to form bromate, and chlorine dioxide degrades to chlorite. Bromate and chlorite both present health concerns. Although the use of UV applications has increased significantly, this method of disinfection typically has high capital and O&M costs.

Summary

Control of THMs in wastewater can be achieved by removing precursors, optimizing chlorination conditions, implementing post-treatment, and using alternative disinfectants. Typical precursor removal methods for drinking water, such as enhanced coagulation, GAC adsorption, ion exchange, and membrane filtration, may not be effective and have high capital and O&M costs for wastewater utilities.

Alternative disinfectants, such as ozone, chlorine dioxide, and UV, do not form THMs to significant levels, but the use of alternative disinfectants for THM control should be carefully evaluated for cost and for their formation of other byproducts.

Wastewater utilities using chlorine for disinfection should focus on optimizing chlorination conditions and post-treatment for controlling THMs. It is critical for utilities to improve chlorine contact tank efficiencies, optimize chlorine dose and contact time, prevent direct sunlight irradiation, and adjust pH in order to reduce THM formation.

In some cases, adding ammonia to form chloramines is a practical method of controlling THM formation, but this method may increase effluent total nitrogen concentrations and produce some toxic nitrogenous and iodinated DBPs in the effluent.

Adding bromide can shift the formation of THM toward bromoform and reduce BDCM and DBCM concentrations. Post-treatment, such as aeration, is a viable method of further reducing THM concentrations in the effluent because of the volatility of THMs.

Overall, controlling THMs in wastewater treatment is a challenging task. More study is needed to determine THM precursors in

treated wastewater, and factors affecting THM formation during wastewater disinfection should be investigated. Optimizing chlorination conditions and post-treatment can reduce THM concentrations in the treated effluent. By employing multiple control strategies and treatment technologies, utilities will improve performance and meet effluent THM limitations.

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