

# THMs Control in Wastewater Treatment Plant Effluent

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## ABSTRACT

Some municipal wastewater treatment plants in New Jersey are facing stringent effluent permit limits for Trihalomethanes (THMs), which are a byproduct of disinfection of fully nitrified effluent with chlorine-bearing compounds. Full scale evaluations at one impacted facility demonstrated that addition of a small dose of ammonia prior to the point of chlorine application (chloramination) prevents generation of THMs, just as it is practiced in the potable water treatment industry. Preliminary evaluations of air stripping and activated carbon treatment, which are another technologies used in water treatment for THMs control, indicated that these processes are not practical or cost-effective when applied to wastewater treatment plant effluent.

## KEY WORDS

THMs, Chlorination Byproducts, Chloramination, Effluent Disinfection, Chloroform, Bromodichloromethane, Dibromochloromethane, Bromoform

## INTRODUCTION

In early 2000' the New Jersey Department of Environmental Protection (NJDEP) began a program for enforcing Surface Water Quality Standards (SWQC) for toxic compounds, including THMs for wastewater dischargers. Table 1 provides the current (2011) New Jersey Surface Water Quality Criteria for THMs, which are regulated by the individual species. It is noted that the current Primary Drinking Water Standards regulate Total THMs at an 80 ug/L level.

Table 1. New Jersey Surface Water Quality Criteria for THMs

	Fresh Water, ug/L	Saline Water, ug/L
Chloroform	68 (h)	2,100 (h)
Bromodichloromethane	0.55 (hc)	17 (hc)
Dibromochloromethane	0.40 (hc)	13 (hc)
Bromoform	4.3 (hc)	140 (hc)

h – based on human health non-carcinogenic effects

hc - based on human health carcinogenic effects

Using the above listed criteria, effluent limits for wastewater treatment plant effluents are being calculated by NJDEP based on the in-stream dilution available under the critical stream and plant flow conditions. If the plant effluent characterization data indicate a potential to exceed the calculated limit, a limit is being imposed with a 59 month compliance schedule. Many fully nitrifying plants, which utilize some form of chlorination for effluent disinfection, are facing new, stringent effluent limits for THMs. One of the impacted plants is the Hanover Sewerage Authority (HSA) plant in northern New Jersey.

HSA plant is an advanced wastewater treatment plant with a design capacity of 4.6 MGD (17,400 m<sup>3</sup>/d) treating domestic wastewater. The treatment train consists of primary clarification, trickling filters with intermediate clarification, nitrifying activated sludge process with final clarification and sand filters. For disinfection sodium hypochlorite is added to the head of the Chlorine Contact Tank (CCT) and at an average dose of approximately 2 mgCl<sub>2</sub>/L with sulfur dioxide used for dechlorination. Table 2 summarizes the calculated Water Quality-based effluent permit limits and typical performance data for THMs for the HSA plant.

Table 2. Calculated Limits and Effluent Data for THMs at HSA plant. All concentrations are in ug/L

	Chloroform	BDCM <sup>(1)</sup>	DBCM <sup>(2)</sup>	Bromoform
Calculated (potential) Water Quality-Based effluent permit limit	221	3.3	2.4	26
Maximum effluent value reported in the period Jan 2004- Dec 2007	33	29	47	36
Median effluent value reported in the period Jan 2004- Dec 2007	8	14.5	11	2
Recommended Quantification Level (RQL) = Enforceable limit	5	5	6	8

1. Bromodichloromethane

2. Dibromochloromethane

Table 2 indicates that for all THMs, with exception of Chloroform, the plant's compliance with the calculated limits was questionable. It should be noted that at present, the future permit limit for BDCM imposed by NJDEP is 1.6 ug/L (based on old SWQC); however, this is being challenged. The plant also has to comply with a 106 ug/L Existing Effluent Quality limit for Bromoform.

Some of the New Jersey plants with a questionable compliance with the THMs limits decided to switch to UV light for disinfection. Some other facilities, however, investigated alternative

methods of bringing the effluent into compliance with the new limits. Air stripping, activated carbon treatment, and chloramination were available technologies which were investigated to develop a practical and cost-effective compliance strategy.

## AIR STRIPPING

Since the THMs are categorized as volatile compounds, air stripping of these compounds in the reaeration facilities available at most plants appeared to be a possibility. To evaluate the amount of air required, theoretical calculations based on the equilibrium considerations (Henry's law) were performed and are summarized in Table 3. Column 3 indicates the volumetric ratio of air to water needed to remove 90% of the individual THMs at 20°C, and assuming no mass transfer limitations.

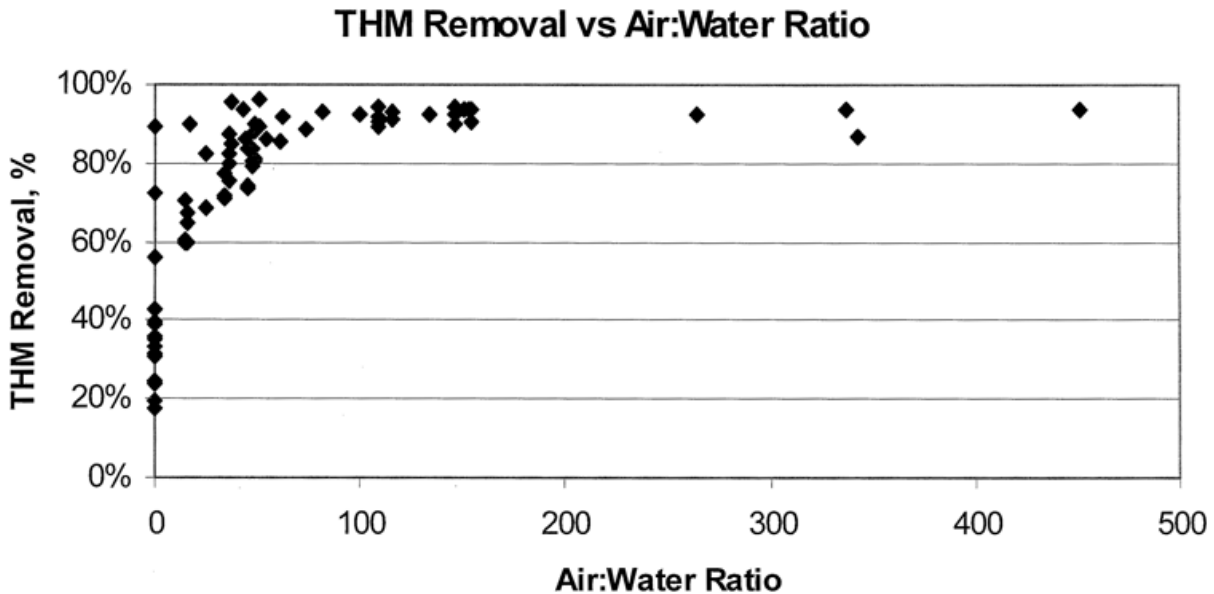
Table 3. Theoretical Air Requirements for THMs Removal

	Henry's Constant, mol/L/atm	Volumetric Ratio of Air to Water Needed for 90% THMs Removal at Equilibrium	Air Flow Required for 90% THMs Removal at a 3,785 m <sup>3</sup> /D (1 MGD) Plant	
			scfm	m <sup>3</sup> /hr
Chloroform	0.25	13	1,200	2,000
Bromodichloromethane	0.45	23	2,100	3,500
Dibromochloromethane	1.0	52	4,800	8,100
Bromoform	1.7	87	8,100	14,000

These air requirements recalculated in terms of air needed for 90% THMs removal at a 3,785 m<sup>3</sup>/d (1 MGD) plant are shown in the last column.

The theoretical calculations shown in Table 3 are consistent with literature information (see Figure 1, taken from Tarquin, 2005), where an approximately 90% removal of THMs (not identified by species) was achieved on a stripping tower at air to water ratio of 50 or more.

Figure 1. Experimental Air to Water Ratios for THMs Removal (after Tarquin, 2005)



The air requirements for THMs removal given above (Table 3) are very high for a diffused aeration system typically used at a wastewater treatment plant re-aeration facilities. For comparison, a typical volume of air needed for activated sludge treatment of typical domestic wastewater, including a complete nitrification, is on order of 1,700 m<sup>3</sup>/hr (1,000 scfm) per 1 MGD (3,785 m<sup>3</sup>/d) treated. Air flow available in a typical re-aeration facility (following chlorine disinfection) is usually significantly (order of magnitude) lower than those used for aeration of activated sludge. Consequently, air stripping in the wastewater re-aeration facilities is not expected to provide significant reduction of THMs concentrations. A dedicated air stripping tower would be required for that purpose, where a large volume of air provided by low pressure fans could be contacted with the effluent.

### ACTIVATED CARBON ADSORPTION

One of the methods used for removal of THMs in a potable water treatment industry is activated carbon treatment. A series of jar tests with HSA effluent was performed to determine the feasibility and approximate cost of utilizing that method.

The carbon isotherm jar test was conducted on final effluent samples utilizing three different carbon types identified by manufacturers as most promising in this application. The effluent was contacted (mixed) for 2 hours at room temperature in sealed bottles (without air space) with a series of activated carbon dosages. Subsequently, the carbon was settled with a help of polymer and supernatants analyzed for THMs.

Removal of the THMs followed an expected, classical model of Freundlich isotherms, as evidenced by approximately straight lines on Figures 2 through 5. The isotherms developed in this way allow an approximate evaluation of the activated carbon use in full-scale, continuous flow activated carbon beds.

Figure 2. Adsorption Isotherms for Chloroform

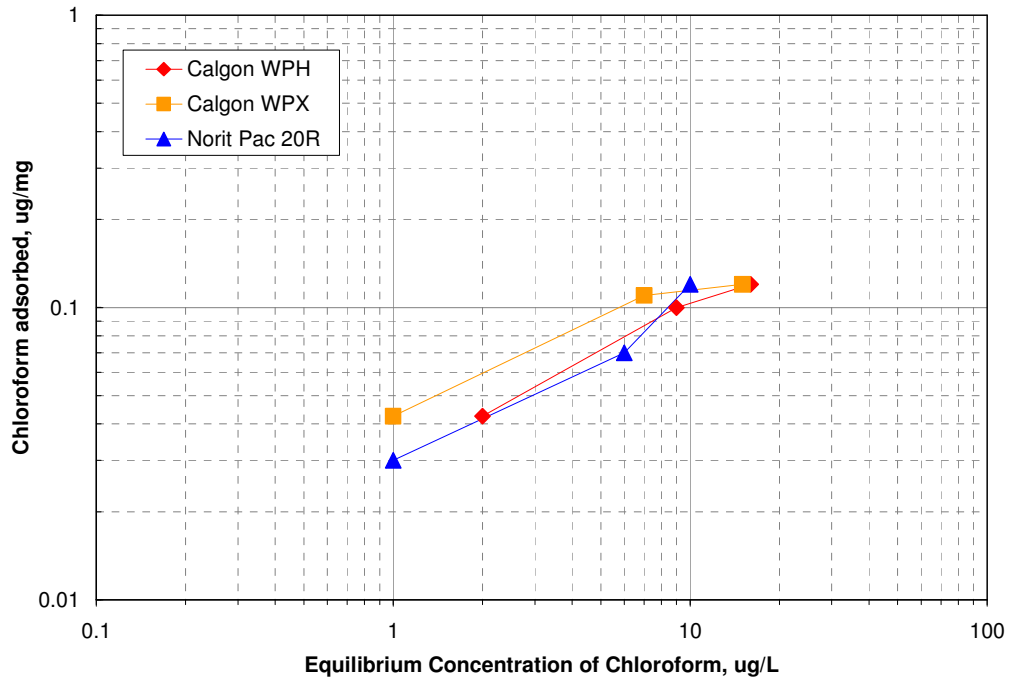


Figure 3. Adsorption Isotherms for Bromodichloromethane

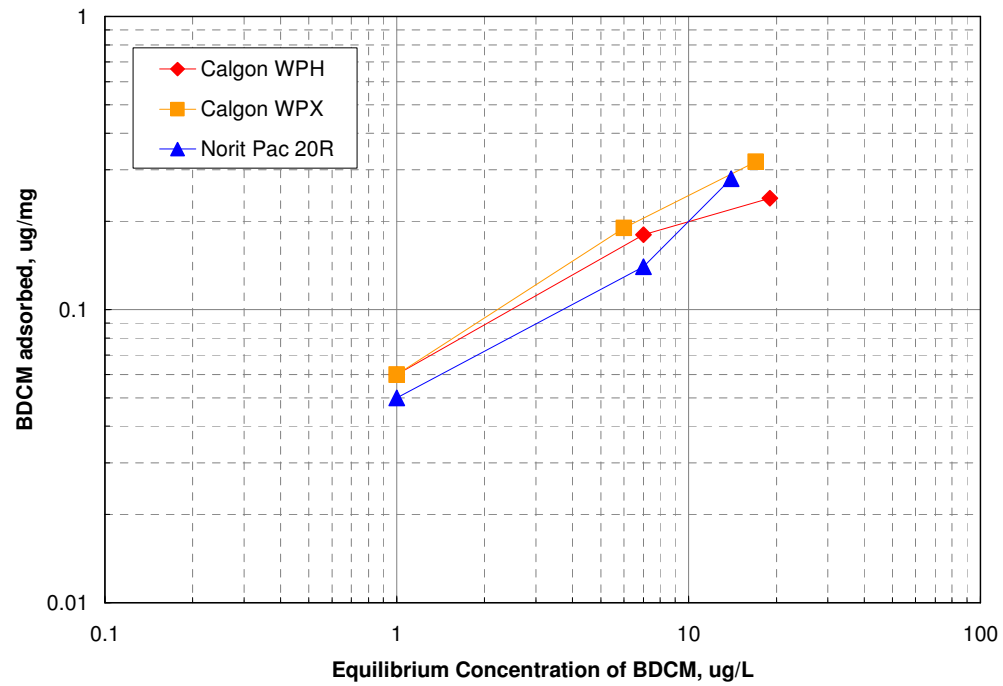


Figure 4. Adsorption Isotherms for Dibromochloromethane

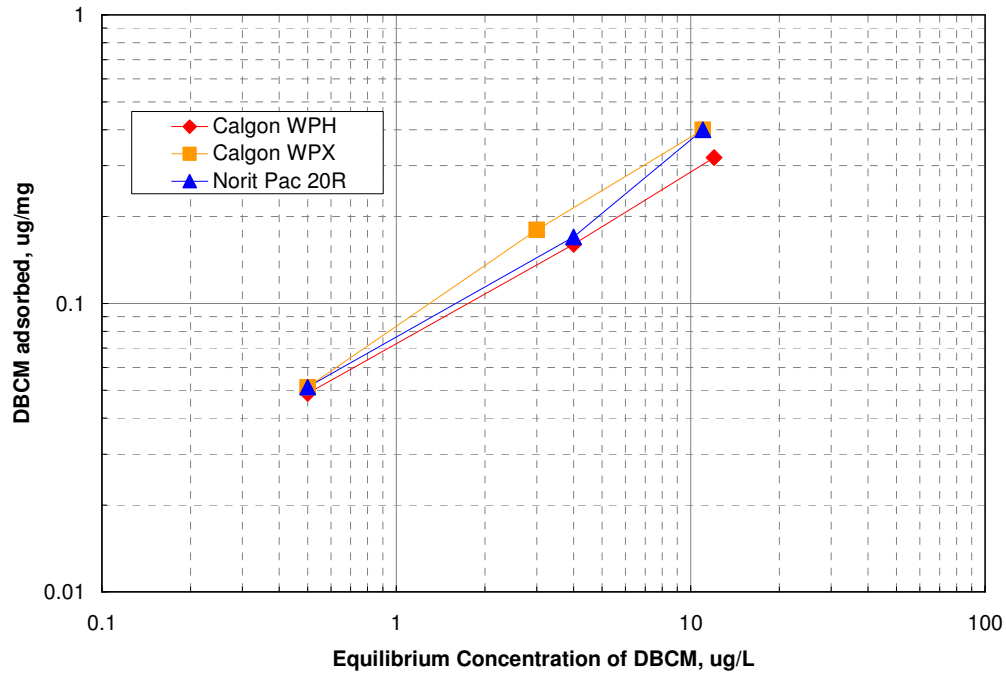
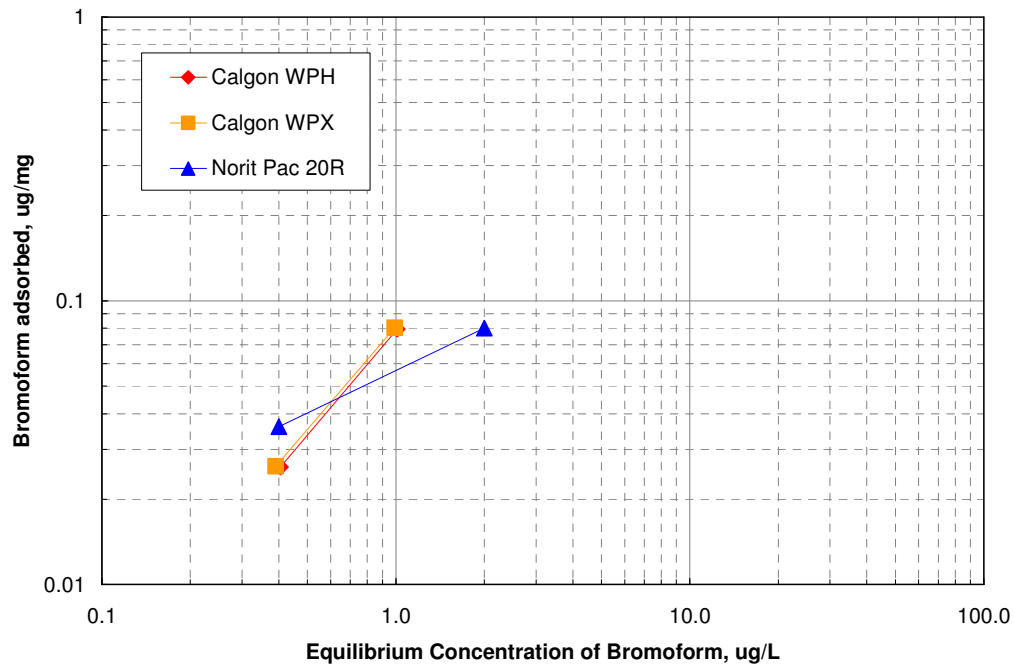


Figure 5. Adsorption Isotherms for Bromoform



For the critical for HSA's compliance parameter Bromodichloromethane (BDCM), Figure 3 indicates that for the design (equilibrium) effluent BDCM concentration of 1 ug/L (present limit = 1.6 ug/L) approximately 0.06 ug of BDCM is adsorbed per mg of both Calgon carbons. Assuming the design influent concentration of 20 ug/L (average from existing data = 15.5 ug/L), the required mass of BDCM to be removed at 3 MGD flow is 0.46 lb of BDCM per day. The carbon use thus calculates to be 6,700 lb of carbon per day, with an associated cost of approximately \$15,000 per day or \$5,500,000 per year, which is cost-prohibitive. It should be noted that carbon use calculated from static isotherm tests is an approximation of the actual use, which could only be properly derived from pilot tests using continuous flow columns. Such pilot tests will take into account adsorption kinetics (depth of adsorption zone) and possible competition from other constituents in the effluent, which could further increase carbon use. The latter aspect may be of particular importance for treated wastewater, which contains residual organics at concentrations much higher than the target compound (BDCM), which are likely to be competing for the same adsorption sites.

Based on the very high cost, activated carbon treatment for THMs was not considered further by HSA.

## **CHLORAMINATION**

### **Experience Elsewhere**

While chloramination is a well-established practice in the potable water industry, its application for THMs control in wastewater treatment plant effluent is not well documented. Some literature sources (Kuo et al., 2003; Aguiar et al. 2002; Bober, 2005; Rebhun et al., 1997; Exter et al., 2002; Wallis-Lage et al., 2004) have reported full scale experiences with addition of ammonia to wastewater treatment plant effluents for various purposes; however, comparative data on effectiveness of full-scale ammonia addition for THMs control in such application are very limited.

### **Theoretical Considerations**

When adequate residual ammonia is present in the effluent ( $\text{Cl}_2$  to  $\text{NH}_3\text{-N}$  ratio of less than 5), chlorine added to wastewater generates monochloramine, a moderately effective and stable disinfectant. At a ratio greater than 7.5 in clean water (in treated effluent that ratio may be somewhat higher), a breakpoint reaction could occur, which is oxidation of chloramines by the chlorine with formation of non-germicidal residuals (free chlorine is used-up in such reaction). This results in a decrease of the residual combined chlorine and in disinfection instability. A further increase in chlorine dose is required to maintain chlorine residual and this residual is in the free chlorine form. At fully nitrifying plants, such as HSA and most plants in NJ, the residual ammonia concentration is usually in the 0.1 mg/L range (at or below detection levels). The typical chlorine demand for disinfection of highly treated effluent is usually in 1.5-5 mg/L range, which translates to chlorine to ammonia ratio of >10. Consequently, breakpoint chlorination conditions are prevalent and chlorine residual present in the CCT is almost exclusively in the free chlorine form, which promotes THMs formation. In summary, when nitrification is complete and little ammonia is present, chlorine addition generates free chlorine, which:

- is much more aggressive than chloramines, thus reacting with organic compounds causing bleaching (could be very fast) and creating disinfection byproducts, including THMs,
- additionally, free chlorine could generate organic chloramines much faster than monochloramine could. Organic chloramines have little if any disinfection power but could be registered as combined chlorine by some colorimetric methods (DPD), thus misleading the chlorination system into thinking that chlorine residual is present, while in fact dechlorination chemical (sulfite) could be present at that time (organic chloramines react slowly with the dechlorination chemicals).

### HSA Experience

The HSA plant completely nitrifies, with activated sludge effluent ammonia concentration typically below 0.2 mg/L. Prior to undertaking chloramination trials, the effluent was disinfected by sodium hypochlorite addition to the head of the CCT tank with a chlorine residual set-point of 1.9 mg/L with an average hypochlorite dose of about 2 mg/L. Under these conditions, the major disinfecting species was free chlorine, which lead to generation of THMs. A complicating factor was the plant's practice to add, in summer months, a small dose of hypo at the weirs of the final clarifiers in order to prevent algae growth. Consequently, some THMs generation was already taking place ahead of the CCT, as seen in Table 4, which provides a profile of THMs concentration through the plant (prior to chloramination trials). Note that when addition of hypo at the clarifier weir was temporarily halted (sample from 9/13/2005), THMs were practically absent ahead of CCT.

Table 4. THMs Profile at HSA Plant

Date	Chloroform			Bromodichloro-methane			Dibromochloro-methane			Bromoform		
	Sand Filter Infl.	CCT Inlet	CCT Effl.	Sand Filter Infl.	CCT Inlet	CCT Effl.	Sand Filter Infl.	CCT Inlet	CCT Effl.	Sand Filter Infl.	CCT Inlet	CCT Effl.
8/30/2005	1	2	7	3	4	18	3	4	20	< 0.8	1	5
9/6/2005	1	2	5	3	5	16	3	7	25	0.9	2	9
9/13/2005*	< 1	< 1	7	< 0.7	0.7	15	< 1	< 1	16	< 0.8	< 0.8	4
9/20/2005	1	2	6	3	5	15	3	5	10	1	1	5
9/27/2005	2	3	7	3	6	16	3	6	17	0.8	1	4
10/4/2005	2	2	7	4	6	17	5	7	23	1	2	7

\* Prechlorination system at final clarifier for algae control not operational



Beginning in early 2009, the plant embarked on a program of adding 30% solution of ammonium sulfate at a target concentration of approximately 0.3 mg/L as N for a total residual ammonia concentration of approximately 0.4 mg/L. Ammonium sulfate solution was initially added to the final clarifier effluent due to the availability of the chemical addition facilities at that location. However, as the sand filters removed some of the ammonia (nitrification), the addition point was moved to the filter clean well. As the trials progressed, the chlorine residual set-point at the head of the CCT was gradually reduced from 1.9 to 0.8 mg/L, resulting in 50% reduction in hypochlorite use.

Table 5 provides a summary of operating conditions from the chloramination trials for October 2010. During that period concentration of THMs in the plant effluent remained at below detection levels (<1 ug/L or less for all THMs, which is a better detection level than a RQL listed in Table 2). Such results are typical for operation in colder months. During the summer months, when hypochlorite is added at the clarifier weir, some THMs formation is still being observed. To eliminate this problem, the plant plans to implement alternative methods of algae control at the final clarifier weir.

Table 5. Effluent Data from Chloramination Trials for October 2010

Parameter (Final Effluent)	Average	Minimum	Maximum
Plant flow at the time of sampling, MGD	3.06	2.30	4.40
NH <sub>3</sub> -N, mg/L	0.37	0.29	0.43
Monochloramine, mg/L	0.61	0.60	0.65
Total Cl <sub>2</sub> residual, mg/L	0.73	0.68	0.78
Free Cl <sub>2</sub> residual, mg/L	0.13	0.10	0.17
Fecal coliforms, #/100 mL	-	0	1

During the initial period of chloramination trials, fecal coliform counts were occasionally elevated, which necessitated an increase in the chlorine residual set-point. In more recent months, fecal coliform counts, if detected at all, rarely exceed single digits.

Based on the results obtained during 2 years of the ammonia addition trials, the plant staff is confident that compliance with THMs limits could be achieved by chloramination. In addition to avoiding significant capital expenditures for UV facilities, operational cost savings associated with lowering the hypochlorite use are practically paying for the cost of ammonium sulfate.

## CONCLUSIONS

The previously discussed evaluations and trials, aimed at development of strategy for compliance with stringent THMs limits at municipal wastewater treatment plants could be summarized as follows:

- THMs present in the effluent from a fully nitrifying wastewater treatment plant are being generated during chlorination,
- ammonia addition at a target concentration at the point of chlorine addition of 0.4 mg/L (including any ammonia already present) resulted in reduction of THMs generation to below detection level, most of the time,
- implementation of chloramination process at the HSA facility resulted in reduction of hypochlorite use by 50%,
- activated carbon treatment of wastewater treatment plant effluent for THMs control is cost prohibitive,
- air stripping of THMs requires large volumes of air, usually provided in a dedicated, low air pressure drop stripping tower. Stripping of THMs in reaeration facilities available at typical municipal wastewater treatment plants is not expected to be effective.

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