THE FORMATION AND FATE OF TRIHALOMETHANES IN POWER PLANT COOLING WATER SYSTEMS

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Prepared By:
Electric Power Research Institute

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Prepared By:
Electric Power Research Institute
K. Zammit
Palo Alto, California
Contract No. 1009486

Prepared For:
California Energy Commission

Joe O'Hagan,
Project Manager

Kelly Birkinshaw,
Program Lead
Energy-Related Environmental Research Program Area
Public Interest Energy Research Program

Marwan Masri,
Deputy Director
Technology Systems Division

Robert L. Therkelsen
Executive Director

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The Formation and Fate of Trihalomethanes in Power Plant Cooling Water Systems

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Sponsor:
Public Interest Energy Research Program (PIER)
California Energy Commission
1516 Ninth Street
Sacramento, CA 95814

PIER Project Manager
J. O'Hagan

EPRI
3412 Hillview Avenue
Palo Alto, CA 94304

EPRI Project Manager
K. Zammit

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Michael N. DiFilippo, Consultant

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CITATIONS

This report was prepared by

Michael N. DiFilippo, Consultant
2803 Woolsey Street
Berkeley, CA 94705

Principal Investigator
M. DiFilippo

This report was prepared for

EPRI
3412 Hillview Avenue
Palo Alto, California 94304

and

Public Interest Energy Research Program (PIER)
California Energy Commission
1516 Ninth Street
Sacramento, CA 95814

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REPORT SUMMARY

Trihalomethanes (THMs) are semi-volatile compounds that form in water when chlorine or bromine reacts with dissolved organic carbon. This report investigates the formation and fate of THM compounds in power plant cooling water systems, THM health risks, a generalized mechanism of THM formation, and the applicability of existing THM research to power plant cooling. The report presents results of a two-site sampling and analytical program designed to identify THM formation potential in cooling towers using fresh water and reclaimed municipal effluent. It also discusses predictive models for THM compounds in domestic water supplies and their applicability to THM formation and fate in cooling towers.

Results & Findings

THM compounds were formed during halogenation in the two cooling systems studied. Site 1 involved fresh water (well water) using sodium hypochlorite for biological control. Site 2 involved a blend of fresh water (well water) and reclaimed municipal effluent using activated bromine for biological control. Data collected at this site, however, was based upon chlorinated samples since the bromine injection equipment was not operable. Intermittent chlorination at Site 1 did not generate a significant amount of total THM compounds (TTHM), and all of it attenuated to nondetectable levels in the cooling water in several hours. Continuous halogenation at Site 2 generated detectable levels of THM on a continuous basis. However, approximately 80 percent of the THM escaped from the cooling tower in the airstream and the rest in blowdown. At both sites, calculated airstream concentrations of TTHM were very low and far below the workplace health-threat level for chloroform (one of four THM compounds).

Existing models for THM compound formation in domestic water supplies were not applicable to cooling towers. While the study did not generate sufficient data to develop a model for THM formation in cooling towers, it appears that two new models will be required. They should address

- Intermittent chlorination and/or bromination for systems using freshwater to model low level THM formation and attenuation
- Continuous chlorination and/or bromination for systems using treated municipal effluent to model steady/residual levels of THM formation and their continuous release to the airstream

Challenges & Objective(s)

THM compounds are of industry interest, since these disinfection byproducts are suspected to cause not only cancer but also liver and kidney damage, retarded fetus growth, birth defects, and possibly miscarriage. The primary goal of the project was to design a sampling and analytical program that would identify THM formation potential in cooling towers using fresh water and reclaimed municipal effluent. Another goal of this study was to compare formation and fate of THM compounds relative to make-up water source, also via sampling and analysis.

Applications, Values & Use

Models have been developed to simulate the formation of THM compounds in domestic water supplies, where chlorine can be in contact with finished/treated water for many hours or even days. The models require an assumption of constant chlorine residuals in a closed system (not open to air) to predict results. The temporal nature of THM formation made this problem especially difficult to evaluate in a cooling tower where circulating water is first exposed to halogens under pressure (closed system), then highly aerated at atmospheric pressure, and lastly placed in a quiescent/open environment. This cycle is repeated in rapid succession every 5 – 10 minutes. It became clear that models developed for THM formation in water supply systems are not applicable to cooling towers.

Possible future work could include another round of sampling at Site 2 using bromination. Sampling at another power plant that uses only reclaimed municipal effluent containing high levels of ammonia and that applies continuous bromination for biological control may also be of value. In particular, the levels of THM generation could be significantly higher, and ammonia interactions with reactive halogens would be noteworthy. Finally, it would be of interest to determine THM formation during no-load events when some plants halt cooling cell fans, allowing for a possible increase in THM levels in the cooling system during these periods.

EPRI Perspective

EPRI research into Advanced Cooling Alternatives has identified many potential water-conserving technologies, one involving the use of degraded water sources in traditional wet cooling systems. Other research has targeted potential scaling, fouling, corrosion, treatment options and disposal issues associated with the use of such sources. This project was funded because the potential for human exposure to THM compounds could be a barrier to adoption of this technology. Results indicate that the risk is negligible.

Approach

The project team first conducted a literature search, but found no references relating to THM formation in cooling towers. They next determined the key questions to be answered by this study, including: What species of THM are formed in cooling systems? How much THM is emitted in the airstream and cooling tower blowdown? Does the water source make a difference in the amount of THM formation, i.e. fresh water versus treated municipal effluent? Do the biological control chemicals make a difference, i.e. sodium hypochlorite, bromine formulations? The team designed a two-site sampling and analytical program to identify THM formation potential in cooling towers using fresh water and reclaimed municipal effluent. The sampling protocol was designed to conduct mass balances within and around critical areas of the cooling system to predict (on a gross scale) how much THM was formed and where it was leaving the system.

Keywords

Trihalomethane
THM Formation
Cooling Water Systems
THM Predictive Models

ABSTRACT

Trihalomethane (THM) compounds are of industry interest, since these disinfection byproducts are suspected to cause not only cancer but also liver and kidney damage, retarded fetus growth, birth defects, and possibly miscarriage. The goal of this project was to investigate the formation and fate of THM compounds in power plant cooling water systems, via sampling and analysis. This report includes a brief discussion of THM health risks, a generalized mechanism of THM formation, and the applicability of existing THM research to power plant cooling. Predictive models – developed for THM formation in water supply systems – and their applicability to THM formation and fate in cooling towers are also discussed. Finally, the report details field studies conducted at two power plants – one using groundwater for cooling tower make-up with intermittent chlorination and the other using treated municipal effluent with continuous bromination (although data collected was based upon chlorinated samples). Sampling was conducted at both plants to determine the degree of THM formation during halogenation. The amount of THM released into the airstream and blowdown was also estimated for each site. Recommendations for further study are provided.

EXECUTIVE SUMMARY

The goal of this project was to investigate the formation and fate of trihalomethanes (THMs) in power plant cooling water systems. THMs are semi-volatile compounds that form in water when chlorine or bromine reacts with dissolved organic carbon.

In the early 1970's, a significant effort was initiated in the US to investigate the formation of disinfection byproducts (DBP). DBPs are formed during the chlorination of drinking water and are primarily comprised of THMs and haloacetic acids (HAA). Early research into health effects showed a relationship between THM exposure (airborne and waterborne) and cancer of the bladder. Currently, THMs are suspected to cause not only cancer, but also liver and kidney damage, retarded fetus growth, birth defects, and possibly miscarriage.

All water sources contain naturally occurring organic matter – usually in the form of humic and fulvic acid formed by the natural decomposition of organic matter. These are relatively large molecules with molecular weights greater than 3,000 to 5,000 daltons. During halogenation (the use of chlorine and/or bromine compounds as disinfectants for biological control), $–CH_3$ (methyl) groups are cleaved from humic and fulvic acids. THMs are formed when these disinfectants react with $–CH_3$. Trihalomethanes are comprised of a mixture of the following compounds:

Chloroform	$CHCl_3$
bromodichloromethane	$CHCl_2Br$
dibromochloromethane	$CHClBr_2$
Bromoform	$CHBr_3$

Models have been developed to simulate the formation of THMs in domestic water supplies where chlorine can be in contact with finished/treated water for many hours or even days. The models also require an assumption of constant chlorine residuals in a closed system (not open to air) to predict results. The temporal nature of THM formation made this problem especially interesting (as well as difficult to evaluate) in a cooling tower where circulating water is first exposed to halogens under pressure (closed system), then highly aerated at atmospheric pressure and lastly placed in a quiescent/open environment. This three-step cycle is repeated in rapid succession every five to ten minutes. It was thus concluded that the models developed for THM formation in water supply systems are not applicable to cooling towers.

A sampling and analytical program was designed to identify the THM formation potential in cooling towers using fresh water and reclaimed municipal effluent. Two power plants were evaluated:

- Site 1 – fresh water (well water) using sodium hypochlorite for biological control
- Site 2 – blend of fresh water (well water) and reclaimed municipal effluent using activated bromine for biological control

One of the goals of this study was to compare formation and fate of THM compounds relative to make-up water source. It was assumed that the organic content of reclaimed municipal effluent would contribute to greater THM levels in cooling water.

The sampling protocol was designed to conduct mass balances within and around critical areas of the cooling system to predict (on a gross scale) how much THM was formed and where it was leaving the system.

Sampling was conducted at Site 1 on June 28, 2002. Site information provided in this report was purposefully kept to a minimum to maintain the confidentiality of the plant. Site 1 utilizes 12.5 percent sodium hypochlorite to periodically chlorinate their cooling system. Typically, the plant chlorinates for 15 minutes once per day to achieve a target FAC (free available chlorine) residual of 0.2 mg/l. The plant will repeat the chlorine injection cycle if the target residual is not sustained after a two-hour period.

Sampling was conducted at Site 2 on September 11, 2003. Site confidentiality was also maintained at this plant. Site 2 utilizes a blend of treated municipal effluent and well water for cooling tower make-up. The blend typically consists of 35 to 50 percent of treated effluent for cooling tower make-up. 12.5 percent NaOCl is blended with 40 percent sodium bromide to generate a mixture of hypobromous acid (HOBr) and hypochlorous acid (HOCl). The plant halogenates continuously to achieve a FAC residual of 0.2 to 0.4 mg/l and total residual chlorine (TRC) of 0.2 to 1.2 mg/l. Oxidation reduction potential (ORP) is continuously monitored to control halogen levels in the circulating water. At the time the testing was conducted, the sodium bromide feed system was not operable. Therefore, the plant used continuous chlorination via 12.5 percent NaOCl solution to maintain its FAC and TRC residuals during THM testing.

THMs were formed during halogenation in the two cooling systems studied. Intermittent chlorination at Site 1 did not generate a significant amount of TTHM and all of it attenuated to non-detectable levels in the cooling water in several hours. Continuous halogenation at Site 2 generated detectable levels of THMs on a continuous basis. Approximately 80 percent of the THM escapes from the cooling tower in the air stream and the rest in blowdown. At both sites, calculated air stream concentrations of TTHM were very low and far below the workplace health-threat level established by OSHA for chloroform (one of the four THM compounds).

Intermittent chlorination appears to generate very little THM which attenuates quickly to non-detectable levels. No conclusions can be drawn regarding THM formation during continuous bromination utilizing treated municipal effluent, since bromine injection equipment was not operable at Site 2. However, during continuous chlorination at Site 2, the cooling water held a steady residual of THM throughout the sampling period.

The study did not generate enough data to develop a model for THM formation in cooling towers. Based on the study results, it appears that two models are required to predict THM formation:

- Intermittent chlorination and/or bromination for systems using freshwater to model low level THM formation and attenuation
- Continuous chlorination and/or bromination for systems using treated municipal effluent to model steady/residual levels of THM formation and their continuous release to the air stream

Model development should include sampling at a number of sites to generate more data and model parameters.

Possible future work could also include another round of sampling at Site 2 using bromination. Sampling at another power plant with the following characteristics may also be of value:

- Utilizes only reclaimed municipal effluent (Site 2 used a blend of freshwater and reclaimed effluent)
- Municipal effluent contain high levels of ammonia
- Continuous bromination (activated or stabilized) is used for biological control

This plant profile would provide information that was not gained at Sites 1 and 2. The levels of THM generation could be significantly higher. Ammonia interactions with reactive halogens would be noteworthy. It would also be of interest to determine THM formation during no-load events when some plant operators stop cooling cells fans. THM levels in the cooling system could increase during these periods.

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1
INTRODUCTION

1.1 Project Objectives

The goal of this project was to investigate the formation and fate of trihalomethanes (THMs) in power plant cooling water systems. The study includes a brief discussion of THM health risks, a generalized mechanism of THM formation, and the applicability of existing THM research to power plant cooling. Prediction models and their applicability to THM formation and fate in cooling towers are discussed in the next section.

Field studies are detailed for two power plants – one plant uses groundwater for cooling tower make-up and the other uses a blend of groundwater and treated municipal effluent. One of the goals of this study was to compare formation and fate of THM compounds relative to make-up water source. It was assumed that the organic content of reclaimed municipal effluent would contribute to greater THM levels in cooling water.

Findings and conclusions are presented in the last section of the study. A bibliography of cited papers and reading recommendations is found in the Appendix A. Sampling results for both sites are found in Appendix B.

1.2 THM Research to Date

In the early 1970's, a significant effort was initiated in the US to investigate the formation of disinfection byproducts (DBP) during the chlorination of drinking water. DBPs are primarily comprised of THMs and haloacetic acids (HAA). Early research into health effects showed a relationship between THM exposure (airborne and waterborne) and cancer of the bladder. Currently, THMs are suspected to cause not only cancer, but also liver and kidney damage, retarded fetus growth, birth defects and possibly miscarriage. The U.S. Department of Health and Human Services has determined that chloroform, a THM compound, may reasonably be anticipated to be a carcinogen. In addition, breathing a level of 900 parts chloroform per million parts air (900 ppm) for even a short time can cause dizziness, fatigue, and headache; and liver and kidney damage can result from breathing air, eating food, or drinking water containing high levels of chloroform for long periods of time. The Occupational Safety and Health Administration (OSHA) has set the maximum allowable concentration of chloroform in workroom air during an 8-hour workday in a 40-hour week at 50 ppm. (ToxFAQs™, 1997)

Today, research into THM formation in drinking water supplies in the United States is minimal (relative to past years) since its formation and fate are fairly well understood. Research and study outside the US continues since many countries are just addressing the issue. Also, the use

of chlorine as a disinfectant has been eliminated by many public utilities in the US, but it is still widely used as a primary disinfectant by the majority of water suppliers.

1.3 Generalized Mechanism of THM Formation

All water sources contain naturally occurring organic matter – usually in the form of humic and fulvic acid. These are relatively large molecules with molecular weights greater than 3,000 to 5,000 daltons. Humic and fulvic acid represent a class of chemicals formed by the natural decomposition of organic matter. During halogenation (the use of chlorine and/or bromine compounds as disinfectants for biological control), $–CH_3$ (methyl) groups are cleaved from humic and fulvic acids. THMs are formed when hypochlorous acid (HOCl) and/or hypobromous acid (HOBr) react with $–CH_3$. (Engerholm and Amy, 1983 and Pourmoghaddas and Stevens, 1995)

Background levels of bromide (Br^{-1}) will also participate in THM formation (trace levels of bromide are found in most natural waters). Trihalomethanes are comprised of a mixture of the following compounds:

chloroform	$CHCl_3$
bromodichloromethane	$CHCl_2Br$
dibromochloromethane	$CHClBr_2$
bromoform	$CHBr_3$

THM concentrations are usually at µg/l levels in municipal water. EPA has set the national standard for THMs in drinking water at 80 µg/l. (EPA ,1998 and EPA, 2001) Lastly, THMs continue to form for hours (even days) in the presence of a chlorine residual. (Müller, 1998)

Some work has been done in speciating the organic compounds found in treated municipal effluent. (Amy et al, 1987) Municipal effluent is regulated with respect to THMs, however, it is usually not a problem because background ammonia competes for chlorine to form chloramines. Also, since THMs are somewhat volatile and municipal effluent is exposed to atmospheric air at certain points in the wastewater treatment process, THM levels are usually reduced.

1.4 Applicability of Assessing THM Formation in Cooling Towers

In a literature review of this topic, no references were found in the literature that relate to THM formation in cooling towers. Almost all cooling towers chlorinate circulating water via the use of sodium hypochlorite (also known as bleach), because it is readily available and inexpensive. Halogens are used to disinfect circulating cooling water to minimize biological growth, which interferes with heat transfer and power plant performance. Cooling towers not only receive organic compounds from source water, they also receive a significant amount of organic airborne matter (bacteria, vegetation and insects) in the air stream. Based on the mechanism described

above, it is prudent to assume that THMs are formed in cooling towers during halogenation. The questions to be answered by this study are:

- What species of THM are formed in cooling systems?
- How much THM is emitted in the air stream and cooling tower blowdown?
- Does the water source make a difference in the amount of formation, i.e. fresh water versus treated municipal effluent?
- Do the biological control chemicals make a difference, i.e. sodium hypochlorite, bromine formulations?

Also, the temporal nature of THM formation makes this problem especially interesting (as well as difficult to evaluate) in a cooling tower where circulating water is first exposed to halogens under pressure, then highly aerated at atmospheric pressure and lastly placed in a quiescent/open environment. This three-step cycle is repeated in rapid succession – every five to ten minutes as described in more detail below:

Step 1. Prior to passing through the condenser, cooling water is halogenated using sodium hypochlorite, activated bromine or stabilized bromine as described below:

- Sodium hypochlorite (12 percent bleach) reacts with water to form HOCl.
- Activated bromine is generated by blending 12 percent sodium hypochlorite with 40 percent sodium bromide solution to form a mixture of HOBr and HOCl.
- Stabilized bromine is a formulation that releases HOBr.

Halogens are typically injected (either intermittently or at continuous low levels) into the circulating water just before or after the circulating water pumps. Halogens are typical of strong oxidants in that they are non-specific, i.e. they react with any compound in cooling water that can be oxidized. THM formation is initiated at the halogenation injection point and continues to form in the presence of a halogen residual. The freshly halogenated water passes through the condenser, where it is under slight pressure, so any gases or volatile compounds that were formed stay in solution.

Step 2. As the circulating water leaves the condenser, it is sent to the cooling tower. The warm circulating water is allowed to fall through and mix with the air stream. Packing is utilized in the cooling tower to " break and spread" the circulating water into small droplets and thin films. The cooling tower packing thus allows for a more intimate contact with the air stream. A portion of the THMs will volatilize in this environment and leave with the air stream.

Step 3. As the cooling water leaves the packing, it usually falls through open air and collects in the cooling tower basin in a relatively quiescent state (slow moving with little turbulence). It then returns to the circulating pumps to repeat the cycle.

In contrast to the three-step process described above, THM formation in municipal water systems forms under very different conditions. After chlorination, the water is usually pumped through a network of distribution piping (closed to the atmosphere). Chlorine may be added along the network to maintain disinfection levels. Disinfection levels may be held for days before the

water is released for use. During this time, THMs are continuously forming. (Müller, 1998) THMs stay in solution because there is no opportunity for release via volatilization to air. Again, research to date has been focused on THM formation in these types of distribution systems.

Two sites were evaluated in this study. Site 1 is a 500 MW power plant that uses groundwater for cooling tower make-up and sodium hypochlorite for halogenation. Site 2 is a 250 MW power plant that uses a blend of treated municipal effluent and well water and activated bromine for halogenation. Both plants are located in the Southwest.

2
PREDICTION MODELS

2.1 Prediction Models and Their Applicability to Cooling Towers

Models have been developed to simulate the formation of THMs in domestic water supplies where chlorine can be in contact with finished/treated water for many hours or even days. Several equations are discussed below which predict THM formation by applying variables that are critical to its formation, e.g. Total Organic Carbon (TOC), chlorine residual, background bromide concentration, contact time, etc. The models also require an assumption of constant chlorine residuals in a closed system (not open to air) to predict results. Lastly, in municipal water supply systems, the water may never be exposed to the atmosphere until point of use so there is no loss of THMs to volatilization.

THM relationships that have been developed and enhanced for the past ten or more years for municipal water systems follow:

$$C_{TTHM} = 0.00309(TOC \times UV_{254})^{0.440} C_{Cl_2}{}^{0.409} t^{0.265} T^{1.05} (pH - 2.6)^{0.715} (C_{Br} + 1)^{0.036}$$

$$\ln(AMW) = 4.46 + 0.48\ln(C_{Br} + 1) - 0.89\ln(UV_{254})$$

$$C_{CHCl_3} = 0.00278(TOC \times UV_{254})^{0.616} C_{Cl_2}{}^{0.391} t^{0.265} T^{1.15} (pH - 2.6)^{0.800} (C_{Br} + 1)^{-2.13}$$

Where:

C_{TTHM}	*Total trihalomethanes, µmoles/liter*
C_{CHCl3}	*Chloroform, µg/liter*
AMW	*TTHM Average molecular weight, g/mole*
TOC	*Total organic carbon, mg/l*
UV_{254}	*Ultraviolet absorbance at 254 nm, cm^{-1}*
C_{Cl2}	*Chlorine residual, mg/l as Cl_2*
C_{Br}	*Bromide, mg/l*
t	*Contact time, hours*
T	*Temperature, ^{o}C*

Formulas for C_{TTHM} and average molecular weight for THM were developed by Harrington, Chowdhury, et al (1992) and C_{CHCl3} prediction can be found in the "Water Treatment Plant Simulation Program, Version 1.21, User's Manual" (EPA 1992).

As stated above, this model applies to closed drinking water distribution systems where a chlorine residual is maintained at all times. As a point of note, some municipal water purveyors are converting to chloramines to disinfect water supply systems to minimize THM concentrations at the tap.

The majority of cooling towers do not operate with a constant chlorine residual. These cooling systems utilize periodic chlorination (two or three times per day for 15 to 60 minute periods) to maintain effective biological control. A handful of plants, using municipal effluent for cooling tower make-up, halogenate continuously to maintain a residual of than 0.5 mg/l (expressed as free available chlorine, FAC). Continuous chlorination is being considered at a number of plants with fresh water supply because of better biological control and reduced disinfection costs.

The first step of the cooling cycle (as described in the previous section of this report) is analogous to a municipal water system, i.e. under pressure in a closed system and allowed to react fully with the halogenating agent (albeit for a short period of time). The other steps of aeration (flow through the packing) and open storage (catchment in the cooling tower basin) do not parallel the domestic water systems that were modeled. *Thus, the models developed to date for THM formation in water supply systems are not applicable to cooling towers.*

3
THM SITE TESTING

3.1 Data Requirements to Evaluate THM Formation and Fate

Two sources of cooling tower make-up water were sampled to evaluate THM formation and fate:

- Groundwater using sodium hypochlorite for biological control
- Reclaimed municipal effluent using activated bromine for biological control

The goal of the project was to design a sampling and analytical program that would identify the THM formation potential in cooling towers using fresh water and reclaimed municipal effluent. As noted previously, THM formation would be difficult to predict in a cooling tower because existing models are designed for closed water distribution systems. The sampling protocol was designed to conduct mass balances within and around critical areas of the cooling system to predict (on a gross scale) how much THM was formed and where it was leaving the system. To perform this analysis, the following information was obtained for each cooling system evaluated:

- Cooling water circulation rate
- Cooling tower air flow
- Treated municipal effluent chemistry – ammonia, bromide, TOC, THM, etc.
- Cooling tower cycles of concentration
- Biological control chemicals
- Biological control procedure, e.g. halogenation schedule, halogenation residual target range, halogenation monitoring equipment, etc.

More data was collected than outlined above, however, this list is felt to be most applicable to meet the project goals.

3.2 Site 1 THM Field Sampling & Test Results

Sampling was conducted at Site 1 on June 28, 2002 to determine total trihalomethane (TTHM) generation during chlorination. Site information provided in this report was purposefully kept to a minimum to maintain the confidentiality of the plant.

3.2.1 Site 1 Profile

Site 1 uses groundwater from wells at the plant site for cooling tower make-up. No analyses were performed to determine TOC or trace levels of THMs in the groundwater since the water is taken directly from the well heads to the cooling tower without pretreatment. It was presumed that the TOC in the groundwater is <0.5 mg/l and no THM compounds are present.

The plant utilizes 12.5 percent sodium hypochlorite to periodically chlorinate their cooling system. Typically the plant chlorinates for 15 minutes once per day to achieve a target chlorine residual of 0.2 mg/l_{Cl2}. The plant will repeat the chlorine injection cycle if the target residual is not sustained after a two-hour period. Chlorine is injected just upstream of circulating water pump forebay located at one end of the cooling tower. Cooling tower blowdown is manually stopped during chlorination (and opened shortly thereafter). Most utilities chlorinate with the blowdown stream valved closed to reduce chemical use and minimize chlorine residual in the discharged water. Refer to Table 3-1 for Site 1 cooling system information.

Table 3-1
Cooling System Information

Circulating Pump Flow Rate, gpm	41,500
Number of Circulating Pumps	4
Circulating Pumps in Operation (typical)	3
Circulating Flow Rate, gpm	124,500
Approx Cooling Water Volume, gallons	635,000
CT Type	Counter Flow
CT Packing	Slat Fill
CT Cycles of Concentration	5
Thermal Load (Steam Turbine), MW	333
Approx Blowdown Rate, gpm (calculated)	833
CT Cells	16
Air Flow per cell, ACFM (1)	1,277,000
Total Air flow, ACFM	20,432,000
Approx Circulating Water TDS, mg/l	4,000

Notes.....
1. ACFM = actual cubic feet per minute.

3.2.2 Sampling Methodology

Chlorine samples were taken at the riser of the cooling tower. THM samples were collected at the riser and the basin of the cooling tower. The riser is the warm water delivery line of the cooling tower, and is the last point in the cooling loop before the water is allowed to mix the air stream. Riser and basin sample points were selected to determine how much THM was lost to the cooling tower air stream via volatilization. Sample points were allowed to flow continuously

to ensure representative concentrations. Riser samples were taken from a tap located at the base of one of the two cooling tower risers. Basin samples were taken from the last cell of the cooling tower (just prior to the circulating-water pump forebay). A siphon was inserted along the outside edge of the cell to draw a continuous sample. The sample was drawn two feet from the edge of the basin and 6 inches below the surface of the cooling water.

Free available chlorine (FAC) and total residual chlorine (TRC) were monitored using a portable Hach colorimeter. Samples were taken on 15-minute intervals for the first two hours and on 30-minute intervals the final two hours. The DPD Method (N,N-diethyl-p-phenylene diamine) was used for this analysis. This method is accepted by EPA for monitoring purposes and is equivalent to EPA Method 330.5 for wastewater and EPA Method 4500-Cl G for drinking water.

THM samples were collected in 40-ml brown-glass VOA (volatile organic acid sample bottle). Each container was pre-preserved with HCl to terminate the organic carbon-chlorine-trihalomethane conversion reaction and maintain sample integrity. Without preservation, THMs would continue to form in the VOAs. VOAs were filled slowly (with minimal overflow) leaving a convex meniscus at the very top of the sample bottle when capped. Care was also taken to minimize air bubble entrainment in the sample. Triplicate samples were labeled, inserted in water-tight zip-lock baggies and immediately placed on ice. Triplicate samples were taken to ensure analytical repeatability. The ice in the chest was maintained above the samples. Samples were analyzed at Curtis & Tompkins, Ltd. Analytical Laboratory in Berkeley, California. Curtis & Tompkins, Ltd. is a commercial laboratory certified by the California Department of Health Services. Refer to Table 3-2 for the chlorine and THM sampling schedule.

Table 3-2
Sampling Schedule – Site 1, June 28,2002

Sequence Number	Riser			Basin THM
	FAC	TRC	THM	
---	6:52 (1)	6:52 (1)	---	---
0	---	---	6:59 (1)	---
---	7:31	---	---	---
1	7:44	7:45	7:38	7:40
2	7:58	7:59	7:53	7:54
3	8:13	8:14	8:08	8:09
4	8:27	8:28	8:23	8:24
5	8:42	8:43	8:38	8:39
6	8:59	8:58	8:53	8:54
7	9:12	9:13	9:08	9:09
8	9:28	9:29	9:23	9:24
9	9:57	9:57	9:53	9:54
10	10:28	10:29	10:23	10:24
11	10:58	10:59	10:53	10:54
12	11:33	11:34	11:23	11:24

Notes.....
1. Pre-chlorination sample to establish baseline conditions.

3.2.3 Residual Chlorine Data

Chlorine injection started at 7:23 am on June 28, 2002 and stopped at 7:38 am (15-minute injection period). Chlorine was injected in the forebay just upstream of the circulating pumps. 55 gallons of 12.5 percent NaOCl (sodium hypochlorite) were added manually since the NaOCl injection pump was out of service the day of sampling (the author monitored injection, start and stop times, and closed the valve to stop injection). The volume of bleach and the injection period were the same as that of the automated system. The chlorine dose was equivalent to 4.21 mg/l_{Cl2} at the point of injection.

FAC is a measure of hypochlorous acid (HOCl) and is expressed as mg/l of Cl_2. TRC is a measure of HOCl and chloramine concentrations (NH_2Cl, $NHCl_2$ and NCl_3). Chloramines also provide biological oxidation, but are significantly less effective than HOCl. FAC and TRC samples (as well as THM) were taken before chlorination started to establish baseline conditions. Refer to Table 3-3 and Figure 3-1 for cooling tower FAC and TRC concentrations.

Table 3-3
Chlorine Concentration

FAC Sample Time	FAC mg/l_{Cl2}	TRC Sample Time	TRC mg/l_{Cl2}
6:52 (1)	0.02	----	0.06
7:23	Chlorine injection started		
7:31	2.65	----	----
7:38	Chlorine injection stopped		
7:44	1.46	7:45	1.67
7:58	1.34	7:59	1.55
8:13	1.19	8:14	1.41
8:27	1.03	8:28	1.27
8:42	0.92	8:43	1.15
8:59	0.76	8:58	1.03
9:12	0.65	9:13	0.93
9:28	0.58	9:29	0.77
9:57	0.34	9:57	0.55
10:28	0.22	10:29	0.46
10:58	0.17	10:59	0.34
11:33	0.06	11:34	0.24

Notes.....

1. Baseline sample prior to chlorine injection.

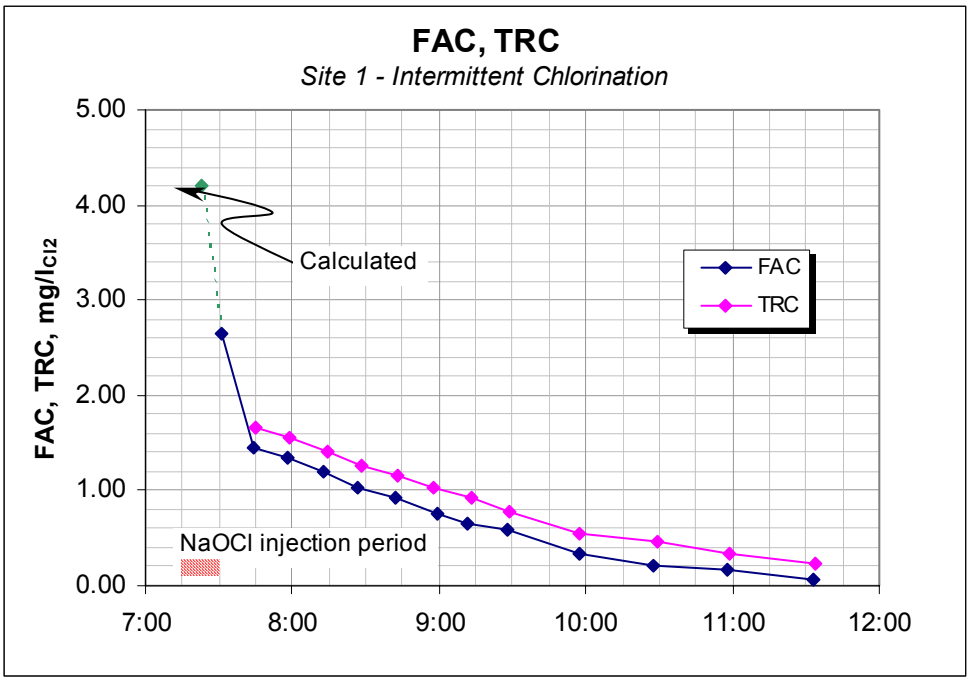

Figure 3-1
FAC, TRC

Before chlorination started, baseline concentrations of FAC and TRC were 0.02 mg/l_{Cl2} and 0.06 mg/l_{Cl2}, respectively. FAC was measured during chlorine injection (approximately midway through the injection step) to determine how well the chlorine residual was being established. TRC was not measured during chlorine injection because of time constraints. The rapid decline in FAC concentration during and just after chlorine injection was probably a result of HOCl flash off (volatilization) from the cooling tower. HOCl is somewhat volatile and a portion will flash off into the air stream. FAC diminished to 0.06 mg/l_{Cl2} after four hours. TRC levels were consistently higher than FAC by 0.2 mg/l_{Cl2} to 0.4 mg/l_{Cl2}. This differential represents the chloramine component of residual chlorine. Trace levels of ammonia from boiler blowdown (which is sent to the cooling tower to conserve water) were likely converted to chloramines.

3.2.4 TTHM Data

Results from THM sampling at Site 1 can be found in Appendix B, Tables B-1 and B-2. Refer to Figure 3-2 for TTHM sampling results. TTHM refers to total trihalomethane compounds, i.e. the sum of the concentrations of $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$. FAC is included in Figure 3-2 to show the relationship between FAC and TTHM formation.

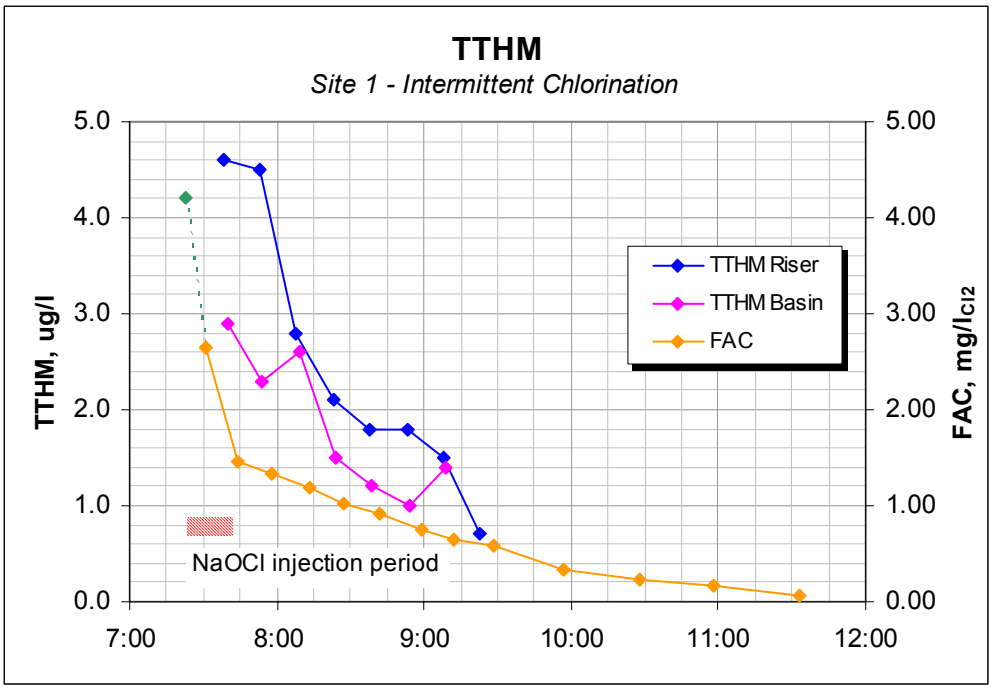

Figure 3-2
TTHM

All THM species with the exception of bromoform ($CHBr_3$) were detected at low levels. Refer to Figures 3-3 and 3-4. $CHBr_3$ was not detected in any of the riser or basin samples (detection limit is 1.0 µg/l). None of the THM species were detectable in the riser two hours and 15 minutes after chlorination and one hour and 46 minutes after chlorination in the basin. Chloroform ($CHCl_3$) concentrations in both the riser and basin quickly dissipated to less-than-detectable levels fifteen minutes after chlorine injection was terminated. Note that TTHM losses (at least at these low concentrations) were not significant across the cooling tower, in some cases less than 1 µg/l. $CHCl_2Br$ and $CHBr_2$ were the predominant THM species and occurred in similar proportions. The concentrations of $CHCl_3$, $CHCl_2Br$ and $CHClBr_2$ were detected at concentrations just above their respective detection limits of 1.0 µg/l, 0.5 µg/l and 0.5 µg/l.

Since the concentrations of three of the THM species were barely above detection limits and $CHBr_3$ was not detected at all, it is likely that the actual concentration of TTHM is greater than the simple sum of the detectable concentrations of the species as presented in Table 3-4. An effort was made to determine potential concentrations of $CHCl_3$, $CHCl_2Br$ and $CHClBr_2$ in the riser and the basin. Potential concentrations were simply extrapolated from the existing values and should provide a more realistic estimate of TTHM generation in the cooling tower. Refer again to Figures 3-3 and 3-4. The dotted lines represent projected values for THM species if they were allowed to attenuate to concentrations below the detection limit. The projection for $CHCl_3$ was trended in the same manner by applying an attenuation curve similar to that of $CHCl_2Br$ and $CHClBr_2$. Since $CHBr_3$ was not detected in any of the samples, it was assumed to be 50 percent of its detection limit in the riser and 35 percent of its detection limit in the basin. These assumptions, although they have no basis, were used to provide a means of calculating TTHM. Both approximations for $CHBr_3$ were trended similarly (shape of attenuation curve) to

$CHCl_2Br$ and $CHClBr_2$. Potential TTHM concentrations were calculated by summing the trended values for THM. Refer to Figure 3-5.

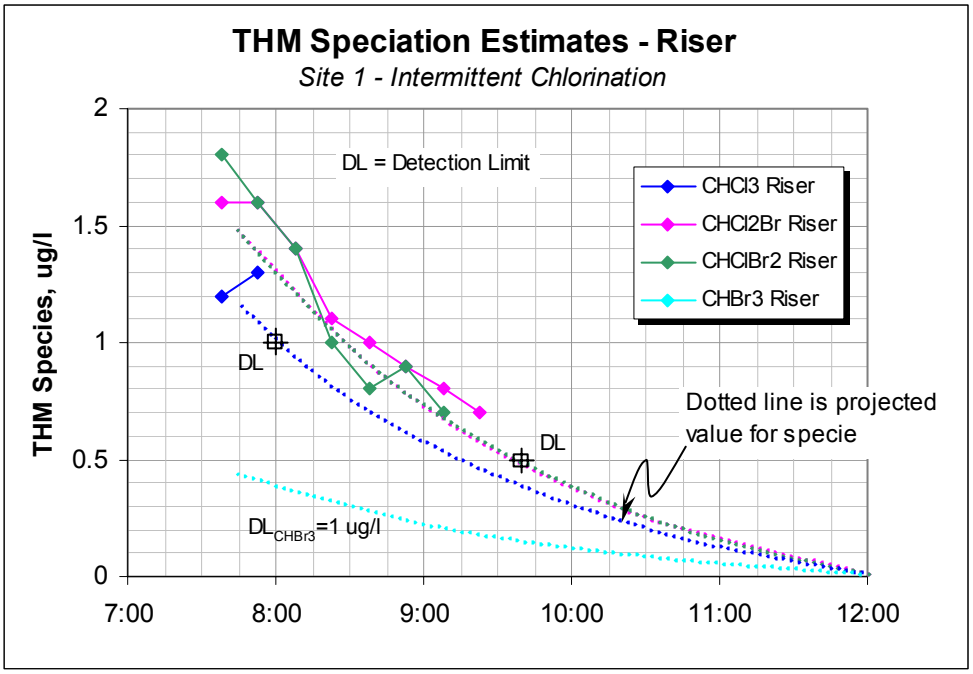

Figure 3-3
THM Speciation Estimates – Riser

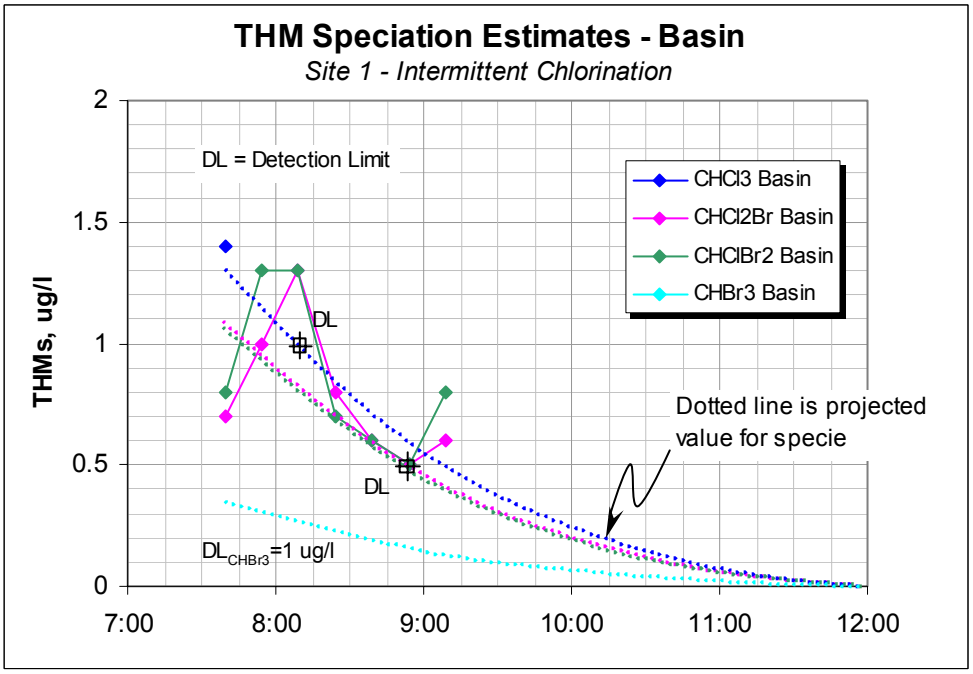

Figure 3-4
THM Speciation Estimates – Basin

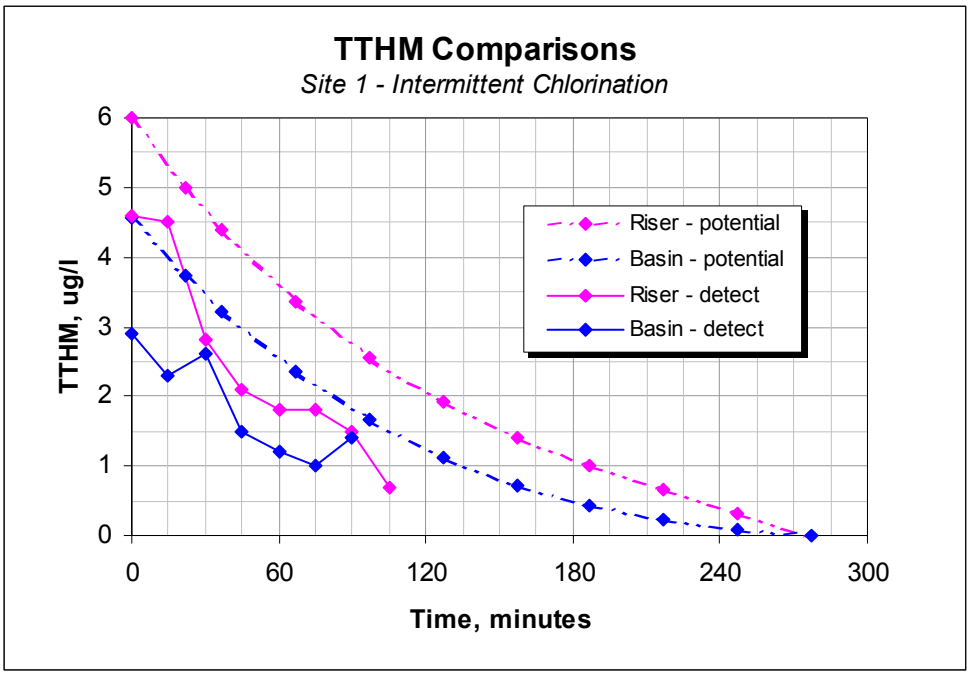

Figure 3-5
TTHM Comparisons

3.2.5 THM Generation

THM generation was estimated by measuring the TTHM lost to the air stream, i.e. the difference in the riser and basin concentrations. Recall that blowdown was valved closed during and after chlorination for two hours when THM concentrations were at their greatest. The amount of TTHM lost to the air stream was calculated by applying the difference in TTHM concentration from the riser to the basin and cooling tower circulating flow rate. Refer to Figures 3-3 and 3-4. The estimated generation of TTHM during and after chlorination using the sampling results (at or just above the detection limit for a period of 1.75 hours) was approximately 60 grams. Based on potential concentrations, the generation of TTHM was approximately 100 grams with an attenuation period of 4.5 hours. The average and maximum concentrations of TTHM in the air stream from the start of chlorination to complete attenuation (including potential concentrations of THMs) were calculated to be 0.00013 and 0.00022 ppb_{Vol}, respectively.

This calculation shows that TTHM was being generated and lost to the air stream throughout the sampling period (recall that cooling tower blowdown was valved off). The concentration of TTHM in the riser (measured just after chlorine injection was stopped) was measured at 4.6 µg/l (approximately 6.0 µg/l potential concentration). Given that the cooling system volume is 635,000 gallons (2,400,000 liters), this calculates to 11.1 grams of TTHM in the circulating water at the completion of chlorine injection (assuming perfect mixing) or 14.4 grams on a potential basis. If TTHM did not continue to form, the early concentrations in the riser and basin would have dropped off dramatically. Recall, that even with a total air flow of 20,000,000 cubic feet per minute and a system-volume circulation time of five minutes (cooling water volume divided by the circulating rate), a dramatic drop in TTHM concentration would have been

expected. Compounds such as chloroform, which have a relatively high vapor pressure, should readily volatilize into the air stream. Instead of an expected rapid decline in TTHM concentration, the drop was gradual and lasted an estimated four hours. Therefore, THMs were forming in the presence of a FAC residual.

3.2.6 Site 1 Findings

Findings for THM formation and fate at Site 1 follow:

1. Field-measured TTHM concentrations in the riser and basin (as a result of intermittent chlorination) were relatively low – initially, 5 µg/l and 3 µg/l , respectively. Concentrations fell to non-detectable levels in less than two hours.

2. $CHCl_2Br$ and $CHClBr_2$ were the predominant species detected in the riser and the basin (both have a detection level of 0.5 µg/l). Both species occurred at approximately the same concentration throughout the sampling period.

3. $CHCl_3$ was detected in the riser and the basin, but quickly attenuated to non-detectable levels (less than 1 µg/l).

4. $CHBr_3$ was not detected in any of the samples (detection level is 1 µg/l).

5. The equivalent of 21,900 grams of HOCl (55 gallons of 12.5% NaOCl solution injected during 15 minutes of chlorination) generated 60 to 100 grams of TTHM.

6. The average and maximum concentrations of TTHM in the air stream during the sampling period (accounting for potential levels of THM species as well) were calculated to be 0.00013 and 0.00022 ppb_{Vol}, respectively.

7. There was a steady decline in THM riser and basin concentrations over time (in concert with FAC). Therefore, while THMs were volatizing into the air stream, they were also forming in the presence of a FAC residual.

8. Since blowdown was valved off for approximately two hours during and after chlorine injection, TTHM was presumed to be completely removed by the air stream.

3.3 Site 2 TTHM Field Sampling & Test Results

Sampling was conducted at Site 2 on September 11, 2003. Site information in this report was purposefully kept to a minimum to maintain the confidentiality of the plant.

3.3.1 Site 2 Profile

Site 2 utilizes a blend of treated municipal effluent and groundwater for cooling tower make-up. The blend typically consists of 35 to 50 percent of treated effluent for cooling tower make-up. Treated effluent is nitrified, i.e. most of the ammonia is converted to nitrate and nitrite

compounds (NO_3^{-1} and NO_2^{-1}). Nitrification reduces the competition for halogens and minimizes chloramine formation. Also, bromide levels in the make-up were at non-detectable levels (<0.40 mg/l). TOC levels in the source water ranged from 3.1 to 3.7 mg/l. TOC is a measure of organic matter in water and source of methyl groups required for THM formation. Refer to Appendix B for source water and cooling system chemical characteristics.

Activated bromine is typically used for halogenation at Site 2. 12.5 percent NaOCl is blended with 40 percent sodium bromide to generate a mixture of hypobromous acid (HOBr) and hypochlorous acid (HOCl). The plant halogenates continuously to achieve a FAC residual of 0.2 to 0.4 mg/l and TRC of 0.2 to 1.2 mg/l. Oxidation reduction potential (ORP) is continuously monitored to control halogen levels in the circulating water. Activated bromine is injected just upstream of circulating water pumps suction in the forebay located at one end of the cooling tower. Sodium bisulfite ($NaHSO_3$) is used to de-haloginate cooling tower blowdown before it is discharged. Refer to Table 3-4 for Site 2 cooling system information.

At the time the testing was conducted, the sodium bromide feed system was not operable. Therefore, the plant used continuous chlorination via 12.5 percent NaOCl solution to maintain its FAC and TRC residuals during THM testing.

Table 3-4
Cooling System Information

Circulating Pump Flow Rate, gpm	35,000
Number of Circulating Pumps	3
Circulating Pumps in Operation	2
Circulating Flow Rate, gpm	70,000
Approx Cooling Water Volume, gallons	680,000
CT Type	Counter Flow
CT Packing	Film Fill
CT Cycles of Concentration	1.5 to 2.5
Thermal Load (Steam Turbine), MW	104
Approx Blowdown Rate, gpm (calculated)	800 to 2,400
CT Cells	4
Air Flow per cell, ACFM (1)	1,200,000
Total Air flow, ACFM	4,800,000
Approx Circulating Water TDS, mg/l	3,000 to 3,600

Notes.....

1. ACFM = actual cubic feet per minute.

THM samples were collected at the base of one of the four risers (nearest the circulating water pumps). Chlorine samples were also taken from this riser. Basin samples were taken from a sample point just downstream of the circulating water pumps (flow-orifice pit). As with Site 1,

these two sample points were established to determine how much TTHM was lost to the cooling tower air stream.

Samples of cooling tower make-up were also taken since a portion of it is treated municipal effluent. Well water and treated effluent are fed to a large common tank. Water from the tank is then filtered and fed to the cooling towers. Ammonia, bromide, and TOC were measured in this stream as well as the cooling tower (samples taken from the riser). Ammonia, which can occur at high levels in treated effluent, interferes with halogens by forming chloramines and bromamines and thus reduces the concentration of available reactive halogens. Bromides were analyzed to determine their input (if any) to the formation of bromoform compounds. As it turned out, bromides were not detected in any streams (concentrations were always less than 0.40 mg/l), and as stated previously, the sodium bromide feed system was inoperable. Thus the role (if any) of background or added bromide could not be determined. Lastly, TOC, which is an indirect measure of organic compounds in water, is found at much higher levels in municipal effluent than fresh water. Generally, the greater the TOC, the higher the potential for THM formation.

FAC and TRC were monitored with the same portable Hach colorimeter (DPD Method) used at Site 1. Samples were taken on 50-minute intervals throughout the nine-hour sampling period.

THM samples were collected in 40-ml brown-glass VOA (volatile organic acid sample bottle). Each container was pre-preserved with sodium thiosulfate ($Na_2S_2O_3$) to terminate the organic carbon-chlorine-trihalomethane conversion reaction and maintain sample integrity (HCl was used for Site 1). Triplicate samples were labeled, inserted in water-tight zip-lock baggies and immediately placed on ice. TOC was also collected in VOA containers (single samples not triplicates) and stored on ice. Ammonia samples were collected in one-liter plastic bottles pre-preserved with sulfuric acid to prevent gaseous ammonia loss. Bromide samples were collected in 500 ml non-preserved plastic bottles. Ammonia and bromide samples were stored at room temperature. The ice in the chest was always maintained above the samples. Samples were analyzed at Curtis & Tompkins, Ltd. Analytical Laboratory in Berkeley, California. Refer to Table 3-5 for the sampling schedule.

3.3.2 Residual Chlorine Data

Halogenation is maintained in the cooling system at Site 2 on a continuous basis. As stated previously, the sodium bromide system was not operable during the testing, therefore, 12.5 percent sodium hypochlorite was the only disinfectant used. Refer to Figures 3-6 and 3-7 for residual FAC and TRC data.

There was a slight decline in FAC concentrations throughout the sampling period with a “spike” toward the end of the period. TRC decline was more pronounced. There is a possible relationship between plant load and FAC (Figure 3-6). The FAC concentration started to drift downward as load increased and sustained during the daylight hours. As cooling water temperature increases with plant load, HOCl flash off increases (volatility increases with temperature). The notable TRC decline was assumed to be a result of increasing ambient temperature and chloramine flash off. Figure 3-7 shows ammonia with respect to TRC and FAC.

Ammonia followed the decline in TRC concentration. Ammonia (in the form of chloramines) comprised most of the TRC concentration.

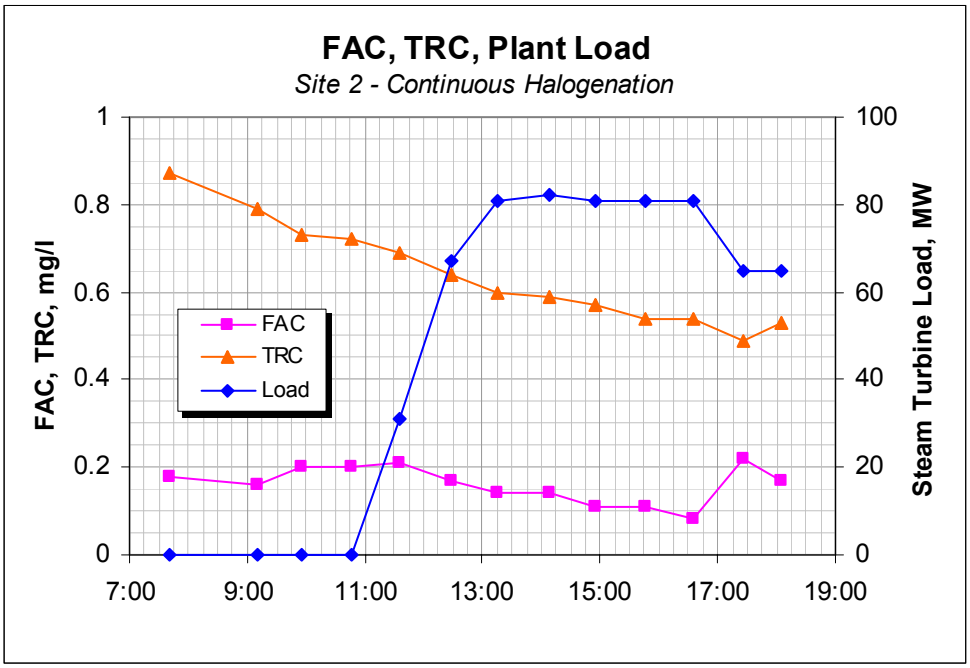

Figure 3-6
FAC, TRC, Plant Load

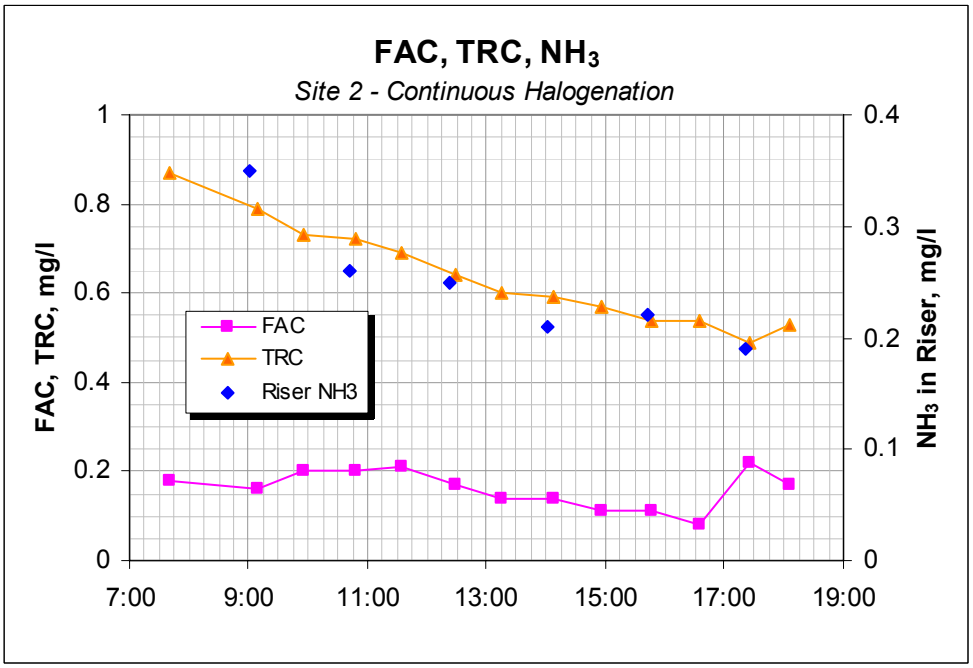

Figure 3-7
FAC, TRC, NH_3

3.3.3 TTHM Data

Results from sampling results for Site 2 can be found in Appendix B, Tables B-3 thru B-11. Analytics include the four THM species (also totalized to TTHM), Total Organic Carbon (TOC), ammonia and bromide.

Figure 3-8 shows the relationship between FAC and detectable TTHM (less-than-detectable concentrations are discussed later). TTHM concentrations in the cooling tower riser and basin generally decreased over time as did FAC. As noted previously there was a spike in FAC concentrations toward the end of the sampling period. While FAC concentrations varied from 0.15 to 0.33 mg/l, detectable levels of TTHM never exceeded 5µg/l. Figure 3-9 shows the relationship between TOC and TTHM in the riser and basin. TOC increased from 4.9 to 6.2 mg/l during the sampling period as a result of a slight increase of cycles of concentration during the sampling period from 2.1 to 2.5 (estimated values). There was no resultant increase in TTHM. From this relationship it appears that TOC provides a passive role in THM formation. TOC at mg/l levels provides enough methyl groups to generate THM at the µg/l concentrations.

Table 3-5
Sampling Schedule – Site 2, September 11,2003

Sequence Number	Steam Turbine MW	Riser		Basin	Make-up	
		FAC, FRC, TTHM, TOC	NH_3, Br	TTHM	TTHM	TOC, Br, NH_3
0	0	7:40 (1)	---	---	---	---
1	0	9:00	9:00	9:15	9:20	9:20
2	0	9:50	---	10:00	10:05	---
3	0	10:40	10:40	10:55	11:00	10:05
4	31	11:30	---	11:40	11:45	---
5	67	12:20	12:20	12:35	12:40	12:40
6	81	1:10	---	1:20	1:25	---
7	81	2:00	2:00	2:15	2:20	2:20
8	81	2:50	---	3:00	3:05	---
9	81	3:40	3:40	3:55	4:00	4:00
10	81	4:30	---	4:40	4:45	---
11	65	5:20	5:20	5:35	5:40	5:40
12	65	6:00	---	6:10	6:15	---

Notes.....

1. Only FAC and TRC were analyzed.

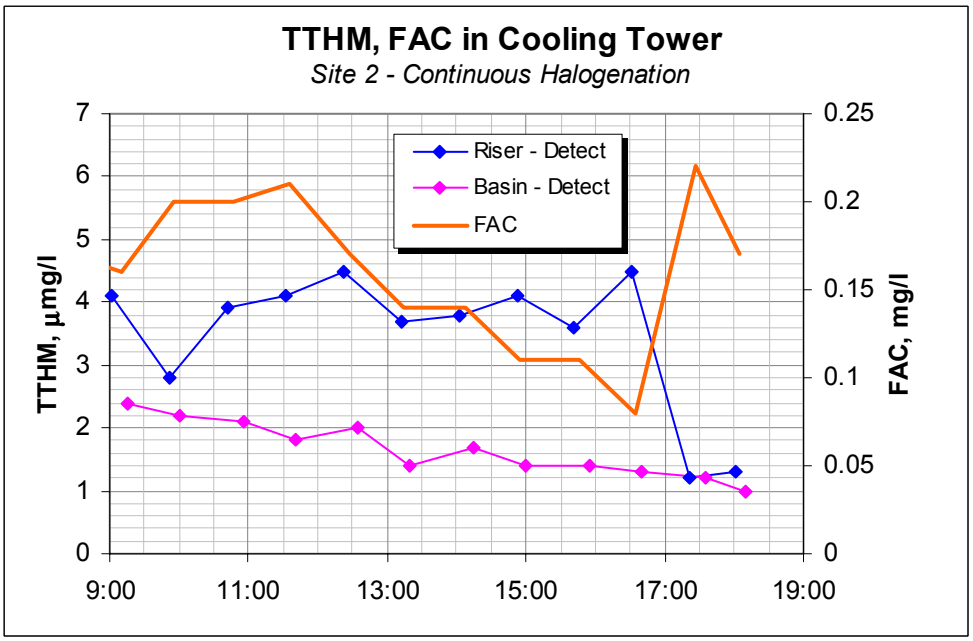

Figure 3-8
TTHM, FAC in Cooling Tower

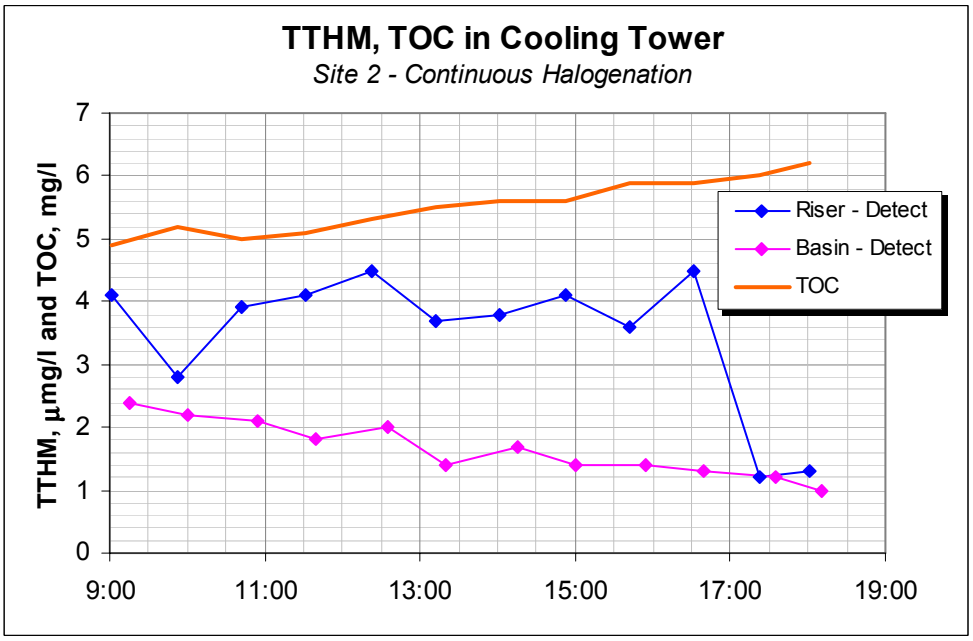

Figure 3-9
TTHM, TOC in Cooling Tower

3.3.4 THM Generation

Refer to Figures 3-10 through 3-13 for THM specie analysis of cooling tower riser, basin and make-up streams. $CHCl_3$ was the predominant specie of THM in the riser. $CHBr_3$ was not detectable in the riser or the basin, but was detected in the make-up stream. Refer to Figure 3-10. Chloroform was the only detectable specie in the basin, i.e. the measurable amounts of $CHCl_2Br$ and $CHClBr_2$ were apparently released to the air stream. Refer to Figure 3-11. Basin concentrations represent THM levels in cooling tower blowdown. Of note are the THM concentrations in the cooling tower make-up water. $CHCl_3$ concentrations in the make-up are twice that of the concentrations in the riser and $CHCl_2Br$ and $CHClBr_2$ levels are ten times that of the riser. Refer to Figure 3-12. $CHBr_3$ was also measurable in the make-up water. Figure 3-13 shows TTHM levels in make-up water.

There was no significant difference between detectable and potential concentrations in the cooling tower riser. Refer to Figure 3-14. With the exception of bromoform, all species were detectable in the riser. As the water left the basin, there was a greater difference between potential and measurable concentrations of TTHM since all species with the exception of chloroform were non detectable. It also points to the fact that constant low levels of halogens (in this case HOCl) can create sustained low levels of THM in the cooling circuit.

Figure 3-15 schematically shows where TTHM enters and exits the cooling system. A mass balance follows:

Cooling System Stream	Stream	Input/Output 9:00 to 18:15	Pct Emitted by Stream
Make-up	A	29 – 30 grams	N/A
Blowdown	B	21 – 50 grams	13.7% - 17.0%
Air Stream	C	161 – 274 grams	86.3% - 83.0%
TTHM Formation	B+C-A	153 – 294 grams	N/A

Relative to the TTHM formed during the nine-hour sampling period, the amount in the feed stream is somewhat negligible. Most of the THM leaving the cooling tower exited via the air stream – 83.0 to 86.3 percent. The remaining THM presumably left the cooling tower in the blowdown stream – 13.7 to 17.0 percent. Blowdown was estimated from operating data supplied by the plant.

Figure 3-16 shows the estimated concentration of TTHM in the air stream based on the difference of detectable levels between the riser and basin. The concentration of TTHM in the riser is superimposed in the graph to show the direct relationship between the two concentrations. The average concentration of TTHM in the air stream was calculated to be 0.60 $\mu g/l_{Vol}$ during the sampling period.

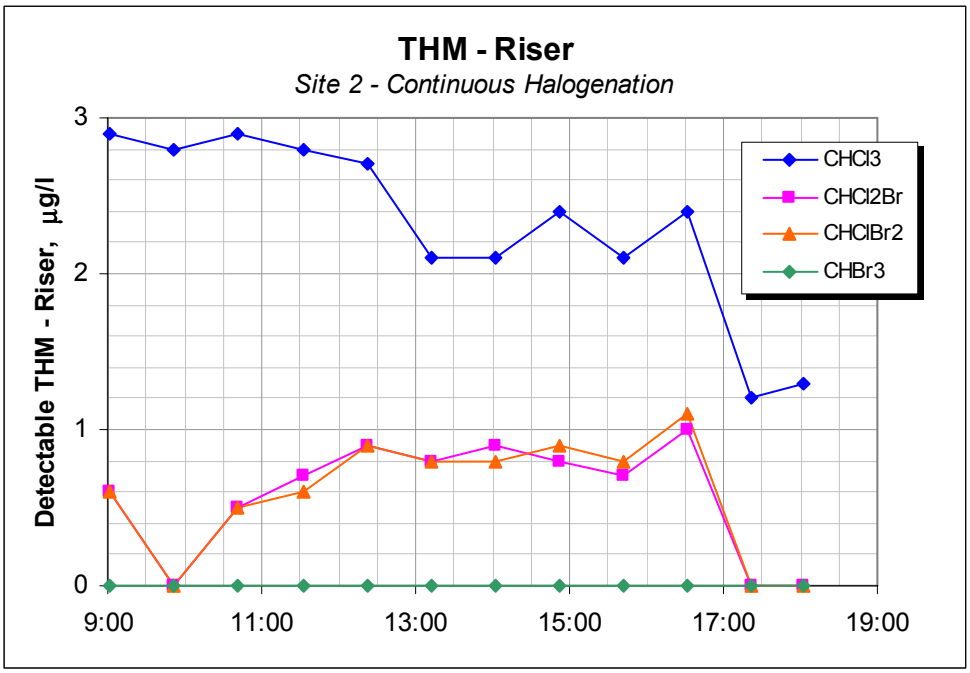

Figure 3-10
THM – Riser

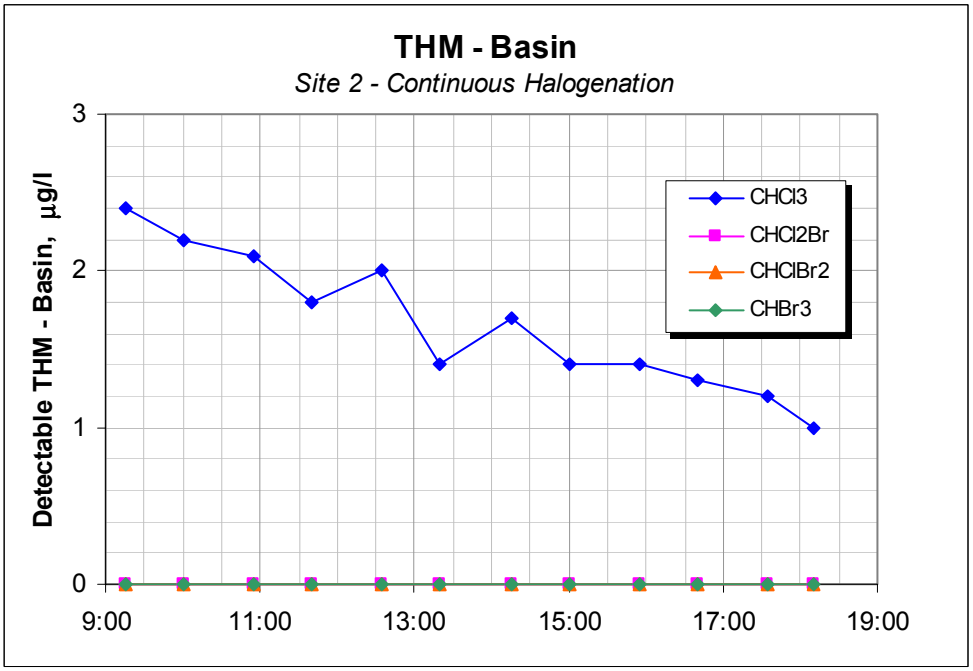

Figure 3-11
THM – Basin

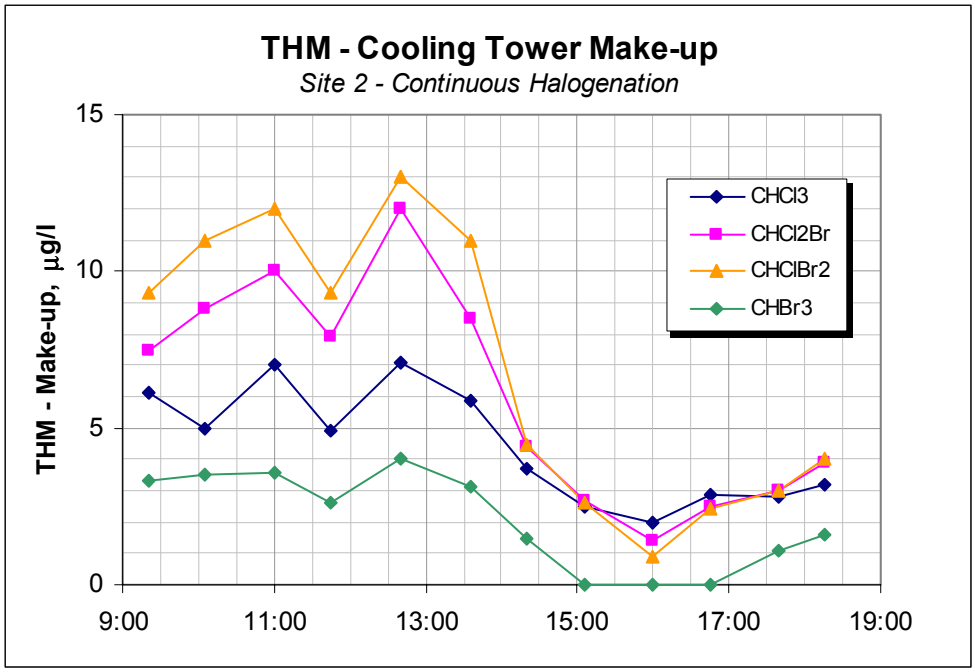

Figure 3-12
THM – Cooling Tower Make-up

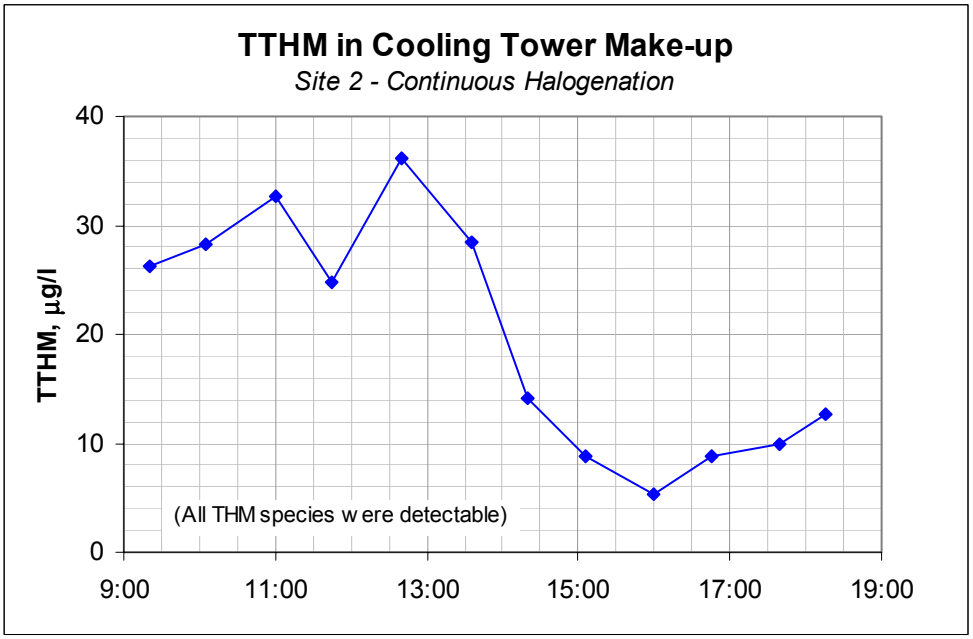

Figure 3-13
TTHM in Cooling Tower Make-up

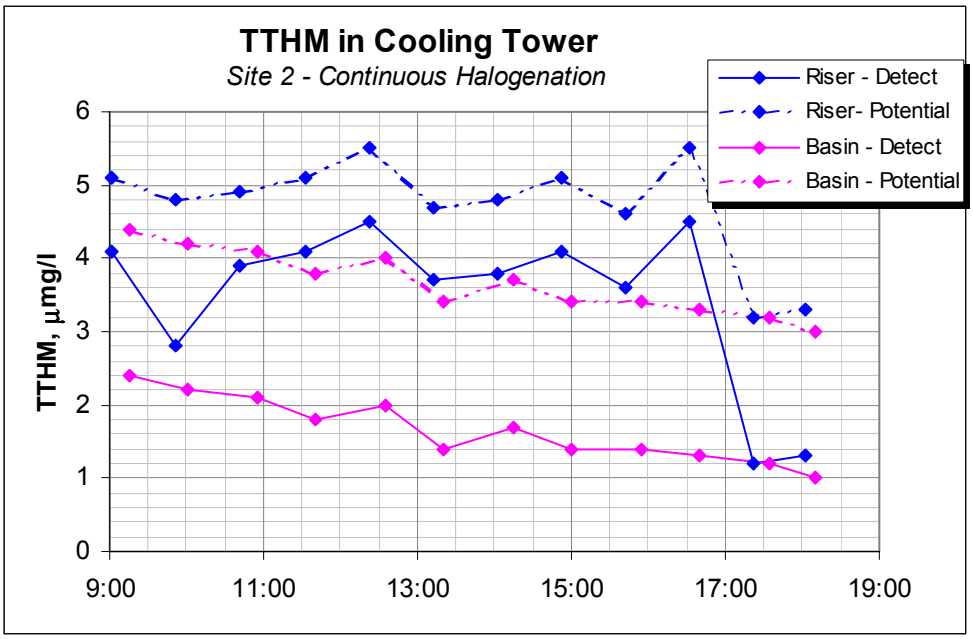

Figure 3-14
TTHM in Cooling Tower

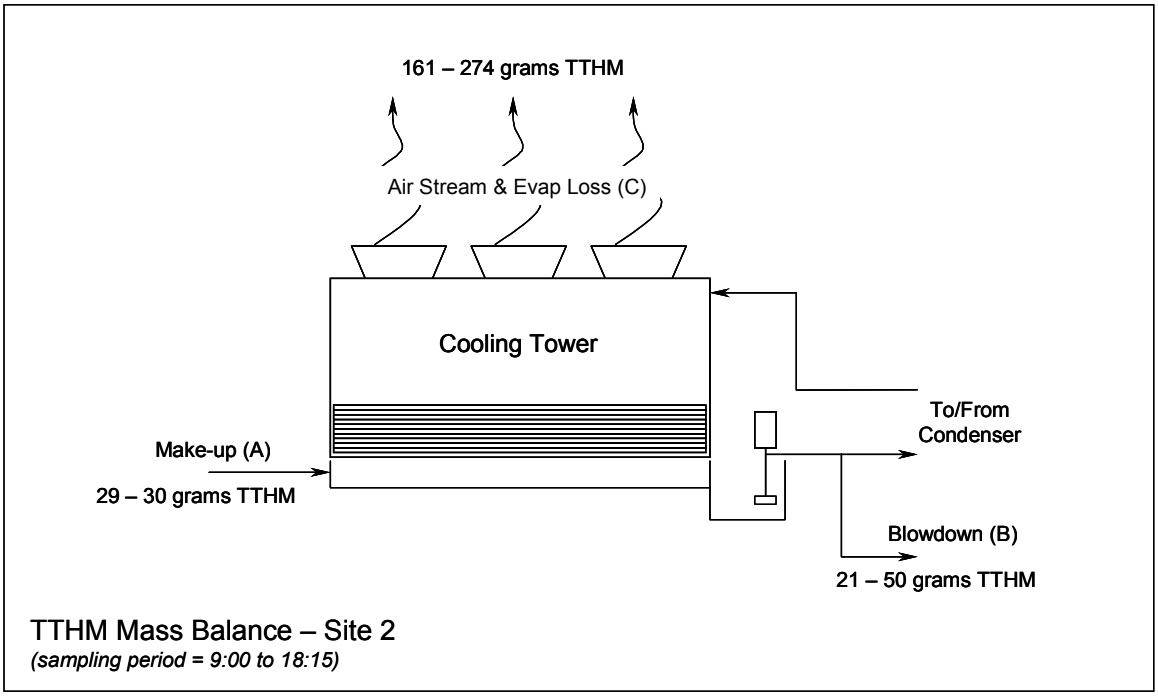

Figure 3-15
TTHM Mass Balance – Site 2

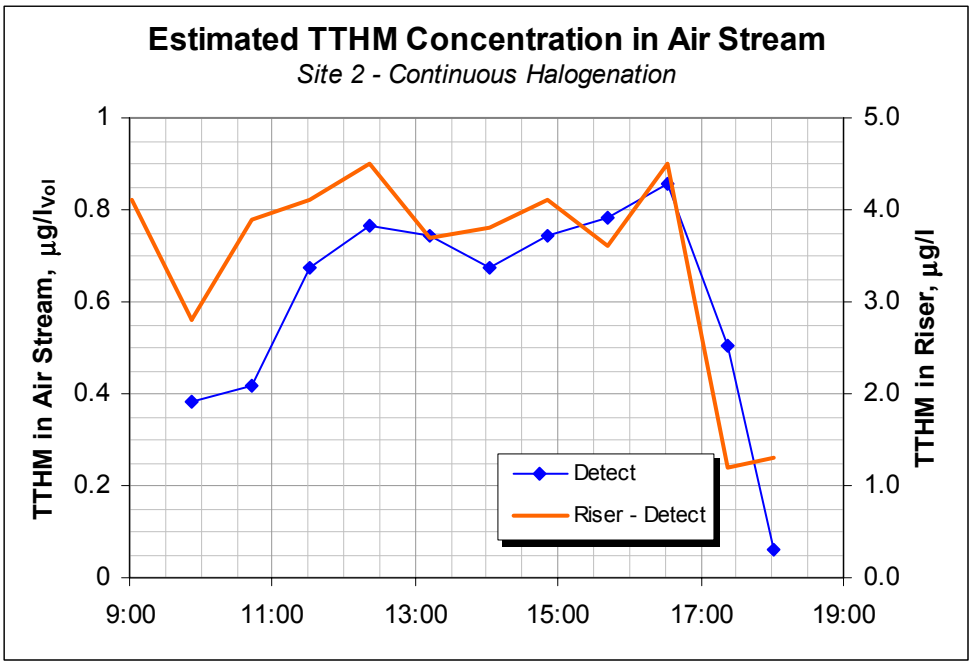

Figure 3-16
Estimated TTHM Concentration in Air Stream

3.3.5 Site 2 Findings

Findings for THM formation and fate at Site 2 follow:

1. Field-measured TTHM concentrations in the risers and basin (as a result of continuous halogenation – in this case chlorination) were relatively low and always measurable. Concentrations in the riser and basin varied from 5 µg/l and 1 µg/l.

2. $CHCl_3$ dominated the THM concentrations in the riser. Recall that $CHCl_2Br$ and $CHClBr_2$ were the predominant species detected in the cooling tower riser (and basin) at Site 1.

3. $CHCl_3$ was the only detectable THM specie in the basin, i.e. all other species volatilized to the air stream.

4. TTHM in the make-up water was relatively high (average concentration of 19.4 µg/l) and all four THM species were present.

5. Over 80 percent of the THM formed in the cooling system exited in the air stream. The balance presumably exited in the blowdown stream.

6. The average concentration of TTHM in the air stream was calculated to be 0.60 $\mu g/l_{Vol}$ during the sampling period.

7. 10 to 20 percent of the THM emitted from the cooling tower (air stream and blowdown) originated from cooling tower make-up.

4
FINDINGS AND CONCLUSIONS

4.1 General

- THMs were formed during halogenation in the two cooling systems studied.
- Models for predicting THM formation in drinking water supplies are not usable for power plant cooling systems.
- There is insufficient information to develop a model of THM formation in cooling towers.
- Intermittent chlorination did not generate a significant amount of TTHM and all of it attenuated to non-detectable levels in several hours.
- Continuous halogenation generated detectable levels of THMs on a continuous basis.
- THM predominantly escapes from the cooling tower in the air stream.
- At both sites, calculated air stream concentrations of TTHM were very low and far below the workplace health-threat level established by OSHA for $CHCl_3$. (ToxFAQs™, 1997)

4.2 Site 1 - Groundwater

- Field-measured TTHM concentrations in the riser and basin (as a result of intermittent chlorination) were relatively low – initially, 5 µg/l and 3 µg/l, respectively. Concentrations fell to non-detectable levels in less than two hours.
- $CHCl_2Br$ and $CHClBr_2$ were the predominant species detected in the riser and the basin. Both species occurred at approximately the same concentration throughout the sampling period.
- $CHBr_3$ was not detected in any of the samples.
- 60 to 100 grams of TTHM were generated during this sampling event.
- The average and maximum concentrations of TTHM in the air stream during the sampling period were calculated to be 0.00013 to 0.00022 $ppbl_{Vol}$, respectively.
- There was a steady decline in TTHM concentrations over time in the riser and basin in concert with FAC.
- Since blowdown was valved off, TTHM was presumed to be completely removed by the air stream.

4.3 Site 2 – Blend of Treated Municipal Effluent and Groundwater

- Field-measured TTHM concentrations in the risers and basin (as a result of continuous halogenation) were relatively low and always measurable – 5 μg/l in the riser and 1 μg/l in the basin.
- $CHCl_3$ dominated the THM concentrations in the riser. $CHCl_2Br$ and $CHClBr_2$ were the predominant species detected in the cooling tower riser (and basin) at Site 1.
- $CHCl_3$ was the only detectable THM specie in the basin.
- THM in the make-up water was relatively high – all four THM species were present.
- Over 80 percent of the THM formed in the cooling system exited in the air stream. The balance presumably exited in the blowdown stream.
- The average concentration of TTHM in the air stream was calculated to be 0.60 $\mu g/l_{Vol}$ during the sampling period.
- 10 to 20 percent of the THM emitted from the cooling tower (air stream and blowdown) originated from cooling tower make-up.

4.4 Further Study

Intermittent chlorination appears to generate very little THM which attenuates quickly to non-detectable levels. No conclusions can be drawn regarding THM formation during continuous bromination utilizing treated municipal effluent, since bromine injection equipment was not operable at Site 2. However, during continuous chlorination at Site 2, the cooling water held a steady residual of THM throughout the sampling period.

The study did not generate enough data to develop a model for THM formation in cooling towers. Based on the study results, it appears that two models are required to predict THM formation:

- Intermittent chlorination and/or bromination for systems using freshwater to model low level THM formation and attenuation
- Continuous chlorination and/or bromination for systems using treated municipal effluent to model steady-residual levels of THM formation and their continuous release to the air stream

Model development should include sampling at a number of sites to generate more data and model parameters.

Possible future work could also include another round of sampling at Site 2 using bromination. Sampling at another power plant with the following characteristics may also be of value:

- Utilizes only reclaimed municipal effluent (Site 2 used a blend of freshwater and reclaimed effluent)
- Municipal effluent contain high levels of ammonia
- Continuous bromination (activated or stabilized) is used for biological control

This plant profile would provide information that was not gained at Sites 1 and 2. The levels of THM generation could be significantly higher. Ammonia interactions with reactive halogens would be noteworthy (even though bromamine is unstable and reverts to HOBr). It would also be of interest to determine THM formation during no-load events when some plant operators stop cooling cells fans. THM levels in the cooling system could increase during these periods.

A
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B
SAMPLING RESULTS

Table B-1
THM Analytical Data Summary – Riser, Site – Intermittent Chlorination

THM Analytical Data Summary - Riser
Site 1 - Intermittent Chlorination

Sample Time	Sequence Number	$CHCl_3$ µg/l	$CHCl_2Br$ µg/l	$CHClBr_2$ µg/l	$CHBr_3$ µg/l	Calc'd TTHM µg/l
6:59 (1)	0	ND	ND	ND	ND	
7:38	1	1.2	1.6	1.8	ND	4.6
7:53	2	1.3	1.6	1.6	ND	4.5
8:08	3	ND	1.4	1.4	ND	2.8
8:23	4	ND	1.1	1.0	ND	2.1
8:38	5	ND	1.0	0.8	ND	1.8
8:53	6	ND	0.9	0.9	ND	1.8
9:08	7	ND	0.8	0.7	ND	1.5
9:23	8	ND	0.7	ND	ND	0.7
9:53	9	ND	ND	ND	ND	
10:23	10	ND	ND	ND	ND	
10:53	11	ND	ND	ND	ND	
11:23	12	ND	ND	ND	ND	
Reporting Limit, µg/l		1.0	0.5	0.5	1.0	

Notes…..

1. Baseline measurement of THMs prior to chlorination.

Table B-2
THM Analytical Data Summary – Riser, Site 1 – Intermittent Chlorination

THM Analytical Data Summary - Riser
Site 1 - Intermittent Chlorination

Sample Time	Sequence Number	$CHCl_3$ µg/l	$CHCl_2Br$ µg/l	$CHClBr_2$ µg/l	$CHBr_3$ µg/l	Calc'd TTHM µg/l
7:40	1	1.4	0.7	0.8	ND	2.9
7:54	2	ND	1.0	1.3	ND	2.3
8:09	3	ND	1.3	1.3	ND	2.6
8:24	4	ND	0.8	0.7	ND	1.5
8:39	5	ND	0.6	0.6	ND	1.2
8:54	6	ND	0.5	0.5	ND	1.0
9:09	7	ND	0.6	0.8	ND	1.4
9:24	8	ND	ND	ND	ND	
9:54	9	ND	ND	ND	ND	
10:24	10	ND	ND	ND	ND	
10:54	11	ND	ND	ND	ND	
11:24	12	ND	ND	ND	ND	
Reporting Limit, µg/l		1.0	0.5	0.5	1.0	

Table B-3
THM Analytical Data Summary – Riser, Site 2 – Continuous Halogenation

THM Analytical Data Summary - Riser
Site 2 - Continuous Halogenation

Sequence Number	Date	Sample Time	TTHM Range µg/l	µg/l	$HCCl_3$ µg/l	$HCCl_2Br$ µg/l	$HCClBr_2$ µg/l	$HCBr_3$ µg/l
1	9/11/2003	9:02	4.1	5.1	2.9	0.6	0.6	ND
2	9/11/2003	9:52	2.8	4.8	2.8	ND	ND	ND
3	9/11/2003	10:42	3.9	4.9	2.9	0.5	0.5	ND
4	9/11/2003	11:32	4.1	5.1	2.8	0.7	0.6	ND
5	9/11/2003	12:22	4.5	5.5	2.7	0.9	0.9	ND
6	9/11/2003	13:12	3.7	4.7	2.1	0.8	0.8	ND
7	9/11/2003	14:02	3.8	4.8	2.1	0.9	0.8	ND
8	9/11/2003	14:52	4.1	5.1	2.4	0.8	0.9	ND
9	9/11/2003	15:42	3.6	4.6	2.1	0.7	0.8	ND
10	9/11/2003	16:32	4.5	5.5	2.4	1.0	1.1	ND
11	9/11/2003	17:22	1.2	3.2	1.2	ND	ND	ND
12	9/11/2003	18:02	1.3	3.3	1.3	ND	ND	ND
			Reporting Limit		1.0	0.5	0.5	1.0

Table B-4
THM Analytical Data Summary – Basin, Site 2 – Continuous Halogenation

THM Analytical Data Summary - Basin
Site 2 - Continuous Halogenation

Sequence Number	Date	Sample Time	TTHM Range µg/l	µg/l	$HCCl_3$ µg/l	$HCCl_2Br$ µg/l	$HCClBr_2$ µg/l	$HCBr_3$ µg/l
1	9/11/2003	9:15	2.4	4.4	2.4	ND	ND	ND
2	9/11/2003	10:00	2.2	4.2	2.2	ND	ND	ND
3	9/11/2003	10:55	2.1	4.1	2.1	ND	ND	ND
4	9/11/2003	11:40	1.8	3.8	1.8	ND	ND	ND
5	9/11/2003	12:35	2.0	4.0	2.0	ND	ND	ND
6	9/11/2003	13:20	1.4	3.4	1.4	ND	ND	ND
7	9/11/2003	14:15	1.7	3.7	1.7	ND	ND	ND
8	9/11/2003	15:00	1.4	3.4	1.4	ND	ND	ND
9	9/11/2003	15:55	1.4	3.4	1.4	ND	ND	ND
10	9/11/2003	16:40	1.3	3.3	1.3	ND	ND	ND
11	9/11/2003	17:35	1.2	3.2	1.2	ND	ND	ND
12	9/11/2003	18:10	1.0	3.0	1.0	ND	ND	ND
				Reporting Limit	1.0	0.5	0.5	1.0

Table B-5
THM Analytical Data Summary – Make-up Water, Site 2 – Continuous Halogenation

THM Analytical Data Summary - Make-up Water
Site 2 - Continuous Halogenation

Sequence Number	Date	Sample Time	TTHM Range µg/l	µg/l	$HCCl_3$ µg/l	$HCCl_2Br$ µg/l	$HCClBr_2$ µg/l	$HCBr_3$ µg/l
1	9/11/2003	9:20	26.2	26.2	6.1	7.5	9.3	3.3
2	9/11/2003	10:05	28.3	28.3	5.0	8.8	11	3.5
3	9/11/2003	11:00	32.6	32.6	7.0	10	12	3.6
4	9/11/2003	11:45	24.7	24.7	4.9	7.9	9.3	2.6
5	9/11/2003	12:40	36.1	36.1	7.1	12	13	4.0
6	9/11/2003	13:35	28.5	28.5	5.9	8.5	11	3.1
7	9/11/2003	14:20	14.1	14.1	3.7	4.4	4.5	1.5
8	9/11/2003	15:05	7.8	8.8	2.5	2.7	2.6	ND
9	9/11/2003	16:00	4.3	5.3	2.0	1.4	0.9	ND
10	9/11/2003	16:45	7.8	8.8	2.9	2.5	2.4	ND
11	9/11/2003	17:40	9.9	9.9	2.8	3.0	3.0	1.1
12	9/11/2003	18:15	12.7	12.7	3.2	3.9	4.0	1.6
				Reporting Limit	1.0	0.5	0.5	1.0

Table B-6
TOC Analytical Data Summary – Riser, Site 2 – Continuous Halogenation

TOC Analytical Data Summary - Riser

Site 2 - Continuous Halogenation

Sequence Number	Date	Sample Time	TOC mg/l	RL mg/l
1	9/11/2003	9:02	4.9	0.50
2	9/11/2003	9:52	5.2	0.50
3	9/11/2003	10:42	5.0	0.50
4	9/11/2003	11:32	5.1	0.50
5	9/11/2003	12:22	5.3	0.50
6	9/11/2003	13:12	5.5	0.50
7	9/11/2003	14:02	5.6	0.50
8	9/11/2003	14:52	5.6	0.50
9	9/11/2003	15:42	5.9	0.50
10	9/11/2003	16:32	5.9	0.50
11	9/11/2003	17:22	6.0	0.50
12	9/11/2003	18:02	6.2	0.50

Table B-7
TOC Analytical Data Summary – Make-up Water, Site 2 – Continuous Halogenation

TOC Analytical Data Summary - Make-up Water

Site 2 - Continuous Halogenation

Sequence Number	Date	Sample Time	TOC mg/l	RL mg/l
1	9/11/2003	9:20	3.6	0.50
2	9/11/2003	11:00	3.6	0.50
3	9/11/2003	12:40	3.6	0.50
4	9/11/2003	14:20	3.7	0.50
5	9/11/2003	16:00	3.1	0.50
6	9/11/2003	17:40	3.2	0.50

Table B-8
NH_3 Analytical Data Summary – Riser, Site 2 – Continuous Halogenation

NH_3 Analytical Data Summary - Riser

Site 2 - Continuous Halogenation

Sequence Number	Date	Sample Time	NH_3 mg/l	RL mg/l
1	9/11/2003	9:02	0.35	0.10
2	9/11/2003	10:42	0.26	0.10
3	9/11/2003	12:22	0.25	0.10
4	9/11/2003	14:02	0.21	0.10
5	9/11/2003	15:42	0.22	0.10
6	9/11/2003	17:22	0.19	0.10

Table B-9
NH_3 Analytical Data Summary – Make-up Water, Site 2 – Continuous Halogenation

NH_3 Analytical Data Summary - Make-up Water

Site 2 - Continuous Halogenation

Sequence Number	Date	Sample Time	NH_3 mg/l	RL mg/l
1	9/11/2003	9:20	0.21	0.10
2	9/11/2003	11:00	0.19	0.10
3	9/11/2003	12:40	0.17	0.10
4	9/11/2003	14:20	0.17	0.10
5	9/11/2003	16:00	0.17	0.10
6	9/11/2003	17:40	0.17	0.10

Table B-10
Br Analytical Data Summary – Riser, Site 2 – Continuous Halogenation

Br Analytical Data Summary - Riser

Site 2 - Continuous Halogenation

Sequence Number	Date	Sample Time	Br mg/l	RL mg/l
1	9/11/2003	9:02	ND	0.40
2	9/11/2003	10:42	ND	0.40
3	9/11/2003	12:22	ND	0.40
4	9/11/2003	14:02	ND	0.40
5	9/11/2003	15:42	ND	0.40
6	9/11/2003	17:22	ND	0.40

Table B-11
Br Analytical Data Summary – Make-up Water, Site 2 – Continuous Halogenation

Br Analytical Data Summary - Make-up Water

Site 2 - Continuous Halogenation

Sequence Number	Date	Sample Time	Br mg/l	RL mg/l
1	9/11/2003	9:20	ND	0.40
2	9/11/2003	11:00	ND	0.40
3	9/11/2003	12:40	ND	0.40
4	9/11/2003	14:20	ND	0.40
5	9/11/2003	16:00	ND	0.40
6	9/11/2003	17:40	ND	0.40