The Pennsylvania State University

The Graduate School

Department of Civil and Environmental Engineering

DISINFECTION BYPRODUCT PRECURSORS FROM WASTEWATER ORGANICS: FORMATION POTENTIAL AND INFLUENCE OF BIOLOGICAL TREATMENT PROCESSES

A Dissertation in

Environmental Engineering

by

Hao Tang

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2011

The dissertation of Hao Tang was reviewed and approved* by the following:

John M. Regan
Associate Professor of Environmental Engineering
Dissertation Co-Advisor
Co-Chair of Committee

Yuefeng F. Xie
Professor of Environmental Engineering
Dissertation Co-Advisor
Co-Chair of Committee

Brian A. Dempsey
Professor of Environmental Engineering

Yen-Chih Chen
Assistant Professor of Environmental Engineering

Peggy A. Johnson
Professor of Civil Engineering
Head of the Department of Civil and Environmental Engineering

*Signatures are on file in the Graduate School

ABSTRACT

Wastewater organics are an important source of various disinfection byproduct (DBP) precursors in downstream potable water supplies. Because of the various biological treatment processes adopted at wastewater treatment plants (WWTPs), the effluents may have a wide range of qualities, especially in DBP precursors. To minimize the risks posed by DBP-related issues, it is necessary to investigate the essence of DBP precursors in wastewater and evaluate the influence of biological treatment processes.

Because conventional practices for evaluating DBP precursors in drinking water cannot be used directly in wastewater due to the complexity of wastewater constituents, a DBP formation potential (FP) quantification method was developed and used for wastewater samples. Sample pretreatment was required to maintain the level of DBPFP and filtration coupled with acidification to pH less than 2 produced stable samples for DBPFP assessment and has advantages for long-term storage. The proposed method for quantification of DBPFP in wastewater is based on the standardized parameters in the chlorination conditions, which include 20 mg/L chlorine dose, pH 7, 25 ℃, and an incubation of 3 days in the dark. Proper dilution is a key to assure that free chlorine residual remains after incubation. It is recommended that the dilution ratio be determined based on the ammonia level. The proposed method was validated by varying chlorine doses and ammonia levels, and could be used to quantify DBPFP for a broad range of wastewater samples.

A survey on DBPFP of treated effluents from various WWTPs was conducted to explore the influence of different biological treatment processes on DBP precursors. The WWTPs that achieved better organic matter removal and nitrification tended to result in low DBPFP in treated effluents. By focusing on a model WWTP that had two biological processes for the same primary effluent treatment, the survey found that haloacetic acid (HAA), trihalomethane (THM) and

chloral hydrate (CH) precursors were in predominant concentrations in wastewater. The combination of trickling filter and modified Ludzack-Ettinger process was more efficient in dissolved organics and DBPFP removal than the activated sludge process. The FPs of haloacetonitriles and haloketones showed the highest removal efficiencies in both systems compared to the FPs of other predominant DBP species such as HAAs and THMs. In addition, WWTP changed the DBPFP speciation profile by lowering the HAAFP/THMFP ratio. The DBP yields and specific ultraviolet absorbance increased after secondary treatment, indicating that the remaining organic matters tend to be more humic. The study implied that oxic and anoxic conditions, soluble microbial products, nitrification, and solid retention time may impact DBPFPs. The study is a comprehensive survey on an assessment of DBP precursor removal efficiencies in a large-scale WWTP.

Three continuously stirred tank reactors (CSTRs) and two sequencing batch reactors (SBRs) were designed to simulate different biological treatment processes in the laboratory. For the three CSTRs, HAAFP decreased as nitrification improved from a poor to a good level. THMFP, however, was not found to be clearly correlated with nitrification. For the two SBRs that were operated at the same SRTs and with complete nitrification, the oxic-anoxic SBR with better denitrification had decreased DBPFP. During an 8-h cycle of an SBR operation, the majority of DBP precursor removal was completed with the bulk removal of wastewater organics. The oxic reactions had a faster removal rate and greater removal efficiency than the anoxic reactions. Although the majority of wastewater organics were removed by biological treatment processes, the remaining organic matter had a higher potential to form DBPs upon chlorination. The study provides information on the effectiveness of wastewater treatment processes on a variety of wastewater parameters, organic matter, and precursors for DBPs. The information can be beneficially used by wastewater and water professionals to minimize the health risks posed by wastewater-derived DBPs.

Materials of human origin (MHOs) are the main constituents of wastewater organics. This research monitored DBPs in an indoor swimming pool over a 1-year period following water change, explored DBPFP from MHOs, and developed a model to simulate DBPs in swimming pool water. As the time since the water change increased, the HAA concentrations increased up to 1650 μg/L while the THM concentrations fluctuated in a range between 40 and 181 μg/L over the 1-year period in the monitored pool. The difference between the concentrations of HAAs and THMs is attributed to three factors: (1) MHOs from pool users; (2) slow HAA reduction; and (3) long water retention. The model developed based on a mass balance and pseudo first-order kinetics achieved a good simulation of a real swimming pool system at long water age. The sensitivity analysis indicates that MHO loadings would impact DBPs in swimming pool water. The research reveals that MHOs contribute to DBP formation and are an important source of DBPs in swimming pools. As MHOs are continuously brought in by swimmers and pools are continuously exposed to disinfectants, pool water represents extreme cases of disinfection that differ from the disinfection of drinking water, and the net-accumulated HAAs could pose negative health risks to human beings. The study can help water professionals to better understand the contribution of MHOs to DBP precursors.

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ACKNOWLEDGEMENTS

This research is made possible by the Pennsylvania State University Office of Physical Plant and Institute of Energy and Environment assistantship.

I would like to express my sincere gratitude to my advisor and life mentor, Dr. Yuefeng Xie. In my life from 20 to 27 years old, I was supported, advised, encouraged, and inspired under his direct guidance. He helped me a lot in a variety of fields such as my course work, research, teaching, networking, and so on. His enthusiasm and achievements in research and teaching give me strong faith of growing into a researcher I want to be.

I'm heartily grateful to my co-advisor, Dr. John Regan. His guidance, patience, and encouragement were indispensible to my journey from the beginning to the end of my study at Penn State University.

I would like to thank Dr. Brian Dempsey and Dr. Yen-Chih Chen for their guidance and serving on my committee. Specifically, I wish to acknowledge Dr. Yen-Chih Chen, for this advice and instructions on many of my projects related to biotechnology.

I'm indebted to all of my colleagues at Environmental Engineering Programs at Penn State Harrisburg, especially Sue Hipple, Mitch Spear, and Alison Shuler, who kindly offer their help on numerous matters.

This dissertation is dedicated to my parents, Zhengwu Tang and Yuelan Lu; my wife, Wen Peng; and my sons, Shunyu (Andy) and Jinyu (Evan). I could not have accomplished this honorable milestone in my life without their love.

Chapter 1

Introduction

DBP-Related Issues from Wastewater Organics

Chlorination is a widely used technique for disinfection of drinking water and wastewater effluents to prevent water-borne diseases such as typhoid, cholera, and dysentery. However, chlorination also produces disinfection byproducts (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs), which have been linked to cancers of the urinary and digestive tracts and a variety of adverse health consequences (Singer, 1999; Boorman et al., 1999). The DBP chemistry and effects of water treatment processes on DBP formation have been discussed (Xie, 2004; Chiang, 2002; Chellam, 2000). Formation of DBPs has been found to be affected by factors such as chlorine dose, chlorination time, pH, temperature, and bromide. It is believed that precursors of DBPs are aquatic organic matter, including humic acids , fulvic acids and other substances, though information on their structures and DBP formation mechanisms are not well understood. They are generally evaluated by formation potential (FP) tests, which maximize DBP formation using a high chlorine dose (Summers et al., 1996).

Because of adverse health effects of DBPs, in drinking water systems, the removal of DBP precursors by utilities is required under the EPA Stage 1 Disinfectants and Disinfection Byproducts (D/DBP) rule (USEPA, 1998), a comprehensive regulation that specifies maximum concentrations for disinfectants and DBPs. To be in compliance with the rule, DBP precursors need to be controlled by a variety of approaches. Among them, enhanced coagulation, lime softening, carbon adsorption, biofiltration, and membrane technologies have shown effectiveness

(Shorney, 1999; Jacangelo et al., 1995; Weiss et al., 2003; Chellam, 2000) in drinking water treatment.

Control of DBP precursors during wastewater treatment has received less attention, since disinfection of wastewater effluents is carried out to prevent the spread of human pathogens rather than for human consumption. Currently, there are no regulations on DBP precursor removal efficiencies by wastewater treatment plants (WWTPs). The National Pollutant Discharge Elimination System (NPDES) discharge limits only regulate some THMs (e.g. chloroform) in WWTP effluents. However, DBP precursors control in wastewater is needed and becoming more and more important, because many treated effluents are indirectly reclaimed as part of water supply in downstream rivers or directly reclaimed by drinking water supplies due to the shortage of fresh water (Tortajada, 2006). Wastewater organics are becoming an important source of pollutants in existing potable water supplies (Chen et al., 2009). When these organics are chlorinated, DBPs are formed. Sirivedhin and Gray (2005a,b) found the wastewater organics are structurally different from the natural organic matter in drinking water, and chlorination of wastewater leads to the formation of various DBPs due to the presence of chlorine-reacting species such as ammonia, organic carbon, organic nitrogen, and bromide at high concentrations. It is expected that high levels of DBPs are formed during chlorination of wastewater effluents, which poses a contamination problem (Rebhun et al., 1997).

Because wastewater organics are a source of various DBP precursors, more attention is given to the DBP-related issues with wastewater, especially the DBP precursor removal by WWTPs:

(1) What are the levels of DBP precursors in raw wastewater and treated wastewater?

(2) Is DBP precursor removal affected by different biological treatment processes adopted by WWTPs?

Many wastewater treatment facilities employ a variety of biological, physical, and chemical processes, which can produce a wide range of treated water qualities in terms of DBP levels, if chlorine disinfection is practiced (Krasner et al., 2008). Few studies have explored DBPs in chlorinated wastewater to date. Krasner et al. (2009b) explored the impact of wastewater treatment processes on DBP precursors and emphasized a profound impact of nitrification on many measures of effluent quality including organic carbon, organic nitrogen, and DBP precursors. Galapate et al. (1999) found that the hydraulic retention time (HRT) and mixed liquor suspended solids (MLSS) were two parameters that could affect THM precursors and chemical properties of organic matter in the effluents of activated sludge processes. Since WWTPs affect wastewater quality in many ways, there is a need for comprehensive studies. For example, the compositions of DBP precursors in wastewater are expected to be different from those found in drinking water, and the fate of DBP precursors during different biological treatment processes has not been studied. It is hypothesized that in addition to the removal of organics, DBP precursors are affected in various ways by different biological treatment processes.

The research herein aims to explore the essence of DBP precursors in wastewater and the influence of biological treatment processes adopted by WWTPs. It is expected that armed with a relatively full understanding of these subjects, we will be able to provide referable information about the capability of DBP precursor removal by WWTPs and to understand the yields and speciation of DBPs in different wastewater. We will also be able to propose favorable design and operational conditions for DBP precursor removal from wastewater, which would better limit the DBP precursors from treated wastewater entering potable water supplies.

Research Summaries

The dissertation mainly focused on the contribution of wastewater treatment processes to DBP precursors. The author developed a reliable method for assessment of DBP precursors in wastewater, evaluated DBP formation potential from wastewater organics, and explored the influence of various biological treatment processes adopted by WWTPs.

The dissertation is composed of six chapters. Chapter 1 describes the author's research summaries. Chapter 2 provides comprehensive background information on DBP precursors from natural organics and wastewater organics. Chapter 3 presents a quantification method to assess DBP precursors in wastewater. Chapter 4 presents results of a survey on DBP precursor removal by various WWTPs and a model WWTP. Chapter 5 is a detailed discussion on the impact of biological treatment processes on DBP precursors. Chapter 6 deals with materials of human origin, a main source of wastewater organics, as DBP precursors.

Quantification of DBPFP in Wastewater

Conventional practices of DBP formation potential (FP) test for drinking water cannot be used directly in wastewater due to the complexity of wastewater constituents. Quantification of DBPFP in wastewater was conducted by several researchers. However, due to different sample preservation and chlorination conditions used, it might be difficult to compare these results. As wastewater samples vary in their characteristics, development of a DBPFP quantification method that can be applied to a broad range of wastewater samples is necessary. The research evaluated three preservation methodologies on wastewater samples: (1) storing samples at 4 ℃ only; (2) filtering samples with 0.45 μm filters and storing at 4 ℃; and (3) filtering samples with 0.45 μm filters, acidifying to pH less than 2, and storing at 4 ℃. Results show that storing samples at 4 ℃

without any pretreatment affected dissolved organic carbon (DOC), Ultraviolet absorbance at 254 nm (UV_{254}), Specific Ultraviolet Absorbance (SUVA), HAAFP and THMFP. This indicates that proper sample pretreatment is required to maintain the level of DBPFP. Filtration coupled with acidification to pH less than 2 has advantages for long-term storage, because it is able to provide the most stable samples for DBPFP assessment. However, both pretreatment methods changed the organic matter constituents which made the samples biased at the beginning. They could not address the DBPFP of the particulate matter and the DBPFP of the organic matter that was lost, likely due to precipitation. The proposed method for quantification of DBPFP in wastewater is based on standardized parameters for chlorination, which include 20 mg/L chlorine dose, pH 7, 25 ℃, and incubation of 3 days in the dark. Proper dilution is a key to assure that free chlorine residual remains after incubation. It is recommended that dilution ratio be determined based on the ammonia level. These dilution ratios were tested on effluent samples from various wastewater treatment plants and were able to produce consistent results. Sample preservation affects the quantification of DBPFP in wastewater. Filtration (0.45 μm) coupled with acidification to pH less than 2 and 4 ℃ storage provides stable levels of DBPFP during long-term storage. However, this pretreatment technique underestimated the original wastewater DBPFP. Proper sample dilution is a key to address sample chlorination conditions. (The research was presented at IWA Micropol & Ecohazard 2011 Conference in Sydney, Australia. It is described in Chapter 3.)

DBPFPs of Wastewater Effluents and Their Removal in WWTPs

The DBPFPs of treated wastewaters from various WWTPs were investigated and the research explored the DBPFP removal by various treatment facilities in a model wastewater treatment plant. Results showed that the WWTPs that achieved better organic matter removal and nitrification resulted in low DBPFPs in treated effluents. HAA, THM, and chloral hydrate (CH)

precursors were in predominant concentrations in wastewater. The chlorinated primary effluent contains 2000 μg/L HAAFP, 1080 μg/L THMFP, and 987 μg/L CHFP. The WWTP removed 82% DBPFP by the activated sludge process and 83% DBPFP by the trickling filter and modified Ludzack-Ettinger process. The haloacetonitrile (HAN) FP and haloketone (HK) FP showed the highest removal efficiencies (95% and 96%) by both systems compared to the FPs of other DBP species. In addition, WWTP could affect the DBPFP speciation profile by lowering the HAAFP/THMFP ratio. The DBP yields and SUVA increased after secondary treatment, indicating that the remaining organic matters tend to be more humic. The survey implies that the oxic & anoxic conditions, soluble microbial products (SMPs), nitrification, and solid retention time (SRT) may impact DBPFPs. (The research is a manuscript in preparation, and is described in Chapter 4.)

Impact of Biological Treatment Processes on DBPFP in Wastewater

To further enhance the understanding of the impact of biological treatment processes on DBPFP in wastewater, bench-scale experiments were carried out to simulate different processes under controlled conditions in the laboratory. Three continuously stirred tank reactors (CSTRs) were designed to achieve various levels of nitrification by varying SRTs, and two sequencing batch reactors (SBRs) were designed to achieve denitrification by oxic-anoxic and anoxic-oxic processes. The five reactors used the same wastewater as influent and were stabilized after more than 180 days of continuous operation under controlled conditions (SRT, HRT, dissolved oxygen, and temperature). The three CSTRs achieved poor, medium, and good levels of nitrification. HAAFPs decreased as nitrification improved from the poor to the good level. THMFPs, however, were not found to be clearly correlated with nitrification. For the two SBRs that were operated at the same SRTs (20 days) and with complete nitrification, the oxic-anoxic SBR with better

denitrification had lower DBPFPs when the two SBRs were compared. During the 8-h cycle of the SBR operation, the DBP precursors of wastewater influent decreased, and the majority of DBP precursor removal was completed with the bulk removal of wastewater organics. Advanced treatment processes including nitrification and denitrification slightly brought down DBP precursors further. The oxic reactions had a faster DBP precursor removal rate and a greater DBP precursor removal efficiency than the anoxic reactions. Although the majority of wastewater organics were removed by wastewater treatment processes, the remaining organic matter had a higher potential to form DBPs upon chlorination. This could be due to two factors: (1) the non-removal of recalcitrant organic matter initially present in wastewater influent; and (2) the production of new DBP precursors that came from SMPs, especially biomass-associated products (BAPs). The study provides information on the effectiveness of wastewater treatment processes on a variety of wastewater parameters, organic matter, and precursors for DBPs. The information can be beneficially used by wastewater and water professionals to minimize the health risks posed by wastewater-derived DBPs. (The research was presented at AWWA 130th Annual Conference in Washington, DC, and is described in Chapter 5.)

Materials of Human Origin as a Source of DBP Precursors

Contribution of wastewater organics to DBPs in drinking water is an important research area because of the increasing wastewater reuse nowadays. Materials of human origin (MHOs) are the main constituents of wastewater organics and they are substantially different from the natural organic matter in drinking water. This research monitored DBPs in an indoor swimming pool over a 1-year period following water change, explored DBPFPs from MHOs, and developed a model to simulate DBPs in swimming pool water. As the time since the water change increased, the HAA concentrations increased up to 1650 μg/L while the THM concentrations were

fluctuating in a range of 40 to 181 μg/L over the 1-year period in the monitored swimming pool. The difference between the concentrations of HAAs and THMs is attributed to three factors: (1) MHOs from pool users; (2) slow HAA reduction; and (3) long water retention. Lab experiments indicate that all MHO samples had high DBPFPs, and MHOs contributed to more HAAs than THMs. The sweat, saliva, skin wash, hair wash, and urine samples had higher DBP yields than NOM. The THM reduction rate coefficient was 0.45 per day while the HAA reduction rate coefficient was 0.023 per day based on the pseudo first order kinetics. There was no net accumulation of THMs taking place in swimming pools. The model developed based on a mass balance and pseudo first-order kinetics achieved a good simulation of a real swimming pool system. Optimized parameters of the model implied approximately 117 ml sweat and 69 ml urine per person were released to the pool. The sensitivity analysis indicates that MHO loadings would impact DBPs in swimming pool water. The experimental results reveal that MHOs contribute to DBP formation and are an important source of DBPs in swimming pools. As MHOs are continuously brought in by swimmers and pools are continuously exposed to disinfectants, pool water represents extreme cases of disinfection that differ from the disinfection of drinking water, and the net-accumulated HAAs could pose negative health risks to human beings. The results can help water professionals to better understand the MHO contribution to DBPs and the fate of DBPs. (The research was submitted to *Water Research*, and is described in Chapter 6.)

Further Research

The methods and tools developed in this research were used to investigate the DBP precursors from dissolved organic matter in wastewater. WWTPs may also produce various qualities of particulate matter. Based on the preliminary research, the particulate matter may also lead to DBP formation upon chlorination. Further research is needed to preserve particulate matter and explore the contribution of particulate matter to DBP formation.

The DBP precursors in wastewater could be characterized based on various fractions of wastewater organics. Further research into the reactivity of each fraction is needed for better characterization of DBP precursors.

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Chapter 2

Literature Review

DBP Precursors from Natural Organics

Disinfection of drinking water and DBP formation

Disinfection kills or inactivates disease-causing organisms and is an important step to ensure that water is safe to drink. Disinfection byproduct (DBP) is a term used to describe a group of organic and inorganic compounds formed during water disinfection (Xie 2004). Since the discovery of DBPs in drinking water in 1970s, numerous researches have been focused on their occurrence, formation, health effects, and control (Karanfil et al., 2008). Because chlorine is still the predominant disinfectant and the bromide levels are low in potable waters, many researches focus on trihalomethane (THMs) and haloacetic acids (HAAs), the two largest classes of halogenated DBPs on weight basis, and their regulations have been well-established and enforced (USEPA, 1998).

The formation of DBPs is briefly illustrated in Eq. 2.1 and 2.2.

Eq. 2.1

$$Cl_2 + H_2O \leftrightarrow HOCl + HCl$$

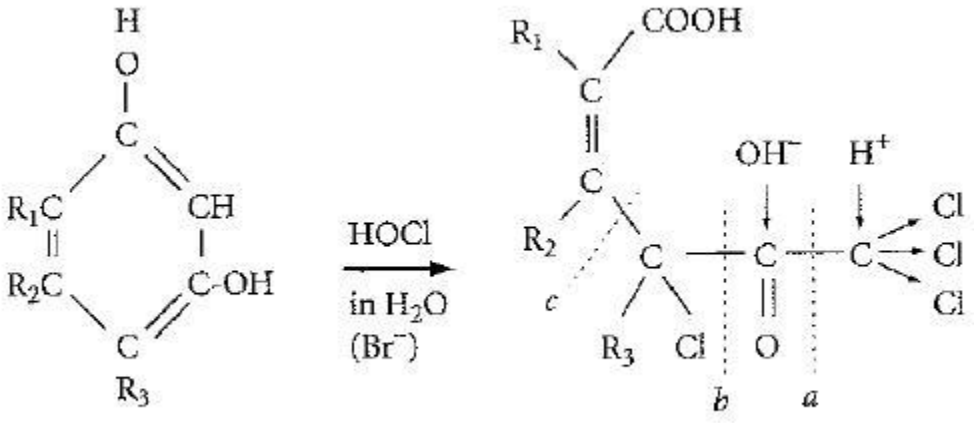
Eq. 2.2

$$HOCl + DBP\ precursor \rightarrow DBPs$$

THMs are obtained by replacing three hydrogen atoms with halogen atoms including chlorine and bromine, and a total of four THMs are formed. They are trichloromethane (chloroform) (CF), bromodichloromethane (BDCM), chlorodibromomethane (CDBM), and tribomomethane (bromoform) (BF).

HAAs are obtained by partially or completely replacing the hydrogen atoms with halogen atoms including chlorine and bromine, and a total of nine HAAs are formed. They are monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetic acid (TCAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), and tribromoacetic acid (TBAA) (Cowman and Singer, 1996).

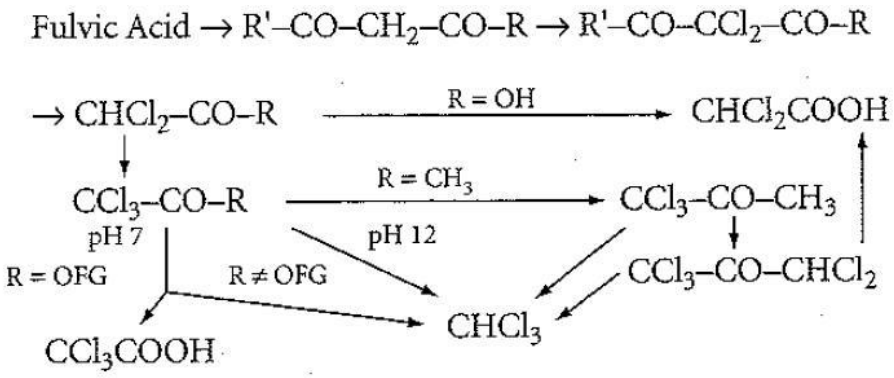
Rook (1977) postulated that the haloform reaction occurred with the resorcinol-type moiety of fulvic acids, a constituent of natural organic matter (NOM). The proposed pathway first involved a fast chlorination of the carbon atoms that are activated by ortho hydroxide (OH) substituents or phenoxide ions in an alkaline environment. Hypochlorous acid (HOCl) is the typical source of electrophilic halogenating species Cl^+. The reaction initially gives the intermediate carbanion, which is rapidly halogenated. After the aromatic structure has been halogenated and opened (Shown in Figure 2-1), cleavage at a will result in formation of THMs. Alternatively, oxidative and hydrolytic cleavages at b will yield an HAA (e.g., TCAA or chloral hydrate). In addition, cleavage at c will result in haloketone (HK) formation.



Source: Adapted from Rook (1977).

Figure 2-2. Haloform reaction with fulvic acids and resorcinol

In the Reckhow and Singer (1985) model (shown in Figure 2-2), oxygenated functional groups (e.g., β-diketone groups) are formed. And the activated carbon will quickly become fully substituted with chlorine. Hydrolysis then occurs rapidly, yielding a monoketone group. If the remaining "R" group is a hydroxyl group, the reaction will stop, yielding DCAA. Otherwise, the structure will be further chlorinated to a trichloromethyl species. This intermediate species is base-hydrolyzable to chloroform. At neutral pH, if the R group is an oxidizable functional group capable of readily donating an electron pair to the rest of the molecule, TCAA is expected to form. In the absence of such as oxidative cleavage, hydrolysis will prevail, yielding chloroform.



NOTE: OFG = oxidizable functional group.
Source: Adapted from Reckhow and Singer (1985).

Figure 2-2. Generalized conceptual model for the formation of major halide products from fulvic acid

Disinfection using chlorine and monochloramine results in different DBP formation. The difference is believed to be due to different formation routes. When using chlorine, the reaction with NOM preferentially forms TCAA in low bromine-containing waters. The formation mechanism with monochloramine is more complex and many models have been proposed in the literature. Karanfil et al. (2007) and Hong et al. (2007) found that the direct reaction between preformed monochloramine and NOM counted for 80% HAA formation while the remaining HAA formation was due to the dissociation of monochloramine to chlorine. Duirk and Valentine (2006) attributed the majority of formed DXAA to the reaction between NOM and chlorine in equilibrium with monochloramine. The presence of bromide complicates the chemistry, because bromide reacts with free chlorine and/or monochloramine to form HOBr-/OBR-, bromamines and bromochloramines (Diehl et al., 2000). They also reported that the formation of THMs and HAAs decreased with an increase in the pH from 6 to 10 and with a decrease in the chlorine-to-ammonia nitrogen (Cl:N) ratio when the bromide concentration increased the production of brominated DBPs.

DBP precursors in drinking water

DBP precursors are sort of materials that react with disinfectants such as chlorine and chloramines, and forms DBPs (Barrett et al., 2000). NOM is a commonly recognized source of DBP precursors in drinking water (White et al., 2003). It typically consists of humic (hydrophobic) substances, such as humic and fulvic acids, and nonhumic (hydrophilic) material, which is often of biological origin. However, it is usually categorized according to its humic content, measured by the specific ultraviolet absorbance (SUVA). Ultraviolet absorbance (UV) and SUVA have been used as surrogates for measuring DBPs as an easier, cheaper and faster approach in different water sources (Goslan et al., 2002; Parsons et al., 2005; Ates et al., 2007). Waters with SUVA of greater than 4 L/mg.m is considered humic while non-humic waters has SUVA of less than 2 L/mg.m (Krasner et al., 2008). Humic waters generally yield more DBPs upon chlorination than non-humic waters.

To better understand these DBP precursors from NOM, researchers have used various methods to fractionate dissolved organic carbon (DOC) into different sub-groups. Thurman and Malcolm (1981) used a series of resins and differentiate DOC into hydrophobic acids, transphilic acids, and hydrophilic constituents. Rosario-Ortiz et al. (2007) used a polarity rapid assessment method (PRAM) to characterize the polarity of DOC using different solid-phase extraction (SPE) sorbent and differentiate it into non-polar, moderate non-polar, moderate polar, and polar substances. Kim and Dempsey (2008) separated DOC based on size and functionality. Based on existing studies, the THM precursors are found to be related with hydrophobic fractions. The DCAA precursors, however, show very little systematic difference among these fractions, because hydrophilic fractions produce a higher level of DCAA compared to other DBPs. Hydrophobic fractions are also responsible for higher reactivity on forming TCAA.

Quantification of DBP precursors in drinking water

The concentrations of DBP precursors need to be quantified in order to better control the formation of DBPs in finished water and distribution systems. Three standardized tests are commonly used for drinking water: the formation potential (FP) test (Xie, 2004), simulated distribution system (SDS) test (Nieminski et al., 1993; Rostad et al., 2000), and uniform formation conditions (UFC) test (Summers et al., 1996). However, the latter two tests were not strictly for DBP precursors, because the SDS and UFC were developed to simulate the DBP formation in distribution system. Only the DBPFP test is good for evaluating the DBP precursors. It is a procedure to assess the levels of precursors rather than the formation of DBPs. The purpose is achieved by adding excess chlorine to ensure the maximum formation of DBPs.

Since the DBP formation can be affected by chlorine dose, chlorination time, temperature and pH, it is important to have the four parameters controlled during the FP test. The standard test conditions are described in Standard Method 5710B (APHA 1998), which controls the chlorine residual in a range of 3-5 mg/L after 7 days incubation at 25±2 ℃ and pH 7. Reckhow (1984) observed a proportional relationship between 3-day and 7-day high dose THMFP concentrations, and other reaction conditions are also used by researcher for quick determination (Hutton, 1992; Li and Chu, 2003; Chu, 2003; Drikas et al., 2008). These conditions include a chlorine dose of 20 mg/L, an incubation time of 3 days, and a temperature of 20 ℃. Since excess chlorine is added (>3 mg/L), the variation of chlorine residuals does not significantly affect the DBPFP (Xie, 2004), and the results are comparable among different systems or laboratories.

Influence of treatment processes on DBP precursors in drinking water

Removal of NOM has been adopted as one of the main mechanisms to remove DBP precursors in drinking water. This has led to the optimization of existing treatment processes and the development of new process which focus on NOM removal. Many studies have determined that some NOM in drinking water cannot be removed by regular processes (Randtke, 1988; Edwards, 1998; Chow et al., 1999, and van Leeuwen, 2002). The remaining organics are referred as recalcitrant organic matter and is primary consisted of low molecular weight hydrophilic neutral organics such as polysaccharides, proteins and amino sugars (Leenheer, 2004; Allpike et al., 2005). These organics exhibit different reactivity with chlorine to produce DBPs.

Chang et al. (2001) characterized the molecular weight distribution of NOM and found that most organics that responsible for the major DBP precursors are small compounds with a molecular weight less than 1kDa. Therefore, effective removal of small molecules prior to disinfection will significantly reduce the DBP formation in finished water. Conventional coagulation is effective in removing large organics, but is limited in eliminating small organics, which have high DBPFP. Therefore, the enhanced coagulation technique is able to provide a decent removal of DBP precursors in drinking water treatment. In addition, powdered activated carbon can be used to remove the low molecular weight organics and taste-odor causing materials in raw water. Uyak et al. (2007) showed that the combination of enhanced coagulation and powdered activated carbon (PAC) adsorption can be more effective than enhanced coagulation alone to meet the Turkish THM limit of 150 μg/L.

In addition, advanced drinking water treatment processes such as nanofiltration (Fu et al., 1994; Chellam, 2000), reverse osmosis (Taylor and Jacobs, 1996), iron exchange (Boyer and Singer, 2005), ozonation and biotreatment (Miltner et al., 1992) are also effective on DBP precursor removal from drinking water.

DBP Precursors from Wastewater Organics

Disinfection of wastewater and DBP formation

Wastewater disinfection is an important public health measure that helps protect human being from exposure to harmful pathogens after treated wastewater is returned to waterways. Although alternative disinfectants such as ozone and UV can be used, many wastewater treatment practices principally rely on the use of chlorine for disinfection due to its availability at a reasonable cost and well established practices.

The DBP formation during the disinfection of wastewater has not yet received much attention, because wastewater is not to be consumed. It is expected that chlorination of wastewater is different from chlorination of water. It involves many reactions due to the presence of various chlorine-reacting species such as ammonia, organic carbon, organic nitrogen, and bromide at substantially high concentrations. These interactions may lead to or interfere with DBP formation (White, 1999). Since more and more treated effluents are indirectly reclaimed as part of water supply in downstream nowadays, the National Pollutant Discharge Elimination System (NPDES) discharge limits regulate some THMs (e.g., chloroform) in WWTP effluents, and investigations on the DBP formation during wastewater disinfection are an important research area.

Yang et al. (2005) explored DBP formation in breakpoint chlorination of wastewater, and found that the concentrations and distribution of THM and HAA species showed variances among different wastewater effluents and different zones of the breakpoint curves of the same wastewater source. Bromide concentrations had great influence on the THM and HAA distribution. The longer reaction time favors the formation of THMs and HAAs, especially the dihalogenated HAAs. Qi et al. (2004) studied factors affecting the formation of HAAs during

monochloramination of wastewater and found the initial Cl:N ratio was related with chlorine demand and HAA formation. The variance observed in the patterns of HAA formation cannot be easily explained by the chlorine chemistry but are likely attributable to the combining effects of the water quality and the characteristics of the organics in the wastewater.

Because of the high chlorine demand of the wastewater organics, wastewater disinfection with chlorine may end up with unintentional chloramination instead of chlorination. The reactions between monochloramine and wastewater organics lead to the formation of other DBPs including haloacetonitriles (HANs), haloketones (HKs), chloropicrin (CP) and N-nitrosodimethylamine (NDMA) (Mitch et al., 2003; Guo and Krasner, 2009) while THMs and HAAs are formed at relatively low concentrations (Krasner et al., 2009a). Common HANs observed in chlorination or chloramination consist of dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN). Major HKs include 1,1-dichloro-2-propanone (1,1-DCP) and 1,1,1-trichloro-2-propanone (1,1,1-TCP) (Krasner et al., 1989). These DBPs including NDMA were found in relatively high concentrations and became an issue particularly in locations where wastewater effluents are used for indirect potable use (Mitch et al., 2003). Since wastewater organics contribute to the formation of various DBPs upon disinfection, it is important to investigate the DBP precursors from those wastewater organics.

DBP precursors in wastewater

Because wastewater organics are sources of various precursors for DBPs (Krasner et al., 2008), adequate knowledge on the characteristics of these organics is critical for the understanding of DBP precursors in wastewater.

Table 2-1 shows the values of typical municipal wastewater characteristics. The term "wastewater characteristics" refers to the partitioning of organic material into biodegradable and

unbiodegradable (inert) portions, the ammonia portion of the total nitrogen and so on (Melcer et al., 2003). Within the biodegradable fraction, the organics are further divided into readily biodegradable and slowly biodegradable compounds. The readily biodegradable compounds are presumed to consist of relatively small molecules (such as volatile fatty acids (VFAs) and low molecular weight carbohydrates, alcohols, peptones and amino acids) (Henze, 1992), which can be easily transported into the cell resulting in an immediate response in the use of electron acceptor (oxygen or nitrate). The slowly biodegradable compounds are assumed to consist of particulate/colloidal material and complex organic molecules, which require extracellular breakdown prior to uptake and utilization (Dold et al., 1980). Dold et al. (1980) also found that filtration (0.45 μm) was able to remove the particulate material, but a significant portion of colloidal materials passed through the filters, because the colloidal material spans a wide range of molecular sizes and weights. Effluent organics are the basis for evaluating plant performance, and they are also made up of a wide range of organic compounds. It can be assumed that the readily biodegradable compounds in wastewater influent have been completely consumed after wastewater treatment, and the remaining organics in the effluents are attributed to the three principle sources: (1) the influent organics (e.g. unbiodegradable compounds); (2) intermediates and end products of various metabolic pathways; and (3) material from cell lysis and death. The latter two sources are the two components of soluble microbial products (SMPs) (Namkung and Rittmann, 1986).

Table 2-2. Typical municipal wastewater characteristic parameter value (Source: Melcer et al., 2003).

Wastewater Characteristic	Concentrations	Concentration Units	Fractions	Fraction Units
Organic Material				
Total COD	250 – 700	g COD m^{-3}	–	–
Readily biodegradable COD	25 – 125	g COD m^{-3}	0.05 – 0.25	g COD / g of total COD
Soluble unbiodegradable COD	20 – 50	g COD m^{-3}	0.04 – 0.16	g COD / g of total COD
Particulate unbiodegradable COD	35 – 110	g COD m^{-3}	0.07 – 0.22	g COD / g of total COD
Slowly biodegradable COD	200 – 400	g COD m^{-3}	0.4 – 0.80	g COD / g of total COD
Nitrogenous Material				
TKN	25 – 70	g N m^{-3}	–	–
Free and saline ammonia	20 – 30	g N m^{-3}	0.50 – 0.75	g N / g TKN
Soluble unbiodegradable TKN	0 – 5	g N m^{-3}	0 – 0.07	g N / g TKN
Biodegradable organically bound TKN	0 – 10	g N m^{-3}	0 – 0.25	g N / g TKN
Particulate unbiodegradable TKN	2 – 8	g N m^{-3}	0.03 – 0.07	g N / g particulate unbiodegradable COD
Phosphorus Material				
TP	4 – 15	g P m^{-3}	–	–
Orthophosphate	2 – 12	g P m^{-3}	0.50 – 0.85	g P / g TP
Soluble unbiodegradable TP	0 – ?	g P m^{-3}	0 – ?	g P / g TP
Biodegradable organically bound TP	0 – 10	g P m^{-3}	0 – 0.25	g P / g TP
Particulate unbiodegradable TP	1 – 4	g P m^{-3}	0.02 – 0.03	g P / g particulate unbiodegradable COD

Sirivedhin and Gray (2005a,b) found the organics in wastewater effluent and NOM were structurally different, and the structurally different organic matrices also behaved differently in the chlorination process. The effluent organic matter was found to be less reactive with chlorine on a DOC concentration basis. Liu and Li (2010) found the biodegradation may effectively remove some DBP precursors, but the biotransformation during the process produces new DBP precursors in the form of SMPs.

Although further information regarding DBP precursors from wastewater organics is scarce, a number of researchers have focused on a major component of wastewater organics – materials of human origin (Judd and Black, 2000; Kim et al., 2002; Judd and Bullock, 2003; Kanan and Karanfil, 2011), which would contribute to DBP formation in chlorinated swimming pool water. However, there is still a need to directly look into the DBP precursors in raw and treated wastewater, and to explore the removal efficiencies by WWTPs.

Quantification of DBP precursors in wastewater

One reason that may limit the investigations into DBP precursors in wastewater is the lack of the standardized method for DBPFP quantification due to the complex constituents of wastewater organics. Wastewater has high levels of ammonia and other inorganic and organic compounds which react with free chlorine. This makes the conventional practices for DBPFP test unadoptable in wastewater because of the high chlorine demand of wastewater and low to none free-chlorine residual after several days of incubation. Using the conventional practices, the halogenated DBPFP of wastewater could easily be under-estimated. In addition, wastewater is not biologically stable (Sundstrom and Klei, 1979) and it could undergo a series of biodegradation and DBPFP may change very quickly. To quantify the DBPFP of wastewater, therefore, pretreatment strategies are also needed in order to maximally preserve DBP precursors.

Various sample pretreatment strategies were found in literature. Yang et al. (2005) preserved their wastewater samples by lowering the temperature to 4 ℃ before the DBPFP test. Sirivedhin and Gray (2005) and Krasner et al. (2009b) immediately filtered their wastewater samples with 0.45 μm filters before the DBPFP test. Standard Methods 5710 (1998) suggested store samples at 4 ℃ and analyze as soon as possible. Since the Standard Methods 5710 was developed for quantifying DBPFP in drinking water, the pretreatment method may be insufficient. Chlorination conditions, such as temperature, reaction time, chlorine dose and residual, and pH, need to be controlled and standardized. For wastewater, dilution may also be considered as a controlled parameter in chlorination conditions. However, literature also shows a wide selection of strategies. Yang et al. (2005) diluted wastewater samples with 0.01M phosphate buffer at a 1:1.5 volume ratio to buffer the pH at 7, and then initiated chlorination by adding a pre-set chlorine dosage. Samples were incubated at room temperature (21±1 ℃) for 24 hours. Sirivedhin and Gray (2005) buffered each sample at pH 7, chlorinated with an excess of free

chlorine and stored them at 25 ℃ for 7 days. Lee et al. (2007) buffered samples to pH 7 with 5 mM phosphate buffer, and then used an initial dose of 5 mg Cl_2 per mg of DOC with 7-day incubation at 20 ℃. Diaz et al. (2008) employed uniform formation conditions (Summers et al., 1996; Boyer and Singer, 2005) in determining DBPFP in wastewater. Those conditions included 1 ±0.4 mg/L free chlorine residual at pH 8 ±0.2 after 24 ±1 h of incubation at 20 ℃. Krasner et al. (2009a) chlorinated wastewater samples according to organic and inorganic chlorine demand and held them for 24 hours at pH 8.2 and 25 ℃. The standard reaction conditions described in Standard Methods 5710 (APHA, 1998) included free-chlorine residual at least 3 mg/L and not more than 5 mg/L at the end of a 7-day incubation period, and the incubation temperature at 25 ± 2 ℃, and pH at 7 ± 0.2. So far, there is no systematic study on the impact of these non-standardized issues on the quantification of DBPFP in wastewater. As wastewater samples vary in their characteristics, development of a DBPFP quantification method that can be applied to a broad range of wastewater samples is essential.

Influence of treatment processes on DBP precursors in wastewater

The performance of treatment processes has a significant impact on the removal wastewater organics. It is suspected that DBP precursors may also be affected. These processes could be conducted in a number of ways, and at different scales, for example, batch, continuous-flow, and sequencing batch reactor (SBR) systems. Typically, batch tests would be conducted at laboratory-scale, but continuous-flow and SBR systems could be either laboratory- or full-scale.

In full-scale studies, Krasner et al. (2009a) found that the DBP formation in wastewater is strongly affected by whether or not the WWTP achieved good nitrification. Chlorine addition to poorly nitrified effluents formed low levels of halogenated DBPs but often substantial amounts of NDMA. Chlorination of well-nitrified effluent typically resulted in substantial formation of

halogenated DBPs but much less NDMA. The results may imply that well-nitrified effluents have less DBP precursors than the poorly-nitrified effluents, and the nitrification process during the wastewater treatment play an important role. However, to truly evaluate the levels of DBP precursors, the effects of reactions between chlorine and inorganic nitrogen (e.g. ammonia) need to be minimized, and there should be excess chlorine to ensure the maximum formation of halogenated DBPs.

In a follow-up full-scale study by Krasner et al. (2009b), 23 WWTPs were surveyed on organic carbon, organic nitrogen, and DBP precursors in wastewater effluents. DBPFP (based on reactivity) was measured to determine the levels of DBP precursors in treated wastewater, and they found nitrification reduced the HAA precursors while the THM precursors were relatively unaffected by the level of treatment. The increase in SUVA was attributed to the preferential removal of the less UV-absorbing (nonhumic) fraction of the DOC during biological treatment.

Very often the information available on full-scale plant (flow rate, sludge age, recycle ratio, etc) may be inaccurate or incomplete, and there is a need to operate a laboratory-scale system which allows for more accurate control of these operating parameters.

The continuous-flow systems could be in a plug-flow design or in a form of continuously stirred tank reactor (CSTR). Plug-flow introduces waste at one end, allows it to flow through the length of the reactor, and the treated effluent exits the other end. In a CSTR, the contents of the reactor are mixed and the concentration of the material in the reactor is equal to that in the effluent exiting the reactor. In terms of laboratory-scale systems, the fill-and-draw SBR system has a few advantages over the continuous flow systems: (1) less equipment is required; (2) no settling tank is needed; (3) Simple to operate; and (4) More accurate control of sludge age. The CSTR has advantages, too. Kim et al. (2002) found that continuously fed lab-scale CSTRs were more stable during variable organic loading rates than reactors which were instead fed once at a time.

The suspended growth systems (e.g. activated sludge) generally adopted by WWTPs are usually in the form of CSTR. CSTRs are operated with continuous feeding, mixing, and wasting so that ideally the concentrations of substrate and active biomass are equal throughout the reactor, and the biomass produced during the treatment equals to those removed from the reactor in the effluent (Rittmann and McCarty, 2001). Part of the wasted biomass may be recirculated back into the reactor to maintain a higher biomass concentration and increase the solid retention time (SRT). CSTRs are also referred to as chemostats, and are frequently used to determine the kinetics of microbial growth and metabolism in laboratory. Grady and Williams (1975) studied a CSTR system without recycle and proposed that the effluent organics are inversely related to the sludge age. Many activated sludge process designs used for biological nitrogen removal have a mixed, non-aerated anoxic reactor in front of the aeration reactor (anoxic-oxic, A/O) to achieve the denitrification. There are numerous other designs (Rittmann and McCarty, 2001), such as O/A, A2O, and various modifications for enhanced nutrient removal from wastewater.

Fixed-film reactors (e.g., trickling filter) are different from suspended growth systems like activated sludge. Fixed-film reactors depend on the colonization of an inert support material with a microbial biofilm. Wastewater is spread onto the top of the reactor and flows downward through the bed of the colonized material where treatment takes place with treated effluent exiting the bottom of the reactor. The design allows separation of the hydraulic retention time (HRT) and SRT by retaining active biomass in the reactor. Reactors with immobilized biomass have been reported to withstand the stress of changing substrate loading conditions better than reactors with a flocculent or suspended growth system (Raposo et al., 2004).

So far, there are no adequate studies on DBP precursor removal influenced by different wastewater treatment processes. Both comprehensive full-scale survey and in-depth laboratory-scale investigation are needed to enhance the understandings about the impact of wastewater treatment processes on DBP precursors.

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Chapter 3

Quantification of Disinfection Byproduct Formation Potential in Wastewater

Abstract

Sample pretreatment methods were evaluated to explore their impacts on the quantification of disinfection by-product formation potential (DBPFP) in wastewater. Results showed that pretreatment was required to maintain the level of DBPFP and filtration coupled with acidification to pH less than 2 produced stable samples for DBPFP assessment and had advantages for long-term storage. The proposed method for quantification of DBPFP in wastewater is based on the standardized chlorination parameters, which include 20 mg/L chlorine dose, pH 7, 25 ℃, and 3-day incubation in the dark. Proper dilution is a key to assure that free-chlorine residual remains after incubation. It is recommended that the dilution ratio be determined based on the ammonia level. The proposed method was validated by varying the chlorine doses and ammonia levels. The method could be used to quantify DBPFP for a broad range of wastewater samples.

Keywords: Chlorination; disinfection by-products; formation potential; disinfection by-product precursor; sample pretreatment; wastewater

Material presented in this chapter was presented at IWA Micropol & Ecohazard 2011 Conference in Sydney, Australia.

Introduction

Disinfection of wastewater is required before treated wastewater is discharged into natural water bodies. Chlorination is a commonly adopted disinfection strategy because of its mature practices and low cost. However, it has been known for decades that chlorine readily reacts with aquatic organic matter, or disinfection by-product (DBP) precursors, to form possibly carcinogenic DBPs. Since organic matter is abundant in wastewater, it is crucial to evaluate its DBP formation or DBP precursors. DBP precursors are usually estimated by the DBP formation potential (DBPFP) (Amy et al., 1990; Galapate et al., 1999; Chu et al., 2002). In drinking water, the DBPFP test is conducted according to standardized chlorination conditions, which allows comparison of results between water systems or laboratories (Xie, 2004). These standardized conditions include a chlorine dose of 20 mg/L, an incubation time of 3 days and/or an incubation temperature of 20 ℃ (Xie, 2004). Wastewater is more complicated due to the complexity of its constituents, including high levels of ammonia and other inorganic and organic compounds which react with free chlorine. This makes the drinking water DBPFP test protocol unadoptable in wastewater because of the high chlorine demand of wastewater which results in low to none free-chlorine residual after several days of incubation. In addition, wastewater is not biologically stable and could undergo a series of biodegradation. To quantify the DBPFP of wastewater, therefore, pretreatment strategies are needed in order to maximally preserve DBP precursors.

Quantification of DBPFP in wastewater has been conducted by several researchers (Li and Chu, 2003; Sirivedhin and Gray, 2005; Yang et al., 2005; Lee et al., 2007; Diaz et al., 2008; Krasner et al., 2009b; Song et al., 2010). However, due to different pretreatment and chlorination conditions used, it might be difficult to compare these results. Various sample pretreatment strategies were found in literature. Yang et al. (2005) preserved their wastewater samples by lowering the temperature to 4 ℃ before the DBPFP test. Sirivedhin and Gray (2005) and Krasner

et al. (2009b) immediately filtered their wastewater samples with 0.45 μm filters before the DBPFP test. Standard Methods 5710 (APHA, 1998) suggested storing samples at 4 ℃ and analyzing as soon as possible. Since Standard Methods 5710 was developed for quantifying DBPFP in drinking water, the pretreatment strategy may be insufficient. Chlorination conditions, such as temperature, pH, reaction time, chlorine dose and residual, need to be controlled and standardized. For wastewater, dilution may also be needed. However, literature also shows a wide selection of strategies. For example, Yang et al. (2005) diluted wastewater samples with a 0.01M phosphate buffer at a 1:1.5 volume ratio to pH 7, and then initiated chlorination by adding a pre-set chlorine dose. Samples were incubated at room temperature (21 ±1 ℃) for 24 hours. Sirivedhin and Gray (2005) buffered each sample at pH 7, chlorinated with an excess of free chlorine and stored them at 25 ℃ for 7 days. Lee et al. (2007) buffered samples to pH 7, and then used an initial dose of 5 mg Cl_2 per mg of DOC with 7-day incubation at 20 ℃. Diaz et al. (2008) employed uniform formation conditions, which were conventionally used in drinking water (Summers et al, 1996), for DBPFP assessment in wastewater. Those conditions included 1 ±0.4 mg/L free-Cl_2 residual at pH 8 ±0.2 after 24 ±1 h of incubation at 20 ℃. Krasner et al. (2009a) chlorinated wastewater samples according to organic and inorganic chlorine demand and held them for 24 hours at pH 8.2 and 25 ℃. The reaction conditions described in Standard Methods 5710 (APHA, 1998) included free-chlorine residual at least 3 mg/L and not more than 5 mg/L at the end of a 7-day incubation period, and the incubation temperature at 25 ± 2 ℃, and pH at 7 ± 0.2. Li and Chu (2003) followed the chlorination conditions described in Standard Methods except that an incubation period of 3 days was used. It is important to investigate how these variable conditions affect the quantification of DBPFP in wastewater. As wastewater samples vary in their characteristics, development of a standardized method for DBPFP assessment in wastewater is essential.

The objectives of this study are: (1) to evaluate the effects of pretreatment methods on DBPFP in wastewater, and (2) to propose a method for quantification of DBPFP in wastewater that can be applied to a broad range of wastewater samples.

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Materials and Methods

Chemicals

All chemical solutions were prepared from reagent-grade chemicals or stock solutions. A free chlorine (sodium hypochlorite) stock solution (1000 mg/L) was prepared from 6% sodium hypochlorite and it was periodically standardized using the n,n-diethyl-p-phenylene diamine (DPD) colorimetric method (APHA, 1998). Trihalomethanes (THMs), haloacetic acids (HAAs), and chloral hydrate (CH) were obtained from Supelco (Bellefonte, Pennsylvania, USA). 200 μg/ml of THMs and 200 μg/ml of HAAs in methyl tert-butyl ether (MTBE) and 150 μg/ml of CH in methanol were made as stock solutions for calibration standards.

Wastewater sampling, pretreatment, and characterization

Wastewater samples were collected from various domestic wastewater treatment systems. To evaluate the pretreatment strategies, non-pretreated samples, filtered samples, and filtered & acidified samples were stored at 4 ℃ before further analyses. Filtration (0.45 μm) was conducted immediately on site. Acidification was conducted by adding a few drops of concentrated sulfuric acid to lower the pH to less than 2. To evaluate the effects of filter pore sizes, 0.1 μm, 0.2 μm, and 0.45 μm filters were used during the filtration process. Total organic carbon (TOC) was

measured with a TOC analyzer (O.I. Analytical Model 1010, Maryland, USA). Ammonia nitrogen was measured using the ammonia-selective electrode method (APHA, 1998). A Hewlett Packard 8453 UV/VIS spectrophotometer was used for measuring ultraviolet absorbance at 254 nm (UV_{254}) based on Standard Method 5910B (APHA, 1998).

Dilution and buffering of wastewater

The dilution ratio was determined based on the ammonia level. To evaluate the effects of dilutions, three volume dilution ratios (1:25, 1:12.5, and 1:5) were tested. Two ml of 1 M phosphate buffer (pH 7) was added to a pre-determined volume of a wastewater sample, and the volume was brought up to 250 ml by distilled water.

Chlorination and incubation of wastewater

After dilution, a chlorine dose of 20 mg/L was applied. The amber bottles were sealed with PTFE-lined screw caps without head space for incubation. A 3-day reaction time in the dark was adopted for DBP formation. Temperatures were set to 25 ℃. At the end of the sample incubation, samples were transferred to two 40 ml vials containing granular ammonia chloride to convert free chlorine to combined chlorine. These vials were sealed with PTFE-lined screw caps without head space and stored at 4 ℃ until sample extractions.

DBP analyses

HAA, THM and CH analyses were conducted using modified EPA method 552.3 and 551.1, and their method detection limits were 0.26, 0.06, and 0.005 μg/L, respectively. For HAA

analysis, each 30 ml sample was acidified with 1.5 ml concentrated sulfuric acid and extracted with 3 ml of MTBE spiked with 300 μg/L 1,2-dibromopropane. Approximately 12 g of sodium sulfate was added to enhance the extraction. Then, 1 ml of the MTBE extract was mixed with 1 ml of 10% sulfuric acid/methanol mix, and incubated for two hours at 50 ℃ for HAA derivatization. After derivatization, the solution was back-extracted with 4 ml of 10% sodium sulfate solution to remove excess methanol. For THM and CH analysis, each 30 ml sample was treated using the protocols above excluding pre-extraction acidification and post-extraction methylation.

DBP measurements

The concentrations of DBPs were determined using gas chromatographs (Hewlett Packard 6890) with electron capture detectors. A DB-1 capillary column (30 m × 0.32 mm i.d., 1.0 μm film thickness) was used for THM and CH analyses. A DB-1701 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used for HAA analysis. The temperature ramping programs were as follows: (1) THMs and CH: Initial at 35 ℃ for 22 minutes, ramp to 145 ℃ at 10 ℃/min and hold at 145 ℃ for 2 minutes; (2) HAAs: Initial at 35 ℃ for 10 minutes, ramp to 75 ℃ at 5 ℃/min and hold 16 minutes, a final ramp to 200 ℃ at 25 ℃/min and hold 5 minutes. DBP concentrations were obtained using the calibration curves developed for THMs, HAAs, and CH. Based on replicate analyses, errors in the measurements were less than 10%, and the relative standard deviation was 8.3% for THMs, 8.9% for HAAs, and 6.4% for CH, respectively. The matrix recoveries for DBPs were within 80-120%.

Statistical analysis

Statistical methods were implemented using Minitab version 15 (State College, Pennsylvania, USA). The level of significance was set to $\alpha \leq 0.05$. Analysis of Means (ANOM) was performed to compare DBPFP data obtained between any two different sample pretreatment or chlorination conditions. Mann-Whitney procedure, a nonparametric method was used if the sample sizes were small. Minitab's Homogeneity of Variances Test was used to test whether the two standard deviations of any two populations were different. If the variances were similar, a pooled variance t-test was used. Otherwise, a separate variance t-test was used.

Results and Discussion

Sample Pretreatment

DBP precursors in drinking water and wastewater are of different origins (Krasner et al., 2009a). In drinking water, organic matter is generally stable and DBP formation is correlated with aromatic moieties (Singer, 1999). DBP precursors in wastewater, however, are mostly non-humic organic matter (Chen et al., 2009), and unstable due to bacteriological activities. Therefore, it is crucial to use a pretreatment method for maximum preservation.

This research employed three preservation methodologies for DBP precursors in wastewater: (1) storing samples at 4 ℃ only; (2) filtering samples with 0.45 μm filters and storing at 4 ℃; and (3) filtering samples with 0.45 μm filters, acidifying to pH less than 2, and storing at 4 ℃. Figure 3-1 shows the DBPFP results during a 14-day preservation. The chlorination conditions include pH 7, 25 ℃, 20 mg/L Cl_2 and 3-day incubation in the dark.

During the 14-day preservation at 4 ℃, the TOC of the non-pretreated samples decreased by 19%. In the meantime, the UV_{254} and specific ultraviolet absorbance (SUVA) also changed.

This indicates that the organic matter in non-pretreated samples was unstable at 4 ℃. Since SUVA correlates with DBP formation (Kitis et al., 2001), the DBPFP may also be affected. For the filtered samples and the filtered & acidified samples, TOC only showed slight decrease. Their UV_{254} and SUVA values were relatively stable. This indicates that the two pretreatment strategies preserve organic matter very well. However, it was also found that they reduced the TOC at the very beginning. Results showed that the filtration instantly removed 17% TOC by retaining the particulate matter on the filters, and the acidification instantly removed 14% TOC further due to potential mineralization. Therefore, the organic matter constituents were changed by the pretreatment.

While the DBPFPs were explored, Figure 3-1d and e show that the 4 ℃ preservation without other pretreatment strategies could not preserve DBP precursors well. In the first 5 days of preservation, the HAAFP and THMFP in the non-pretreated samples increased by 32% and 35%, respectively. This indicates that although the bacteriological activities might be limited at 4 ℃, there still existed slow reactions that converted some organic matter to DBP precursors. The possible mechanism is the formation of soluble microbial products (SMPs). The SMPs can react with chlorine and are an important source of wastewater-derived DBP precursors (Liu and Li, 2010). Because some SMPs can be degraded further, the experiments observed a decline of HAAFP and THMFP after 5 days of preservation. Filtration can remove a majority of bacteria. With filtration, increases of HAAFP and THMFP were still observed. However, the increases were not as significant as those of the non-pretreated samples. Filtration coupled with acidification was found to result in most stability on DBPFP. It appears to be an efficient strategy to produce stable samples for DBPFP assessment. However, the method could not address the DBPFP from the particulate matter and the mineralized organics.

Literatures show that different size organic matter fractions, such as particulate organic matter, colloidal organic matter, and dissolved organic matter have different chemical properties (Guo et al., 2003) and different reactivity in forming DBPs (Chow et al., 2006). Filters with a pore size of 0.45 μm are widely used for filtration of wastewater samples. It is believed dissolved organic matter (DOC) remains in the filtrate while suspended solids are retained on filters. Hu et al. (2010) used 0.2 μm filters to eliminate particles. The use of 0.1 μm membrane retains all colloid materials on filter (Roeleveld and van Loosdrecht, 2002). Chow et al. (2005) found that a finer pore size filter is able to provide more homogeneous DOC properties and enables a better characterization of DBP precursors. Therefore, filters with three pore sizes were tested in this study. After filtration with these filters on site, samples were also acidified immediately to maximally preserve DBP precursors. Figure 3-2 shows three major DBPFPs including THMFP, HAAFP, and CHFP in 0.1 μm, 0.2 μm, and 0.45 μm filtered samples. The results indicate that filtration with a finer pore size filter appeared to produce lower DBPFPs. The Mann-Whitney test determined that the difference between 0.1 μm and 0.2 μm and the difference between 0.2 μm and 0.45 μm were 0.1914 and 0.3313, respectively. They were not significant at the significance level of 0.05, although a marginal increase was observed. The 0.45 μm filters were preferably chosen because the 0.45 μm pore size was commonly used as a cutoff point for defining DOC.

By exploring the DBPFP levels in the preserved samples, the research data supports that for longer storage, further pretreatment was required to maintain the level of DBPFP. In addition to the 4 ℃ described in Standard Methods 5710, both filtration (0.45 μm) and acidification (pH<2) could be used for better characterization and maximal preservation of wastewater samples for DBPFP determination.

Chlorination Conditions

The chlorination conditions in the DBPFP test include chlorine dose, pH, temperature, and incubation time. All of them affect the formation of DBPs (Xie, 2004). High pH generally results in a higher level of THM formation but a lower level of HAA formation. High temperature generally results in a higher level of DBP formation. Both 20 ℃ and 25 ℃ have been reported in protocols. In accordance with Standard Methods 5710, the authors recommend selected pH 7 and 25 ℃. The authors also recommend an incubation time of 3 days, which is in accordance with the method generally used for quantification of DBPFP in drinking water.

A chlorine dose of 20 mg/L is normally used since it is sufficient to drive all DBP precursors to DBPs for a broad range of drinking water samples. However, it may not be the case for wastewater. The free-chlorine demand of wastewater could range from tens of milligram per liter to hundreds of milligram per liter. If sufficient chlorine residual is not maintained, DBPFP can be under-estimated (Dieh et al., 2000; Hong et al., 2007). Therefore, dilution becomes a pre-requisite step before chlorine is added.

A well-nitrified effluent sample from Annville Wastewater Treatment Plant (Annville, Pennsylvania, USA) was diluted in three volume ratios (1:25, 1:12.5, and 1:5) during the DBPFP test. The chlorine doses were 20 mg/L, and the free chlorine residuals after incubation were 19.4, 18.5, and 16.0 mg/L, respectively. Figure 3-3a shows that a high dilution tended to result in higher DBPFP, which could be due to the slightly higher chlorine residual. However, dilution also cannot be too low, because the chlorine demand may consume all free chlorine and result in much lower DBPs. Proper dilution has to assure that free-Cl_2 residual remains after incubation and to accommodate individual sample characteristics and laboratory limitations. For the Annville sample, dilution ratios of 1:12.5 and 1:5 were all acceptable, since statistically there were no significant difference between the resulting DBPFPs according to the Mann-Whitney

test. For the poorly-nitrified effluent sample from Middletown Wastewater Treatment Plant (Middletown, Pennsylvania, USA), the dilution ratio of 1:5 was un-acceptable due to the severe under-estimation of DBPFP (Figure 3-3b). The free-Cl_2 residual after 3-day incubation was zero mg/L.

The authors recommend that the dilution ratio be selected based on the concentration of ammonia, which accounts for the majority of inorganic chemical demand in wastewater. Table 3-1 shows the recommendations of the dilution ratios based on different ammonia levels.

Method Validation

Two tests by varying chlorine doses and ammonia levels were designed to validate the proposed method. In the chlorine dose test, two chlorine doses were applied to the samples while other conditions remained the same. Since the ammonia level is a key factor in determining the DBPFP of wastewater, the effects of ammonia need to be explored to validate the proposed method as well. In the ammonia level test, two ammonia levels were spiked to the samples to produce different levels of ammonia while other conditions remained the same. The samples would result in the same DBPFPs after chlorination, if the proposed method was valid.

For the chlorine dose test, the study compared two chlorine doses, including Dose 1 at 20 mg/L and Dose 2 at 20 + 8×(NH_3-N) mg/L. Dose 2 was based on the inorganic (i.e., NH_3) chlorine demand, because for breakpoint chlorination, 7.6 mg Cl_2 was needed to oxidize 1 mg NH_3-N. Dose 2 had included the ammonia level into consideration so that there were sufficient free-Cl2 residual after incubation (Krasner et al., 2009a). Table 3-2 shows the results of DBPFP test on six different effluent samples from wastewater treatment systems. The samples were divided into two groups based on their ammonia content. Group 1 (No. 1-3) had less than 0.5 mg/L NH_3-N, and Group 2 (No. 4-6) had 27.8, 11.9 and 13.2 mg/L NH_3-N, respectively. A 1:5

volume ratio dilution was applied to all the samples. Apparently, when Dose 1 was applied, according to Table 3-1, the dilution was sufficient for Group 1, but was insufficient for Group 2. All samples in Group 2 had zero free-Cl_2 residuals. For the samples of Group 1 which had high free-Cl_2 residuals, the two chlorine doses did not impact DBPFP data. This was because proper dilutions were made and free-Cl_2 residuals were maintained. The variation of chlorine dose does not significantly affect the DBPFP. When Group 2's DBPFP data was explored, chlorine dose was found to be an issue. Because Group 2 did not maintain free-Cl_2 residual due to insufficient dilution, the DBPFP data using Dose 1 was much lower compared to the data obtained by using Dose 2. The results supported that: (1) when wastewater samples had low ammonia concentrations and high free-Cl_2 residuals, both chlorine doses had no significant impact on DBPFP; (2) The 20 mg/L chlorine dose became an issue when wastewater samples had high ammonia concentrations and low free-Cl_2 residual. Therefore, the 1:25-1:50 dilution ratio should be used as suggested by the authors in Table 3-1.

For the ammonia level test, the study compared three levels (low, medium, and high levels) of NH_3-N concentrations. Figure 3-4 shows the DBPFP data of a well-nitrified effluent. Originally, the sample had 0.6 mg/L NH_3-N. Results were obtained after the addition of 0, 5 and 15 mg/L of NH_3-N into the sample before the DBPFP test. The chlorination conditions included pH 7, 25 ℃, 1:10 volume ratio dilution, 20 mg/L chlorine dose, and 3-day incubation in the dark. It was found that, statistically, there was no significant difference among the DBPFPs of the three samples. This indicated that ammonia itself did not impact DBPFP when a proper dilution was made. The impact of ammonia on DBPFP came from the low free-Cl_2 residuals as a result of the high ammonia levels.

Conclusions

The following main conclusions were obtained from this study:

- Sample pretreatment and the selection of filter pore size affected the quantification of DBPFP. Filtration (0.45 μm) coupled with acidification to pH less than 2 provided stable samples for DBPFP assessment and had advantages for long-term storage of wastewater samples.
- The proposed method for quantification of DBPFP in wastewater was based on a series of standardized chlorination conditions, which include 20 mg/L chlorine dose, pH 7, 25 ℃, and 3-day incubation in the dark.
- Proper sample dilution is a key to DBPFP quantification in wastewater. It is an effective way to maintain free-Cl_2 residual after incubation. It is recommended that the dilution ratio be determined based on the ammonia level.
- The proposed method was validated by varying chlorine doses and ammonia levels. The method can be used to quantify DBPFP for a broad range of wastewater samples.

Acknowledgements

This study was supported by Office of Physical Plant and Institutes of Energy and the Environment at the Pennsylvania State University.

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List of Figure and Table Captions

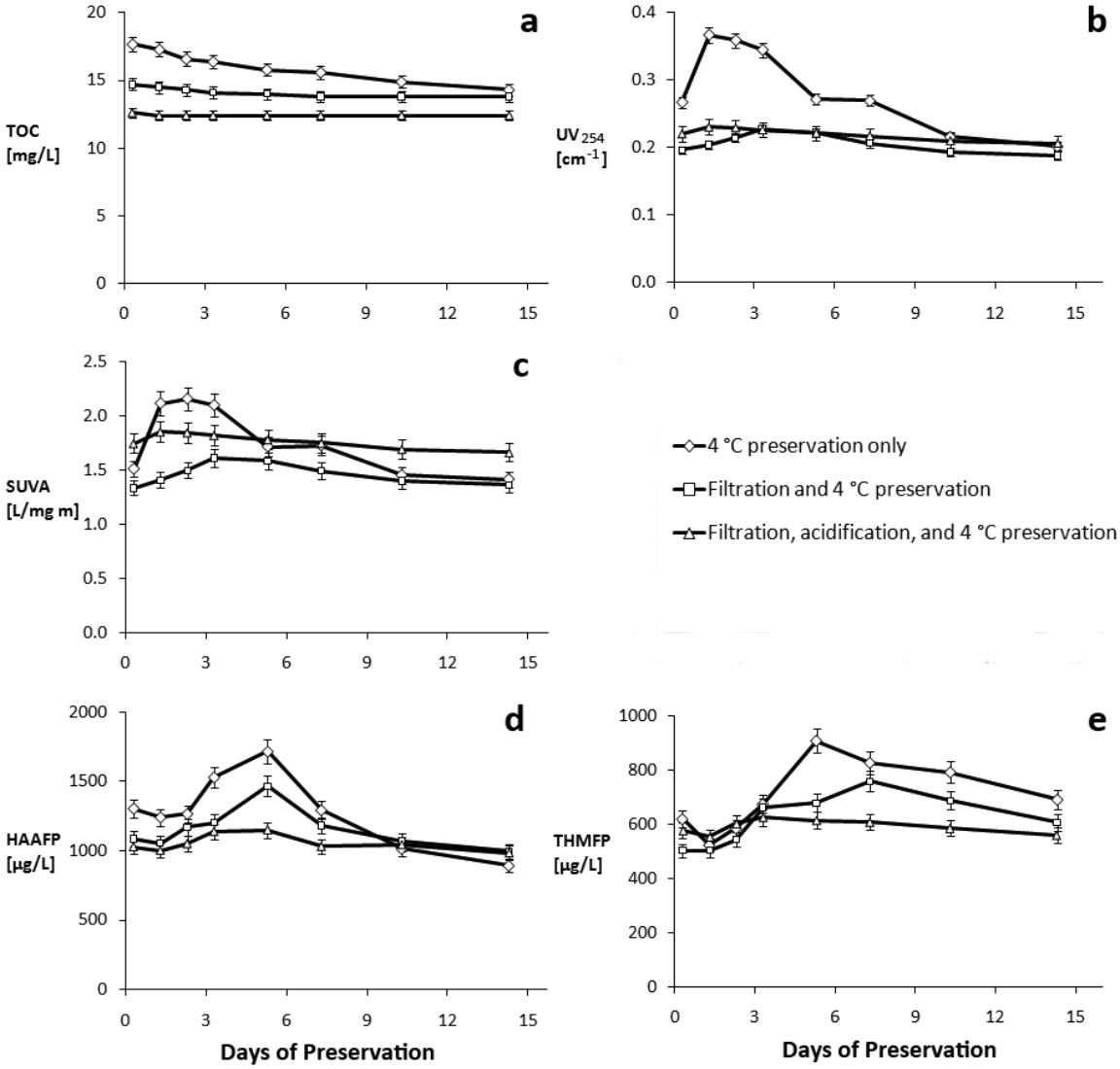

Figure 3-1. Impact of sample pretreatment on DBPFPs of wastewater samples

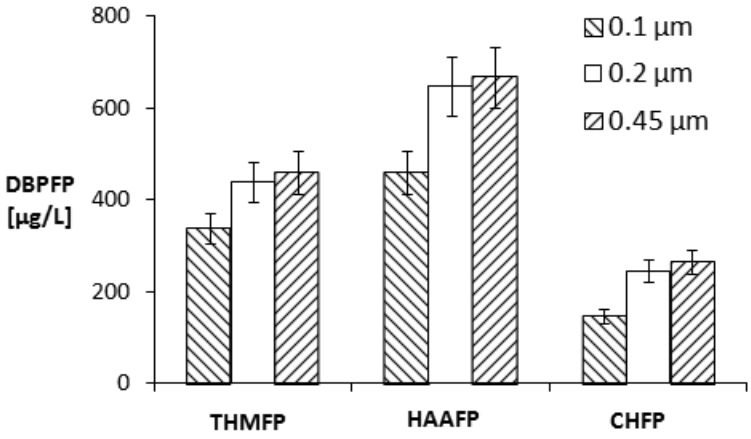

Figure 3-2. Impact of filter pore size on DBPFPs of wastewater samples

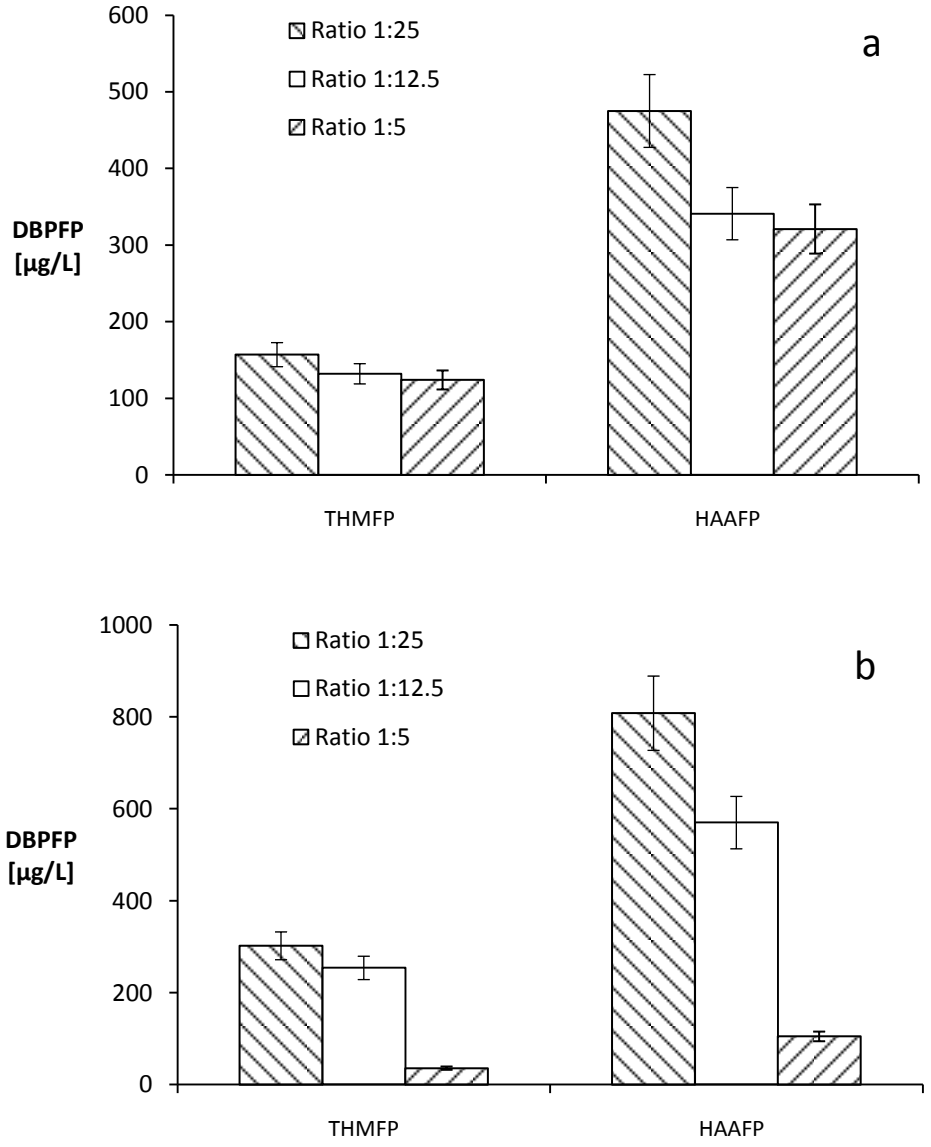

Figure 3-3. Impact of dilution ratio on DBPFPs of wastewater samples: (a) Effluent from Annville Wastewater Treatment Plant; (b) Effluent from Middletown Wastewater Treatment

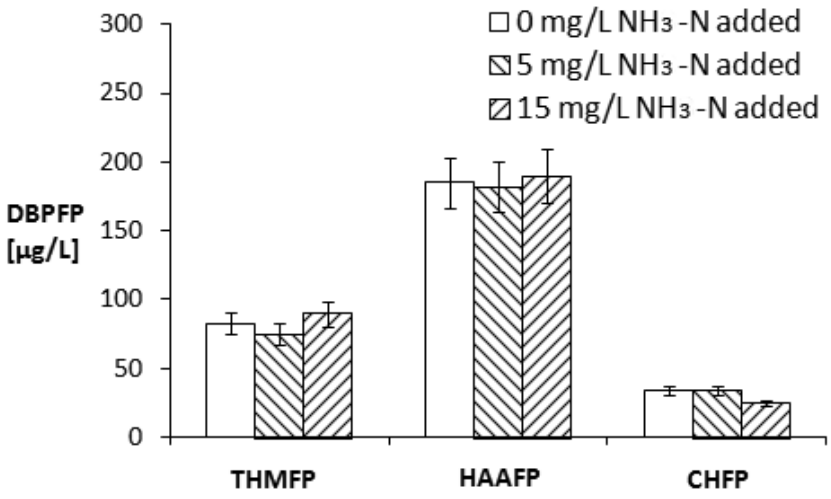

Figure 3-4. Ammonia level test on DBPFPs of wastewater samples

Table **3-1**. Suggested dilution ratio for wastewater with different ammonia levels

NH_3-N	Dilution ratio
<5 mg/L	1:5
5-15 mg/L	1:10-1:20
15-30 mg/L	1:25-1:50

Table **3-2**. Chlorine dose test on the DBPFPs of six wastewater samples

Sample ID	Free-Cl_2 residual		DBPFP		HAAFP		THMFP		CHFP	
	Dose 1	Dose 2	Dose 1	Dose 2	Dose 1	Dose 2	Dose 1	Dose 2	Dose 1	Dose 2
Group 1: Samples had low ammonia concentrations										
No. 1	17.4	18.4	262	257	138	140	75	83	18	21
No. 2	17.5	18.6	260	258	139	156	72	71	18	18
No. 3	18.7	19.5	265	247	148	144	70	71	17	18
Group 2: Samples had high ammonia concentrations										
No. 4	0	18.8	94	456	45	251	17	136	5	49
No. 5	0	14.8	196	360	99	206	44	104	16	32
No. 6	0	13.1	121	346	48	191	35	104	8	30

Dose 1: 20 mg/L Cl_2, pH 7, 25 ℃, 1:5 volume ratio dilution, and 3 day incubation time in the dark
Dose 2: 20+8×[NH_3-N] mg/L Cl_2, pH 7, 25 ℃, 1:5 volume ratio dilution, and 3 day incubation time in the dark

Chapter 4

Disinfection Byproduct Formation Potentials of Wastewater Effluents and Their Removal in a Model Wastewater Treatment Plant

Abstract

The disinfection byproduct formation potentials (DBPFPs) of treated wastewaters from various wastewater treatment plants (WWTPs) were analyzed and the DBPFP removal by different treatment processes in a model WWTP was studied. Results showed that the WWTPs that achieved better organic matter removal and nitrification resulted in low DBPFPs in treated effluents. In the model WWTP, the combination of trickling filter and modified Ludzack-Ettinger process was more efficient in dissolved organics and DBPFP removal than the activated sludge process. The FPs of haloacetonitriles and haloketones showed the highest removal efficiencies in both systems compared to the FPs of other predominant DBP species such as haloacetic acids (HAAs) and trihalomethanes (THMs). In addition, WWTP changed the DBPFP speciation profile by lowering the HAAFP/THMFP ratio. The DBP yields and specific ultraviolet absorbance increased after secondary treatment, indicating that the remaining organic matters tend to be more humic. The study implied that the oxic and anoxic conditions, soluble microbial products, nitrification, and solid retention time may impact DBPFPs.

Keywords: disinfection by-products; formation potential; wastewater treatment plants

Material presented in this chapter is a manuscript in preparation.

Introduction

In recent years, increased wastewater discharges pose a serious threat to drinking water supplies (Krasner et al., 2008). As rivers, lakes and groundwater are accepting more and more treated wastewater, the drinking water quality is affected and a notable impact on disinfection byproduct (DBP) precursors was observed (Chen et al., 2009). Some of DBPs are carcinogenic (Bull, 1982; Singer, 1999) and have been regulated. The removal of DBP precursors by utilities in drinking water systems is required under the EPA Stage 1 Disinfectants and Disinfection Byproducts (D/DBP) rule (USEPA, 1998), which specifies maximum concentrations for disinfectants and DBPs in drinking water. Although wastewater is a source of various DBP precursors, currently there are no regulations on DBP precursor removal efficiencies by wastewater treatment plants (WWTPs). The National Pollutant Discharge Elimination System (NPDES) discharge limits only regulate some THMs (e.g. chloroform) in WWTP effluents. Because chlorination of wastewater involves many reactions due to the presence of various chlorine-reacting species such as ammonia, organic carbon, organic nitrogen, and bromide at high concentrations, various DBPs can be formed at high levels (Diehl et al., 2000; Yang et al., 2005; Lee et al., 2007; Hong et al., 2007; Hu et al., 2010; Song et al., 2010). A non-removal or poor-removal of DBP precursors from wastewater would impact the downstream water treatment systems.

Assessment of DBP precursors can be completed by a formation potential (FP) test (APHA, 1998; Rostad et al., 2000; Chu et al., 2002; Li and Chu, 2003; Xie, 2004; Diaz et al., 2008). The DBP precursors in wastewater are generally estimated by analyzing the FPs of the DBPs, including trihalomethanes (THMs), haloacetic acids (HAAs), oxygenated DBPs and nitrogenous DBPs. Because wastewater organics are substantially different from the natural organic matter in drinking water, the types and amounts of DBPFPs in wastewater could be different from those found in drinking water (Sirivedhin and Gray, 2005a,b). Krasner et al.

(2009b) explored the impact of wastewater treatment processes on DBP precursors and emphasized a profound impact of nitrification on effluent quality including organic carbon, organic nitrogen, and DBP precursors. Galapate et al. (1999) found that the hydraulic retention time (HRT) and mixed liquor suspended solids (MLSS) were two parameters that could affect THM precursors and chemical properties of organic matter in the effluents of activated sludge process. Since WWTPs affect wastewater quality in many ways, there is a need for comprehensive studies. To date, few studies evaluated the DBPFPs in various wastewater effluents and the fate of DBP precursors during the biodegradation processes remains unclear.

In this study, a survey on DBPFPs was conducted on WWTP effluents of various levels of organic removal and nitrification. In addition, the survey focused on a model WWTP, which employs two independent process trains to treat the same wastewater influent. The objectives were (1) to evaluate the levels of DBPFPs in various wastewater effluents; and (2) to explore the DBPFP removal efficiencies during the biodegradation trains in the model WWTP. The target species of DBPFPs were chloroform (CF), bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (BF), chloral hydrate (CH), monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), chloropicrin (CP), 1,1-dichloro-2-propanone (DCP), and 1,1,1-trichloro-2-propanone (TCP). Since some of these compounds such as THM and HAA species are regulated in drinking water (USEPA, 1998), the research into THMs and HAAs is of particular interest.

Materials and Methods

WWTPs Surveyed

Nine domestic WWTPs in Pennsylvania USA were selected for a survey on DBPFPs in treated wastewater. All WWTPs had grit removal and primary treatment. A description of secondary treatment by the WWTPs is presented in Table 4-1. In December 2008, grab samples of secondary effluents prior to disinfection were collected from these plants. Due to the different biological treatment processes, the WWTPs produced various effluent qualities. The levels of carbon, nitrogen and DBPFPs were evaluated.

The model WWTP

The University WWTP (University Park, Pennsylvania, USA) was selected as a model WWTP for the intensive study. The plant has a treatment capacity of 4.0 mgd. It accepts domestic wastewater from the Pennsylvania State University and a portion of State College Borough. The WWTP provides primary treatment, carbonaceous oxidation, nitrification, and denitrification. Wastewater receives preliminary treatment via vortex grit removal and primary treatment with primary clarifiers prior to the secondary treatment. It has two independent process trains to treat the same primary effluent and a series of facilities are involved. Approximately, 50% of the flow is treated by a trickling filter and a modified Ludzack-Ettinger activated sludge process (TF/MLE) that operate in tandem while the other 50% is treated by an activated sludge process (ASP). The TF/MLE side flow is split between two parallel-operating trickling filters and the anoxic zone of an MLE process. The trickling filter effluent and anoxic zone effluent combine and enter the aerobic reactors of the MLE process. The ASP side flow enters an oxic reactor of the activated sludge process, and then it enters an anoxic zone and a second oxic reactor

sequentially. Eleven sampling points, illustrated in Figure 5-1, covered all outlet flows of the secondary treatment facilities. Grab sampling of the process trains were finished in 2 hours and it was conducted in April 2009 when the WWTP had full operation. The experiments were repeated in May 2009 and June 2009 when the WWTP had reduced flows, for which reason the anoxic zone and the second oxic reactor in the ASP side flow were shut down, and again in October 2009 when the WWTP resumed normal operation.

Sample preservation and the FP test

Samples collected from the WWTPs were preserved at 4 ℃ on site. After they were transported to the laboratory, samples were filtered (0.45 μm) and acidified to pH<2 by adding a few drops of concentrated sulfuric acid. Samples were then stored in a 4 ℃ until analysis.

The DBPFP test was conducted by applying a chlorine dose of 20 mg/L to the diluted and buffered samples. The dilution ratio was determined based on the ammonia level. A phosphate buffer solution (1M, pH 7) was used. Incubation was completed at 25 ℃ in amber glass bottles for 3 days in absence of light. Then samples were transferred to 40 ml vials containing granular ammonia chloride to quench the free chlorine residuals. The vials were sealed with PTFE-lined screw caps without head space and stored at 4 ℃ before extractions.

DBP extractions and measurements

Sample extractions were conducted using modified EPA method 552.3 and 551.1. For HAAs, each 30 ml sample was acidified with 1.5 ml concentrated sulfuric acid and extracted with 3 ml of MTBE spiked with 300 μg/L 1,2-dibromopropane. Approximately 12 g of sodium sulfate was added to enhance the extraction efficiency. Then, 1 ml of the MTBE extract was mixed with

1 ml of 10% sulfuric acid/methanol mix, and incubated for two hours at 50 ℃ for HAA derivatization. After derivatization, the solution was back-extracted with 4 ml of 10% sodium sulfate solution to remove excess methanol. For other DBPs, each 30 ml sample was treated using the protocols above excluding pre-extraction acidification and post-extraction methylation.

The concentrations of DBPs were determined using gas chromatographs (Hewlett Packard 6890) with electron capture detectors. A DB-1701 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used for HAA analysis. A DB-1 capillary column (30 m × 0.32 mm i.d., 1.0 μm film thickness) was used for the analysis of other DBPs. The temperature ramping programs were as follows: (1) HAAs: Initial at 35 ℃ for 10 minutes and ramp to 75 ℃ at 5 ℃/min and hold for 15 minutes, ramp to 100 ℃ at 5 ℃/min and hold 5 minutes, a final ramp to 135 ℃ at 5 ℃/min; (2) Other DBPs: Initial at 35 ℃ for 22 minutes, ramp to 145 ℃ at 10 ℃/min and hold 2 minutes. Minimum reporting levels (MRLs) for the DBPs were determined to be 1.0 μg/L.

Data and statistical analysis

Duplicate sets were analyzed and only average data were presented. The standard deviations were below 10% of the average value. For comparisons of those surveyed WWTPs, statistical methods were implemented using Minitab version 15 (State College, Pennsylvania, USA). Mann-Whitney procedure, a nonparametric method was used and the level of significance was set to $\alpha < 0.05$.

Results and Discussion

Effluents of the nine WWTPs

Carbon and nitrogen levels

The carbon content was evaluated by the dissolved organic carbon (DOC) in this study. The DOC levels of the nine WWTP effluents were in the range of 5.1 and 14.3 mg/L (Table 4-1). For the nitrogen content, the ammonia nitrogen concentrations (NH_3-N) were used as a parameter to evaluate the process efficiencies on nitrification. Based on the NH_3-N levels, the nine surveyed WWTPs were divided into two categories: five WWTPs (Plants #1, #2, #3, #4, and #5) that had insufficient nitrification with NH_3-N greater than 2 mg/L and four WWTPs (Plants #6, #7, #8, and #9) that had complete nitrification with non-detected NH_3-N in their effluents.

Plants #1, #2, #3, #4, and #5, which belonged to the category of insufficient nitrification, had relatively high DOC in their effluents. Plants #6 and #8 achieved DOC as low as 5.1 mg/L and 6.3 mg/L and non-detected NH_3-N in effluents, indicating that the two WWTPs had superior performances on organic matter removal and nitrification. This also implies that while nitrification was in progress, additional organic matter removal could be observed. Plant #9, although had complete nitrification, showed the highest DOC as 14.3 mg/L among the 9 surveyed WWTPs. This was related with the tertiary membrane system in Plant #9. The membrane treated a portion of the plant's secondary effluent. It rejected 99% of organics and recycled them to the primary effluent. The high DOC observed in secondary effluent of Plant #9 implied that the rejected unbiodegradable organics were returned.

DBPFP levels

Of all WWTPs analyzed, the data showed that their effluents had higher HAAFPs than THMFPs. This was possibly due to the characteristics of wastewater organics, which were substantially different from the natural organic matter in drinking water (Sirivedhin and Gray, 2005a). Plants #6 and #8, which achieved better organic matter removal and nitrification, also had low DBPFPs including HAAFPs (321 and 302 μg/L) and THMFPs (132 and 197 μg/L) in effluents. Plants #1, #2, #3, #4, and #5, which had high organic matter level and insufficient nitrification, had high DBPFPs. The HAAFPs of the five WWTPs ranged between 400 and 710 μg/L, and the THMFPs ranged between 248 and 305 μg/L. Specifically, Plants #2 and #3 had effluents high in HAAFPs. Their THMFPs, however, were not significantly different from the other three insufficiently nitrified WWTP effluents based on the Mann-Whitney test at the significance level of 0.05. Plant #2, which adopted pure oxygen activated sludge process, had a short solid retention time (SRT) with a maximum of 4.3 days. In addition, the relatively low pH also limited the efficiency of nitrification and possible degradation of HAA precursors. According to USEPA (1993), the maximum nitrification rate for Plant #7 which had pH 7.0 could be 10% lower than other WWTPs which had pH higher than 7.5 in bioreactors. Plant #3, which adopted trickling filter process, relied on the slime layer of filter media to achieve nitrification. However, there was also denitrification due to the existence of anoxic conditions. The anoxic reactions and the limited capabilities of biomass retention may be the cause for the poor removal of HAA precursors. In addition, production of new HAA precursors from the formation of SMPs (Liu and Li, 2010) could be another factor. Plant #9's effluent had extraordinarily high THMFPs. This was due to the high concentrations of recalcitrant organic matters (Krasner et al., 2009a) from the recycled flow of the tertiary membrane system. The hydrophobic portions of those

organics had been related with THM precursors (Galapate et al., 1999; Chiang et al., 2002; Chow et al., 2005, 2006).

DBP yields

DBP yields are calculated per carbon basis. The parameter normalizes the DBPFPs based on the organic matter concentrations. Compared to a low DBP yield, a high DBP yield in wastewater effluent would indicate that the remaining organics have high reactivity in forming DBPs, or the remaining organics were more associated with DBP precursors. Plants #2 and #3 resulted in high HAA yields (78.0 and 78.8 μg/mgC) in their effluents. This implies that the pure oxygen activated sludge and trickling filter processes produced effluent organics that had relatively high reactivity in forming HAAs. Compared to other plants' effluents, Plant #9's effluent appeared to have a high THM yield (34.9 μg/mgC) even though the increase of DOC tend to offset the increase of THMFP. However, according to the Mann-Whitney test, the difference was not significant.

By investigating the DBPFP levels in effluents of the nine WWTPs, the research data supports that a wastewater treatment process that is able to achieve better organic matter removal and complete nitrification (e.g. Plants #6 and #8) tends to result in low DBPFPs in the effluent. Although all of these plants mainly treat domestic wastewater, it would be difficult to compare the removal efficiencies of the different WWTPs because of their variable influent quality. It is necessary to investigate a model WWTP with various treatment processes and the same wastewater influent.

The model WWTP

Primary effluent

The primary treatment facilities of the model WWTP resulted in an effluent COD of 268 mg/L. The DOC of samples for the DBPFP test was 52.7 mg/L. Because the NH3-N level was in the 25 mg/L range, a high dilution ratio (1:50) was applied to accommodate a 3-day chlorine demand. Results of the DBPFP test (Table 4-3) shows that the wastewater sample prior to biological treatment was high in DBP precursors. HAA, THM and CH precursors were in predominant concentrations. 2000 μg/L HAAFP, 1080 μg/L THMFP and 987 μg/L CHFP were found in the chlorinated primary effluent. The FPs of individual species were 1280, 700, 1080, 987 μg/L, 99, 56, 18, and 4 μg/L for DCAA, TCAA, CF, CH, TCP, DCAN, CP, and BDCM, respectively. MCAA, MBAA, DBAA, DBCM, BF, DCP, TCAN, BCAN and DBAN were below the MRLs in chlorinated samples during the DBPFP test, since dilutions were applied. The specific ultraviolet absorbance (SUVA) (0.89 L/mg-m) of the primary effluent were relatively low. As SUVA lower than 2 L/mg-m would indicate non-humic organic matter in drinking water systems (Krasner et al., 2008), the wastewater organics of primary effluent would be classified as "non-humic" since they were mostly biodegradable organic matter.

Secondary effluents

Because both the ASP and TF/MLE treated the same primary effluent, the qualities of their secondary effluents could be compared. The SRTs of the two processes were 11.9 and 12.3 days, respectively. The long SRTs ensured complete nitrification in both systems and NH_3-N was not detected in their secondary effluents. However, their carbon removal capabilities were

different. The TF/MLE had lower DOC (5.6 mg/L) in secondary effluent compared to the ASP (7.7 mg/L), indicating that the TF/MLE was more efficient on organic matter removal.

The two processes also behaved differently on DBPFP removal efficiencies. The TF/MLE had lower DBPFP in secondary effluent compared to the ASP, indicating that the TF/MLE was also more efficient on DBPFP removal. The HANFP and HKFP showed the highest removal efficiencies (greater than 95%) by both systems compared to the FPs of other DBP species. This could be due to the properties of the precursors. The HK precursors were primarily small molecules such as ketones which were easily biodegradable. Therefore, greater removal efficiencies could be achieved compared to those hard-to-decompose compounds such as HAA precursors and THM precursors.

The DBPFP speciation profile also changed after treatment by the WWTP. While the relative abundance of DBP precursors was explored, the HAA precursors and THM precursors, which were two major DBP precursors in wastewater, demonstrated different ratios before (1.9:1 for primary effluent) and after the secondary treatment (1.5:1 for ASP effluent and 1.4:1 for TF/MLE effluent). This implies that the HAA precursors were more associated with those biodegradable organic matters in the primary effluent and more HAA precursors were removed by the secondary treatment compared to THM precursors. The TF/MLE, which achieved higher DOC removal, resulted in a lower HAAFP/THMFP ratio (1.4:1) than the ASP (1.5:1),

Although the DBPFPs were removed by both systems, the DBP yields increased from 80.6 to 102 μg/mgC by ASP and to 127 μg/mgC by TF/MLE. The DBP yield increase in this study implies that the organic matter removed in this secondary treatment was less associated with DBP precursors. The TF/MLE, which removed more organic matter, resulted in higher DBP yield than the ASP. The SUVA, a parameter normally used to predict DBP formation in drinking water systems (Kitis et al., 2001; White et al., 2003), also correlated well with the change of DBP yield in wastewater, and the SUVA increased from 0.89 to 1.55 L/mg-m by ASP and to 1.70

L/mg-m by TF/MLE. As the value were approaching 2 L/mg-m, below which would be classified as less-humic organic matter, the effluent organic matter tend to have more-humic constituents.

Investigations on the removal of DBPFPs by the model WWTP indicate that the TF/MLE was more efficient on DOC and DBPFP removal. WWTP could remove more percentages of HKFP and HANFP than the FPs of other DBP species and could affect the DBPFP speciation profile by lowering the HAAFP/THMFP ratio. The DBP yields and SUVA increased after secondary treatment, indicating that the remaining organic matters tend to be more humic.

Implications of the process impact

The investigation on the DBPFP removal efficiencies by exploring the start point and end points of secondary treatment illustrated the effectiveness of the two processes. As each process consisted of one or more reactors, to better understand the fate of DBP precursors during the biodegradation, it was important to evaluate how the DBPFP removal was affected by each treatment reactor in the process trains. The samplings from the eleven locations, which covered the outlet flows of all secondary treatment reactors made the evaluation possible. Because the influents to some reactors were diluted in various ratios by recycled flows, the following discussion on the process impact would be limited due to the influent discrepancy. For better comparisons, the study divided the treatment reactors of the two process trains into two stages: (1) Stage 1 included the reactors which directly accepted primary effluent. The first oxic tank in the ASP, the trickling filter and the anoxic tank in the TF/MLE were included. The three reactors used the primary effluent and recycled flows as influent and their influent organic matter concentrations were relatively high; (2) Stage 2 included the second reactor (the anoxic tank) and the third reactor (the second oxic tank) in the ASP, and the second reactor (the oxic tank) in the TF/MLE. The three reactors accepted influents after Stage 1 biological treatment and therefore

had relatively low organic matter concentrations. The effects of dilution from recycled flows were addressed by calculating DBP precursors in mass, so that the DBP precursor removal by each reactor can be determined. By defining Stage 1 and Stage 2 reactors, one may obtain some implications about the process impact on DBPFPs. But for accurate comparison, well designed and experimentally controlled WWTP operation would be needed. For example, operation of laboratory-scale systems would allow for more accurate control of operating parameters (e.g. flow rate, sludge age, recycle ratio, etc).

Oxic and anoxic conditions

Analysis of the Stage 1 reactors implies that the oxic and anoxic conditions of the reactors would impact the DBPFP removal. The first tank in ASP and the trickling filter in TF/MLE, which were oxic or partially oxic reactors, removed more kilograms DBPFPs per MGD treated flows from the primary effluent than the anoxic tank in TF/MLE (Figure 4-2a). The mass removal of HAAFP, THMFP, and CHFP was greater than that of HANFP and HKFP due to the large amount of the first three precursors in primary effluent. For the DBPFP removal percentages, Figure 4-2b shows that the first tank in ASP had the highest removal efficiency (60% for the overall DBPFP removal). The reason could be that the fully aerated condition in the oxic reactor was favorable for the biodegradation of the hard-to-decompose DBP precursors. The trickling filter in TF/MLE had 41% overall DBPFP removal. The trickling filter is an attached growth system, which has the combination of oxic and anoxic conditions for nitrification in the outer slime layer and denitrification in the inner slime layer. The presence of anoxic condition in the trickling filter would limit the oxygen utilization rate (OUR) and resulted in less DBP precursor removal. No significant overall DBPFP removal was observed in the anoxic tank in TF/MLE due to lack of oxygen in the reactor. Some DBPFP species (THMFP, HANFP, and

HKFP) even showed slight increase after treatment by the anoxic reactor. This would indicate that new DBP precursors were formed in anoxic reactions. Figure 4-2b also shows that although HANFP and HKFP had low concentrations, their removal percentages were high (82% and 92%, respectively). This is in accordance with the previous discussion on the HANFP and HKFP concentrations in the secondary effluents. The results imply that the majority of HAN and HK precursors, which were likely small molecules such as ketones, were largely removed by the first oxic reactors in the process trains.

Soluble microbial products (SMPs)

SMPs were intermediates and end products of various metabolic pathways and materials from cell lysis and death (Namkung and Rittmann, 1986). The SMPs could react with chlorine and were found to be associated with wastewater-derived DBP precursors (Liu and Li, 2010). As the Stage 1's oxic reactors removed the majority of organic matter and DBPFPs, it is suspected that the role of SMPs became significant. Figure 4-3 demonstrates that although there was DBPFP removal by the Stage 2 reactors (Figure 4-3a), the DBP yields increased significantly (Figure 4-3b). Because the organic matter removal by the Stage 2 reactors was relatively low, the DBP yield increase implies that new DBP precursors were generated. The generation of new DBP precursors could be attributed to the formation of SMPs.

For the removal of DBPFP species by the Stage 2 reactors, it was found that the second reactor in ASP, which was an anoxic reactor, had less percentage of HAAFP, THMFP, CHFP, HANFP, and HKFP removal than the second reactor in TF/MLE, which was an oxic reactor. The results coincided with the previous discussion about the Stage 1 reactors that oxic conditions are favorable for DBP precursor removal.

The HK and HAN yields decrease after treatment by the second reactor in TF/MLE (Figure 4-3b) indicates that the newly formed HK and HAN precursors were degraded further. It has been discussed (Laspidou and Rittmann, 2002) that there were two classes of SMPs: utilization-associate products (UAPs) and biomass-associated products (BAPs). UAPs are the intermediate and end products of biodegradation which can be degraded further. They may not contribute to DBP precursors in the long term view. HK and HAN precursors are likely associated with UAPs, since they are intermediate products of biodegradation and they are easily biodegraded. BAPs are formed due to cell lysis and they are hard to be biodegraded. It is speculated that BAPs are associated with the majority of the remaining DBP precursors in treated wastewater including HAA and THM precursors and could be the reason for the DBP yield increase.

Nitrification and SRTs

The impact of nitrification on DBP precursors in treated wastewater was evaluated by Krasner et al. (2009b), and the survey results in this study also indicate a possible relationship between nitrification and DBPFPs. Figure 4-4 shows that the WWTPs that achieved good nitrification resulted in lower HAAFPs. However, it was not necessarily true for the THMFPs, because the range of THMFPs in the effluents of the surveyed WWTPs was relatively wide (Figure 4-4b). Since WWTPs normally achieved nitrification by using long SRTs, it is suspected that SRTs would also have impact on the THMFPs. Further studies are needed to investigate the effect of SRT on DBPFP removal.

Conclusions

The following conclusions were obtained from this study:

(1) WWTPs with better organic matter removal and complete nitrification tend to result in low DBPFPs in the effluent.

(2) The TF/MLE was more efficient on DOC and DBPFP removal. The WWTP removed more percentages of HKFP and HANFP than the FPs of other DBP species, and affected the DBPFP speciation profile by lowering the HAAFP/THMFP ratio. The DBP yields and SUVA increased after secondary treatment, indicating that the remaining organic matters tend to be "more humic".

(3) The whole plant analysis lead to three implications of the process impact: (a) The oxic condition appears to be more favorable than anoxic condition on DBPFP removal. (b) The role of SMPs becomes significant after the majority of organic matter and DBPFPs were removed, and the DBP yield increase was likely due to the formation of SMPs. (c) Nitrification and SRTs may affect DBPFPs in treated wastewater.

Acknowledgements

This study was supported by Office of Physical Plant and Institutes of Energy and the Environment at the Pennsylvania State University. The authors acknowledge Mr. Joe Swanderski and the staff at University Park Wastewater Treatment Plant for providing access to the plant facilities. The authors thank Kevin Frank from AECOM Technology Corporation for assistance on GPS-X.

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List of Figure and Table Captions

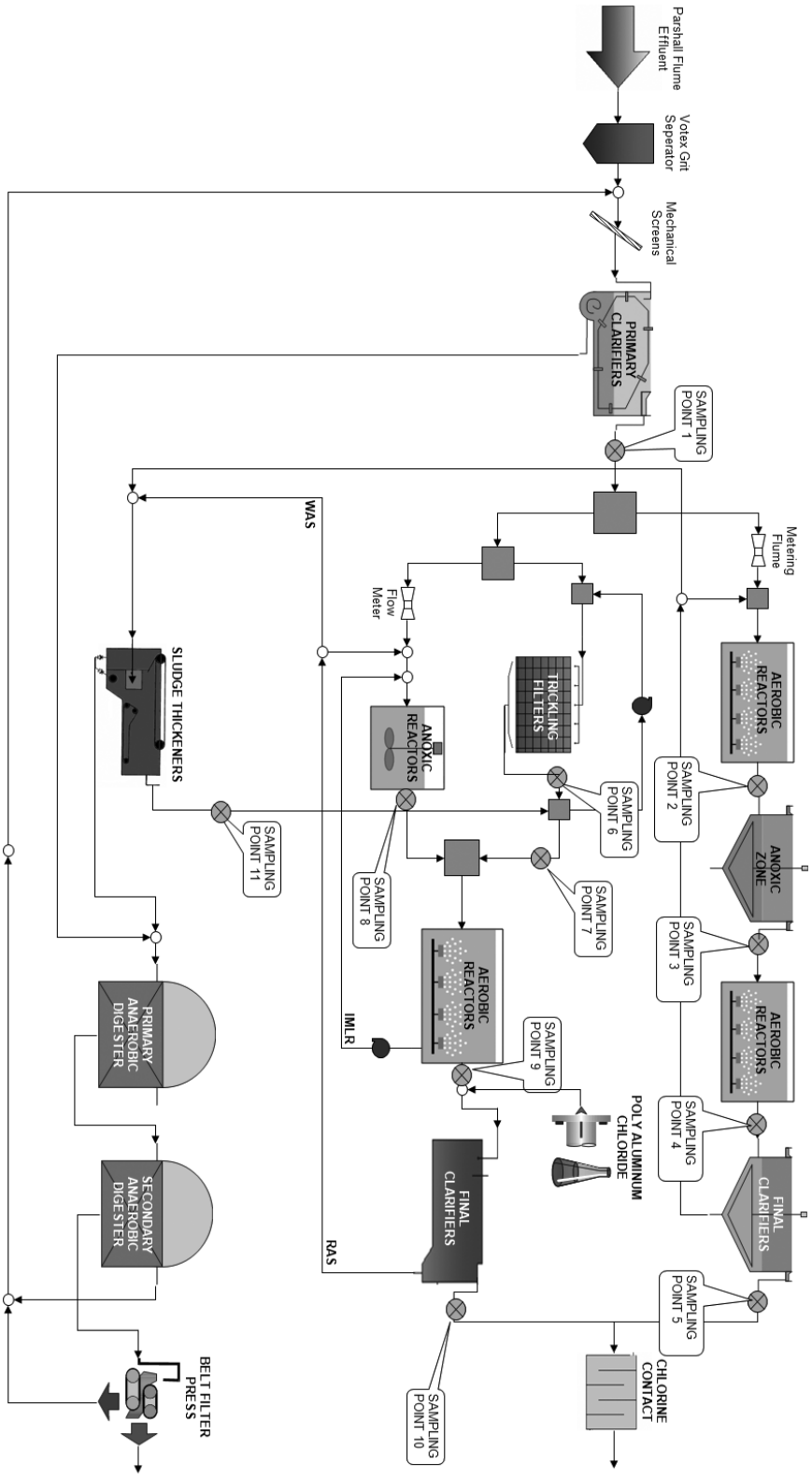

Figure 4-1. Flows and sampling points of the model WWTP

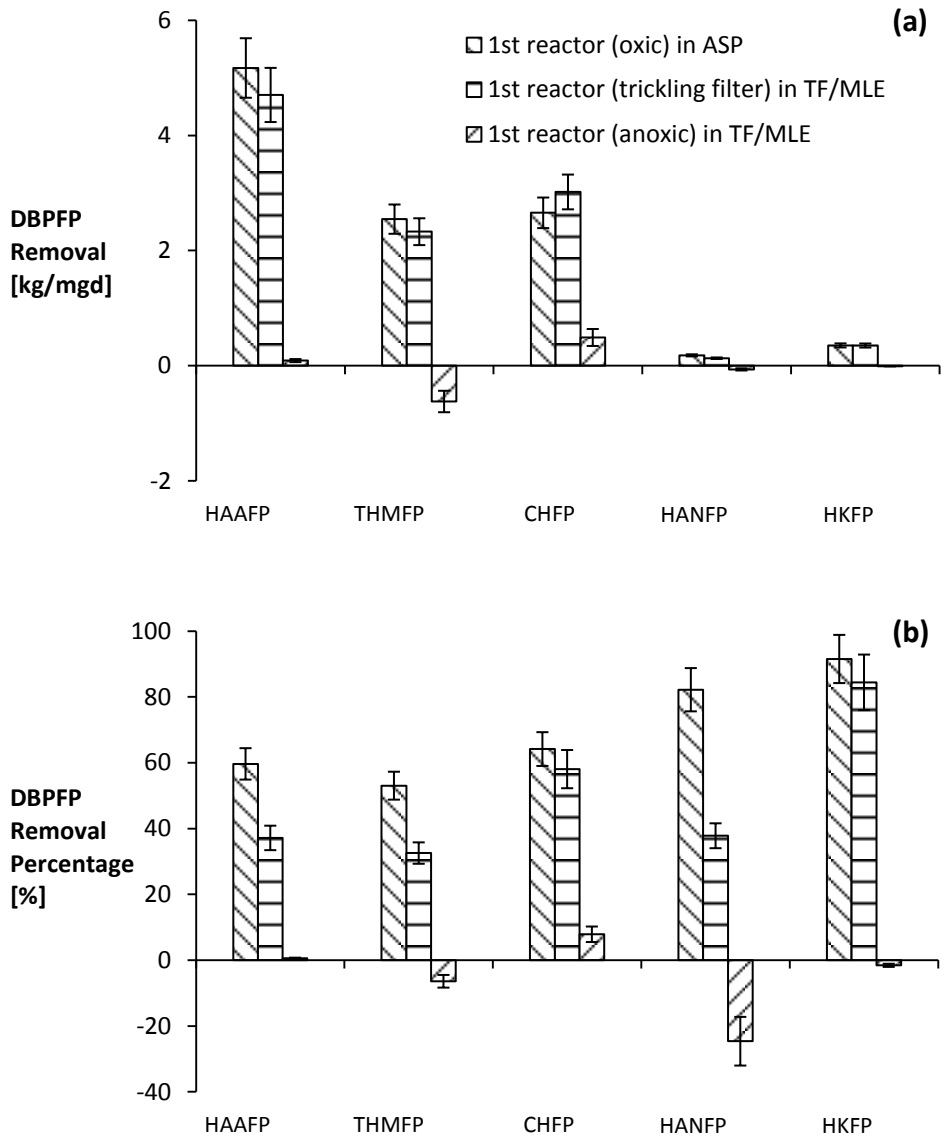

Figure 4-2. (a) Mass and (b) percentage removal of DBPFPs by the Stage 1 reactors

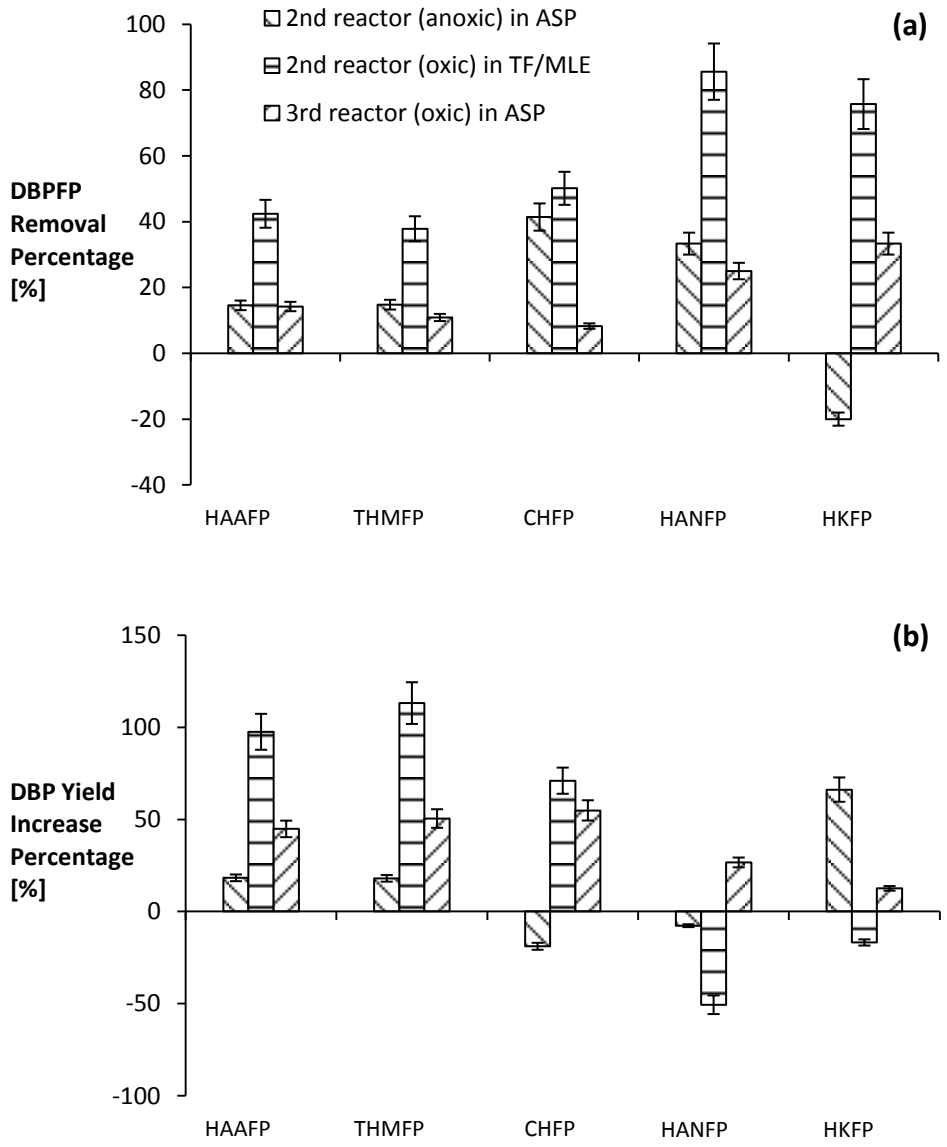

Figure 4-3. Change of (a) DBPFPs and (b) DBP yields by the Stage 2 reactors

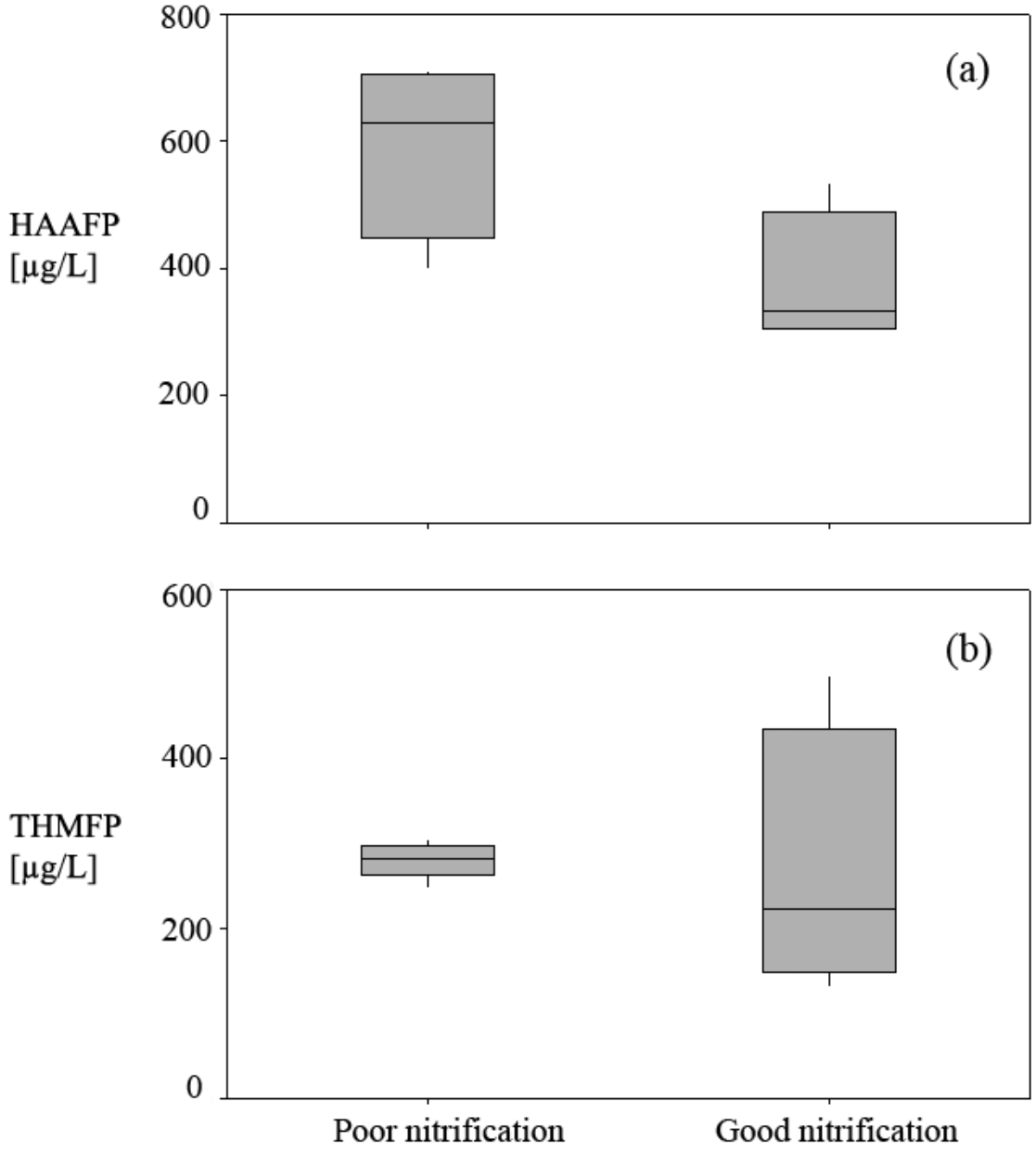

Figure 4-4. Correlations between nitrification and DBPFPs including (a) HAAFP and (b) THMFP

Table **4-1**. Description of the nine surveyed WWTPs

WWTP	Capacity(MGD)	Biological treatment processes
WWTP #1	2.0	Conventional activated sludge
WWTP #2	37.7	Pure oxygen activated sludge
WWTP #3	2.08	Trickling filter
WWTP #4	5.02	Anoxic-Oxic activated sludge
WWTP #5	2.2	Conventional activated sludge
WWTP #6	0.75	Contact stabilization and extended aeration
WWTP #7	2.0	Oxic-Anoxic-Oxic activated sludge
WWTP #8	2.0	Trickling filter and activated sludge in tandem
WWTP #9	6.0	Anaerobic-Anoxic-Oxic activated sludge

Table 4-2. Effluents of the nine WWTPs

WWTP Effluent[2]	DOC [mg/L]	NH_3-N [mg/L]	HAAFP [µg/L]	THMFP [µg/L]	HAA Yield [µg/mgC]	THM Yield [µg/mgC]
Plant #1	8.9	4.1	400	305	44.9	34.3
Plant #2	9.1	3.6	710	281	78.0	30.9
Plant #3	8.9	3.2	701	293	78.8	32.9
Plant #4	9.5	4.3	629	283	66.2	29.8
Plant #5	8.9	4.3	496	248	55.7	27.9
Plant #6	5.1	ND[1]	321	132	62.9	25.9
Plant #7	7.2	ND[1]	347	249	48.2	34.6
Plant #8	6.3	ND[1]	302	197	47.9	31.3
Plant #9	14.3	ND[1]	536	498	37.5	34.9

Data presented are average values of duplicate sets collected in December 2008. ND: not detected.

Table **4-3**. Primary effluent and secondary effluents of the model WWTP

Parameter	Primary effluent[2]	ASP effluent[2]	TF/MLE effluent[2]	ASP removal efficiency (%)	TF/MLE removal efficiency (%)
MCAAFP [µg/L]	<MRL	<MRL	<MRL	-	-
MBAAFP [µg/L]	<MRL	<MRL	<MRL	-	-
DCAAFP [µg/L]	1280	199	179	84	86
TCAAFP [µg/L]	700	174	147	75	79
BCAAFP [µg/L]	25	19	21	24	16
DBAAFP [µg/L]	<MRL	<MRL	<MRL	-	-
CFFP [µg/L]	1078	262	249	76	77
BDCMFP [µg/L]	4	<MRL	<MRL	100	100
DBCMFP [µg/L]	<MRL	<MRL	<MRL	-	-
BFFP [µg/L]	<MRL	<MRL	<MRL	-	-
CHFP [µg/L]	987	117	106	88	89
TCANFP [µg/L]	<MRL	<MRL	<MRL	-	-
DCANFP [µg/L]	56	3	2	95	96
BCANFP [µg/L]	<MRL	<MRL	<MRL	-	-
DBANFP [µg/L]	<MRL	<MRL	<MRL	-	-
DCPFP [µg/L]	<MRL	<MRL	<MRL	-	-
TCPFP [µg/L]	99	4	4	96	96
CPFP [µg/L]	18	5	3	72	83
HAAFP [µg/L]	2000	392	347	80	83
THMFP [µg/L]	1080	262	249	76	77
O-DBPFP [µg/L]	1000	122	109	88	89
HANFP [µg/L]	56	3	2	95	96
HKFP [µg/L]	99	4	4	96	96
DBPFP [µg/L]	4250	783	711	82	83
DOC [mg/L]	52.7	7.7	5.6	85	89
DBP Yield [µg/mgC]	80.6	101.7	127.0	-26	-58
NH_3-N [mg/L]	23.7	ND	ND	100	100
UV_{254} [cm^{-1}]	0.469	0.119	0.095	75	80
SUVA [L/mg-m]	0.89	1.55	1.70	-74	-91
HAAFP/THMFP	1.9	1.5	1.4	19	25

Data presented are average values of duplicate sets collected in April 2009.
MRL: minimal reporting level. N.D.: not detected.

Chapter 5

Impact of Biological Treatment Processes on Disinfection Byproduct Formation Potential in Wastewater

Abstract

Three continuously-stirred tank reactors and two sequencing batch reactors were designed to simulate different wastewater treatment processes in the laboratory. For the continuously-stirred tank reactors with different solid retention times and resultant levels of nitrification, haloacetic acid formation potentials decreased as retention time increased and nitrification level improved. Trihalomethane formation potentials, however, showed an opposite trend due to the influence of soluble microbial products. For both sequencing batch reactors with complete nitrification, the oxic-anoxic reactor with better denitrification resulted in lower disinfection byproduct formation potentials compared to the anoxic-oxic reactor. By comparing oxic and anoxic phases in a cycle of their operations, oxic phases were found to have faster removal rates and greater removal efficiencies than anoxic phases. Major reductions of disinfection byproduct formation potentials were accompanied with bulk removal of wastewater organics, and contribution of soluble microbial products became significant thereafter.

Keywords: disinfection byproduct formation potential; biological treatment processes; sequencing batch reactor; continuously stirred tank reactor; wastewater

Material presented in this chapter was presented at AWWA 130th Annual Conference in Washington, DC.

Introduction

Wastewater disinfection is an important public health measure that helps protect human being from exposure to harmful pathogens after treated wastewater is returned to waterways. Because wastewater is a source of various disinfection byproduct (DBP) precursors, DBP formation is a major concern. Nowadays more and more wastewater is accepted by potable water supplies (Chen et al., 2009). Control of DBPs and DBP precursors in wastewater is becoming an important research area because of adverse health effects of DBPs.

In drinking water systems, the removal of DBP precursors by utilities is required under the EPA Stage 1 Disinfectants and Disinfection Byproducts (D/DBP) rule (USEPA, 1998), which specifies maximum concentrations for disinfectants and DBPs. Because natural organic matter (NOM) is regarded as a source of DBP precursors in drinking water (White et al., 2003), removal of NOM has been adopted as one of the main mechanisms to remove DBP precursors in drinking water. This has led to the optimization of existing treatment processes and the development of new process which focus on NOM removal. Among them, enhanced coagulation, lime softening, carbon adsorption, ion exchange, biofiltration, and membrane technologies have shown effectiveness (Chang et al., 2001; Uyak et al., 2007; Chellam, 2000; Boyer and Singer, 2005; Miltner et al., 1992).

Currently, there are no regulations on DBP precursor removal efficiencies by wastewater treatment plants (WWTPs). The National Pollutant Discharge Elimination System (NPDES) discharge limits only regulate some trihalomethanes (THMs) (e.g. chloroform) in WWTP effluents. Sirivedhin and Gray (2005a,b) found the organics in wastewater effluent and NOM were structurally different, and the structurally different organic matrices also behaved differently in the chlorination process. Because many wastewater treatment facilities employ variety of biological, physical, and chemical processes, a wide range of treated wastewater qualities are

expected in terms of organic carbon, organic nitrogen, and DBP precursor levels (Imai et al., 2002; Krasner et al., 2008), and chlorination of wastewater leads to the formation of various DBPs at high levels due to the presence of various chlorine-reacting species at high concentrations (Mitch et al., 2003; Lee et al., 2007; Guo et al., 2009; Song, et al., 2010). Since biological treatment processes have a significant impact on the removal wastewater organics, it is hypothesized that DBP precursors may also be affected (Rostad et al., 2000; Chu et al., 2002; Diaz et al., 2008). Liu and Li (2010) found that biodegradation may effectively remove some DBP precursors, but the biotransformation process also produces new DBP precursors in the form of soluble microbial products (SMPs). Galapate et al. (1999) found that hydraulic retention time (HRT) and mixed liquor suspended solids (MLSS) were two parameters that can affect THM precursors and chemical properties of organic matter in the effluents of activated sludge processes. The optimum removal of THM precursors was achieved at HRT of 24 h and at MLSS of 2500 mg/L, and the activated sludge process preferentially removed the hydrophilic organic substances. Krasner et al. (2009a,b), on the other hand, found that the DBP formation in wastewater is strongly affected by whether or not the WWTP achieved good nitrification. Upon chlorination, WWTPs with poor nitrification normally did not achieve breakpoint chlorination due to high ammonia-nitrogen levels; and therefore low-to-none free-chlorine residuals and low DBPs were produced, if a regular chlorine dose was applied.

Since biological treatment processes can result in treated water with various DBP precursors, there is a need for comprehensive studies. Very often the information available on full-scale plant (flow rate, sludge age, recycle ratio, etc) may be inaccurate or incomplete, and it is necessary to operate a lab-scale system which allows for more accurate control of these operating parameters. Many activated sludge process designs used for biological nitrogen removal have a mixed, non-aerated anoxic reactor in front of the aerated reactor (anoxic-oxic, A/O) with mixed liquor recirculation to achieve the denitrification. Designs such as oxic-anoxic

(O/A), anaerobic-anoxic-oxic (A2O), and many others are also used for enhanced nutrient removal from wastewater (Rittmann and McCarty, 2001). Kim et al. (2002) found that continuously fed lab-scale continuously stirred tank reactors (CSTRs) were more stable during variable organic loading rates than reactors that were fed-batch reactors, such as fill-and-draw sequencing batch reactors (SBRs). However, SBR does possess advantages, including: (1) less equipment is required; (2) no separate settling tank is needed; (3) they are simple to operate; and (4) they allow more accurate control of sludge age in a lab-scale setting.

The objective of this study was to explore the impact of biological treatment processes on DBP precursors. Lab-scale CSTRs and SBRs were used to simulate different aerobic and anoxic processes to achieve various levels of nutrient removal, and the fate of DBP precursors was evaluated. The target species of DBP precursors were chloroform (CF), bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (BF), chloral hydrate (CH), monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), chloropicrin (CP), 1,1-dichloro-2-propanone (DCP), and 1,1,1-trichloro-2-propanone (TCP). Since some of these compounds such as THM and HAA species are regulated in drinking water (USEPA, 1998), the research into THMs and HAAs is of particular interest.

Materials and Methods

Wastewater

Synthetic wastewater was used in this study. The recipe was adapted based on Irvin and Li (2007): 300 mg/L milk powder, 60 mg/L ammonia chloride, 11.3 mg/L urea, 11.3 mg/L potassium monobasic phosphate, and 5.65 mg/L sodium acetate. The recipe resulted in approximately 400 mg/L COD, 20 mg/L ammonia nitrogen, 5 mg/L organic nitrogen, and 3 mg/L phosphorus.

Reactors for nitrification

Three 2-L reactors were operated as CSTRs. The reactors' set-up is shown in Figure 5-1a. Baffle walls were used to create sludge settling zones in the CSTRs. The baffles were taken out from the reactors every day for complete sludge mixing. While the baffles were removed, 500 ml, 200 ml and 100 ml mixed liquors were withdrawn and decanted from each reactor. After that, the baffles were placed back into the reactors. This maintained three distinct solid retention times (SRTs) (4, 10, and 20 days) to achieve different levels of nitrification. The flow rates were controlled at 3.1 ml/min by peristaltic pumping from an influent tank for all three reactors giving an HRT of 10.7 hours. Effluents were withdrawn from the top of the sludge settling zones through vacuum tubes maintained by level regulators.

Reactors for O/A and A/O processes

Two 2-L reactors were operated as SBRs. The reactors' set-up is shown in Figure 5-1b. Two combinations of oxic and anoxic conditions were used to achieve nitrification and

denitrification at SRT of 20 days. This resulted in two biological treatment processes: O/A and A/O. Table 5-1 shows the parameters of the two SBRs. A volume of 1.5 L was refilled and decanted in each cycle, and the HRT of the two reactors was 10.7 hours. The SBRs were operated 3 cycles per day and were controlled by digital timers. Programming of the timers is presented in Table 5-2. Timer 1 controlled the influent feed pump; Timer 2 controlled the air compressor for aerating the O/A SBR; Timer 3 controlled the stirring plates for mixing in the O/A and A/O SBRs; Timer 4 controlled the methanol feed pump for the O/A SBR; Timer 5 controlled the effluent withdrawal pump; Timer 6 controlled the air compressor for aerating the A/O SBR. Each cycle of the O/A SBR consisted of aerated filling (0.5 h), aeration (3.5 h), anoxic mixing (2.5 h), settling (0.75 h), decanting (0.5 h) and aerated idling (0.25 h). The aerated filling and idling were used to avoid pre-denitrification and thus achieve the desired O/A operation. Methanol was used as the external carbon source for the O/A SBR. The ratio was 3.5 gram methanol per gram nitrate nitrogen being reduced, considering the net effect of mixed liquor, endogenous decay, and residual dissolved oxygen (DO). Each cycle of the A/O SBR consisted of filling (0.5 h), anoxic mixing (2.5 h), aeration (3.5 h), settling (0.75 h) and idling (0.25 h).

Measurements of operational conditions

DO, temperature, and MLSS were measured regularly. The on-off switches of Timers 2 and 6 for aeration control created two combinations of oxic and anoxic conditions for biological treatment processes. Figure 5-2 presents the DO profile in a cycle of the two SBRs. Because the reactors were considered anoxic under 2 mg/L DO, one can obtain similar lengths of anoxic phases (3.5 hours) in both SBRs from Figure 5-2. It was found that in addition to the same wastewater influents, working volumes and recycle ratios, the two SBRs had the same lengths of

oxic and anoxic phases. All of these features of the two processes made it possible to conduct a comparative analysis.

Influent and effluents of the reactors were filtered through a 0.45 μm membrane prior to chemical analyses. Then dissolved organic carbon (DOC) was measured with a Total Organic Carbon Analyzer (O.I. Analytical Model 1010, Maryland, USA). Ammonia nitrogen was measured using the ammonia-selective electrode method 4500-NH_3 (APHA, 1998). UV absorbance at 254 nm was measured using with a UV/Vis spectrophotometer (Agilent 8453 spectrophotometer) with a 10 mm quartz cuvette.

Formation potential test

The research used a formation potential test (Li and Chu, 2003; Xie, 2004) to quantify DBP precursors in wastewater. Samples were buffered at pH 7 and a chlorine dose of 20 mg/L was applied. A 3-day reaction time at 25℃ in the dark was adopted. After the incubation was complete, samples were transferred to 40 ml vials containing granular ammonia chloride to convert free chlorine to combined chlorine. These vials were sealed with PTFE-lined screw caps without head space and stored at 4℃ before DBP extractions.

Because high ammonia levels in wastewater could lead to low-to-none free-chlorine residuals given insufficient sample dilutions and thus had an indirect impact on quantification of DBPFPs (Tang et al., 2011), it is very important that all wastewater samples have been properly diluted in order to ensure that free-chlorine residuals remain after sample incubation. In this study, all wastewater samples contained no more than 25 mg/L ammonia nitrogen including raw wastewater prior to biological treatment, poorly nitrified wastewater, and completely nitrified wastewater. Therefore, a 1:25 dilution ratio was applied to all samples and it was found to be able to produce sufficient free-chlorine residuals in all samples that were to be compared. Table 5-3

presents the free-chlorine residuals and demands of the chlorinated samples in an 8-h cycle of the two SBRs. The free-chlorine residuals in the wastewater samples were as low as 9.1 mg/L for raw wastewater, which was still sufficient after 3 days of incubation given a dilution ratio of 1:25.

DBP extraction and analyses

Sample extractions were conducted using modified EPA methods 552.3 and 551.1. For HAAs, each 30 ml sample was acidified with 1.5 ml concentrated sulfuric acid and extracted with 3 ml of MTBE spiked with 300 μg/L 1,2-dibromopropane. Approximately 12 g of sodium sulfate was added to enhance the extraction efficiency. Then, 1 ml of the MTBE extract was mixed with 1 ml of 10% sulfuric acid/methanol mix, and incubated for two hours at 50 ℃ for HAA derivatization. After derivatization, the solution was back-extracted with 4 ml of 10% sodium sulfate solution to remove excess methanol. For other DBPs, each 30 ml sample was extracted using the protocols above excluding pre-extraction acidification and post-extraction methylation.

The concentrations of DBPs were determined using gas chromatographs (Hewlett Packard 6890) with electron capture detectors. A DB-1701 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used for HAA analysis. A DB-1 capillary column (30 m × 0.32 mm i.d., 1.0 μm film thickness) was used for the analysis of other DBPs. The temperature ramping programs were as follows: (1) HAAs: Initial at 35 ℃ for 10 minutes and ramp to 75 ℃ at 5 ℃/min and hold for 15 minutes, ramp to 100 ℃ at 5 ℃/min and hold 5 minutes, a final ramp to 135 ℃ at 5 ℃/min; (2) Other DBPs: Initial at 35 ℃ for 22 minutes, ramp to 145 ℃ at 10 ℃/min and hold 2 minutes.

Results and Discussion

Effect of SRT

The CSTRs were used to simulate biological treatment processes with different levels of nitrification. Because the CSTRs for nitrification were continuously aerated, sufficient DO was maintained and this avoided unwanted denitrification. In addition, because the nitrification levels were varied by maintaining various SRTs, the study, on the other hand, explores the impact of SRT on DBP precursors. Samples for water quality and DBPFP analyses were consecutively collected from each CSTR after the systems reached steady state. Poor (12.0 mg/L NH_3-N), medium (6.8 mg/L NH_3-N) and good levels (0.3 mg/L NH_3-N) of nitrification were produced by varying SRTs (Figure 5-3a). The MLSS concentrations were 600, 800, and 1400 mg/L, respectively for the CSTRs with 4-day, 10-day, and 20-day SRTs, and after treatment, the effluent DOC values were 6.3, 5.2, and 4.2 mg/L, respectively. Reactors with longer SRTs or better nitrification tend to achieve lower DOC and higher MLSS (Figure 5-3b and c).

The DBPFPs that were explored in this study included the FPs of HAAs, THMs, CH, HANs and HKs. Figure 5-3d shows the overall DBPFPs in the effluents of the three reactors. There was no significant difference among the overall DBPFPs in the effluents. However, by looking into each group of DBP species (Figure 5-4a), it was found that HAAFP decreased from 938 to 539 μg/L as SRT increased from 4 to 20 days and nitrification improved from the poor to the good level. This implies that elongated SRT was accompanied with better removals of NH_3-N and organics, and the removed organics are likely more associated with HAA precursors. The results indicate that HAA precursors could be slowly biodegradable compounds, because they can degrade, but it may take longer time. THMFP, on the other hand, demonstrated an opposite

trend, because it increased from 319 to 524 μg/L. It appears that THMFP may be affected by other factors. One possible reason for the increased THMFP was that the longer SRT may result in the release of more SMPs and the SMPs were likely more associated with THM precursors. In addition, it appears THM precursors are difficult to be biodegraded compared to HAA precursors, even more time is given. It has been recognized that there are different precursor types that give rise to DCAA that has two halogens and TCAA that has three halogens (Reckhow et al., 2008), there is a need to study the two species independently. Figure 5-4b compares DCAAFP and TCAAFP removals affected by different SRTs. Their removals were generally in accordance with the overall HAAFP removal. The results imply that long SRT is one of optimum conditions for removing precursors of HAA species.

Effect of Denitrification

In this section, the O/A and A/O processes were compared according to their abilities on removals of nitrogen and DBPFPs. The two SBRs for O/A and A/O processes were operated at 20-day SRT with complete nitrification. Under the experimental settings described in Table 5-1, the O/A process was supposed to have higher nitrogen removal capability, because all NO_3-N formed in the oxic phase had a potential to be denitrified by the followed anoxic reactions. For the A/O process, only the portion of nitrified wastewater that was recycled to the front anoxic phase had potential to be denitrified. The denitrification efficiency of the A/O process was closely related to the recycle ratio. Although O/A process was theoretically better than A/O process on denitrification, two problems need to be addressed in field applications: (1) low carbon content after oxic phase; and (2) poor sludge settling capability. To solve the potential problems, the O/A SBR in this research used methanol as an external carbon source to promote the denitrification and a 3-minute bubbling period was provided prior to the settling phase to avoid floating sludge.

Effluent NO_3-N levels of the O/A SBR were stabilized at 3.9 mg/L with a standard deviation of 0.9 mg/L, while those of the A/O SBR were stabilized at 7.5 mg/L with a standard deviation of 1.3 mg/L (Figure 5-5a). Because lower effluent DOC levels were observed for the O/A SBR (Figure 5-5b), the dosed methanol for promoting denitrification had shown complete utilization. Furthermore, comparisons of the two SBR's effluents imply that besides bulk removal of organics in aerobic phase, there was additional removal of organic matter for the O/A SBR with better denitrification. This may be correlated with the findings that the DBPFPs in effluents of the O/A SBR were also lower (Figure 5-5d). For individual groups of DBP species, Figure 5-6 shows that the O/A process, which had better denitrification, resulted in effluents with lower HAAFP (including DCAAFP and TCAAFP), THMFP and CHFP. The results imply that denitrification affect removals of these DBP precursors.

Fate of DBP precursors

To explore how DBP precursors change during wastewater treatment processes and the fate the DBP precursors, the research focused on one 8-h cycle of the two SBRs. In that cycle, liquids from both reactors were withdrawn at a 30 min interval. Samples were immediately filtered and preserved for DBPFP characterization.

DOC and NH_3-N

Both reactors had been continuously operated for more than 180 days and had demonstrated steady removal of carbon and nitrogen. The DOC and NH_3-N profiles in an 8-h cycle are shown in Figure 5-7. For the O/A process, sharp decline of DOC occurred within the first half hour and sharp decline of NH_3-N occurred within the first two hours when the SBR was

in oxic phase. In 2.5 hours, complete nitrification was achieved. For the A/O process, the DOC removal was slow in anoxic phase. In the meantime, there was slight decline of NH_3-N due to cell synthesis. The aeration started at the 3rd hour and nitrification was completed in 1.5 hours.

DBPFPs and speciation

Figure 5-8 presents the changes of major DBPFPs including FPs of DCAA, CF, TCAA and CH in the 8-h cycle of O/A and A/O SBRs. The wastewater influent had 544 μg/L DCAAFP, 496 μg/L CFFP, 404 μg/L TCAAFP, and 215 μg/L CHFP. The FPs showed substantial changes under the influence of biological processes. For the O/A SBR, 66% DCAAFP, 40% CFFP, 68% TCAAFP and 58% CHFP were finally removed from the influent, and the remaining FPs in treated effluent were 184, 300, 130, and 91 μg/L, respectively. Figure 5-8a shows that substantial decline of FPs were observed in the first half hour of aeration while the reactor demonstrated sharp decline of DOC. This indicates that the portion of removed organics was related with these DBP precursors. The substantial DOC and DBP precursor removals at the beginning of each cycle may be due to direct biodegradation or adsorption by MLSS. As time went on, DCAAFP and TCAAFP showed decreases at slower rates. CFFP and CHFP, however, did not show much removal within the experimental time frame. This could be due to the characteristics of their precursors. It is believed that THM (e.g. CF) precursors are mostly humic-like recalcitrant organic matter (Singer, 1999). This explains why they are difficult to degrade. In anoxic phase of the O/A SBR, removals of the remaining FPs were limited. This implies that these precursors were preferably removed in oxic conditions other than anoxic conditions. The fluctuations of FPs in anoxic phase could be due to the formation and degradation of SMPs. Researchers concluded that primary and secondary metabolites are the major contributor of the effluent organics (Laspidou and Rittmann, 2002). It can be assumed that the readily biodegradable compounds in

wastewater influent have been completely consumed after wastewater treatment, and the remaining organics in the effluents are attributed to the three principle sources: (1) the influent organics (e.g. unbiodegradable compounds); (2) intermediates and end products of various metabolic pathways; and (3) material from cell lysis and death. The latter two sources are the two components of SMPs (Namkung and Rittmann, 1986). And SMPs start to play a significant role after the majority of organics is removed. The intermediates and end products of biodegradation and cell lysis products could be a source of new DBP precursors (Liu and Li, 2010).

For the A/O SBR, 26% DCAAFP, 15% CFFP, 38% TCAAFP and 54% CHFP were finally removed from the wastewater influent, and the remaining FPs in treated effluent were 405, 421, 250, and 99 μg/L, respectively. Although FP removals were observed in both anoxic and oxic phases, without an oxic phase in the beginning, their removal rates were much slower. This coincides with previous discussions that oxic conditions were favorable for DBP precursor removal. Fluctuations of CFFP in the cycle could be due to the formation and degradation of SMPs.

Figure 5-9 presents changes of HKFP and HANFP in the SBR cycles. Although their FP levels were low, their removal efficiencies were 93% and 97% for the O/A SBR and 91% and 90% for the A/O SBR, respectively, and they were largely removed at the beginning of the processes regardless of oxic or anoxic conditions. This indicates that HK and HAN precursors are readily biodegradable compounds, which consist of relatively small molecules (such as volatile fatty acids) and low molecular weight carbohydrates, alcohols, peptones and amino acids (Henze, 1992).

DBP yields

DBP yields were calculated per carbon basis. The parameter normalizes DBPFPs based on organic matter concentrations. A yield increase indicates that the removed organics are less associated with DBP precursors, and vice versa. The yield profiles of the two SBRs are shown in Figure 5-10. The yields of DCAA, CF, TCAA, and CH demonstrated steady increases under the influence of biological treatment processes. An exception to this was the sharp decline between the 4th and 5th hour in the O/A SBR. This was due to the addition of external carbon source, which significantly enlarged the denominator during the yield calculations. Greater yield increase rates were observed in oxic phase than anoxic phase, as revealed in both O/A and A/O SBRs. The theoretical bases of the phenomena could be: (1) the biological processes preferentially removed readily biodegradable organics which are usually less associated with DBP precursors; and (2) oxic reactions removed readily biodegradable organics more quickly than anoxic reactions.

Changes of HK and HAN yields, which are presented in Figure 5-11, can be explained by the first basis. Because HK and HAN precursors are readily biodegradable, the yields showed decrease at the beginning of cycles in both O/A and A/O SBRs. After the majority of readily biodegradable compounds were removed, the yield changes were due to the formation and degradation of SMPs.

The second basis can be explained by the concept of aerobic and anoxic (anaerobic) respiration. As deduced from previous discussions, some DBP precursors are slowly biodegradable compounds. The slowly biodegradable compounds are assumed to consist of particulate/colloidal material and complex organic molecules, which require extracellular breakdown prior to uptake and utilization (Dold et al., 1980). Compared to the anoxic respiration which uses nitrate as electron acceptor, the aerobic respiration uses oxygen as electron acceptor

and more energy is released. This facilitates quick breakdown of the slowly biodegradable compounds.

Implications

Substantial removals of carbon and nitrogen were achieved in the lab-scale reactors. Evaluation and characterization of DBP precursors during the biological processes help professionals to better understand the relationship between wastewater organics and DBP precursors.

In water, correlations between NOM and DBP precursors are revealed by specific ultraviolet absorbance (SUVA), which defines humic (>4 L/mg-m) and non-humic (<2 L/mg-m) water. In wastewater, SUVA is normally less than 2 L/mg-m and it would be classified as non-humic. However, high levels of DBPs are still formed upon chlorination. This implies that in addition to NOM, wastewater organics are also important sources of DBP precursors. Because of the deficiency of existing characterization method, new methods are needed to characterize DBP precursors in wastewater. For instance, Galapate et al. (1999) characterized DBP precursors based on the hydrophobicity and hydrophilicity of wastewater organics.

Results of the study reveal that wastewater organics contribute to a level of 2000 μg/L DBP precursors according to the FP test, including precursors of HAAs, THMs, HKs, HANs and CH. Biological treatment processes can only remove about half of HAA, THM and CH precursors without significantly changing their relative abundance (Figure 5-12), although DOC has been substantially removed. HK and HAN precursors can be removed with the bulk removal of wastewater organics, because they are readily biodegradable compounds. Other precursors are primarily slowly biodegradable compounds. There are either influent organics that are initially present or the SMPs that are primarily cell debris.

The experiments used a special design for comparing different processes. Results reveal that oxic condition is more favorable for DBP precursor removal than anoxic condition. Advanced treatment processes including nitrification and denitrification appear to affect levels of DBP precursors, although there could be other reasons, such as SRT and levels of DOC.

SMPs play an important role on DBP precursors during the wastewater treatment processes. Their impact becomes significant when the majority of wastewater organic matter is degraded and cells start to starve. The intermediate and end products of biodegradation belong to one class of SMPs --- Utilization-associated products (UAPs). UAPs can be degraded further and will not contribute to DBP precursors in the end. What matters is the other class of SMPs --- Biomass-associated products (BAPs). BAPs are formed due to cell lysis and they are slowly-biodegradable compounds. It is speculated that BAPs contributes to the majority of the remaining DBP precursors in treated wastewater. Further investigations on BAPs and their removal strategies may result in enhanced DBP precursor removal.

Conclusions

The three CSTRs with nitrification and the two SBRs with denitrification behaved differently on nutrient and DBPFP removal. The CSTRs with longer SRT resulted in better HAAFP removal including DCAAFP and TCAAFP, but THMFP might be increased due to the release of more SMPs. The O/A SBR with better denitrification resulted in lower DOC and DBPFPs.

DBP precursors of wastewater influent decreased during biological treatment processes. HK and HAN precursors were readily biodegradable and they had greater removal efficiencies than other remaining precursors which were slowly-biodegradable. Oxic reactions had faster removal rates and greater removal efficiencies than anoxic reactions.

Although DBPFPs were removed by wastewater treatment processes, DBP yields increased. After the bulk removal of organics, the yield changes were affected by the formation and degradation of SMPs.

Because advanced treatment processes including nitrification and denitrification were accompanied with greater organic matter and DBP precursor removal capabilities, wastewater treatment facilities with enhanced nutrient removal are able to reduce the wastewater-derived DBPs.

Acknowledgements

This research was supported by Office of Physical Plant and Institutes of Energy and the Environment at the Pennsylvania State University.

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List of Figure and Table Captions

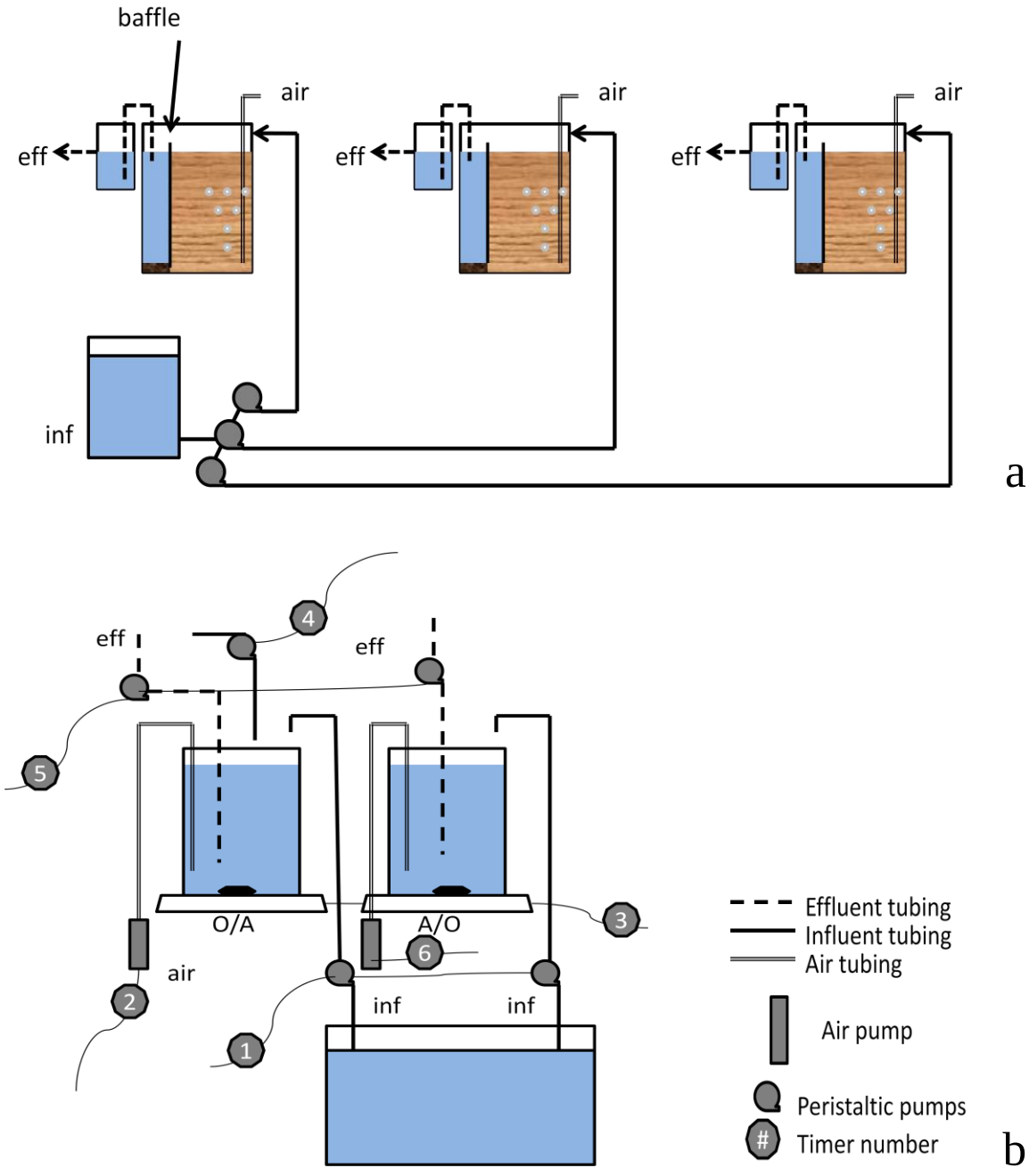

Figure 5-1. Set-up of reactors for experiments: a) three CSTRs; b) two SBRs

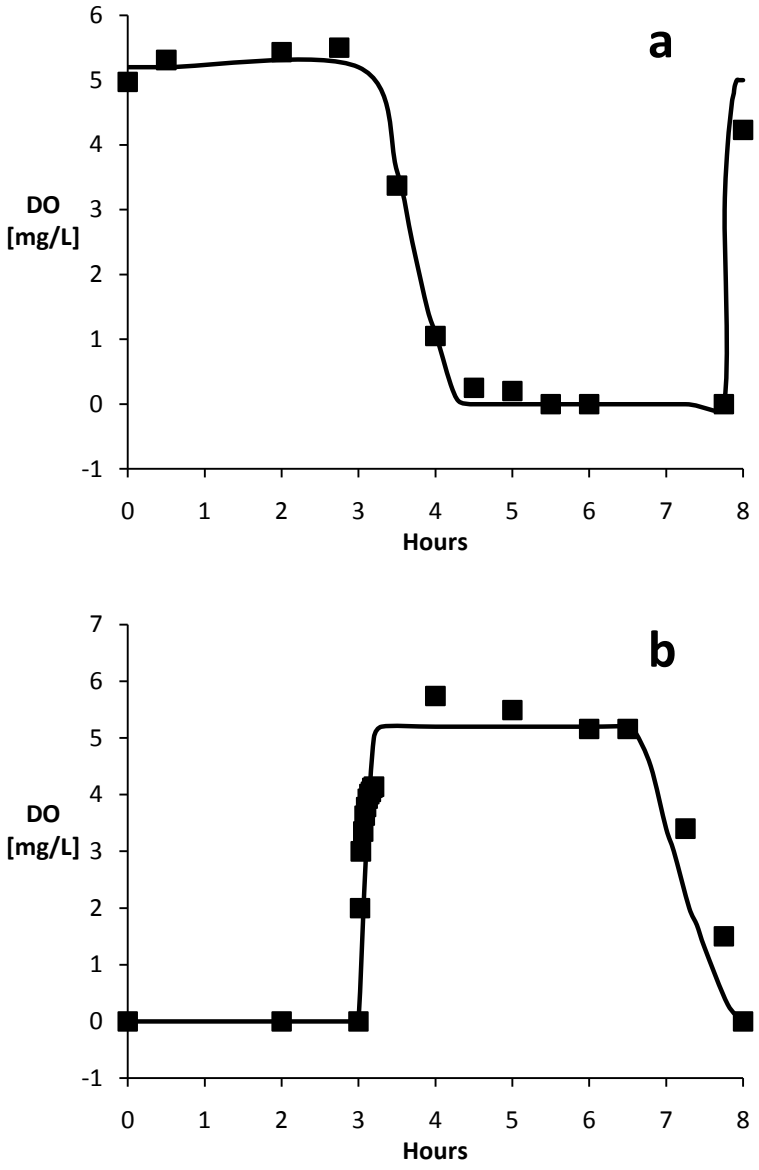

Figure 5-2. The DO profile in an 8-h cycle of two SBRs: (a) O/A SBR; (b) A/O SBR

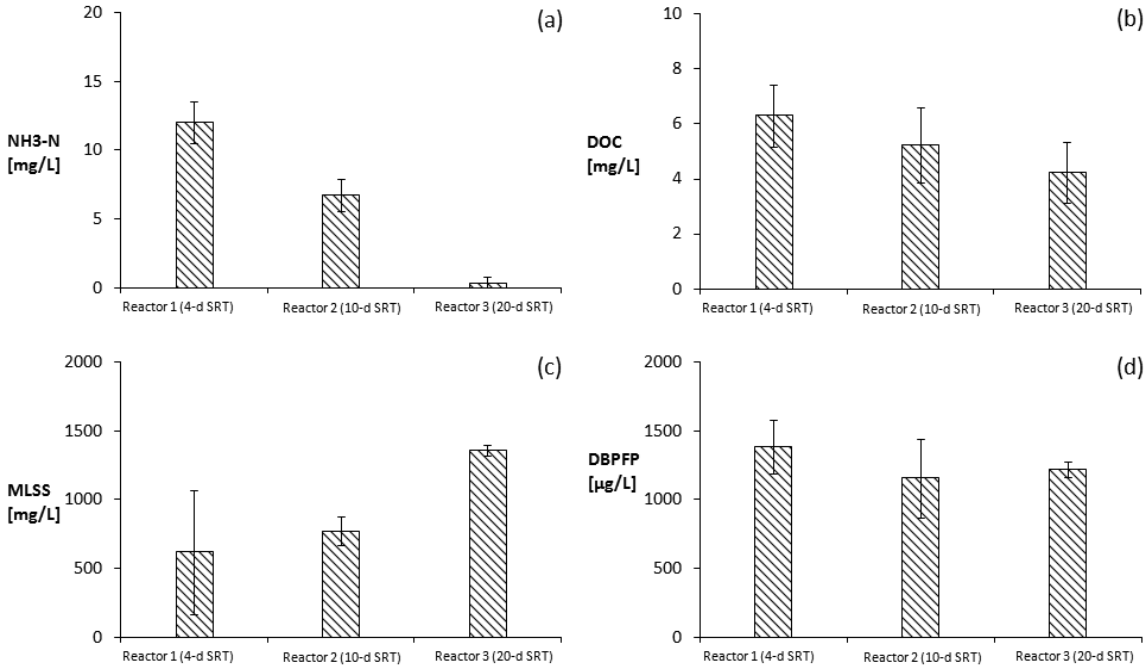

Figure 5-3. MLSS of the three CSTRs and removal of NH_3-N, DOC and DBPFP

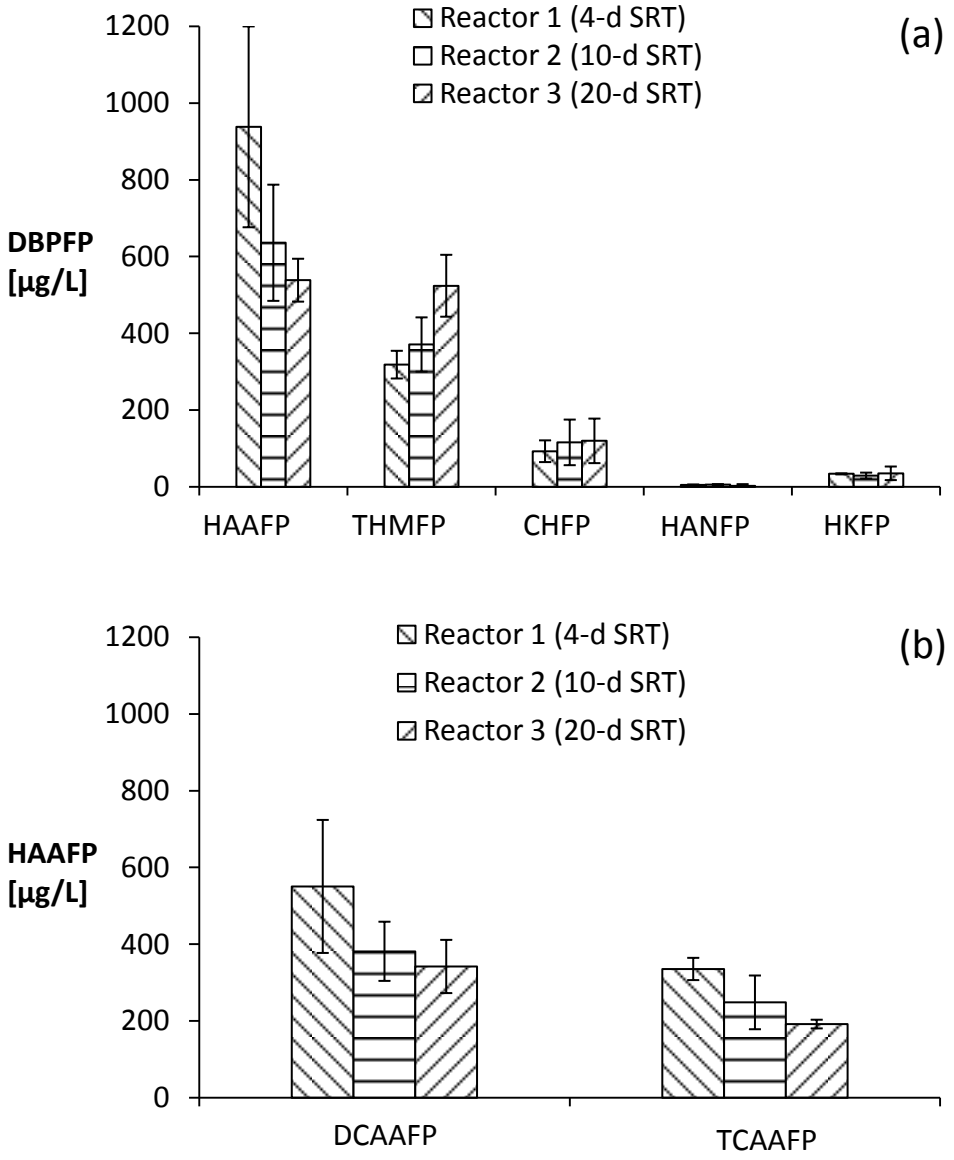

Figure 5-4. Species of DBPFPs in the effluents of the three CSTRs

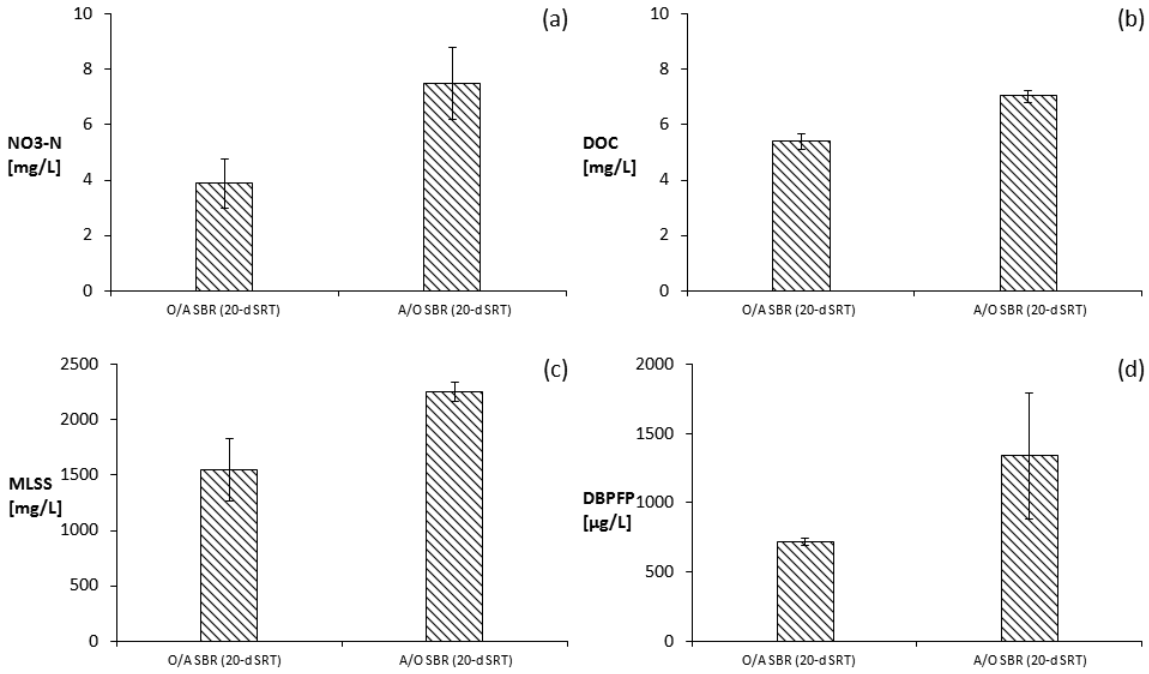

Figure 5-5. MLSS of the O/A and A/O SBRs and removal of NO_3-N, DOC and DBPFP

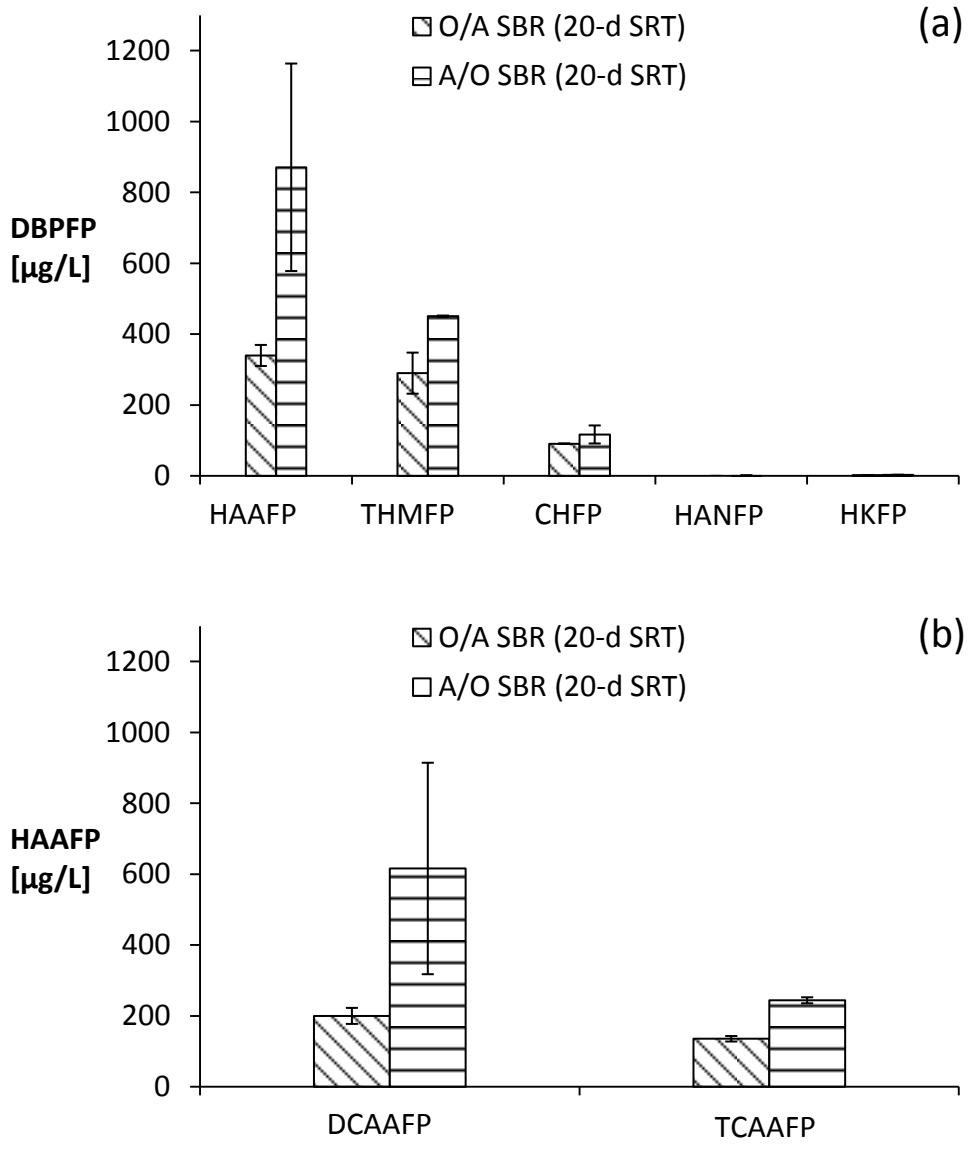

Figure 5-6. Species of DBPFPs in the effluents of the O/A and A/O SBRs

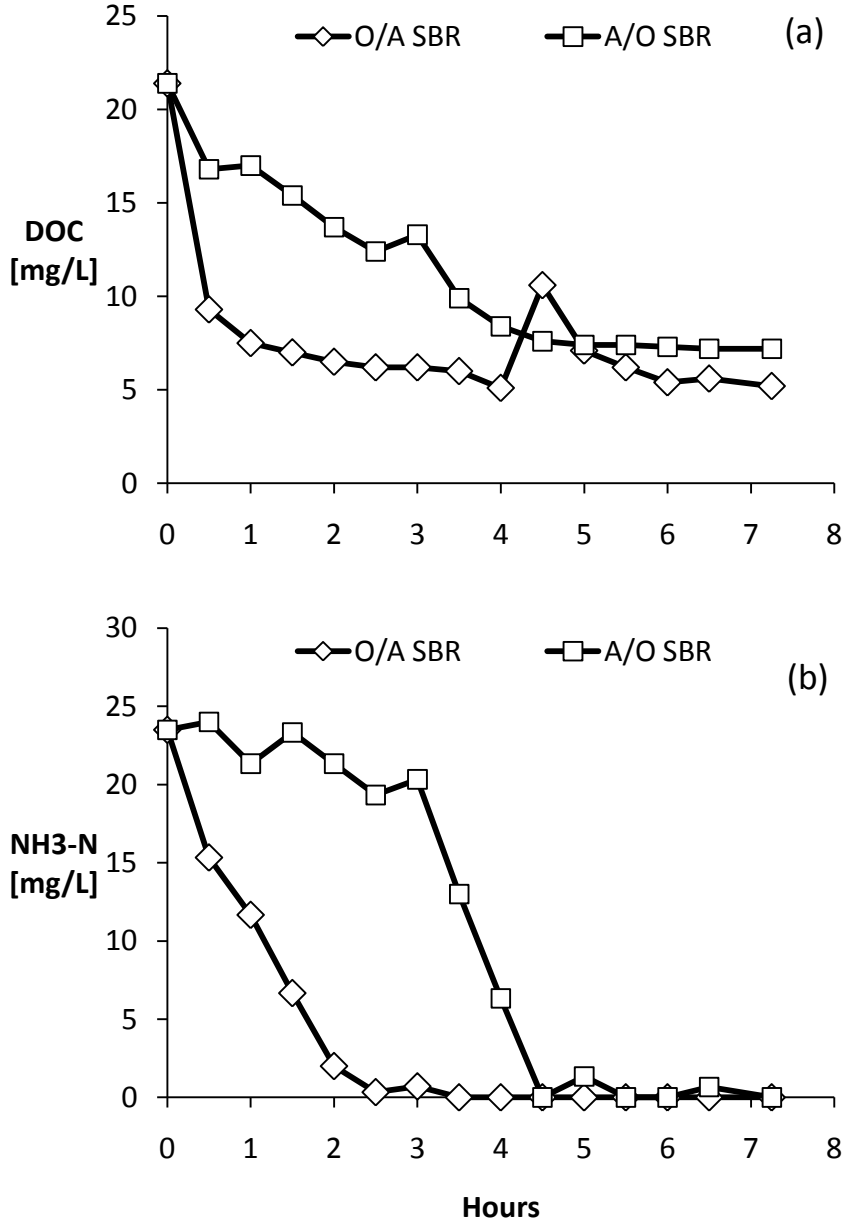

Figure 5-7. (a) DOC and (b) NH_3-N profile in an 8-h cycle of the O/A and A/O SBRs

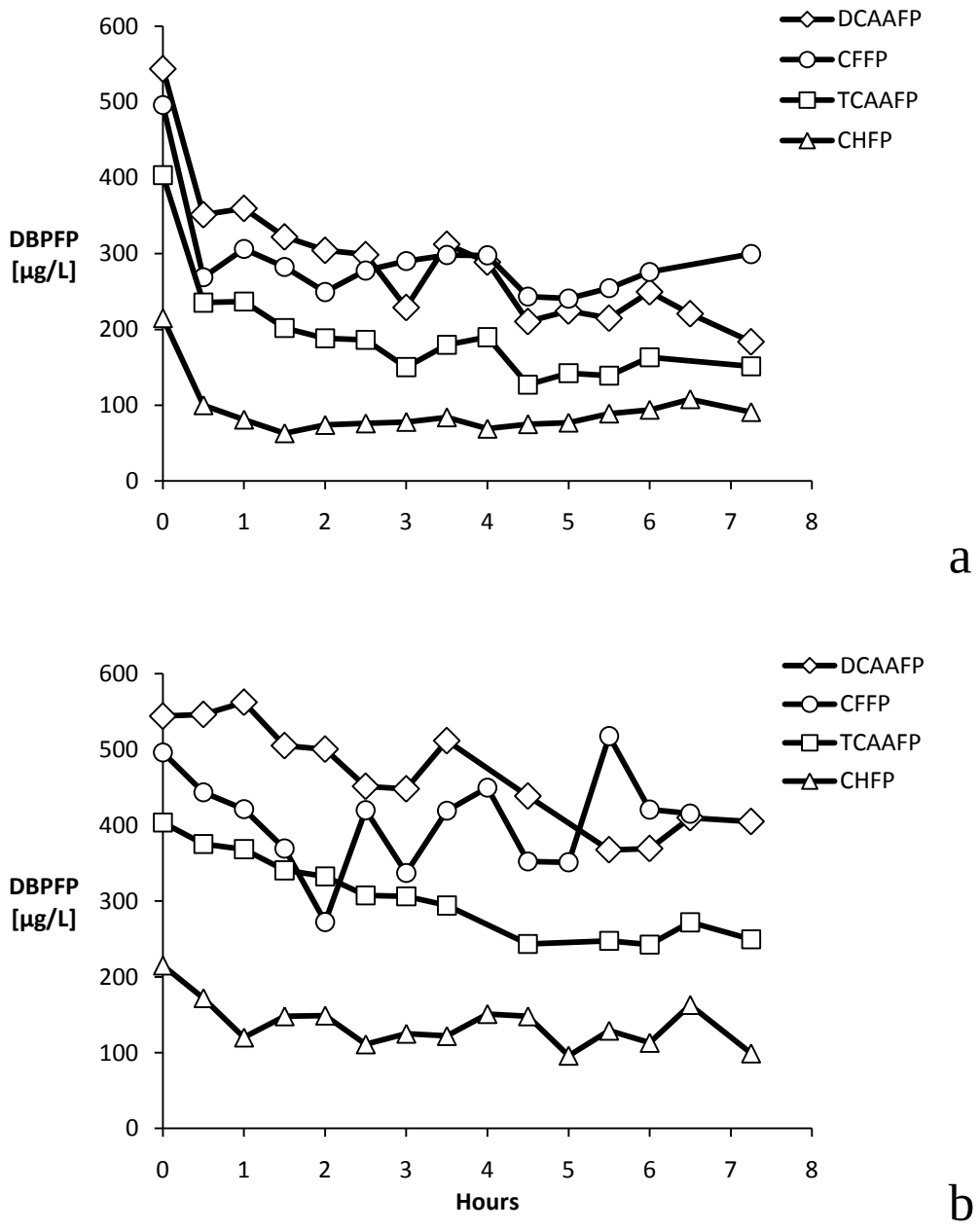

Figure 5-8. DCAA, TCAA, CF and CH profile in an 8-h cycle of the (a) O/A SBR and (b) A/O SBR

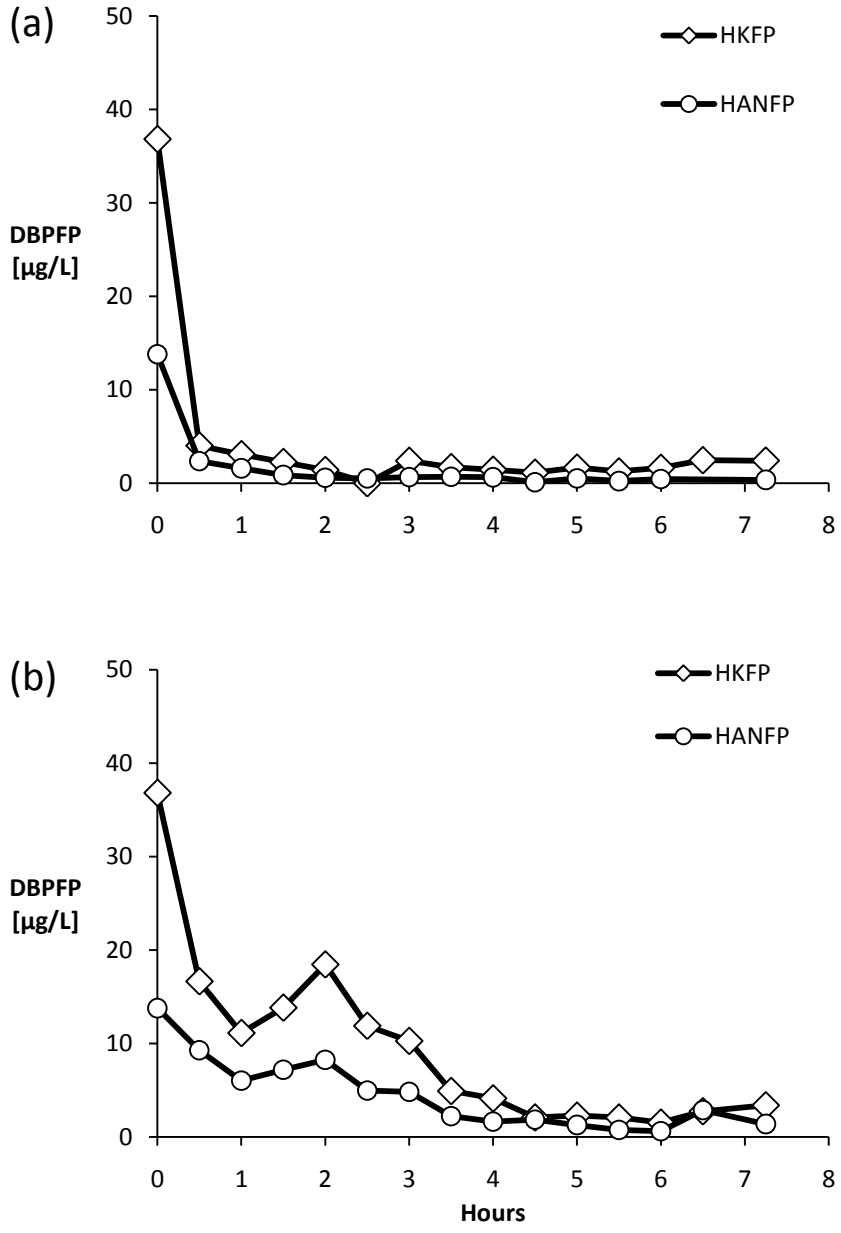

Figure 5-9. HK and HAN profile in an 8-h cycle of the (a) O/A SBR and (b) A/O SBR

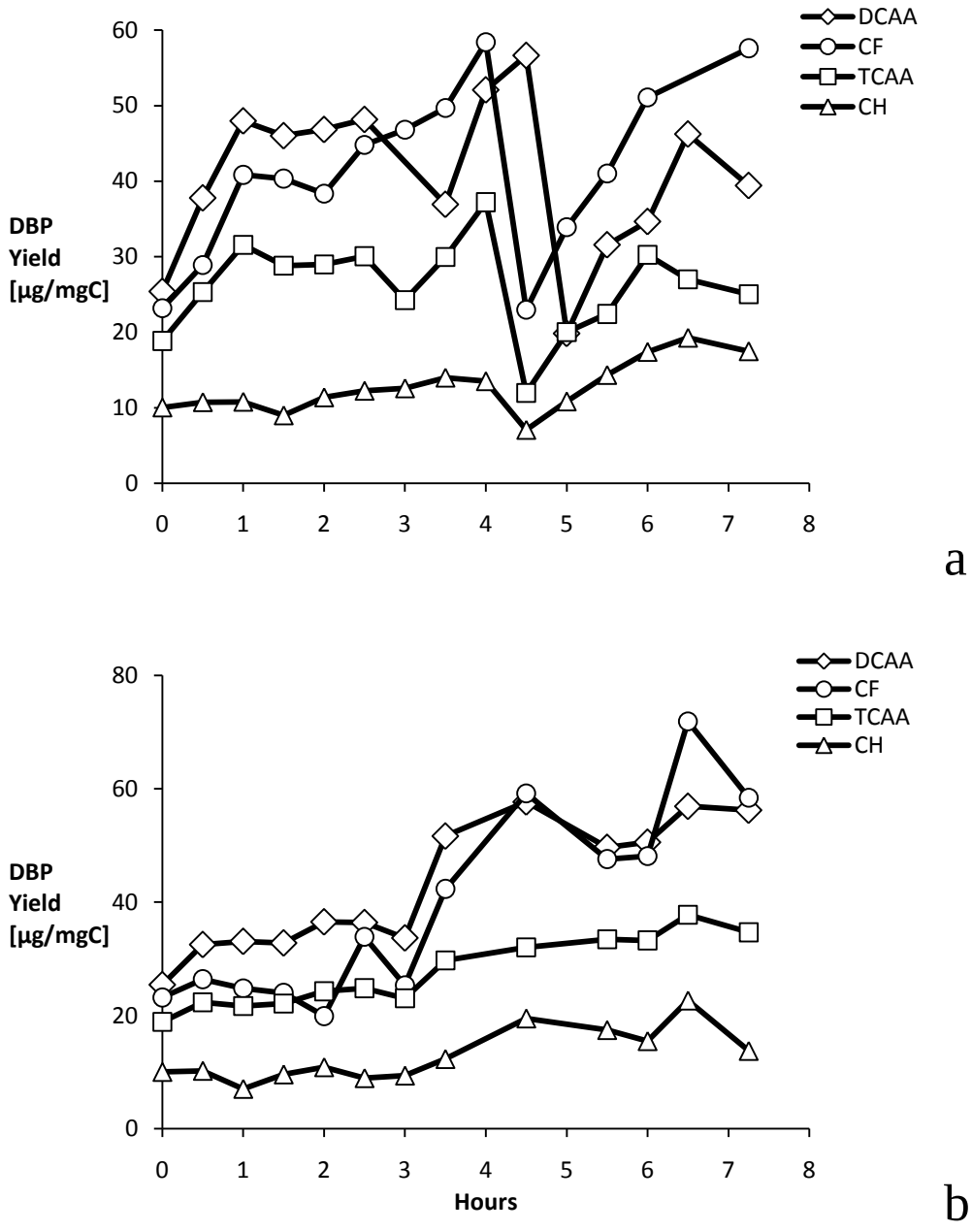

Figure 5-10. DCAA, TCAA, CF and CH yield profile in the (a) O/A SBR and (b) A/O SBR

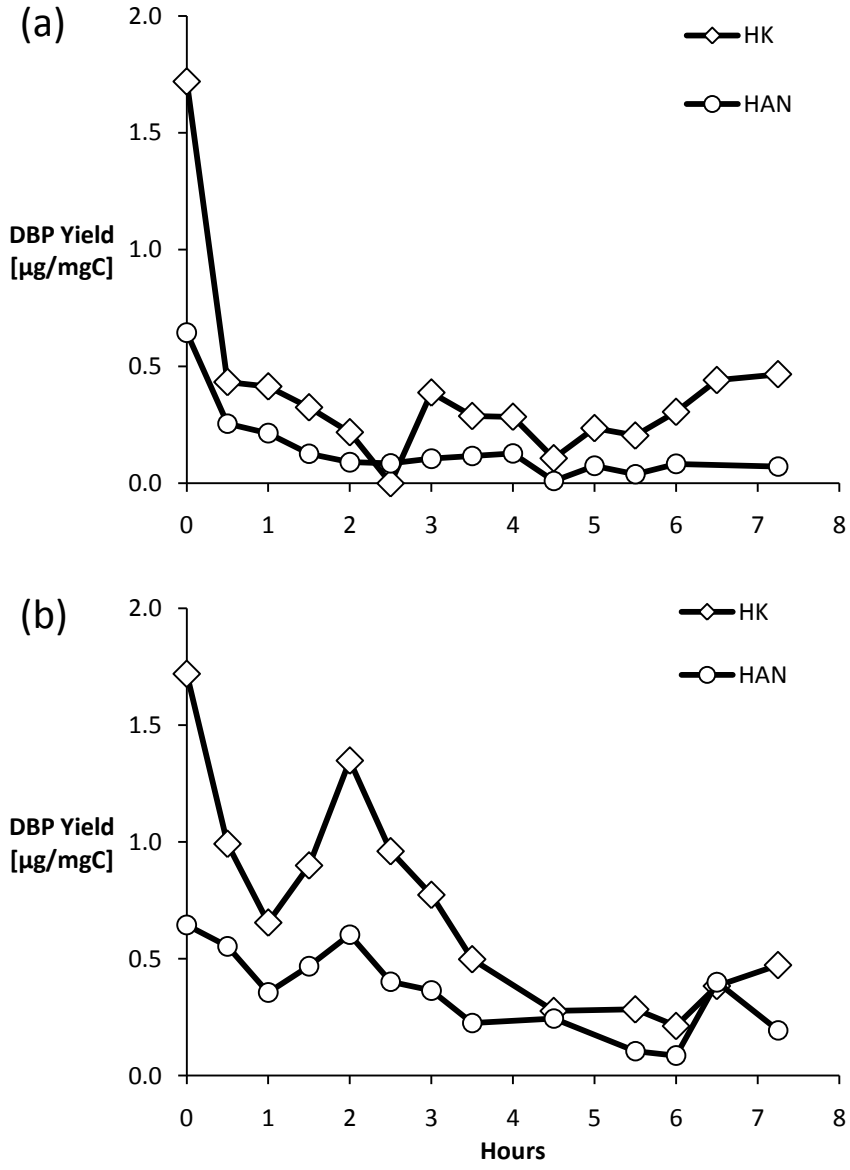

Figure 5-11. HK and HAN yield profile in the (a) O/A SBR and (b) A/O SBR

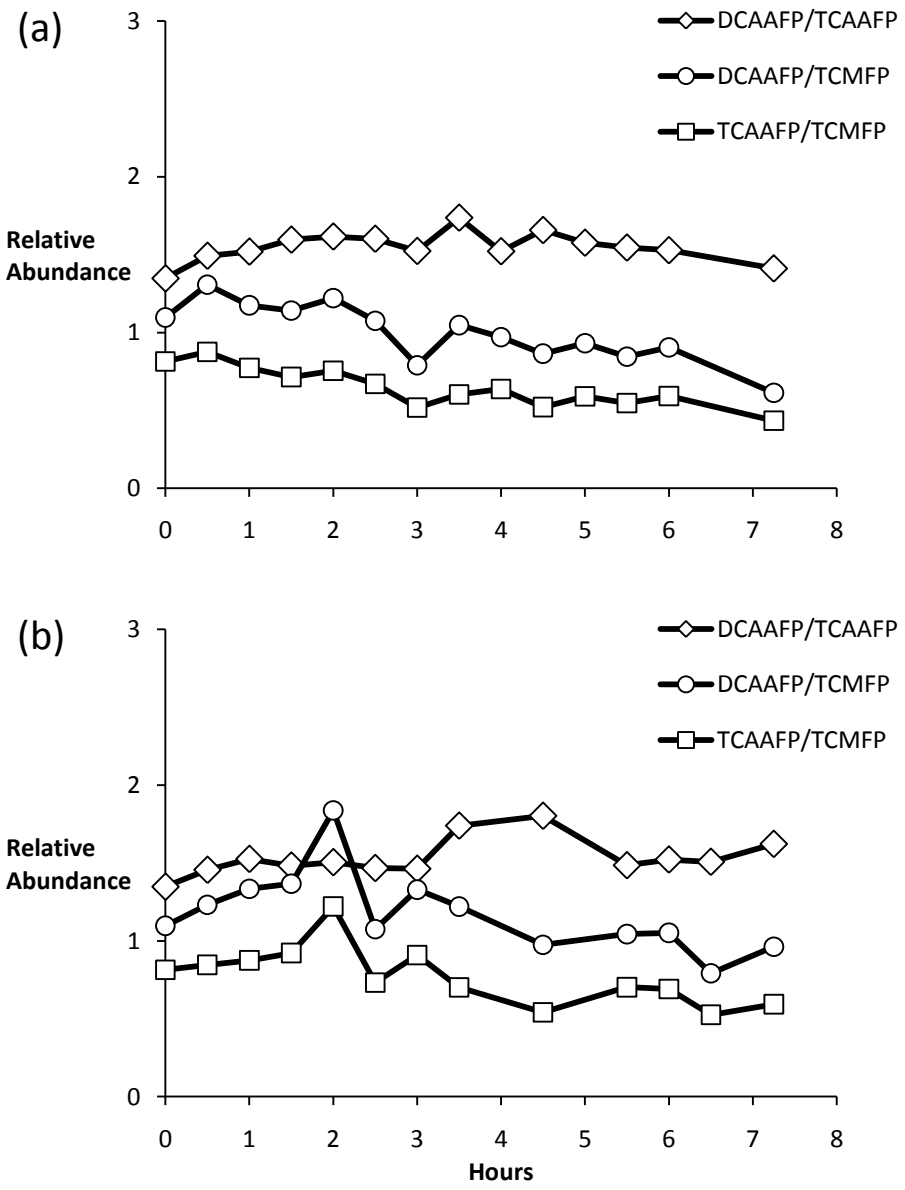

Figure 5-12. Relative abundance of DBPFPs in the (a) O/A SBR and (b) A/O SBR

Table 5-1. Parameters of the two SBRs

	O/A SBR	A/O SBR
Working volume	2 L	2 L
Temperature	20±2 °C	20±2 °C
HRT	10.7 h	10.7 h
SRT	20 d	20 d
Hours per cycle	8 h	8 h
Cycles per day	3	3
Days of continous operation	180 d	180 d
Filling volume per cycle	1.5 L	1.5 L
Discharge volume per cycle	1.5 L	1.5 L
Retained volume per cycle	0.5 L	0.5 L
Recycle ratio	0.33	0.33
Filling time	30 min	30 min
Settling time	45 min	45 min
Decanting time	30 min	30 min
Idling time	15 min	15 min
Anoxic reaction time	3 h	3 h
Oxic reaction time	3.5 h	3.5 h

Table **5-2**. SBR programming in an 8-h cycle during a day

	12:00	12:30	3:00	4:30	4:40	6:30	7:15	7:45	8:00
Timer 1	ON	OFF							
Timer 2			OFF					ON	
Timer 3						OFF		ON	
Timer 4				ON	OFF				
Timer 5							ON	OFF	
Timer 6			ON			OFF			

Table 5-3. Free-chlorine residuals and demands of the chlorinated samples in an 8-h cycle of the two SBRs (Dilution ratio: 1:25)

Sampling time	O/A SBR		A/O SBR	
	Free-Cl_2 residual [mg/L]	Free-Cl_2 demand [mg/L]	Free-Cl_2 residual [mg/L]	Free-Cl_2 demand [mg/L]
0 h	9.1	273	9.1	273
0.5 h	13.9	153	11.3	218
1 h	15.0	125	12.1	198
1.5 h	16.5	87.5	11.5	213
2 h	17.9	52.5	12.1	198
2.5 h	18.4	40.0	12.7	183
3 h	17.7	57.5	12.4	190
3.5 h	19.0	25.0	14.6	135
4 h	19.5	12.5	16.6	85.0
4.5 h	19.3	17.5	18.5	37.5
5 h	19.9	2.5	18.1	47.5
5.5 h	19.7	7.5	19.4	15.0
6 h	19.9	2.5	19.3	17.5
6.5 h	19.4	15.0	18.3	42.5
7.25 h	19.5	12.5	18.6	35.0

Chapter 6

Materials of Human Origin as a Source of Disinfection Byproduct Precursors

Abstract

The research monitored disinfection byproducts (DBPs) in an indoor swimming pool over a 1-year period since water change, explored DBP formation potentials (FPs) from materials of human origin (MHOs), and developed a model to simulate DBP formation in the pool water. As the pool was admitting more and more swimmers, the haloacetic acid (HAA) concentrations increased up to 1650 μg/L while the trihalomethane (THM) concentrations fluctuated in a range of 40 to 181 μg/L during the 1-year observation. High HAA levels and the difference between the concentrations of HAAs and THMs was attributed to three factors: (1) MHOs from swimmers. MHOs yielded more DBPs than the natural organic matter in drinking water, and they contributed to more HAAs than THMs; (2) slow HAA reduction. Laboratory simulations of swimming pools indicated that the HAAs had a much longer half life than THMs; and (3) long water retention time. By implementing the model with the data from 1-year observation and optimized parameters, a good simulation on DBP formation was achieved. The sensitivity analysis indicated that MHO loadings had a major impact on HAAs in swimming pool water.

Keywords: Materials of human origin, Chlorination; disinfection by-products; formation potential; swimming pool

Material presented in this chapter was submitted to *Water Research*.

Introduction

Hygienic safety of swimming pool water is critical not only because of a number of outbreaks of diseases caused by microorganisms in pool water (Friedman et al., 1999; Leoni et al., 1999), but also because of the unintended consequences of disinfection, known as disinfection byproducts (DBPs). DBPs that are escaped into the atmosphere, absorbed through inhalation, ingestion, bathing, showering and swimming have negative effects on human health (Villanueva et al., 2007; Karagas et al., 2008; Richardson et al., 2010). Two major groups of DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) are of keen interests by researchers. Trihalomethanes (THMs) are the best known and most intensively investigated class of DBPs. Reports on THMs in swimming pools first appeared in 1980. Since then, THMs have been measured in pool waters around the world (Zwiener et al., 2007). Fantuzzi et al. (2001) found the THMs ranged from 17.8 to 70.8 μg/L in five indoor swimming pools in Italy. Chu and Nieuwenhuijsen (2002) found the THMs averaged at 132.4 μg/L in forty four indoor swimming pools in UK. In addition to THMs, HAAs are also of toxicological concern, but information regarding their concentrations is rare and their formation kinetic in swimming pools remains unclear.

DBP formation in drinking water is related with a number of environmental factors. Chlorine concentration and reaction time are two of them (Xie, 2004). In Germany, the chlorine concentration must be kept in the range of 0.3-0.6 mg/L in swimming pools and 0.7 - 1.0 mg/L in spas (Zwiener et al., 2007). In the UK and Australia, chlorine concentrations of 1-3 mg/L are recommended. Although there are no strictly enforced regulations in US, a survey shows that the median chlorine concentration was 3.0 mg/L in indoor public pools (Kanan and Karanfil, 2011). Due to continuous addition of chlorine in swimming pools, the water represents a special case of disinfection. Swimming pool water differs from the disinfection of drinking water that is regulated under the USEPA's D/DBP Rule (USEPA, 1998). In swimming pool systems, water

has two distinctive characteristics: (1) The precursors that may account for DBPs not only include the natural organic matter (NOM) in drinking water, but also include the organic constituents that are continuously brought in by swimmers; (2) In contrast to short water ages in drinking water systems, pool water is not frequently changed, and the continuous reaction with the added chlorine have a potential to drive all DBP precursors to form DBPs. Because of these two characteristics, an intensive investigation into the organics in swimming pools regarding their DBP formation potentials (FPs) becomes essential.

A number of researchers (Judd and Jeffrey, 1995; Kim et al., 2002; Judd and Bullock, 2003; Li and Blatchley, 2007; Kanan and Karanfil, 2011) have associated swimming pool organics to the materials of human origin (MHOs) from the pool users. MHOs such as sweat and urine are main constituents of organics in the pool water. The MHO release during an average swim session per person is 25-30 ml urine (Gunkel and Jessen, 1988) and 200-1000 ml sweat (Erdinger et al., 1997). These values were not accurately determined and the actual values may show great variance among different studies, because the MHO release is difficult to measure. For instance, Erdinger et al. (1997) found the urine release into the indoor swimming pool per person was estimated to be 77.5 ml and in outdoors the amount was about 60 ml. Reactions between chlorine and MHOs have been reported by Kim et al. (2002). However, some of their samples had no free chlorine residuals after incubation due to a low chlorine dose and no dilution of samples, therefore, their DBPFPs of MHOs may be underestimated because the free chlorine residual is around 3 mg/L in typical swimming pools. As MHOs are continuously brought in by swimmers and pools are continuously exposed to disinfectants, an FP test that ensures sufficient free chlorine residual and long reaction time may result in a better simulation of chlorination in a real swimming pool system. In addition, it is important to investigate HAAFPs of MHOs because of the exceptionally high HAA concentrations found in swimming pools (Ristau, 2007).

The objective of this research was to monitor DBPs, explore the DBPFPs from MHOs, and develop a model to simulate DBPs in swimming pool water. As the contribution of wastewater organics to DBPs in drinking water is an important research area due to the increasing wastewater reuse nowadays, the research can help water professionals to better understand the contribution of MHOs and the fate of DBPs in drinking water sources where source water is impacted by swimming and wastewater.

Materials and Methods

Swimming pool

The swimming pool under investigation was located in Capital Union Building at The Pennsylvania State University, Middletown, Pennsylvania, USA. The pool has a volume of 440 m3 and accepts an average of 1500 persons per month. The water in the pool was changed on June 7th, 2009. Since then, grab samples were collected monthly and analyzed for DBPs. The free-chlorine residuals in the pool were in the range of 1 to 4 mg/L. There was no water change during the experimental period except that a small amount of make-up water (approximately 1.8 m^3) was added weekly to replace the water lost through evaporation. Pool users were suggested to take a shower prior to their entries to the pool but the shower was not enforced.

MHOs

Samples of MHOs were prepared using distilled water and five kinds of MHOs (sweat, saliva, skin wash, hair wash, and urine) collected from a 26-year-old man. Raw samples were filtered through 0.45 μm membranes. Then dissolved organic carbon (DOC) was measured with a

TOC analyzer (O.I. Analytical Model 1010, Maryland, USA). Ammonia nitrogen was measured using the ammonia-selective electrode method 4500-NH3 (APHA, 1998). UV absorbance at 254 nm was measured using with a UV/Vis spectrophotometer (Agilent 8453 spectrophotometer) with a 10 mm quartz cuvette. The DPD colorimetric method 4500-Cl G (APHA, 1998) was used to measure the concentrations of free chlorine in swimming pool water. Table 6-1 shows the water quality parameters. Samples were acidified to pH 2 and stored at 4 ℃ during the preservation.

DBPFP test

To accommodate the chlorine demand of MHO samples, dilution ratio needs to be determined before the chlorination. After dilution, samples were buffered to pH 7 by a phosphate buffer and a chlorine dose of 20 mg/L was applied. Incubation took 3 days at 25 ℃ in the dark. After the incubation was complete, samples were transferred to 40 ml vials containing granular ammonia chloride to convert free chlorine to combined chlorine. These vials were sealed with PTFE-lined screw caps without head space and stored at 4 ℃ before DBP extractions.

DBP extractions and analyses

DBP extractions were conducted using modified EPA method 552.3 and 551.1. For HAA analysis, each 30 ml sample was acidified with 1.5 ml concentrated sulfuric acid and extracted with 3 ml of MTBE spiked with 300 μg/L 1,2-dibromopropane. Approximately 12 g of sodium sulfate was added to enhance the extraction. Then, 1 ml of the MTBE extract was mixed with 1 ml of 10% sulfuric acid/methanol mix, and incubated for two hours at 50 ℃ for HAA derivatization. After derivatization, the solution was back-extracted with 4 ml of 10% sodium sulfate solution to remove excess methanol. For the analyses of THMs and other DBPs, each 30

ml sample was treated using the protocols above without pre-extraction acidification and post-extraction methylation.

The concentrations of DBPs were determined using gas chromatographs (Hewlett Packard 6890) with electron capture detectors. A DB-1701 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used for HAA analysis. A DB-1 capillary column (30 m × 0.32 mm i.d., 1.0 μm film thickness) was used for the analyses of THMs and other DBPs. The temperature ramping programs were as follows: (1) HAAs: Initial at 35 ℃ for 10 minutes and ramp to 75 ℃ at 5 ℃/min and hold for 16 minutes, a final ramp to 200 ℃ at 25 ℃/min and hold 5 minutes; (2) THMs and other DBPs: Initial at 35 ℃ for 22 minutes, and ramp to 145 ℃ at 10 ℃/min and hold for 2 minutes..

Modeling approach

The conceptualization of a swimming pool system is based on a mass balance and kinetic-based model (Judd and Black, 2000; Sohn et al., 2004). The Shuffled Complex Evolution (SCE-UA) (Duan et al., 1993), a global optimization method, is used to optimize the parameters for the model. The amounts of sweat and urine released by the pool users are to be optimized by the algorithm. Each of the variable parameter is pre-assigned a value to start the simulation. Then the simulated data are compared with the observed data. If the simulation performance does not meet certain criteria, values of the variable parameters are adjusted. After each calibration of variable parameters, the model is evaluated again to examine whether the simulation performance is improved. Simulation and calibration are repeatedly performed until the simulation performance is the best. Then the model is considered to be in good shape to get the closest response of swimming pool DBPs. Root Mean Squared Error, which is defined in Eq. 6-1, is used to evaluate the simulation performance of the model.

Eq. 6-1: $Root\ Mean\ Squared\ Error = \sqrt{\frac{\sum_{i=1}^{n}(O_{sim}-O_{obs})^2}{n}}$

Where Osim = the simulated output; Oobs = the observed output; n = the number of data

Results and Discussion

DBPs in the monitored swimming pool

Figure 6-1a shows the HAAs and THMs profile in the monitored indoor swimming pool since water change. The initial HAA and THM concentrations (81 μg/L and 87 μg/L) were close to the finished water from a typical water treatment plant (maximum contaminant levels: 60 μg/L for HAAs and 80 μg/L for THMs). As time went on and the pool was admitting more swimmers, the HAA concentrations increased significantly. In August, two months since water change, 939 μg/L HAAs were found in the pool. During November 2009 and January 2010 (the 6th and 8th months since water change), the HAA level appeared to have reached a plateau and it fluctuated at 1600 μg/L. This may be due to the fact that less people used the pool in December during the winter break. After January 2010, HAAs declined. Figure 6-1b shows the number of pool users each month. It was suspected that the HAA decline since February 2010 may be correlated with the declining number of pool users and possible HAA degradation. In contrast to HAAs, THMs did not show the increase trend in the pool. During the one-year period, the THM concentrations were only averaged at 68 μg/L with a standard deviation of 40 μg/L. Therefore, there was a substantial difference between the concentrations of HAAs and THMs in the swimming pool water. Similar observations on the difference of HAA and THM concentrations were also reported by Kanan and Karanfil (2011) when 23 indoor pools were surveyed. Three factors were suspected to be the reason: (1) MHOs introduced by pool users; (2) slow HAA degradation, and

(3) long water retention time. The impacts of the three factors on DBPs in swimming pools were discussed in the following sections.

DBPFPs and DBP yields from MHOs

Table 6-2 shows the DBPFPs from the MHO samples. All analyzed MHOs were found to contribute to DBP formation, which was consistent with results reported by Kim et al. (2002). In the DBPFP test, 1930 μg/L, 3050 μg/L, 3420 μg/L, 1750 μg/L, and 1610 μg/L HAAFP was found in chlorinated sweat, saliva, skin wash, hair wash, and urine samples, respectively. Their corresponding THMFPs were 427 μg/L, 1010 μg/L, 875 μg/L, 563 μg/L, and 971 μg/L. Therefore, MHOs could be important sources of DBP precursors in pool water. When the relative abundance of HAAFPs and THMFPs were explored, the data shows all analyzed MHOs contributed more to HAAFPs than THMFPs. The HAAFP/THMFP ratios were between 1.7 and 4.5. Specifically, the sweat, saliva, skin wash and hair wash samples had higher ratios than the urine sample. The results indicate that these MHOs may have more HAA precursors than THM precursors, and may partially explain the difference between the concentrations of HAAs and THMs found in pool water.

Because THM and HAA species are regulated in drinking water (USEPA, 1998), the research into THMs and HAAs is usually of particular interest. Other species also need investigation. For example, Weaver et al. (2009) analyzed 11 DBPs in chlorinated swimming pool water. In this study, besides regulated DBPs, other investigated DBP species included: chloral hydrate (CH), haloacetonitriles (HANs) including trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), and haloketones (HKs) including 1,1-dichloro-2-propanone (DCP) and 1,1,1-trichloro-2-propanone (TCP). Data shows that HANs and HKs were in much lower concentrations compared

to THMs and HAAs. CH, however, was in great abundance, and the CHFPs, which were 1150 μg/L, 1300 μg/L, and 1470 μg/L in the sweat, skin wash, and hair wash samples, were higher than THMFPs.

Table 6-2 also indicated that the MHO samples had much higher free-chlorine demands than NOM in drinking water, which is usually less than 20 mg/L. The 3-day free-chlorine demands per DOC for sweat, saliva, skin, hair and urine were in the range of 21 to 33 mg Cl_2 per mg carbon. This was similar to the results of body fluid analogs reported by Kanan and Karanfil (2011). The majority of the chlorine demands of MHOs were not necessarily from inorganic matter (i.e. ammonia nitrogen), but could be from organic matter. A 1:25 or even higher dilution ratio was required to maintain sufficient free-chlorine residual after 3-day incubation during the DBPFP tests. In addition, the free-chlorine demand of urine is much higher than other MHOs. This could be due to the rich nitrogenous compounds in the urine that react with free chlorine during the incubation (De Laat et al., 2011).

Because it is difficult to collect large amounts of MHOs, the obtained samples in this research were diluted MHOs. The concentrations of these organics, denoted by dissolved organic carbon (DOC), may show substantial variance during multiple collections. Therefore, there is a need to normalize the obtained DBPFPs based on DOC. DBP yield is such a parameter, and it can be used to compare different MHOs regardless of their dilution ratios during collections. The DBP yields were 547 μg/mgC for sweat, 562 μg/mgC for saliva, 615 μg/mgC for skin wash, 340 μg/mgC for hair wash and 304 μg/mgC for urine samples. The authors also studied the DBP yields of waters containing various levels of humic acid, a component of NOM, and found the DBP yield was 153 μg/mgC based on the FP test. Therefore, the DBP yields of MHOs were higher than that of NOM. Sweat, saliva and skin wash samples also showed higher DBP yields than hair wash and urine samples. Figure 6-2 presents the yields of HAA, THM and CH after the FP tests. Urine had the lowest HAA yields (161 μg/mgC) compared to others, and the HAA

yields for sweat (301 μg/mgC), saliva (391 μg/mgC) and skin wash (376 μg/mgC) were all high compared to the yields of other DBP species. The THM yields were in the range of 51 and 129 μg/mgC, which were much higher than Kim et al. (2002)'s data on THM yields in the range of 16 to 32 μg/mgC for hair, saliva, skin and urine samples.

Simulations on DBP formation and reduction

Lab-scale experiments were conducted to simulate a swimming pool environment in order to confirm the contribution of MHOs to DBP formation. A lab-scale swimming pool built with an 8-L reactor with occasional water agitation was used to simulate the swimming pool. MHOs were manually added to the open reactor and free-chlorine residuals were maintained in a range of 1-4 mg/L all the time. Analysis of grab samples from the simulated pool over the time (Figure 6-3) showed that the introduction of MHOs was the cause for HAAs increase. However, in the open air environment with intermittent water agitation, THMs did not show high concentrations, but instead was relatively stable compared to HAAs. It was suspected that THMs were partially lost due to the water agitation while being formed. Benoit and Jackson (1987) observed unchanged THMs while exploring the THM concentrations in 25 whirlpool spas affected by heat, aeration, and agitation. The water agitation by pool users, thought difficult to measure, may play an important role on DBPs.

Lab-scale experiments were used to simulate THM and HAA reductions due to water agitation. The mechanisms involved in real swimming pool systems may include evaporation and possible degradations such as biodegradation (Tung and Xie, 2009) and photodegradation (Lifongo et al, 2004) in outdoor pools. Water samples were taken out from the real swimming pool and placed in an open container after quenching free-chlorine residual with ammonium chloride. Occasional water agitation was applied every day and no external MHOs were added

during the experiment. The THM concentration in the freshly collected swimming pool water was 45 μg/L. It decreased to 11 μg/L after 3 days. The data was plotted in Figure 6-4a. A pseudo first-order kinetic equation (Eq 6-2) was applied to the experimental data to determine the reduction rate coefficient. Based on laboratory simulations, the THM reduction rate coefficient was 0.45 day^{-1}, and the half life of THMs was 1.5 days during the simulation of swimming pool.

Eq 6-2: $C = C_0 e^{-kt}$

The pseudo first-order kinetic equation based on the experimental data of HAA reduction (Figure 6-4b) shows that the rate coefficient of HAAs reduction was 0.023 day^{-1}. And the half life of HAAs in the simulation of swimming pool was 30 days. Because the half life of HAAs is much longer than that of THMs, HAAs can be accumulated while THMs were quickly lost. This explains the particular DBP profile in swimming pools: high HAA and low THM concentrations.

The swimming pool DBP model

Numerous models on DBP formation have been presented by Sohn et al. (2004), and computer-based simulation is a useful tool for a number of tasks performed by water and wastewater professionals (Melcer et al., 2003; Lee et al., 2002). In this study, the conceptualization of a swimming pool system is based on a mass balance and kinetic-based model, which is presented in Eq. 6-3. The DBP_{in} is calculated based on the experimentally determined DBP yields from MHOs in the DBPFP tests. The $DBP_{reacted}$ is based on pseudo first-order kinetics, and the DBP reduction rate coefficients are experimentally determined according to laboratory simulations. Three assumptions were made for the model: (1) All DBP precursors from MHOs have been converted to DBPs; (2) DBP_{out} is zero because water in the swimming pool is not changed in a given time t; (3) The DBP reaction kinetics between the laboratory simulation and the real swimming pool are the same.

Eq. 6-3: $d[DBP] = YC - [DBP] \times \exp(-kt)$

Where Y = DBP yields from MHOs; C = Concentrations of MHOs; [DBP] = DBP concentrations; k = DBP reduction rate coefficient; t = time

Description of the parameters in the swimming pool DBP model is presented in Table 6-3. The model input includes three parameters from observations (Number of pool users per day, days, and swimming pool volume) and six stoichiometric and kinetic paramaters (HAA and THM yields from sweat and urine and the rate coefficients of HAA and THM reductions), which must be defined in order to apply the model to predict system behavior. These stoichiometric and kinetic parameters do not change dramatically among different systems, and they are obtained by indirect techniques (e.g. laboratory experiments). The initial concentrations of HAAs and THMs are assumed to be 60 and 80 μg/L, respectively, based on the MCLs in drinking water. The model output includes the estimated HAA and THM concentrations. The variable parameters are the amounts of released sweat and urine per person and each of them was assigned an initial value to start the simulation. The computational algorithm (i.e. for HAAs) is shown in the following steps based on a daily input of pool users in a 365-day time frame. And the computation was completed using MATLAB (The Mathworks, Inc.).

At Day 0, $HAA_0 = 60$

At Day 1, $HAA_1 = \frac{N_1(H_{YS}C_S+H_{YU}C_U)}{V} + HAA_0 e^{-K_H}$

At Day 2, $HAA_2 = \frac{N_2(H_{YS}C_S+H_{YU}C_U)}{V} + \frac{N_1(H_{YS}C_S+H_{YU}C_U)}{V} e^{-K_H} + HAA_0 e^{-2K_H}$

At Day 3,

$$HAA_3 = \frac{N_3(H_{YS}C_S+H_{YU}C_U)}{V} + \frac{N_2(H_{YS}C_S+H_{YU}C_U)}{V} e^{-K_H} + \frac{N_1(H_{YS}C_S+H_{YU}C_U)}{V} e^{-2K_H} + HAA_0 e^{-3K_H}$$

…

At Day i,

$$HAA_i = \frac{N_i(H_{YS}C_S+H_{YU}C_U)}{V} + \frac{N_{i-1}(H_{YS}C_S+H_{YU}C_U)}{V} e^{-K_H} + \frac{N_{i-2}(H_{YS}C_S+H_{YU}C_U)}{V} e^{-2K_H} + \cdots +$$

$$\frac{N_1(H_{YS}C_S+H_{YU}C_U)}{V} e^{-(i-1)K_H} + HAA_0 e^{-iK_H}$$

i=365.

If all of the input data were perfect, there would be an approximate prediction but not necessarily an exact match. In calibrating the model to take care of small discrepancies, small adjustments were made to the variable parameters until the simulated data matches the observed data. The SCE-UA algorithm ensured that the root mean squared value (168.25) between the simulated and observed data was the lowest. The parameters after optimization were that 701 mg carbon from sweat per person and 415 mg carbon from urine per person were released to the pool. This indicated that an overall estimate of 1120 mg carbon from MHOs per swim per person was released. According to available literature (Judd and Black, 2000), a carbon content of 6000 mg/L is used to simulate body fluids, the optimized parameters implied that each pool user released approximately 117 ml sweat and 69 ml urine into the pool. These values were in the range reported by Erdinger et al. (1997).

Figure 6-5 shows the HAA and THM levels in the swimming pool simulated by the model with optimized parameters. The model simulations on HAAs are close to the experimental

results and they capture the rising trend and declining trend well. Therefore, the model is competent to simulate HAAs in swimming pools. However, while exploring the simulated and observed THM data, the model's performance on THMs simulation appears to be limited. This is because the THM reduction rate is so high that the monthly observation data could not reveal its relationship with the MHO input and could not capture the trend.

The swimming pool DBP model was implemented to obtain simulated DBP data given lower or higher MHO loading scenarios to explore the impact of MHOs on DBP concentrations in swimming pools. Besides the three assumptions for the model, the fourth assumption made here is that the daily MHO loading is constant. Sensitivity analysis in Figure 6-6 shows that the MHO loading plays an important role on DBPs, especially HAAs, in swimming pool systems. A high loading tends to achieve a higher HAA plateau, but it takes longer time to reach the plateau than a low loading (Figure 6-6a). A high loading also tends to achieve higher THM formation (Figure 6-6b). However, due to the high THM reduction rate coefficient, the THM concentrations will be stable and low given a constant MHO loading scenario. Various MHO loadings do not differentiate the HAA/THM ratio, as revealed in Figure 6-6c. The ratio will increase regardless of the high or low MHO loadings, and will finally be stabilized given a constant MHO loading scenario in a conceptual swimming pool system.

Conclusions

The following conclusions were obtained from this study:

- Monitoring of an indoor swimming pool over a 1-year period revealed HAA levels up to 1650 μg/L and stable THMs at 68 μg/L in average in the pool water. High HAA levels and the difference between the concentrations of HAAs and THMs was attributed to three factors: (1) MHOs from pool users; (2) slow HAA reduction; and (3) long water retention time.
- All MHO samples were found to have high DBPFPs, and MHOs contributed more HAAs than THMs. The sweat, saliva, skin wash, hair wash, and urine samples had higher DBP yields than NOM in drinking water.
- The THM reduction rate coefficient was 0.45 per day while the HAA reduction rate coefficient was 0.023 per day based on laboratory pool simulations.
- The model achieved a good simulation of a real swimming pool system. Optimized parameters of the model implied approximately 117 ml sweat and 69 ml urine per person were released to the pool. The sensitivity analysis indicated that MHO loadings had a major impact on HAAs in swimming pool water.

Acknowledgements

This study was supported by the Office of Physical Plant and Institutes of Energy and the Environment at The Pennsylvania State University. The authors thank the staff at Penn State Harrisburg Aquatic Center for providing access to the swimming pool.

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List of Figure and Table Captions

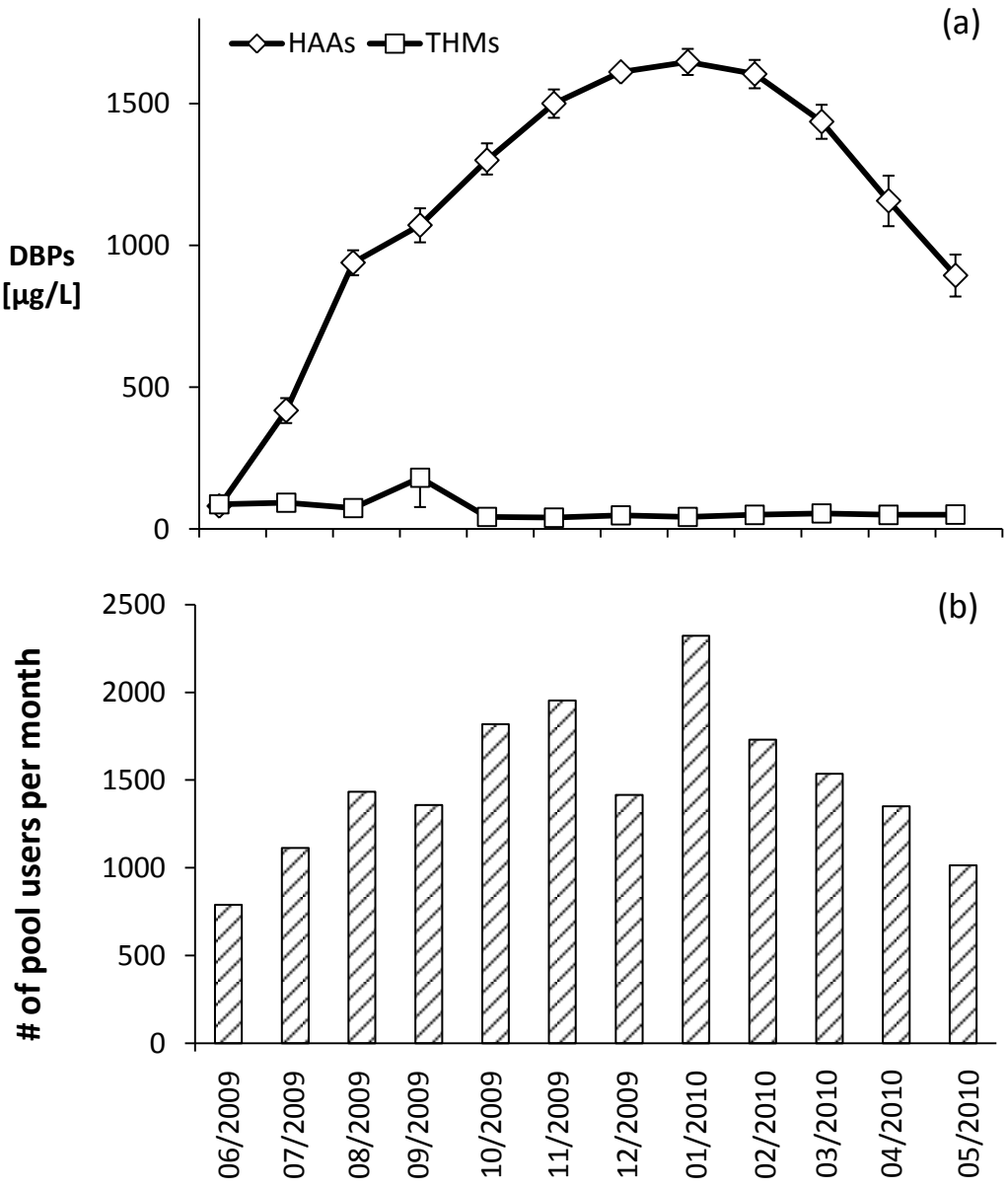

Figure 6-1. (a) HAAs and THMs in an indoor swimming pool since water change and (b) Number of pool users. Error bars are based on duplicate samples and are sometimes smaller than symbol size.

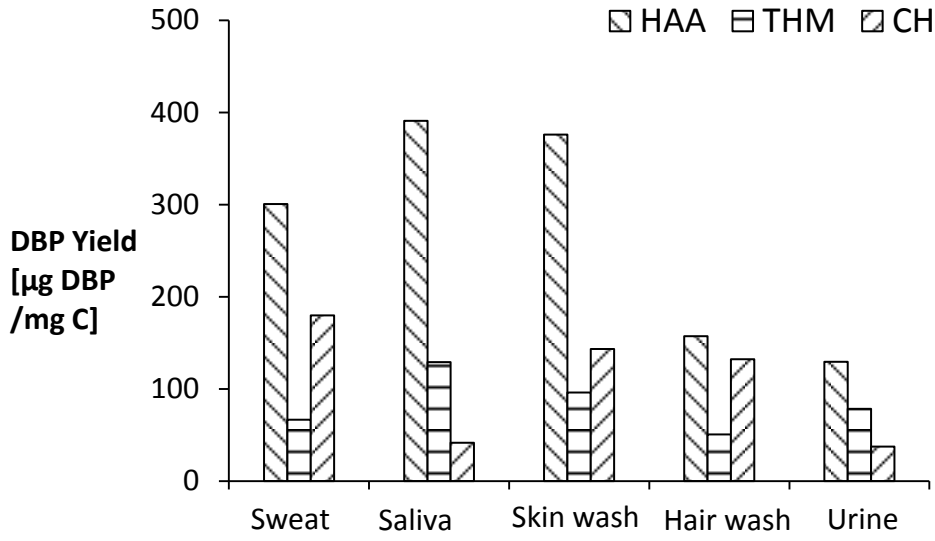

Figure 6-2. DBP yields of MHO samples

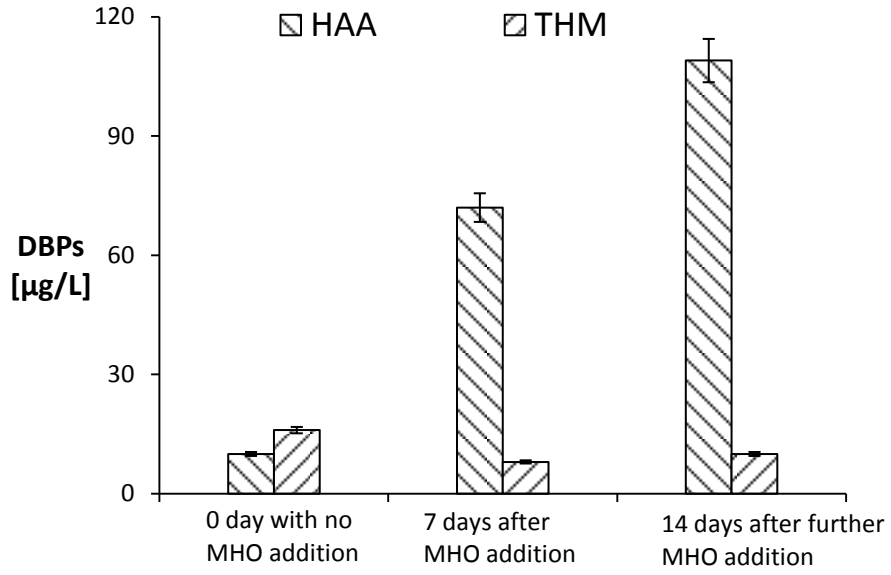

Figure 6-3. DBPs in the simulation of a lab-scale swimming pool. Error bars are based on duplicate sets.

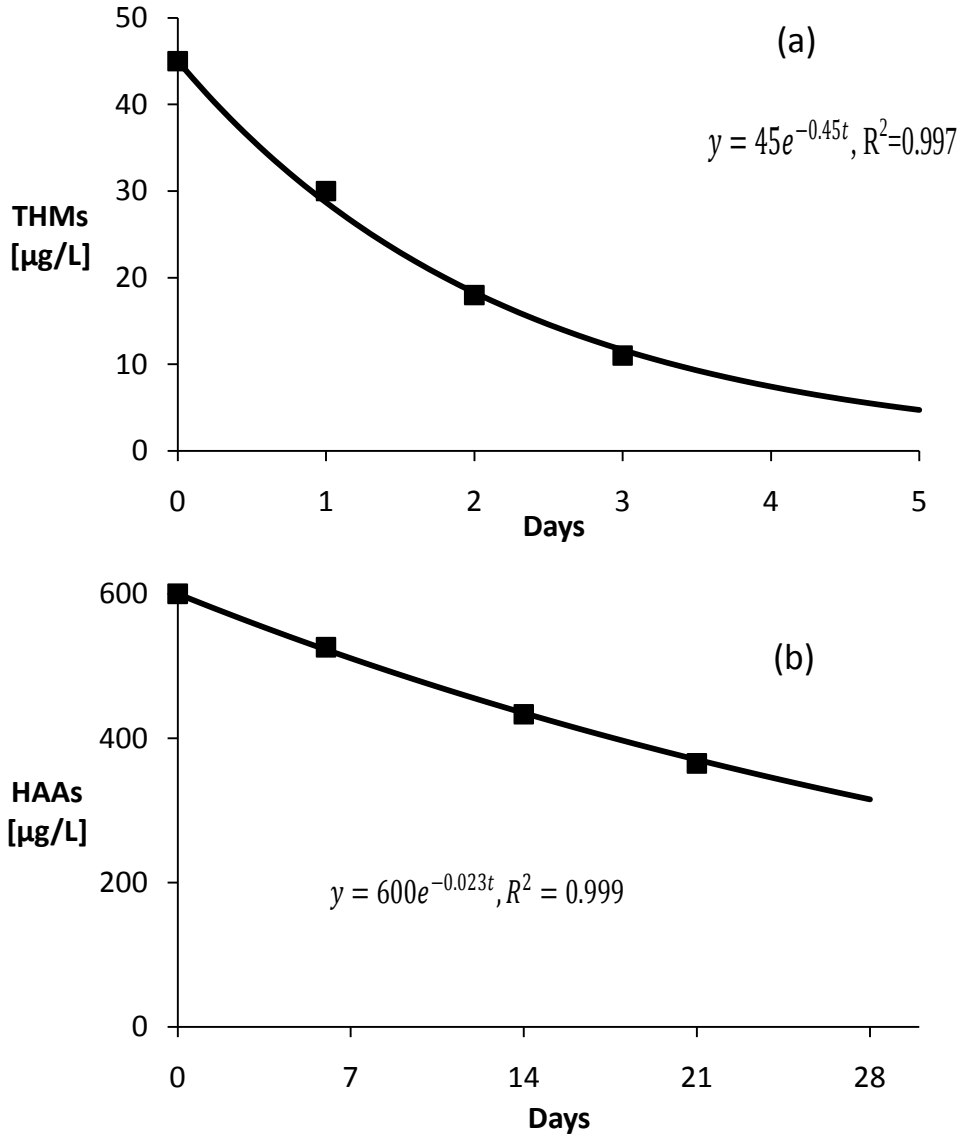

Figure 6-4. THMs and HAAs in the simulation of DBP reduction in lab-scale experiments

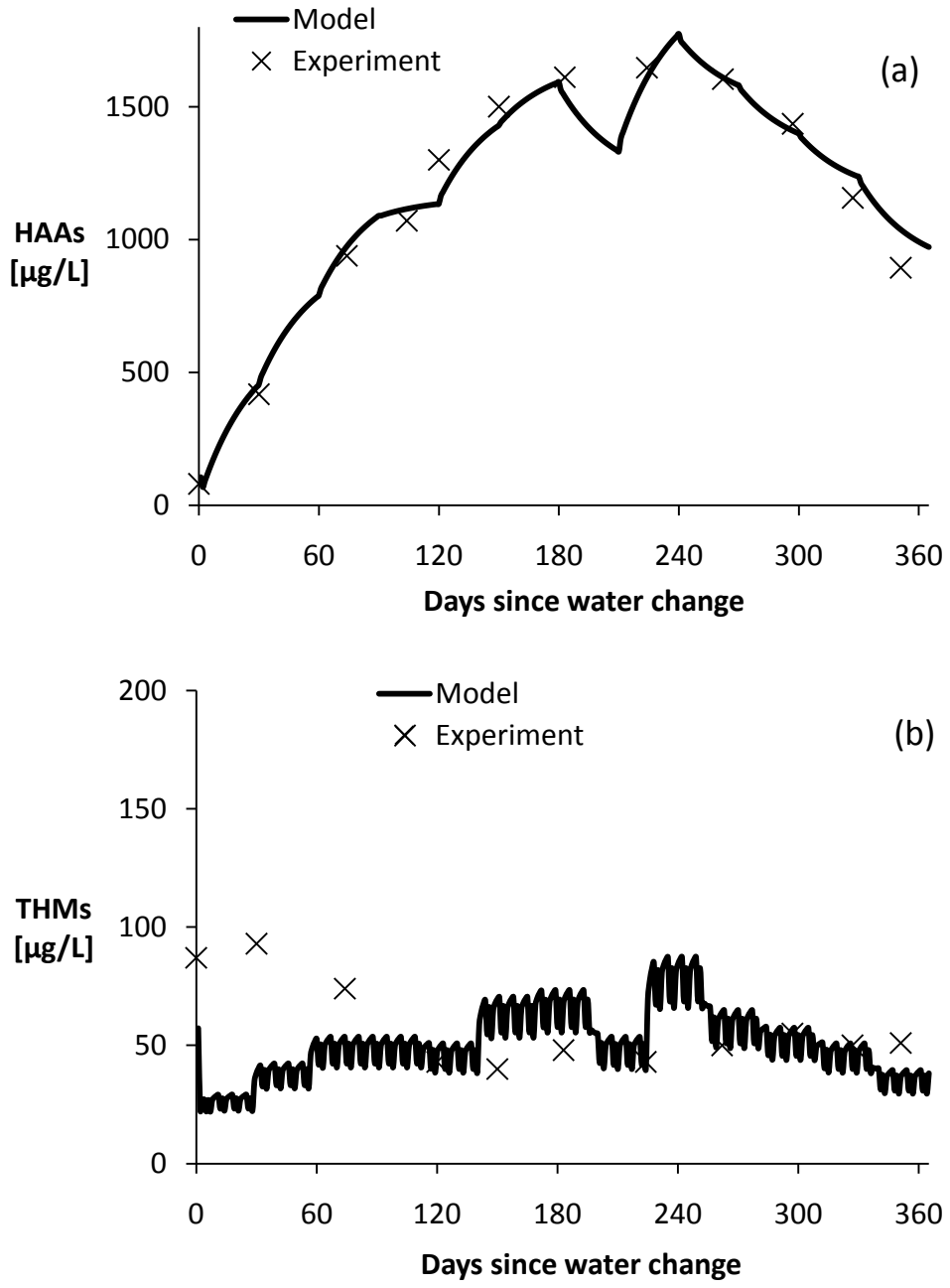

Figure 6-5. Model performance on the simulation of swimming pool DBPs

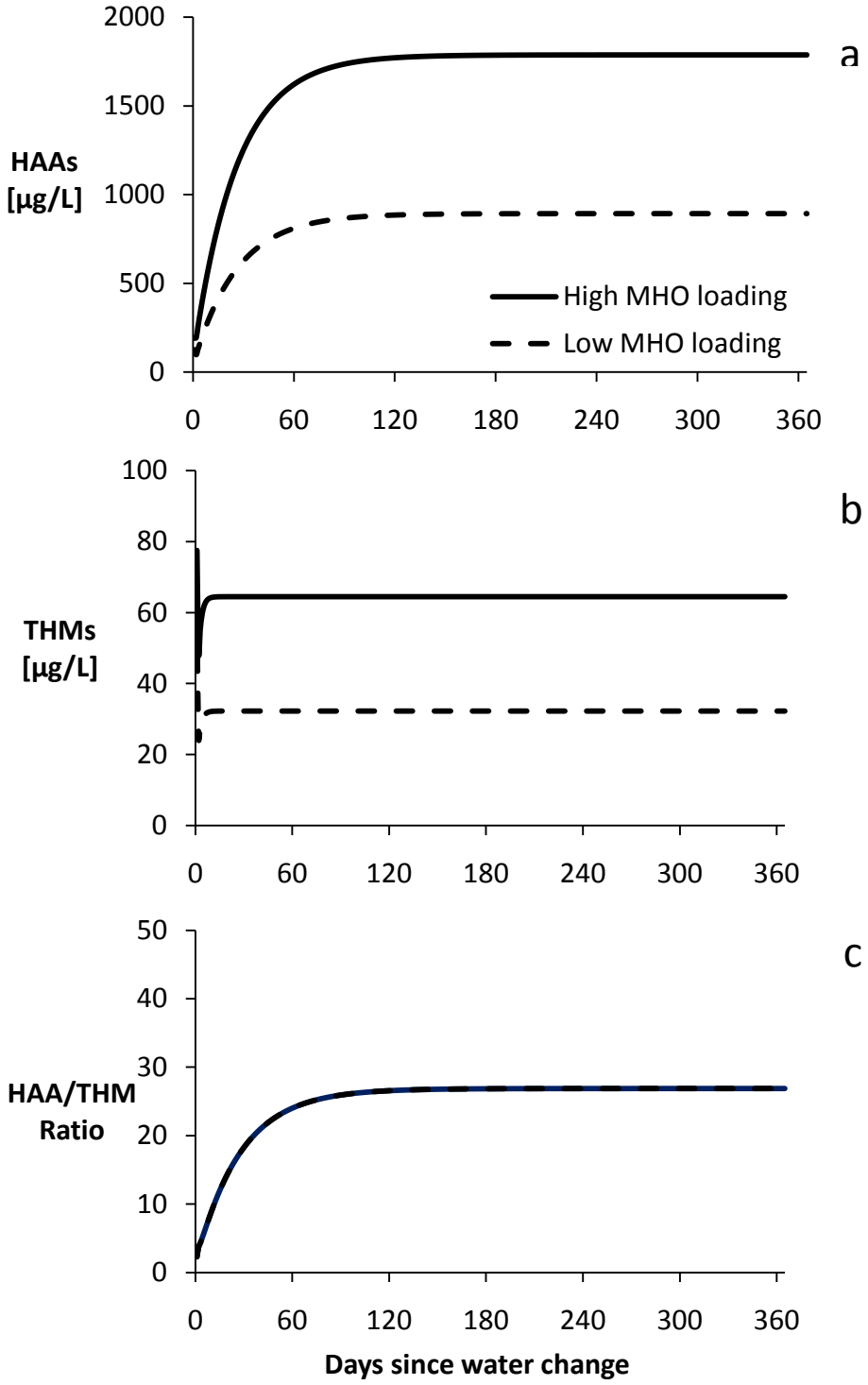

Figure 6-6. Sensitivity analysis on the impact of MHO loadings on DBPs in swimming pool

Table **6-1**. Water quality of the MHO samples

MHO samples	DOC [mg/L]	UV_{254} [cm^{-1}]	SUVA [L/mg-m]	NH_3-N [mg/L]
Sweat	6.4	0.107	1.67	0.9
Saliva	7.8	0.134	1.72	2.4
Skin wash	9.1	0.204	2.24	0.9
Hair wash	11.1	0.229	2.06	1.9
Urine	10.0	0.222	2.22	1.3

Data presented are average values of duplicate sets

Table **6-2**. DBPFPs from the MHO samples

MHO samples	Dilution ratio for DBPFP test	3-day Cl_2 demand [mg/L]	Cl_2 demand per DOC [mg Cl_2/ mg C]	THMFP [µg/L]	HAAFP [µg/L]	CHFP [µg/L]	DCANFP [µg/L]	DCPFP [µg/L]	TCPFP [µg/L]	HAAFP/ THMFP
Sweat	1:25	168	26.3	427	1930	1150	10	12	42	4.5
Saliva	1:25	170	21.8	1010	3050	324	37	11	42	3.0
Skin wash	1:25	208	22.9	875	3420	1300	32	18	43	3.9
Hair wash	1:25	233	21.0	563	1750	1470	4	18	45	3.1
Urine	1:33	408	32.9	971	1610	466	8	6	75	1.7

Data presented are average values of duplicate sets

Table **6-3**. Description of parameters for the swimming pool DBP model

Parameter	Symbol	Description	Unit	Source
Input	N	Number of pool users per day	Person	Observation
	i	Days	day	Observation
	V	Volume of swimming pool	m^3	Observation
	H_{YS}	HAA yield of sweat	μg DBP/ mg C	Experiment
	H_{YU}	HAA yield of urine	μg DBP/ mg C	Experiment
	T_{YS}	THM yield of sweat	μg DBP/ mg C	Experiment
	T_{YU}	THM yield of urine	μg DBP/ mg C	Experiment
	K_H	HAA reduction rate coefficient	day^{-1}	Experiment
	K_T	THM reduction rate coefficient	day^{-1}	Experiment
Output	HAA	HAA concentration	μg/L	Model
	THM	THM concentration	μg/L	Model
Instate	HAA_0	Initial HAA concentration	μg/L	MCL
	THM_0	Initial THM concentration	μg/L	MCL
Variable	C_S	Released carbon from sweat	mg C / person	To be optimized
	C_U	Released carbon from urine	mg C / person	To be optimized

Appendix: Abbreviations

This appendix summarizes the abbreviations used throughout the dissertation.

A2O	Anaerobic-Anoxic-Oxic
ANOM	analysis of means
A/O	Anoxic-oxic
APHA	American Public Health Association
ASP	Activated sludge process
BAP	biomass-associated products
BCAA	bromochloroacetic acid
BCAAFP	bromochloroacetic acid formation potential
BCAN	bromochloroacetonitrile
BCANFP	bromochloroacetonitrile formation potential
BDCM	bromodichloromethane
BDCMFP	bromodichloromethane formation potential
BF	bromoform
BFFP	bromoform formation potential
CF	chloroform
CFFP	chloroform formation potential
CH	chloral hydrate
CHFP	chloral hydrate formation potential
Cl_2	chlorine
COD	chemical oxygen demand
CP	chloropicrin
CPFP	chloropicrin formation potential

DBAA	dibromoacetic acid
DBAAFP	dibromoacetic acid formation potential
DBCM	dibromochloromethane
DBCMFP	dibromochloromethane formation potential
DBP	disinfection byproduct
DBPFP	disinfection byproduct formation potential
DCAA	dichloroacetic acid
DCAAFP	dichloroacetic acid formation potential
DCAN	dichloroacetonitrile
DCANFP	dichloroacetonitrile formation potential
DCP	1,1-dichloro-2-propanone
DCPFP	1,1-dichloro-2-propanone formation potential
DO	dissolved oxygen
DOC	dissolved organic carbon
DPD	n,n-diethyl-p-phenylene diamine
ECD	electron capture detector
EPA	Environmental Protection Agency
FP	formation potential
GC	gas chromatograph
HAA	haloacetic acid
HAAFP	haloacetic acid formation potential
HAN	haloacetonitrile
HANFP	haloacetonitrile formation potential
HK	haloketone
HKFP	haloketone formation potential

HRT	hydraulic retention time
MCAA	monochloroacetic acid
MCAAFP	monochloroacetic acid formation potential
MBAA	monobromoacetic acid
MBAAFP	monobromoacetic acid formation potential
MGD	million gallons per day
MLSS	mixed liquor suspended solids
MRL	minimum reporting level
MTBE	methyl tert-butyl ether
NDMA	N-nitrosodimethylamine
NH_3	ammonia
NH_3-N	ammonia nitrogen
NO_2-N	nitrite nitrogen
NO_3-N	nitrate nitrogen
NO_x-N	nitrite and nitrate nitrogen
NOM	natural organic matter
NPDES	National Pollutant Discharge Elimination System
O/A	Oxic-anoxic
OUR	oxygen utilization rate
PAC	powdered activated carbon
PRAM	polarity rapid assessment method
SCE-UA	shuffled complex evolution – University of Arizona
SDS	simulated distribution system
SMP	soluble microbial products
SPE	solid phase extraction

SRT	solid retention time
SUVA	specific ultraviolet absorbance
TCAA	trichloroacetic acid
TCAAFP	trichloroacetic acid formation potential
TCAN	trichloroacetonitrile
TCANFP	trichloroacetonitrile formation potential
TCM	trichloromethane
TCP	1,1,1-trichloro-2-propanone
TCPFP	1,1,1-trichloro-2-propanone formation potential
TF/MLE	Trickling filter and modified Ludzack-Ettinger process
THM	trihalomethane
THMFP	trihalomethane formation potential
TKN	total Kjeldahl nitrogen
TOC	total organic carbon
UAP	utilization-associated products
UFC	uniform formation condition
USEPA	United States Environmental Protection Agency
UV	ultraviolet absorbance
UV_{254}	ultraviolet absorbance at 254 nm
VFA	volatile fatty acid
WWTP	wastewater treatment plant

VITA

Hao Tang

EDUCATION

Ph.D. in Environmental Engineering, Penn State University, University Park, PA. 2011
M.S. in Environmental Engineering, Penn State University, University Park, PA. 2008
B.S. in Water Supply and Drainage Engineering, Hunan University, Changsha, China. 2004

EXPERIENCE

Graduate Research Assistant, Penn State University, University Park, PA. Jan. 2005 to Aug 2011.
Visiting Scholar, University of Massachusetts, Amherst, MA. May 2011 to Jun 2011.

AWARDS

Student Research Award, Pennsylvania Water Environment Association, 2010.
2nd Place Award in poster contest, Pennsylvania American Water Works Association, 2010
Student Research Award, Pennsylvania Water Environment Association, 2006.
2nd Place Award in poster contest, Pennsylvania American Water Works Association, 2006
Scholarship Award, Hunan University, 2001-2004
3rd Place Award in speech contest, Hunan University, 2003

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PROFESSIONAL AFFILIATIONS

American Water Works Association (AWWA)
American Society of Civil Engineers (ASCE)
Water Environment Federation (WEF)
Association of Environmental Engineering and Science Professors (AEESP)
Chinese-American Professors in Environmental Engineering and Science (CAPEES)