CONTROL OF CHLORINOUS ODOR IN DRINKING WATER BY OXIDATION PROCESSES AND CHARACTERIZATION OF CHLORINOUS ODOR PRECURSORS BY FRACTIONATION TECHNIQUE

Songkeart Phattarapattamawong

2010

Abstract

The increase in customer's complaints about chlorinous odor in drinking water has led water utilities to seek methods to improve the water quality. A promising treatment process known for musty odor removal is ozonation. During ozonation, ozone (O_3) and its decomposition product ($\cdot OH$) are utilized to oxidize micropollutants prior to chlorination. Ozonation, however, produces bromate ion, a probable carcinogen in humans. The simplest way to elevate $\cdot OH$ and minimize bromate ion at the same time is an advanced oxidation process (AOP). This study attempted simultaneous control of chlorinous odor and bromate ion in drinking water treated by ozonation and AOP (O_3/H_2O_2 process) with operation in batch and continuous modes. The contribution of trichloramine (NCl_3, a suspected odor compound causing chlorinous odor in drinking water) to chlorinous odor in drinking water was evaluated using the triangle sensory test and headspace GC-MS analysis. Furthermore, to effectively formulate treatment process for chlorinous odor control, aquatic organic matter in Yodo River was characterized using a fractionation technique in order to seek the major contributors to chlorinous odor.

To evaluate the effectiveness of ozonation and AOP in controlling chlorinous odor, a bench-scale ozonation reactor was operated in batch mode under various reaction conditions. The strength of chlorinous odor, indicated by "Threshold Odor Number (TON)", decreased by approximately 50% for the water treated by ozonation and AOP compared to chlorination alone. Changes in the concentrations of ammonium ion and bromide ion, as well as pH, had no effects on odor strength reduction. Increasing the O_3 dose to extremely high levels led to slight improvement of chlorinous odor removal, while typical O_3 doses (1-2 mg/L) seemed to have no effect on chlorinous odor reduction. Trichloramine was minor odor compound in chlorinous odor.

The effect of ozonation and AOP on chlorinous odor removal in a more practical setup was evaluated with an ozone column contactor. Results of chlorinous odor removal obtained using this continuous reactor quantitatively corresponded with those

obtained using the bench-scale reactor, indicating that differences in operation mode have no effect on chlorinous odor reduction. Although trichloramine was a minor odorous compound in water treated by conventional treatment processes, trichloramine can cause a limitation of odor control by ozonation and AOP (note that ammonium ion, which is a trichloramine precursor, cannot be oxidized by O_3 and •OH). The lowest odor strength of source water treated by ozonation and AOP was approximately 30. The molar ratio of H_2O_2 to O_3 at 0.5 (AOP0.5) was found to be effective for the formation of •OH. Furthermore, it was observed that the oxidation of organic compounds in natural river water leads to the formation of ammonium ion. Based on the musty odor removal by ozoantion and AOP, AOP0.5 with an O_3 dose of 1 mg/L should be utilized for simultaneous control of musty odor and bromate ion below their Japanese standard values when the concentrations of musty-odor compounds (e.g., geosmin and 2-methylisoborneol (2-MIB)) in source water increase to 77 ng/L and 40 ng/L for geosmin and 2-MIB, respectively. When the concentrations of geosmin and 2-MIB are higher than 125 ng/L and 83 ng/L, respectively, AOP0.5 with higher O_3 dose is necessary.

Source water treated by rapid sand filtration (RSF) mainly consisted of hydrophobic acid (HoA), hydrophilic acid (HiA), and transphilic (Trs), while in the water treated by ozonation, hydrophilic fractions (HiA, hydrophilic neutral (HiN), and Trs) were dominant. Base fraction (Bas), including hydrophilic base (HiB) and hydrophobic base (HoB) fractions, was the major fraction causing chlorinous odor in water treated by RSF. Chlorinous odor in ozonated water was mainly produced during the chlorination of HiA and HiN fractions. With the fact that ozonation followed by granular activated carbon (GAC) or biological activated carbon (BAC) is normally used, and trichloramine formation from ammonium ion in ozonated water may not be negligible. Thus, the treatment of ion exchange after ozonation/AOP and GAC is recommended in order to eliminate the remaining odor precursors such as ammonium ion.

To my parents, brother and sister, and all of my friends

Acknowledgements

Table of Contents

Chapter 3 Simultaneous Control of Bromate Ion and Chlorinous Odor in Drinking Water by Ozonation and Advanced Oxidation Process (O₃/H₂O₂ Process) with Batch Reactor   28

Chapter 4 Minimization of Chlorinous Odor and Bromate Ion Formation by Ozonation and Advanced Oxidation Process (O_3/H_2O_2) with an Ozone Bubble Contactor   55

Chapter 5 Characterization of Chlorinous Odor Precursors by a Comprehensive Fractionation Technique 79

Chapter 6 Conclusions   109

Chapter 7 Future Research   112

References   114

List of Figures

List of Tables

Chapter 1

Introduction

1.1 Background

Drinking water treatment requires the removal of numerous compounds and microorganisms from source water. In order to produce safe drinking water, effective disinfection is an important unit operation. Chlorine is widely used for the inactivation of harmful microorganisms before the water is supplied to the public. Residual chlorine is needed in water distribution systems to protect drinking water from the regrowth of pathogens. However, a high dose of chlorine can lead to customer's complaints about the taste and smell of the tap water, and raise the risk of undesired disinfection byproduct (DBP) formation (Krasner and Barrett, 1984; Nikolaou et al., 1999).

Organoleptic properties of drinking water are greatly related to customer's satisfaction on drinking water quality. Because people naturally judge that odor-containing water is unsafe for consumption, bad taste and odor can prompt complaints and loss of consumer confidence on drinking water quality. Accordingly, the American Water Works Association in 1996 conducted a survey with in the drinking water industry and found that approximately 40% of water treatment plants had received customer complaints on the taste and odor of their water (Suffet et al., 1996). Such complaints have resulted in water treatment plants in the US spending on average more than 4% of the total budgets on addressing the organoleptic problems. A similar situation also happened in France (Welte and Montiel, 1999). People have complained about the drinking water quality due to the presence of an odor, even when the water had been produced using advanced treatment technology (e.g., nanofiltration). It has led to growing attentions on the identity of precursors of odor compounds for several years

1

(Freuze et al., 2004; Freuze et al., 2005; Freuze et al., 2006). Furthermore, Bhandari and Grant (2007) reported that the level of customer satisfaction with water quality influenced the estimation of willingness to pay for the operation and maintenance of water treatment plant. Thus, organoleptic issue has to be included in drinking water production for achievement of both customer's satisfaction and maintenance of water treatment plant.

Organoleptic problems in drinking water are caused by natural, industrial or treatment processes (Bartels, et al., 1986). Natural odor compounds produced from algal metabolism (e.g., geosmin and 2-methylisoborneol (2-MIB)) have been identified as contributors to bad taste and odor for decades. The odor threshold level (minimum concentration at which human can feel odor) of these compounds is extremely low (20 ng/L or less) (Matsui et al., 2009 and reference therein). There are numerous researches that focus on the removal of these natural odor compounds (Hargesheimer and Watson, 1996; von Gunten, 2003a and references therein; Matsui et al., 2009). With the development of treatment technologies, ozonation has been found to be an effective process for removing natural odor compounds (von Gunten, 2003a and reference therein), and the demand for ozonation use has increased.

Unpleasant taste and odor can be produced not only from compounds in the natural water source, but also unintentionally during processes in treatment plants and distribution systems. While chlorine is applied in conventional treatment processes to inactivate pathogenic microorganisms, chlorination often causes unpleasant odor called chlorinous odor that has an odor descriptor as "chlorine-like" or "bleach" odor (Suffet et al., 2004). Chlorinous odor is the smell of not only chlorine itself but also the reaction products during water chlorination.

In Japan, a survey of 462 people on dissatisfaction in drinking water quality showed that taste and odor comprised approximately 30% and 15% of the complaints, respectively, and approximately 25% of customers disliked the use of chlorine in drinking water (Mizkan company, 2009). This dissatisfaction may lead to the decrease number of people who directly drink tap water. In another survey on water usage, only

37.5% of 1839 people were found to consume tap water directly, whereas the rest used additional treatments (e.g., boil, filtration) prior to consumption (Cabinet Office, 2009). Itoh et al. (2007) surveyed 3186 people on water usage by questionnaire, and reported that more than 80% of customers (both male and female) did not consume tap water directly even if water was treated by advanced treatment processes (ozonation followed by granular activated carbon (GAC)). These surveys imply that the presence of odor causes the distrust on the drinking water quality. Hence, to enhance the reliability of people on drinking water quality, safe and odor-free water is needed. One possible solution is the removal of precursors of chlorinous odor before the water is chlorinated.

Trichloramine, a chlorination byproduct, is generally formed when the chlorination process is applied to water containing ammonium ions or organic-nitrogen compounds (Shang and Blatchley, 1999). It has been suspected that trichloramine is a major odorous compound in drinking water since its odor threshold concentration was found to be the lowest among chlorine species (Welte and Montiel, 1999). Its odor threshold level detected by human-sensory test is approximately 20 µg/L or less (Bruchet et al., 2004, Yanagibashi, 2008). It can be rapidly formed at a high chlorine-to-nitrogen molar ratio (more than 1), which is usually used in drinking water chlorination treatment (Donnermair and Blatchley III, 2003). However, there is no report on the contribution of trichloramine to odor in drinking water. As such, trichloramine and its odor considered as tap water odor (odor contribution) should be studied in order to avoid aesthetic problems (i.e., odor).

Chlorinous odor has become a challenging issue for water quality control since people complain on odor in drinking water. One proposed solution is the application of a strong oxidant to oxidize the precursors of chlorinous odor before chlorination. Oxidation by O_3 and hydroxyl radical (•OH) seems to be an appropriate solution when treatment by a strong oxidant is needed.

Ozonation is a typical oxidation process that can produce •OH. The process can be incorporated into conventional water treatment processes. Because O_3 is a strong

oxidant, it is applied to water treatment for several purposes, including decoloration, taste and common odor control, elimination of micro-pollutants (von Gunten, 2003a). However, the effect of O_3 on the control of chlorinous odor has not been fully investigated. In order to produce odor-free water using eco-friendly technology (no waste after treatment), knowledge of the effect of ozonation on chlorinous odor is essential.

Bromate ion (BrO_3^-), a brominated disinfection byproducts (DBPs), has been a major concern on the ozonation of bromide-containing waters because it has been classified as a probable carcinogen in humans. The WHO has set the guideline value of bromate ion at 10 µg/L (WHO, 2008). The European Union, the US and Japan have set the standard for bromate ion at the same level (10 µg/L) (von Gunten, 2003b and references therein; MHLW, 2008). Conversion of bromide ion to bromate ion during ozonation is affected by natural organic matter (NOM), O_3 dose, pH, hydrogen peroxide (H_2O_2), bromide ion, ammonium ion, temperature, and alkalinity (von Gunten, 2003a; 2003b).

While O_3 is a selective oxidant, •OH is a nonspecific and much stronger oxidant. In order to increase the oxidation capability, the formation of •OH is generally preferred. •OH is formed during the self-decomposition process of molecule O_3. The •OH formation highly depends on various parameters such as NOM, O_3 dose, pH, and bromide concentration (von Gunten, 2003a). To achieve the oxidation of precursors of chlorinouse odor and control of bromate ion formation below the standard of drinking water quality, an upgrade from conventional ozonation to advanced oxidation processes (AOPs) may be necessary (von Gunten and Oliveras, 1998; Camel and Bermond, 1998; von Gunten, 2003a).

Advanced oxidation processes (AOPs) can offer effective water purification in term of not only the inactivation of microorganisms but also the elimination of common odor compounds (i.e., geosmin and 2-MIB) (Kim et al., 2004). Several variations include: the combination of O_3 and hydrogen peroxide (H_2O_2), O_3/H_2O_2 process; the combination of O_3 and ultraviolet (UV), O_3/UV process; the combination of H_2O_2 and

UV, H_2O_2/UV process (von Gunten, 2003b). AOPs can oxidize refractory pollutants into smaller and more biodegradable compounds that can be further treated by a process such as GAC (Jung and Madjid, 2004).

Because the O_3/H_2O_2 process has the capability to produce high levels of •OH, it is particularly promising for the decomposition of recalcitrant compounds (von Gunten, 2003a). Several studies showed that an O_3/H_2O_2 process with a H_2O_2-to-O_3 ratio of 0.5 was the most effective in producing •OH (Acero and von Gunten, 2000; Acero and von Gunten, 2001). The addition of H_2O_2 can also suppress bromate ion formation during ozonation (von Gunten, 2003b).

Dissolved organic matter (DOM) is a complex mixture of organic compounds in source water that makes up a major component of DBP precursors and has properties that may influence the water treatment process. Previous studies reported that hydrophilic acid fraction was main precursors of trihalomethanes (THMs), and hydrophobic neutral fraction was the most reactive precursor to the formation of haloacetic acids (HAAs) (Marhaba et al., 2000; Imai et al., 2003). Moreover, chlorination of DOM can cause unpleasant odor (Zazouli et al., 2007 and references therein), but its mechanisms are not clearly understood. In order to formulate a treatment process suited for chlorinous odor removal, DOM fractions in natural water should be examined so that the major contributors to chlorinous odor can be identified.

In this study, the conventional ozonation and AOP (O_3/H_2O_2 process) with bench and pilot scale experiments were conducted to simultaneously control disinfection byproducts (DBPs), particularly bromate ion, and chlorinous odor in drinking water. The main purpose of this research was to investigate treatment processes that produce drinking water with less chlorinous odor and a lower concentration of bromate ion. Furthermore, the contribution of trichloramine to chlorinous odor in drinking water was evaluated. The study determined the effects of various operating parameters (e.g., O_3 dose, ratio of H_2O_2 to O_3, Ct-value) and water quality conditions (e.g., pH, concentration of bromide ion and ammonium ion) on the simultaneous control of

chlorinous odor and bromate ion formation. In addition, the organic fractions contributing to chlorinous odor in water treated with and without ozonation were identified using a fractionation technique.

1.2 Research Objectives

This research aims to achieve the simultaneous control of chlorinous odor and ozonation byproduct (bromate ion) using an advanced oxidation process. Also, the characterization of major organic fractions causing chlorinous odor is attempted.

Specific purposes include:
1. To evaluate the effect of ozonation and AOP (O_3/H_2O_2 process) on the control of chlorinous odor
2. To study the effects of operating parameters for ozonation and AOP on the removal of chlorinous odor
3. To evaluate the contribution of trichloramine to the odor of chlorinated water
4. To assess the possibility of the simultaneous control of bromate ion and chlorinous odor formation
5. To investigate the effect of •OH on the removal of chlorinous odor
6. To investigate the effect of ozonation and AOP on odor control by the use of an ozone column reactor
7. To identify the major fraction of DOM, with and without ozonation, causing chlorinous odor in drinking water

1.3 The structure of this dissertation

Chapter 1 presents general background, objectives, and the structure of this thesis. Chapter 2 provides the available information from previous studies and basic knowledges related to this work. Chapter 3 discusses the use of a bench scale reactor operated in batch mode to examine the possibility of using ozonation and an advanced oxidation process or AOP (O_3/H_2O_2 process) to simultaneously minimize chlorinous

odor and bromate ion formation. The effects of operating parameters (i.e., O_3 dose, concentration of ammonium ion, initial bromide concentration, and pH) on the simultaneous control of chlorinous odor and bromate ion are also discussed in this chapter. In addition, the effect of hydroxyl radical (•OH) on chlorinous odor control in each oxidation processes (e.g., ozonation and AOP) are discussed. In chapter 4, a series of experiments in continuous mode with a pilot scale ozone bubble column is conducted in order to study the control of chlorinous odor and bromate ion at the same time in a more practical set up. Furthermore, the formation of •OH, indicated by oxidation of pCBA, in ozonation and O_3/H_2O_2 process is evaluated with tracer test and a tank-in-series model. Chapters 3 and 4 also discusses the contribution of trichloramine to odor in chlorinated water. Chapter 5 provides the informations of fractions causing the chlorinous odor in water treated by RSF and ozonation. Additionally, treatment processes for the control of chlorinous odor are purposed. In chapters 6 and 7, conclusions and suggested future works are presented, respectively.

Chapter 2

Literature Review

This chapter aims to present the basic knowledge and available information on drinking water odor, ozonation, advanced oxidation processes (AOP), and aquatic organic matter. Furthermore, the factors related to the formation of bromate ion and hydroxyl radical (•OH) are summarized based on previous studies.

2.1 Odor in drinking water

The production of drinking water has to take into consideration not only the safety issues (Camel and Bermond, 1998; Chiang et al., 1999; Croué et al., 1999; Boyer and Singer, 2008), but also aesthetic issues. The odor issues have become increasingly important since people started to concern on physical properties of drinking water. People naturally assume that water with an odor is unsafe for consumption (McGuire, 1995; Young et al., 1996; Suffet et al., 2004, Dietrich, 2006). Therefore, to meet the expectations of water consumers in terms of safe and aesthetic water, odor issues have to be addressed.

Odor compounds in drinking water can be classified into two groups based on their sources: naturally produced odor compounds (e.g., geosmin, 2-methylisoborneol (2-MIB)) and unintentionally human-made products (chlorination byproducts) such as trichloramine, *N*-chloroaldimines, aldehydes. The information on these compounds is provided below.

2.1.1 Natural odor compounds

Natural odor, "earthy/musty-like" odor, was found to originate mainly from alicyclic alcohols (e.g., geosmin and 2-MIB) and it was one of the major causes of the odor problems (Kajino and Sakamoto, 1995). Their odor intensity may increase under warmer climate (Terauchi et al., 1995). Geosmin and 2-MIB, produced by microbiological processes and blue-green algae, can cause taste and odor problems in the range of 10-20 ng/L (Bao et al., 1996 and references therein). In Japan, both geosmin and 2-MIB are regulated at 10 ng/L by the standards of drinking water quality (MHLW, 2008). A sequential treatment of ozonation and granular activated carbon (GAC) is the most common technique to remove 2-MIB and geosmin. Advanced oxidation technologies, however, can effectively and better remove these common odor compounds than ozonation because of higher •OH production (Camel and Bermond, 1998; von Gunten, 2003a; Bruchet et al., 2004; Lee, 2006; Peter and von Gunten, 2007). The reaction rate constants of geosmin ($k_{•OH/geosmin}$) and 2-MIB ($k_{•OH/2-MIB}$) to •OH are 7.8 and 5.09×10^9 $M^{-1}s^{-1}$, respectively (Peter and von Gunten, 2007).

2.1.2 Chlorinous odor compounds

Chlorination is usually used for the inactivation of microorganisms carrying waterborne diseases, and is the final treatment step before water is distributed through the pipeline network. Because of its residual effects, chlorine can preserve the water quality from bacterial regrowth along the distribution system. However, the excess use of chlorine can lead to the formation of not only harmful disinfection byproducts (DBPs) such as THMs, HAAs (Glaze, 1987; Ueno et al., 1996; William et al., 1997; Bruchet et al., 2004; Dietrich, 2006; Ates et al., 2007; Deborde and von Gunten, 2008; Hrudey, 2009), but also odorous compounds (Bruchet et al., 2004; Froese et al., 1999; Freuze et al., 2004; Freuze et al., 2005; Freuze et al., 2006).

Chlorinous odors, "chlorine-like" odor, are often considered as a cause of off-flavor of

tap water (Froese et al., 1999; Welte and Montiel, 1999). Chlorinous odor is formed when odor precursors react with chlorine. The compounds causing chlorinous odor in tap water are roughly categorized into two groups: trichloramine (an inorganic chlorination byproduct) and other odorous chlorination byproducts (e.g., aldehydes and *N*-chloroaldimines). These have been believed to be major contributors of off-flavors in tap water (Bruchet et al., 2004; Freuze et al., 2005; Yanagibashi, 2008).

2.1.2.1 Trichloramine

Among the various byproducts of water chlorination, trichloramine (NCl_3), an inorganic chlorination byproduct, has been considered one of the major odor compounds due to its high volatility. It has the lowest odor threshold concentration among chlorine species, as shown in Table 2.1. Trichloramine can form from the chlorination of waters containing trichloramine precursors. Trichloramine precursors in raw water can be categorized into two groups: ammonium ion (NH_4^+); and organic-nitrogen compounds (e.g., amino acids and proteins). Previous researches has found that the oxidation of glycine or serine (free amino acids) by •OH can produce ammonium ion as an end-product (Berger et al., 1999; Karpel et al., 2002; Leitner et al., 2002).

Table 2.1 Detected odor threshold value of chlorine species

Compound	Odor threshold (μg/L)	References
Trichloramine	20	Bruchet et al., 2004; Weaver et al., 2009
	2 or less	Yanagibashi, 2008
Dichloramine	150	Bruchet et al., 2004
Monochloramine	650	Bruchet et al., 2004
Hypochlorous acid	280	Bruchet et al., 2004

The formation of trichloramine highly depends upon pH, the molar ratio of chlorine to

10

ammonia-nitrogen (Cl/N), temperature, and contact time (Wolfe et al., 1984; Kirmeyer et al., 1993). The formation scheme of trichloramine by chlorination is shown in eqs. 2.1 - 2.4 (Yiin and Margerum, 1990). Neutral pH is suitable for monochloramine formation, whereas acidic condition are preferred in dichloramine and trichloramine formation (Jafvert and Valentine, 1992).

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3 \tag{2.1}$$

$$NH_3 + Cl_2 \rightleftharpoons NH_2Cl \quad \text{monochloramine} \tag{2.2}$$

$$NH_2Cl + Cl_2 \longrightarrow NHCl_2 \quad \text{dichloramine} \tag{2.3}$$

$$NHCl_2 + Cl_2 \longrightarrow NCl_3 \quad \text{trichloramine} \tag{2.4}$$
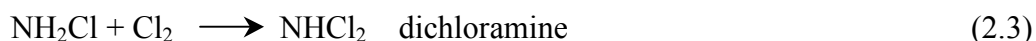
The formation of chloramines also relates to the Cl/N ratio. Donnermair and Blatchley III (2003) reported that monochloramine was produced at low Cl/N, and further addition of free chlorine resulted in the increase of Cl/N and enhanced the formation of dichloramine and trichloramine. In the case of the chlorination of amino acids, a high ratio of chlorine (Cl) to amino acids leads to the formation of trichloramine (Bruchet et al., 1992).

Several researches found that trichloramine is a potentially harmful compound to human through inhalation in swimming pool (Massin et al., 1998; Bernard et al., 2003). Trichloramine has also been found to induce changes in enzymes and tissues within the organs of mammals when water containing high concentration of trichloramine was administrated (e.g., mild changes in enzymes within the kidney, thyroid, and liver of rats when trichlormine concentration was above 2 mg/L) (Nakai et al., 2000). However, the odor threshold values have been estimated to be much lower than the recommended value of airborne trichloramine concentration (0.5 mg/m^3) (WHO, 2006), which usually indicates the harmful level. Thus, trichloramine plays an important role as an odor compound rather than to a hazardous compound. Because there has been no report on the relationship between trichloramine concentration and the odor strength of

drinking water, the relationship between odor strength and trichloramine concentration should be investigated in order to better understand the impact of trichloramine on the odor in drinking water.

Although trichloramine concentration can be determined by UV absorbance measurement at high concentration (Gazda et al., 1995), its concentration in drinking water is usually much lower. Also, conventional titrimetric techniques (DPD ferrous titration) cannot precisely measure trichloramine concentration because of the interference by organic chloramines (Shange and Blatchley III, 1999; Donnermair and Blatchley III, 2003). Kosaka et al. (2009) has, however, developed a selective analytical method for precise trichloramine measurement using headspace-gas chromatography/mass spectrometry (HS-GC/MS).

2.1.2.2 Other organic odorous byproducts

Recently, organic chlorination byproducts (e.g., aldehydes, *N*-chloroaldimines) have also been suspected to be odorous DBPs that cause off-flavor in drinking water (Froese et al., 1999; Freuze et al., 2004; Freuze et al., 2005; Freuze et al., 2006, Dotson and Westerhoff, 2009). Organic odorous byproducts can be generated from the chlorination of amino acids, and their odor threshold levels in drinking water are very low (Brosillon et al., 2009). Thus, amino acids seem to be important precursors of odorous chlorination byproducts.

The chlorination of amino acids can produce various species of *N*-chlorination byproducts, depending on the amino acids (e.g., alanine, valine, phenylalanine, glycine) (Freuze et al., 2004; Freuze et al., 2005; Freuze et al., 2006). The odor of nitrogenous chlorination byproducts relied on starting compounds (i.e., odor precursors). Several studies have found that the threshold odor concentrations of the various chlorination byproducts of amino acids differ as shown in Table 2.2. Hisamoto (2009) similarly reported that the odor strengths of chlorination byproducts from amino acids were different as shown in Table 2.3.

Table 2.2 Odor threshold concentration of the chlorination by-products of amino acids in water (µg/L)

Amino acids	Aldehyde		Nitrile	Chloroaldimine
	Freuze et al. (2005)	Froese et al. (1996)	Freuze et al. (2005)	Freuze et al. (2005)
Phenylalanine	30	4	1200	3
Valine	4	0.9-2.3	430	0.20
Leucine	5	0.15-2.0	210	0.25

Previously, aldehydes (R-CH=O) have been reported to be odorous DBPs that result from the chlorination of amino acids (Hrudey et al., 1988; Froese et al., 1999). Aldehyde formation from the chlorination of nitrogenous organic compounds depends on the reaction conditions, such as Cl/N, pH, temperature, and reaction time. The optimum conditions for aldehydes formation from a previous study were as follows: the molar ratio of Cl/N, 1.5; pH, 9; reaction time, 2 hrs; temperature, 20 ℃ (Froese et al., 1999). Although aldehydes are also well-known as ozonation byproducts, the formation of aldehydes during ozonation was insignificant as the cause of chlorinous odor (Froese et al., 1999). Because aldehydes are biodegradable, they are easily removed by GAC or biological activated carbon (BAC), which is usually utilized after ozonation (Froese et al., 1999, von Gunten, 2003a). Welte and Montiel (1999) investigated the formation of odor compounds in water supplied from a water treatment plant in Paris. They found that aldyhydes did not have an effect on chlorinous odor in drinking water. Therefore, the contribution of aldehydes to odor in drinking water may be negligible.

Table 2.3 Threshold odor values of various chlorination byproducts from amino acids
(concentrations, 0.1 μM; pH, 7; residual chlorine after 24 hrs, 1 mg/L)
(Hisamoto, 2009)

Chlorinated amino acids	Odor Strength (TON)
Lysine (Lys)	22
Tryptophan (Trp)	24
β-Alanine (β-Ala)	24
Glutamine (Gln)	28
Threonine (Thr)	30
Alanine (Ala)	33
Cysteine (Cys)	36
Serine (Ser)	38
Isoleucine (Ile)	41
Glycine (Gly)	43
Aspartic acids (Asp)	44
Histidine (His)	48
Glutamic acids (Glu)	48
Arginine (Arg)	58
Methionine (Met)	58
Proline (pro)	62
Valine (Val)	67
Leucine (Leu)	69
Asparagine (Asn)	71
Phenylalanine (Phe)	101
Tyrosine (Tyr)	102

Recently, *N*-chloroaldimines (R-CH=NCl) have been suspected to be odorous DBPs in drinking water. The odor of *N*-chloroaldimines is characterized as "unexplainable" (Freuze et al., 2006 and references therein). *N*-chloroaldimines has several characteristics that potentially create odor in drinking water: long half-life of approximately 50 hrs at 20 ºC, and extendable to 500 hrs at 25 ºC; low odor threshold

level, less than 1 µg/L; formation at high Cl/N, more than 1 (Freuze et al., 2004; Freuze et al., 2005). Brosillon et al. (2009) reported that the detected N-chloroaldimines levels in real drinking water complained on odor in France was close to or higher than the odor threshold values detected in laboratory conditions. Therefore, the minimization of N-chloroaldimines is a necessary step in producing odorless water (Freuze et al., 2006).

Although several researches focused on the contribution of specific odorous compounds to the odor of drinking water, the major contributor to odor has not been reported. At the same time, odor is usually generated from several odorous compounds together in tap water odor, so evaluation by chemical analysis of a specific compound is very difficult to achieve. In addition, the detection limit of odor using chemical analysis is somewhat higher than that of human sense. Thus, in order to properly determine the contribution of major odorous compounds to heterogeneous odor in drinking water, odor analysis using the human sense of smell is appropriate.

2.2 Odor evaluation method for drinking water

The threshold odor test (Standard Method 2150B) is the most common method for odor analysis of drinking water (APHA, 2005). "Threshold value" is the lowest level of concentration or the highest dilution that panels can detect. Thus, the threshold odor test, commonly referred as "Threshold odor number (TON)", is used to determine odor strength of water samples. For TON analysis, the sample is diluted with odor-free water until the minimum detectable odor is achieved. The analysis typically occurs at 40 ºC to 60 ºC (APHA, 2005). In order to accurately determine odor in sample, the triangle sensory test was developed (Yanagibashi, 2008).

During the triangle sensory test, the sample under investigation is presented with other two odor free samples. These three samples are identical by appearance. Then, panels are asked to choose the sample with different smell from others two times. The position of odor sample is randomly changed for the selection of the second time. Panels can proceed to a sample with a higher dilution if they can correctly select the

test sample twice. The measurement of threshold values depends on a number of factors: experimental methodology, experience of' panels, purity of odor/flavor chemical, sex, and age. Also, APHA (2005) recommends that the number of panels should be 5 or more for precise analysis.

2.3 Ozonation

Ozonation is mainly used for disinfection of microorganisms and oxidation of micropollutants (e.g., for taste and odor control). When ozonation is applied to water, it can produce two primary oxidants: molecular ozone (O_3) and hydroxyl radical (•OH), a stronger oxidant. O_3 is generally used for disinfection, while •OH is used for the oxidation of trace pollutants (von Gunten, 2003a).

Several researches found that ozonation was a very effective process to remove natural odor compounds (i.e., geosmin and 2-MIB) (Camel and Bermond, 1998; von Gunten, 2003a; Bruchet et al., 2004; Peter and von Gunten 2007). The efficiency of trace organics removal by ozonation during full-scale water treatment is shown in Table 2.4. However, no information on chlorinous odor removal by ozonation is available. Ozonation can play both positive (e.g., oxidation of odor compounds in raw water and oxidation of amino acids to nitrate ion) and negative roles (e.g., generation of ammonium ion) in terms of the odor of finished water (Leitner et al., 2002 and references therein). However, our present knowledge does not include information on which role is more dominant under the conditions commonly found in drinking water treatment practice.

Table 2.4 Degree of removal of organic micropllutants during ozonation in full-scale drinking water treatment plants (Gottschalk et al., 2000)

Substances	Removal efficiency (%)	Remarks
Musty odor compounds (i.e., 2-MIB and geosmin)	≤ 95	AOP improves the efficiency removal
Aromatic compounds	≤ 100	
Aldehydes, alcohols	Low	Typical products of ozonation, easily biodegradable
N-containing organic compounds	≤ 50	AOP may increase oxidation rate
Polyaromatic hydrocarbons (PAH)	High	

Because •OH is a reactive and nonselective oxidant to micropollutants, its formation is needed in order to increase the oxidation capability with regard to the removal odor compounds (Acero and von Gunten, 2001; Peter and von Gunten, 2007). •OH formation depends on many factors, including bromide ion and ammonium ion concentrations, O_3 dose, and characteristics of natural organic matter (NOM) (Camel and Bermond, 1998; Acero and von Gunten, 2001; von Gunten 2003a). The improvement of oxidation capability can be observed when pH and O_3 dose are increased (Acero and von Gunten, 2000). Furthermore, suspended particles should be removed before ozonation is applied in order to avoid the reduction of oxidation efficiency and the increase of O_3 demand (Gottschalk et al., 2000).

Normally, studies on ozonation efficiency are conducted in a simple reactor in semi-batch or batch mode, in which oxidation reaction occurs in a transient state (i.e., O_3 concentration during reaction is time-dependent). On the other hand, actual ozonation in water treatment plant is operated in steady state (continuous mode), O_3 concentration is much independent of time because of continuous injection of O_3 gas. Previous research found that the difference of mixing condition between operation in

batch mode and continuous mode leads to the change of O_3 decomposition or •OH formation (Buffle et al., 2006). However, there is no report of the effect of reaction mode (i.e., batch and continuous modes) on the oxidation of odor precursors and bromate ion formation has been available.

Although the removal of micropollutants and pathogens by ozonation depends on O_3 dose and reaction time, the optimum condition for ozonation is hard to define by these two operating parameters because the change of these two parameters affect the formation of undesirable DBPs especially bromate ion (note that bromate ion formation relates to residual O_3 and •OH). The study of the mechanism of •OH formation or O_3 decomposition is difficult to achieve because •OH is difficult to measure due to its highly reactivity, which leads to the extremely low concentration in water (Elovitz and von Gunten, 1999). Thus, a new approach to evaluate the ozonation performance with regard to oxidation capability has come up with the use of •OH exposure or Ct-value (C, concentration of •OH; t, reaction time) (Camel and Bermond, 1998; Elovitz and von Gunten, 1999; Acero and von Gunten, 2001; von Gunten, 2003a; 2003b; Zhang et al., 2005). This assessment can also be used as a tool to optimize ozonation (involving both oxidation-disinfection and bromate ion formation control). Because the reactivity of *p*-chlorobenzoic acid (pCBA) is very low to O_3 (Elovitz and von Gunten, 1999), the only reactant to oxidize pCBA is •OH during ozonation and AOP. Thus, the formula to calculate •OH exposure ($\int [•OH]dt$) for batch mode is as follows :

$$\frac{d[pCBA]}{dt} = -k_{•OH/pCBA}[pCBA][•OH] \qquad (2.5)$$

Integration of eq. 2.5 yields

$$\ln\left(\frac{[pCBA]}{[pCBA]_0}\right) = -k_{•OH/pCBA}\int_0^t [•OH]dt \qquad (2.6)$$

where $k_{•OH/pCBA}$ is the reaction rate of •OH with an ozone-resistant probe (pCBA). Its

value is 5×10^9 $M^{-1}s^{-1}$ (Elovitz and von Gunten, 1999). The term Ct-value represents the time-integrated concentration of •OH.

2.3.1 Advantages for the application of ozonation

Because O_3 is a strong oxidant, it can be a better option than chlorine in controlling some waterborne pathogens. Former studies have shown that O_3 can effectively inactivate oocysts of the protozoa parasite-*Cryptosporidium*, which is highly resistant to free chlorine and monochloramine (Kim et al., 2004). Furthermore, several researches have found that ozonation can control harmful DBPs (e.g., THMs and HAAs), pesticides, and pharmaceuticals products (Camel and Bermond, 1998 and references therein; von Gunten, 2003a and references therein; 2003b and references therein). Furthermore, ozonation can control not only taste and common odors (e.g., geosmin and 2-MIB), but also decoloration of water (von Gunten, 2003a and references therein).

Another important factor that has contributed to the increase in O_3 use is the reduced chlorine dose needed in water after ozonation (Glaze, 1987). With the decrease in Cl/N, a reduction in odorous DBPs is expected, while the disinfection capability remains the same (Chin and BéruBé, 2005). Knowing that the chloramines form in water with lower ratio of Cl/N, including monochloramine and dichloramine, are less odorous than the chloramines formed in higher Cl/N (trichloramine) (Donnermair and Blatchley III, 2003; Bruchet et al., 2004), a decrease in chlorinous odor can be expected due to the reduction in chlorine dose.

Ozonation has several advantages in the control and improvement of drinking water quality. However, as shown below, there are some drawbacks as well (von Gunten, 2003a; 2003b).

2.3.2 Ozonation byproducts

Ozonation byproducts are a complex class of chemicals, but bromate ion (BrO_3^-), aldehydes, ketones, carboxylic acids, hydroxyl acids, alcohols and esters are most common (von Gunten, 2003b). The most important DBP that forms during ozonation of bromide-containing waters is bromate ion. It is a probable carcinogen to human (IARC, 1999). The WHO has set the guideline concentration of bromate ion at 10 µg/L for drinking water quality (WHO, 2008). The US and Japan have also regulated bromate ion at the same level (10 µg/L) (von Gunten, 2003b; MHLW, 2008)

Figure 2.1 shows the reaction scheme of bromate ion formation during ozonation. Both oxidants (O_3 and •OH) act in sequence on the oxidation of bromide ion (Br^-). O_3 oxidizes bromide ion to form hypobromous acid (HOBr) and hypobromite (OBr^-). Then, the oxidation of hypobromite by O_3 leads to the formation of bromite (BrO_2^-), followed by the formation of bromate ion. •OH plays an important role in the oxidation of bromide ion and HOBr/OBr^-, to form bromide radical (Br•) and bromide oxide radical (OBr•), respectively. Then, both intermediate radicals (Br• and OBr•) react with O_3 to form bromate ion (von Gunten and Oliveras, 1998).
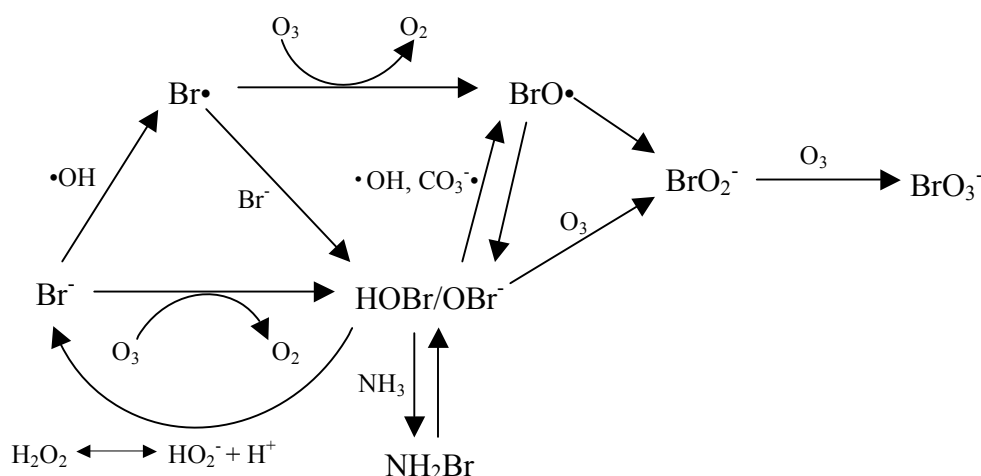
Figure 2.1 Reaction scheme for bromate ion formation during ozonation of bromide-containing waters. Adapted from von Gunten and Oliveras, 1998; Pinkernell and von Gunten, 2001; and von Gunten, 2003b.

The formation of bromate ion by ozonation highly depends on O_3 dose, pH, bromide ion concentration, ammonium ion concentration, hydrogen peroxide (H_2O_2) dose, dissolved organic matter (DOM), and temperature (von Gunten, 2003b). Prior studies suggested that the formation of bromate ion could become significant during ozonation of water with a bromide ion concentration above 100 μg/L (von Gunten, 2003b). Addition of ammonium ion to suppress bromate ion is suitable for water at low ammonia concentration because of the limitation of bromate ion suppression by ammonium ion (Pinkernell and von Gunten, 2001). The use of an optimum O_3 dose is one option for simultaneous disinfection, micro-pollutant removal, and control of bromate ion formation (Neumann et al., 2007). Likewise, lowering pH during ozonation is a simple and effective option for the control of bromate ion formation (Krasner et al., 1995; Huang et al., 2003; von Gunten, 2003b). Echigo et al. (2009) indicated that ozonation under acidic conditions is the best way to simultaneously control ozonation byproducts (e.g., aldehydes, total organic bromines (TOBr), and bromate ion). However, the endeavor to decrease bromate ion by the change of operating conditions (e.g., O_3 dose, pH) may affect the oxidation capacity related to the control of odor in drinking water.

Because •OH is a highly reactive and nonspecific oxidant, an increase in •OH formation may successfully control chlorinous odor. Hence, advanced oxidation processes (AOPs), an upgraded treatment process from the conventional ozonation to increase •OH formation, are challenging and interesting option.

2.4 Advanced oxidation processes (AOPs)

AOPs are oxidation processes that can increase •OH formation (von Gunten, 2003a). It can also decrease bromate ion formation due to the consumption of O_3 (von Gunten, 2003b). Common AOPs include: the combination of O_3 and H_2O_2 (O_3/H_2O_2 process), O_3/UV process, and H_2O_2/UV process (von Gunten and Oliveras, 1997). The simplest way to modify conventional ozonation into an AOP is by combining O_3 and H_2O_2.

Although H_2O_2 can increase •OH formation, the overdose of H_2O_2 may inhibit the •OH formation depending on the concentration of radical scavengers in water (Kosaka et al., 2001). Thus, H_2O_2 can be either promoters or inhibitors of •OH formation. As shown in eqs. 2.7 and 2.8, H_2O_2 can accelerate O_3 decomposition to produce •OH by reacting with O_3 as HO_2^- (Gottschalk et al., 2000). The overall equation for •OH formation shown in eq. 2.9 shows that two molecules of O_3 can produce two molecules of •OH. On the other hand, H_2O_2 can play as •OH scavengers (shown in eq. 2.10) when the concentration of •OH scavengers is too high (Acero and von Gunten, 2000).

$$H_2O_2 \longleftrightarrow HO_2^- + H^+ \qquad\qquad pK_a = 11.8 \qquad\qquad (2.7)$$

$$O_3 + HO_2^- \longrightarrow \;•OH + O_3•^- \qquad\qquad k = 2.2 \times 10^6 \; M^{-1}s^{-1} \qquad\qquad (2.8)$$

$$2O_3 + H_2O_2 \longrightarrow 2•OH + 3O_2 \qquad\qquad\qquad\qquad\qquad (2.9)$$

$$H_2O_2 + •OH \longrightarrow HO_2• + H_2O \qquad\qquad k = 2.7 \times 10^7 \; M^{-1}s^{-1} \qquad\qquad (2.10)$$
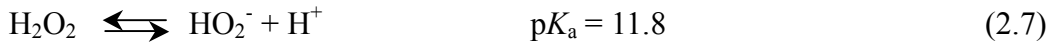
The optimum ratio of H_2O_2 to O_3 is an important operating condition. Previous studies have found that the optimum molar ratio of $O_3/\ H_2O_2$ for producing •OH is in the range of 0.35 to 0.5 (Acero and von Gunten, 2000; Acero and von Gunten, 2001). Also, the mass ratio of $O_3/\ H_2O_2$ for the effective removal of taste and common odor compounds (e.g., geosmin and 2-MIB) has been found to be in the range of 0.4 to 1.0 (Bruchet et al., 2004).

Addition of H_2O_2 not only enhances •OH formation, but also suppresses bromate ion formation. H_2O_2 can convert intermediate substances of bromate ion formation (i.e., HOBr/OBr$^-$) back to bromide ion (Br$^-$), and this reduction reaction leads to a decrease in bromate ion concentration (Figure 2.1). The mechanism in the H_2O_2-HOBr reaction system of the reduction of bromate ion is explained by eqs. 2.11 and 2.12. However, the control of bromate ion by additional H_2O_2 can possibly sacrifice some •OH if an

excess concentration of H_2O_2 is present.

$$OBr^- + H_2O_2 \longrightarrow Br^- + H_2O + O_2 \qquad\qquad (2.11)$$

$$HOBr + HO_2^- \longrightarrow Br^- + H_2O + O_2 \qquad\qquad (2.12)$$

Although some odorous compounds (e.g., aldehydes) produced during ozonation can later be removed by GAC (Froese et al., 1999), customers may still find odor and quality of drinking water treated by advanced water purification (e.g., ozonation and GAC) to be unsatisfactory (Itoh et al., 2007). To design water treatment process for odor control, information on chlorinous odor precursors after treatment by advanced water purification is required.

2.5 Fractionation of Dissolved Organic Matter (DOM)

Dissolved organic matter (DOM) is a complex mixture of organic compounds including humic substances, hydrophilic acids, proteins, lipids, hydrocarbons and amino acids. It has been found to be a main precursor of DBPs. Also, some studies report that the chlorination of DOM may produce an unpleasant odor, taste, and color in drinking water (e.g., Zazouli et al, 2007). In order to control odorous DBP formation, the behavior of NOM during chlorination needs to be understood.

Aquatic humic substances (AHS) are a common component of DOM in river water. They are yellow-brown, non-volatile organic acids, and many of them are classified as hydrophobic organics (Pomes et al., 2000; Imai et al., 2001). It has been discovered that chlorination of AHS produces DBPs (e.g., THMs and HAAs) (Pomes et al., 2000; Nikolaou and Lekkas, 2001; Imai et al., 2003). Chiang et al. (2002) found that the hydrophobic acid fractions are the main precursors of THMs, whereas another study (Imai et al., 2003) reported that the main precursors of THMs are hydrophilic acid fraction. AHS can be easily removed by a conventional treatment process: coagulation, flocculation, sedimentation, and sand filtration (Fabris et al., 2008).

While AHS serve as DBP precursors, non-humic fractions or hydrophilic groups, including amino acids, have been found to be precursors of chlorinous odor, and they can not be sufficiently eliminated in conventional treatment processes (Marhaba et al., 2000; Freuze et al., 2006). Also, Imai et al. (1998) reported that hydrophilic acids are the predominant fraction in Lake Biwa, which serves as the source of the Yodo river. Hydrophilic fractions are mostly biodegradable compounds (Buchanan et al., 2005), so they can potentially cause biological regrowth in the distribution system. Therefore, in order to provide safer drinking water without odor, it is recommended that fractions contributing to harmful DBPs and odor formation should be controlled before water is chlorinated and distributed to consumers.

In each unit treatment process, DOM displays various behaviors, depending on its physical and chemical properties. For example, a previous study reported that coagulation is effective in removing high MW compounds of DOM (more than 50% removal), whereas the removal of smaller compounds of DOM using this process is negligible (Chiang et al., 2002). In contrast, ozonation can convert large organic compounds into smaller compounds, which are more biodegradable (Chiang et al., 2002). Once the relationship between DOM properties and removal in each treatment unit is understood, an effective water treatment process can be designed.

For more than three decades, many researches have attempted to study the physical properties and chemical reactions of DOM during chlorination. Leenheer (2004) found that free amino groups significantly consumed chlorine demand, which may affect the Cl to N ratio and lead to the formation of different odorous DBPs (e.g., aldehydes, *N*-chloroaldimines). However, little information on chlorinous odor precursors is available due to the complexity and heterogeneity of DOM. In order to minimize chlorinous odor formation, it is necessary to determine which fractions are responsible for chlorinous odor.

There are several methods for categorizing and studying the behavior of DOM fractions: MW separation, hydrophobic-hydrophilic separation (also known as ion

exchange separation), ultraviolet (UV) spectroscopy, and carbon-13 nuclear magnetic resonance (^{13}C NMR) (Nikolaou and Lekkas, 2001). The method most widely used for categorizing DOM is separation based on hydrophobic-hydrophilic and acid-base properties. This technique utilizes polar and non-polar properties of each molecule at different pH conditions.

DOM fractions separated through ion exchange can be categorized into 7 classes: hydrophobic bases (HoB), hydrophobic acids (HoA), hydrophobic neutrals (HoN), hydrophilic bases (HiB), hydrophilic acids (HiA), hydrophilic neutrals (HiN) and transphilic organic carbon (Trs) (Leenheer, 2004). Because of the difficulty in completely separate hydrophobic compounds from hydrophilic compounds, the "transphilic fraction" is operationally defined to represent organic fraction between the hydrophobic and hydrophilic fractions. A classification of organic compounds according to the 5 DOM fractions can be seen in Figure 2.2 (Imai et al., 2001 and references therein).
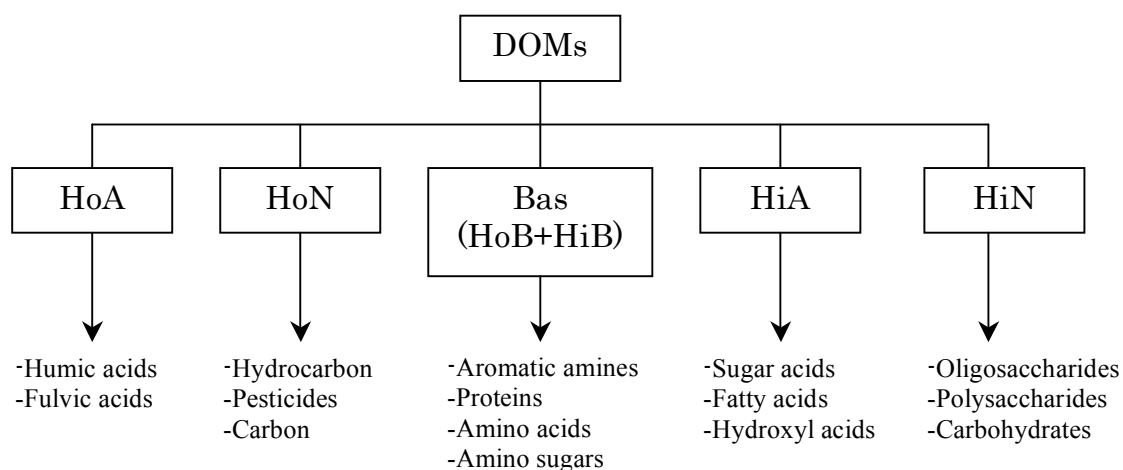
Figure 2.2 Classification of organic solutes for dissolved organic matters (DOMs)

(Imai et al., 2001)

2.6 The effect of ozonation on DOM fraction

With the fact that non-humic fractions and small MW organics (amino acids) are not significantly removed by conventional treatment processes (Chiang et al., 2002; Fabris et al., 2008), the remaining fractions of small MW compounds may contribute to the formation of chlorinous DBPs after chlorination such as aldehydes or N-chloroaldimines. Thus, these small MW compounds should be removed before chlorination.

Ozonation has been found to be more effective in removing DBPs precursors than conventional treatment processes due to its oxidation capability (Chiang et al. 2002). Ozonation could reduce DBP formation by more than 40%. Furthermore, ozonation can oxidize odorants produced by microorganisms, hydrogen sulfide aldehydes, and phenols (Chang et al., 2002 and references there in; von Gunten, 2003a). However, a previous work has shown that the ozonation of some amino acids (e.g., glycine, serine) can produce either nitrate ion or ammonium ion as end-products, with the increase in ammonium ion concentration possibly leading to an increase in chlorinous odor (Donnermair and Blatchley III, 2003). A similar study also found that ozonation of nitrogenous organic compounds in water could produce odorous aldehydes such as isobutyraldehyde and 2-methylbutyraldehyde (Huang et al., 2005).

Because ozonation of larger organic compounds can produce smaller and more biodegradable organic compounds, ozonation can sometime improve the treatment efficiency of other treatment units. For example, the oxidation of organic compounds through ozonation enhances the performance of GAC adsorption (Chiang et al., 2002). Each treatment unit has different effects on the removal of organic compounds and micropollutants (Yee et al., 2009). While coagulation removes large MW and hydrophobic DOM, GAC can remove lower MW and hydrophilic fractions. In addition, membrane filtration may be able to control DBP formation. As such, the study of odor produced from each organic fraction is an important step in designing treatment processes for odor control.

2.7 Summary

This chapter provided the available information on odor problems in drinking water, ozonation, AOP, and ozonation byproducts. The new and exciting challenges obtained from the information of this chapter are listed below.

- Information on how the parameters used in the application of ozonation and AOP affect chlorinous odor control should be sought out, as this knowledge may be very useful in helping water utilities produce odorless water.
- The effects of ozonation under different operating conditions (batch and continuous modes) on the oxidation capability and bromate ion control should be addressed.
- Among chlorine species, trichloramine has been suspected to be a major odorous compound causing chlorinous odor, but this hypothesis has not yet been proven for the heterogeneous odor of tap water, which may consist of several odorous compounds. Trichloramine's contribution to chlorinous odor should be further investigated.
- To provide the information of precursors of chlorinous odor, the removed and remaining DOM in each treatment process should be studied and determined with odor sensory test.

Chapter 3

Simultaneous Control of Bromate Ion and Chlorinous Odor in Drinking Water by Ozonation and Advanced Oxidation Process (O_3/H_2O_2 Process) with Batch Reactor

Abstract - Simultaneous control of chlorinous odor and bromate ion formation was attempted by using ozonation and advanced oxidation process (AOP, O_3/H_2O_2 process). A bench-scale ozonation reactor in batch mode was operated with various parameters (pH, O_3 dose, ammonium ion and bromide ion concentrstions). Also, the relationship between trichloramine (NCl_3, a suspected odor compound in drinking water) and chlorinous odor in drinking water was studied by a headspace GC-MS analysis and the triangle sensory test. Odor strength after chlorination decreased by more than 50% for the samples pretreated with conventional ozonation and AOP compared to samples treated only by chlorination. The change in hydroxyl radical exposure ($\bullet$OH-ct) when AOP was applied did not show the clear difference in chlorinous odor removal compared with conventional ozonation. Trichloramine seemed to be a minor odorous compound in the chlorinated water. Changes in pH and ammonium ion and bromide ion concentrations did not clearly affect the efficiency of odor removal, whereas a slight improvement in odor removal was observed when the O_3 dose was increased to an extreme level. AOP could be an option for the simultaneous control of chlorinous odor and disinfection byproducts (DBPs).

3.1 Introduction

Chlorinous odor is an important component of the public's perception on drinking

28

water quality. Ozonation and advanced oxidation processes (AOPs) are possible and simple options for the removal of odor precursors in raw water prior to chlorination. However, the effect of ozonation and AOP on chlorinous odor formation has not yet been understood.

Trichloramine (NCl_3) has been considered one of the major odorous compounds (Bruchet et al., 2004; Yanagibashi, 2008). The traditional method of evaluating drinking water odor is a sensory test with human subjects, and this method is not capable of differentiating trichloramine. Hence, a headspace GC-MS analysis and the triangle sensory test need to be simultaneously applied to evaluate the contribution of trichloramine to chlorinous odor in drinking water.

In addition, ozonation can produce bromate ion (BrO_3^-) as a disinfection byproduct (DBP). Bromate ion formation is affected by several parameters, including pH, O_3 dose, ammonium ion concentration, and bromide ion concentration. Because changes in operating parameters result in a different oxidation capability, the influence of the various parameters on odor control should be evaluated.

The objectives of this chapter are (1) to evaluate the effect of ozonation and the O_3/H_2O_2 process (hereinafter called AOP) on chlorinous odor following chlorination, (2) to assess the possibility of the simultaneous control of bromate ion and chlorinous odor, and (3) to evaluate the contribution of trichloramine to the odor of chlorinated water. In order to meet these objectives, a series of ozonation (or AOP)/chlorination sequential experiments were performed under various operating conditions. For the preliminarily study of trichloramine's contribution to tap water odor, a small survey of the trichloramine concentration in tap water was carried out before the ozonation and AOP experiments were performed.

3.2 Materials and Methods

3.2.1 Source water

For the survey of trichloramine in tap water, water samples were collected from 6 locations (hereinafter called A, B, C, D, E, and F) in the Kansai area. The samples were stored in a glass bottle at 4 ℃ until the analysis, which included chlorine residual and trichloramine measurements, as well as a sensory test. To test the hypothesis that the odor in surveyed tap water is only contributed from trichloramine, the sample collected at the location D was determined odor strength compared to trichloramine in the stock solution at the same concentration.

For the ozonation and AOP experiments, raw water was collected from the Yodo River (Osaka, Japan) three times, and stored at 4 ℃ after filtration through 0.45 µm membrane filters (mixed cellulose ester, ADVANTEC). For the experiments to study the effects of bromide ion and ammonium ion concentrations on the simultaneous control of odor and DBP formation, the raw water (dissolved organic carbon (DOC), 2.6 mg/L; bromide ion, 28 µg/L; ammonium ion, 36 µg/L) collected on October 6, 2008 (hereinafter called YRW1) was used. For the experiments to study the effects of O_3 dose (under typical doses, 1 and 2 mg/L), the water (DOC, 2.4 mg/L; bromide ion, 38 µg/L) collected on January 19, 2009 (hereinafter called YRW2) was used. Finally, to study the effect of pH and O_3 doses (a typical O_3 dose and an extreme condition, 1, 3, and 5 mg/L), a conventional ozonation was carried out only with the raw water (DOC, 2.5 mg/L; bromide ion, 33 µg/L) collected on May 14, 2009 (hereinafter called YRW3).

3.2.2 Chemical preparation

All the chemicals used in this study were purchased from Wako Pure Chemical Industries, except *o*-dianisidine dihydrichloride (Tokyo Kasei Kogyo Co., Ltd). Stock

chemical solutions were prepared by ultra pure water (Milli-Q water) produced by a Millipore (Tokyo, Japan) Acadamic-A10 purification system. The concentration of sodium hypochlorite (NaOCl) solution (at least 5%) was determined by the DPD-Ferrous titration method (APHA et al., 2005). Trichloramine stock solution was synthesized by mixing ammonium solution and sodium hypochlorite solution at a molar ratio of 1:3.15 under an acidic condition (adjusted with sulfuric acid to pH 3-4) with a T-mixer, and stored in the dark for 24 hours without headspace. Trichloramine concentration of the stock solution was measured by direct UV measurement at 336 nm ($\varepsilon = 190$ M^{-1}cm^{-1}) (Schurter et al., 1995).

3.2.3 Procedure

In order to study the effect of trichloramine on odor in tap water, a two-part survey was conducted to study the assumptions that trichloramine is only major odorous compounds in tap water. First, tap water from 6 locations (labeled as A-F) was collected, and odor contribution from trichloramine was evaluated. Second, to investigate an odorous compound in tap water, trichloramine solution was diluted to the actual concentration of the sample collected at the location D (note that water treated by conventional process) with Milli-Q water. Then, the odor strength of both samples (tap water and trichloramine solution) was analyzed by the triangle sensory test.

The study involving ozonation and AOP consisted of three sets of experiments. First, to study the effects of bromide ion and ammonium ion concentrations on the simultaneous control of odor and DBPs, YRW1 was treated at an O$_3$ dose of 2 mg/L and pH 7 under various conditions (i.e., elevated bromide ion or ammonium ion concentrations to 100 μg/L) compared with the baseline condition (DOC, 2.6 mg/L; bromide ion, 28 μg/L; ammonium ion, 36 μg/L). Second, to study the effect of O$_3$ dose, YRW2 was treated at an O$_3$ dose of 1 or 2 mg/L (a typical ozone dose applied in water treatment) at pH 7. Finally, to study the effects of pH and extreme O$_3$ doses on chlorinous odor control, YRW3 was treated by conventional ozonation at an O$_3$ dose of

1, 3, and 5 mg/L with pH 6 or 7. Ozonation and AOP treatment were conducted in batch mode. Figure 3.1 shows the schematic of the ozonation and AOP experiments. The stock solution of O_3 was prepared in an ice-bathed bottle through the bubbling of O_3 gas into Milli-Q water. The stock O_3 solution was injected to the samples through a syringe. The injection volume of stock O_3 solution varied depending on the dose of O_3. The molar ratios of H_2O_2 to O_3 were set at 0.0 (i.e., conventional ozonation, hereinafter called Ozone), 0.5 (AOP0.5), 1.0 (AOP1), and 3.0 (AOP3). After injection of O_3 solution, ozonated samples were chlorinated at approximately pH 7 for 24 hours. The source water was also chlorinated without ozonation/AOPs (AOP0.5, AOP1, and AOP3) as the control experiment (Control). Chlorine residual after 24 hours was controlled at 1 mg/L. As the probe compound of •OH, p-chlorobenzoic acid (pCBA, 0.5 μM) was used. The remaining H_2O_2 after treatment by AOP was quenched through the addition of a sufficient amount of sodium hypochlorite (NaOCl). All the experiments were duplicated for quality control. Operating conditions for ozonation of each water sample are shown in Table 3.1.
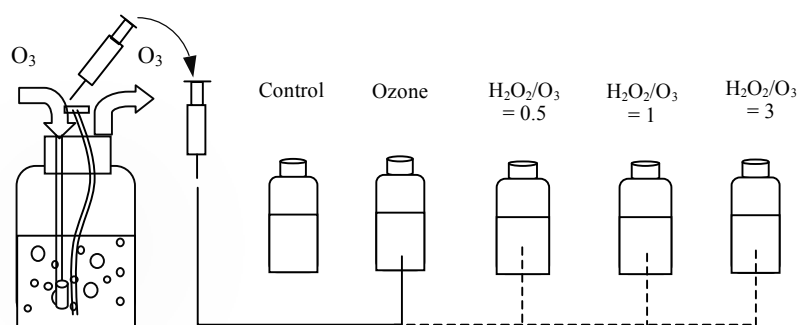
Figure 3.1 Schematic of the ozonation and AOP (No treatment by AOP for YRW3)

Table 3.1 Operating conditions for ozonation of each water sample

Parameters	YRW1[*] (DOC, 2.6 mg/L; Br$^-$, 28 µg/L; NH$_4^+$, 36 µg/L)	YRW2 (DOC, 2.4 mg/L; Br$^-$, 38 µg/L)	YRW3 (DOC, 2.5 mg/L; Br$^-$, 33 µg/L)
O$_3$ dose (mg/L)	2	1, 2	1, 3, 5
H$_2$O$_2$/O$_3$ molar ratio	0, 0.5, 1, 3	0, 0.5, 1, 3	0
pH	7	7	6, 7
pCBA (µM)	0, 0.5	0, 0.5	0, 0.5

Note: [*] *Elevated Br$^-$ or NH$_4^+$ concentrations to 100 µg/L before ozonation*

3.2.4 Analytical Methods

-Trichloramine analysis

Headspace gas chromatographic mass spectrometry (HS-GC/MS) was used for trichloramine analysis (Kosaka et al., 2009), with several modifications. In this analysis, a gas chromatograph (GC) (6890 Plus, Agilent) was connected to a mass spectrometer (MS) (JMS-AX505H, JEOL). Trichloramine was separated with an HP1MS capillary column (15m × 0.25mm i.d. × 0.32 µm, J&W Scientific). For the headspace extraction, 40 mL of sample was sealed in a 50 mL-vial bottle with a TEF-lined septum and an aluminum cap. The sample was then incubated in a water bath for 45 min at 35 ºC, before 3 mL of headspace was removed and injected into the GC-MS. The GC-MS was operated under the following conditions: injection mode, pulsed-split; carrier gas, helium; flow rate, 1.1 mL/min; initial temperature, 30 ºC; initial isothermal stage, 1.5 min; time program after the initial isothermal stage, to 90 ºC at 30 ºC/min. Trichloramine was monitored at selected ion monitoring mode (*m/z* =118.9096 for quantification; 84 and 86 for confirmation). A calibration curve was prepared through the dilutions of the trichloramine stock solution in sulfuric acid solution (pH 3). The detection limit was 15 µg/L as NCl$_3$ or 9 µg/L as Cl$_2$.

33

-Triangle sensory method

Panels

Panels were volunteers from Kyoto University (Kyoto, Japan). All volunteers were healthy during the time of examination. For precise work, 6 panels who passed the preliminary test with odor-surrogate solutions were selected from the volunteers (APHA et al., 2005). Sensory tests were conducted in a well-ventilated room at 25 $\pm$ 2 ºC. Panels were asked not to smoke or eat at least 15 min before the session.

Sensory Test

The odor strength of samples was evaluated without quenching chlorine. The samples were diluted with Milli-Q water using various dilution ratios (ranging from 5 to 400), with two blanks prepared for each sample. Before dilution, 300 mL-flasks were heated at 70 ºC for 45 min and then rinsed with Milli-Q water 2-3 times (APHA et al., 2005). The sample and blank flasks were incubated at 40 ºC for at least 20 min. Then, six panels were separately asked to select the flask with an odor out of the three flasks (identical in appearance). If they selected the correct flask, the order of the flasks was changed and the same procedure was repeated, so as to confirm that they had not coincidentally selected the correct one. The panels who answered correctly twice for the same sample set were then asked to run the same procedure for a sample set with a higher dilution ratio. This process was repeated until the panel gave a wrong answer. No information on the sample or purpose was provided to the panels during the sensory test. The highest dilution ratio that a panel could detect, or the odor strength (dimensionless number), is referred to as the Threshold Odor Number (TON). The TON value reported for each condition was the geometric mean of the TON values from four panels, excluding the highest and lowest values. As a preliminary experiment, stock trichloramine solution was diluted with Milli-Q water at various dilution ratios, and the odor threshold value of trichloramine was measured by the triangle sensory test.

-Bromide ion, bromate ion, and pCBA analysis

The concentrations of bromide and bromate ions were determined with an ion chromatograph (HPLC, Shimadzu). Bromide ion was analyzed with a Shim-pack-IC-SA2 column and a guard column (IC-SA2) with a carbonate buffer (mobile phase, 12 mmol/L $NaHCO_3$ and 0.6 mmol/L Na_2CO_3; detection, UV at 210 nm; and injection volume, 200 μL). For bromate ion analysis, a Shim-pack-IC-SA3 column protected with an IC-GA3 guard column was used for separation with a post-column derivertization method (post column reagent, *o*-dianisidine solution; detection, UV/Visible at 450 nm; injection volume, 200 μL). A reverse phase HPLC analysis was performed for pCBA analysis with an inertsil-ODS-3 column (eluent, 60% of methanol and 40% of 0.1% phosphoric acid; detection, UV at 254 nm; injection volume, 200 μL).

- O_3, H_2O_2, and dissolved organic carbon (DOC) analysis

The DOC of the samples was analyzed with a TOC-5000A analyzer (Shimadzu). Dissolved O_3 concentration was measured using the Indigo colorimetric method with a Multispec-1500 spectrophotometer (Shimadzu) (APHA et al., 2005). Stock H_2O_2 concentration was determined by direct UV measurement at 240 nm (Bader et al., 1988; $\varepsilon = 40$ $M^{-1}cm^{-1}$) with a Multispec-1500 spectrometer (Shimadzu).

3.3 Results and Discussion

3.3.1 Survey of trichloramine in tap water

Residual chlorine concentrations in the tap water from 6 locations are shown in Table 3.2. The concentration of residual chlorine ranged from 0.2 to 0.6 mg/L. These concentrations met the minimum level of free chlorine residual listed in the regulation for Japanese water quality (0.1 mg/L). The residual chlorine levels indicated that the

amount of chlorine addition was high enough to prevent bacterial regrowth in tap water. In contrast, the excess dose of residual chlorine may react with odor precursors and cause an off-flavor problem as seen in Figure 3.2. The higher residual chlorine levels resulted in the enhancement of odor strengths.

Table 3.2 Residual chlorine concentrations in representative samples at each location

Locations	Residual Chlorine (mg/L)
A	0.22
B	0.37
C	0.36
D	0.51
E	0.31
F	0.59
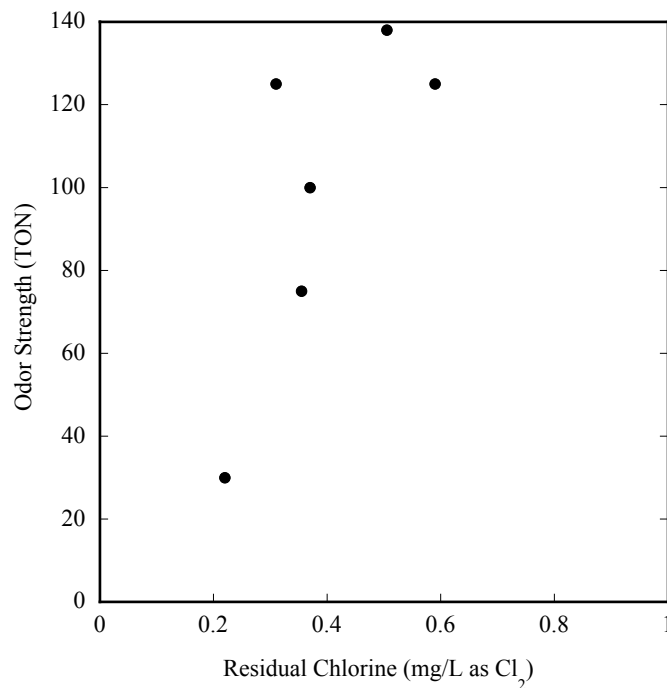
Figure 3.2 The relationship between odor strength and residual chlorine concentration in the survey of tap water

Figure 3.3 shows the relationship between odor strength and trichloramine concentration. It implies that higher trichloramine enhanced the odor strength in tap water. Thus, trichloramine can be a major chlorinous odor compound in tap water.
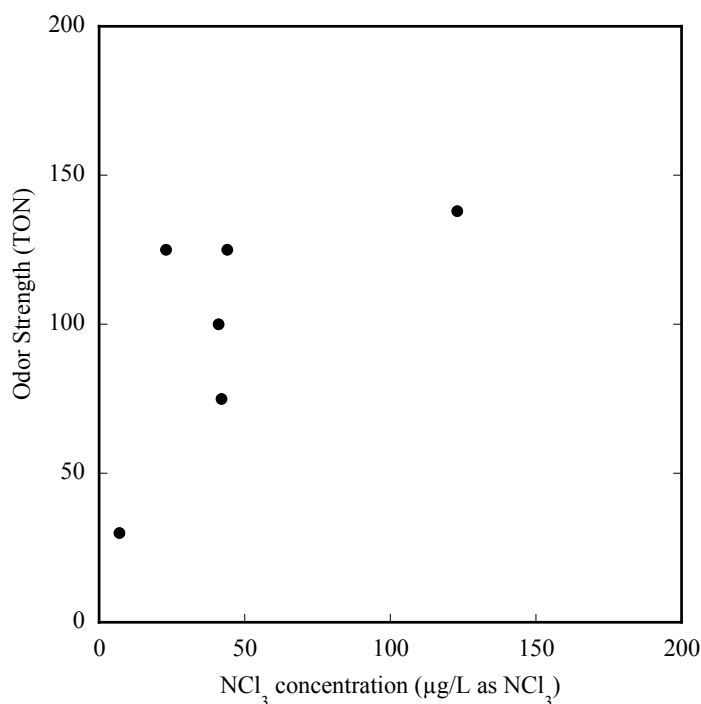
Figure 3.3 The relationship between odor strength (TON) and trichloramine (survey samples)

To determine whether trichloramine is predominant odorant among various chlorinous odor compounds, the odor threshold concentration of a trichloramine stock solution was compared to the actual threshold concentration in tap water treated by a conventional treatment process. Table 3.3 summarizes the threshold level of the trichloramine stock solution and tap water collected at location D. The TON value (dilution factor) of trichloramine solution, after the trichloramine concentration was adjusted to the same level as tap water, was approximately two times higher than tap water. The threshold level of the trichloramine stock solution was 22 μg/L as NCl_3 or 13 μg/L as Cl_2, which was similar to the finding of a previous study (Bruchet et al.,

2004). The detected concentration of trichloramine in tap water was 51 µg/L as NCl_3 or 30 µg/L as Cl_2. The difference in detected trichloramine concentration between the trichloramine stock solution and tap water can be explained by the assumption that other odor compounds (e.g., *N*-chloroaldimines) serve as predominant odorants (odor threshold values of a few µg/L or less, which are much lower than trichloramine) (Freuze et al., 2005) and therefore interfere in the test of trichloramine's odor contribution to heterogeneous odor. In other words, humans have a difficulty in distinguishing the trichloramine odor from other odors present in the tap water. Thus, chlorinous odorants in tap water may involve not only trichloramine, but other odorous compounds as well.

Table 3.3 Average detected odor threshold level (6 panels).

Parameters	Trichloramine	
	Tap Water	Stock solution
TON value	14	32
Threshold level, µg /L as NCl_3 (as Cl_2)	50 (30)	22 (13)

3.3.2 Odor threshold value of trichloramine

The average odor threshold value of trichloramine of six panels was 22 µg/L as NCl_3 (13 µg/L as Cl_2). The difference between this result and those in previous studies (Bruchet et al., 2004; Yanagibashi, 2008) may be due to the varying sensitivities of the panels, which depended on many factors such as age, gender, and experience with the sensory tests. To avoid underestimating the contribution of trichloramine, the odor threshold concentration of trichloramine is considered as the lowest value, 2 µg/L as Cl_2 or 3.4 µg/L as NCl_3 (Yanagibashi, 2008).

3.3.3 Influence of ammonium ion and bromide ion concentrations on the simultaneous control of chlorinous odor and bromate ion formation at an O_3 dose of 2 mg/L

The odor strength of chlorinated water (Control) without ozonation/AOP was around 100, whereas YRW1 itself without chlorination presented relatively low odor strength (TON≈7) (Figure 3.4). This result indicated that the main part of the odor in tap water after chlorination was mostly attributed to chlorinous odor. Comparison of the odor strengths between samples treated with chlorination alone and other conditions clearly showed that ozonation and AOP could reduce the odor strength by 50% or more for a fixed chlorine residual. On the other hand, no clear difference was observed in odor removal efficiency between ozonation and AOPs, even when the water samples were exposed to different amounts of •OH (Figures 3.4 and 3.5). This observation can be explained by the hypothesis that a major fraction of chlorinous odor precursors is reactive wiht both molecular O_3 and •OH, while the rest is resistant to both molecular O_3 and •OH. Thus, the removal of chlorinous odor may be unaffected by changes in •OH exposure. Changes in ammonium ion and bromide ion concentrations in raw water did not have major impacts on the odor strength. The average TON after chlorination of ozonated and AOP water was below 40.
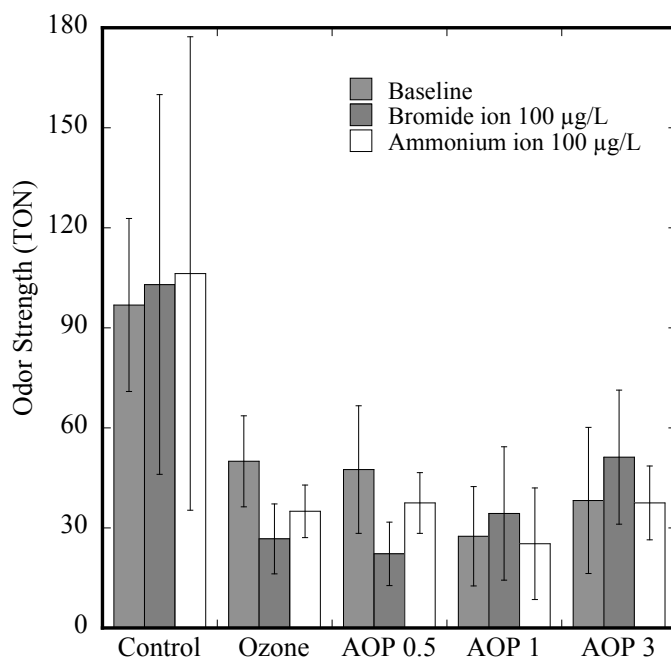
Figure 3.4 Odor strengths after chlorination for various oxidation conditions (YRW1)

In order to study the effect of •OH on the removal of chlorinous odor, the •OH exposure was calculated based on eq 2.6. Figure 3.5 shows the •OH exposure at different oxidation conditions. Ozonation was the most effective process for the formation of •OH indicated by •OH exposure for YRW1. When H_2O_2 was added, •OH exposure decreased by 15-30% (AOP0.5-AOP3). These results were unexpected by the author because additional H_2O_2 generally improves •OH formation (Acero and von Gunten, 2001; von Gunten, 2003a; 2003b). However, this result was similar with one previous study. Wert et al. (2009) mentioned that the presence of high concentration of •OH scavengers might cause a 10-40% reduction in •OH exposure. In addition, Kosaka et al. (2001 and references therein) reported that H_2O_2 could be either a promoter of •OH formation or a scavenger of •OH, depending on the concentration of the scavenger in the water. Thus, it was deduced that the concentration of promoters in YRW1 was sufficient for •OH formation, and H_2O_2 added to YRW1 served as scavengers.
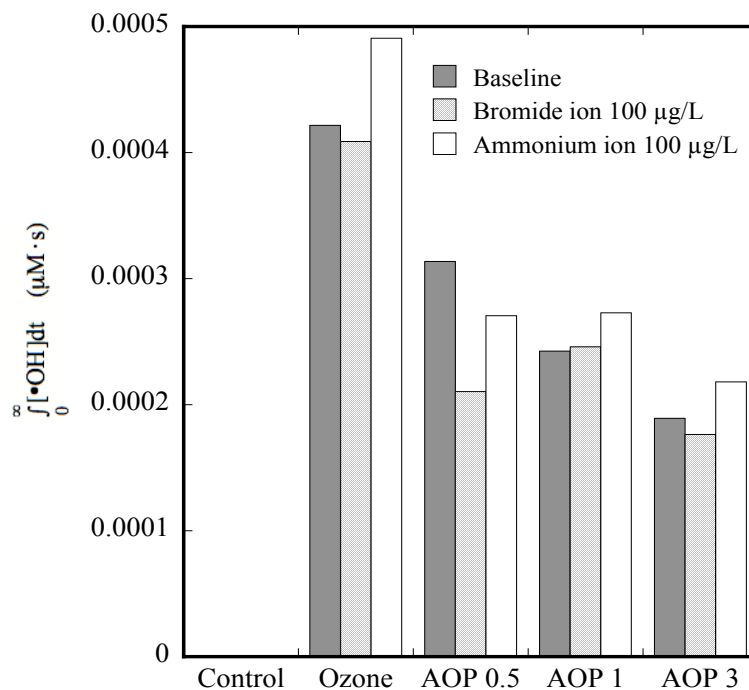
Figure 3.5 •OH exposure for various oxidation conditions (YRW1, pCBA$_{t=0}$ 0.5 μM)

Figure 3.6 shows the bromate ion formation under various oxidation conditions. Clearly, the use of ozonation increased the bromate ion concentration compared with the control. When the bromide ion concentration was elevated to 100 μg/L, the bromate ion concentration exceeded the Japanese standard values. This result was in agreement with the previous works that ozonation of water with a bromide ion concentration above 100 μg/L could produce a significant concentration of bromate ion (von Gunten, 2003b). However, bromate ion formation could be reduced with AOPs by the addition of H_2O_2. von Gunten and Oliveras (1996) reported that H_2O_2 possibly suppressed bromate ion formation by reducing hypobromous acid (HOBr) or hypobromite (OBr⁻) to bromide ion.
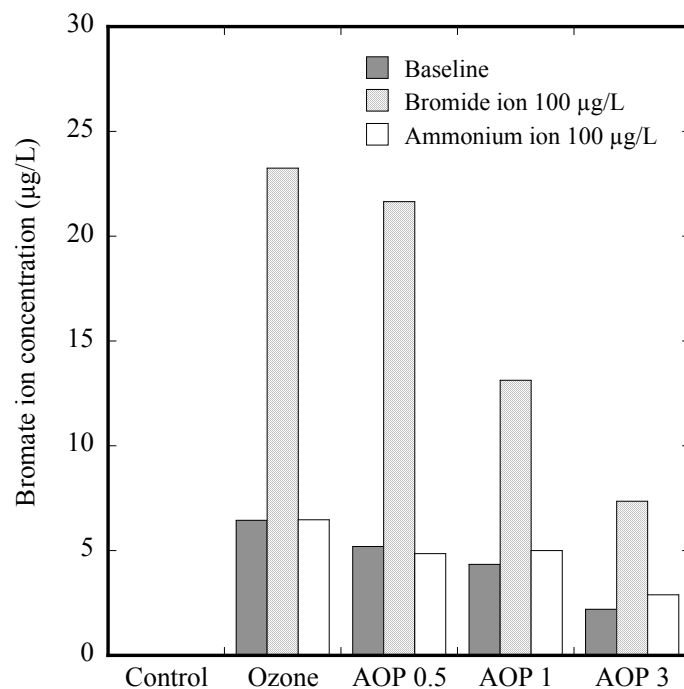
Figure 3.6 Bromate ion formation in various oxidation conditions (YRW1)

Ammonium ion addition did not clearly reduce bromate ion formation. As was described previously, the effect of ammonium ion addition on bromate ion control though the conversion of HOBr to NH_2Br is limited, and depends on the initial ammonium concentration (Pinkernell and von Gunten, 2001). Thus, YRW1 (ammonium ion concentration = 36 µg/L) may have contained a sufficient amount of ammonium to scavenge HOBr, and the addition of ammonium ion to 100 µg/L did not further reduce the bromate ion concentration.

For this set of experiments with YRW1, conventional ozonation and AOP0.5 could produce a sufficient exposure of •OH as indicated by the pCBA removal, and keep the bromate ion concentration below the Japanese standard value when operated under low bromide conditions. When water contains bromide ion above 100 µg/L, the higher ratio of H_2O_2 to O_3 (e.g., AOP3) is needed to suppress the bromate ion in accordance with the Japanese standard value.
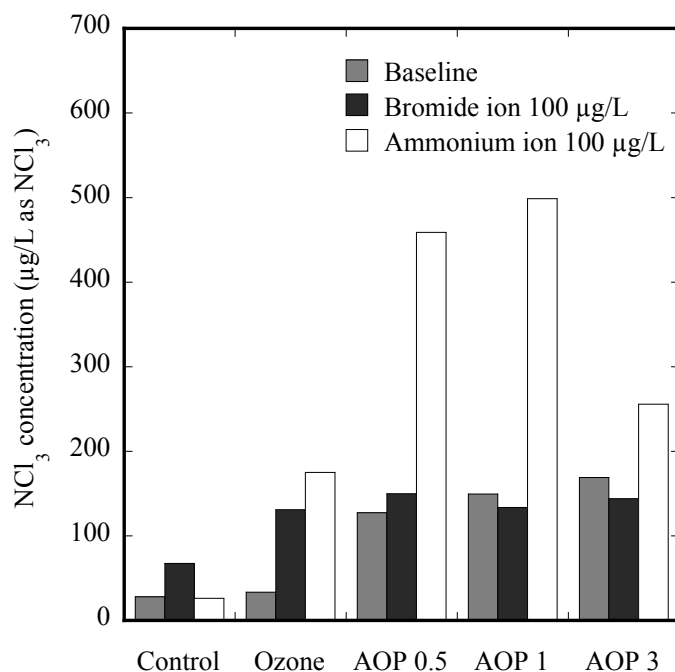
Figure 3.7 The formation of trichloramine in various oxidation conditions (YRW1)

The effects of oxidation conditions on the trichloramine formation after chlorination are summarized in Figure 3.7. The addition of ammonium ion greatly enhanced trichloramine formation in samples pretreated with ozonation and AOPs before chlorination, whereas the others (baseline and bromide ion addition) showed a slight increase in trichloramine concentration. Since trichloramine formation directly depends on the ratio of chlorine to nitrogen (Cl/N) and initial nitrogen concentration (Jafvert and Valentine, 1992), the application of a high chlorine dose to quench excess H_2O_2 during AOPs may have resulted in a much higher conversion ratio to trichloramine. A theoretical calculation with a Complex Pathway Simulator (COPASI) for varying ammonium ion concentration at a fixed chlorine residual (1 mg/L) showed that when the ammonium ion concentration was increased from 40 µg/L to 1000 µg/L, the difference in trichloramine concentration was 9 µg/L or less as NCl_3 (Satoh et al., 2009). Thus, no clear change in trichloramine formation was shown for chlorination alone when the ammonium ion concentration was adjusted to 100 µg/L.
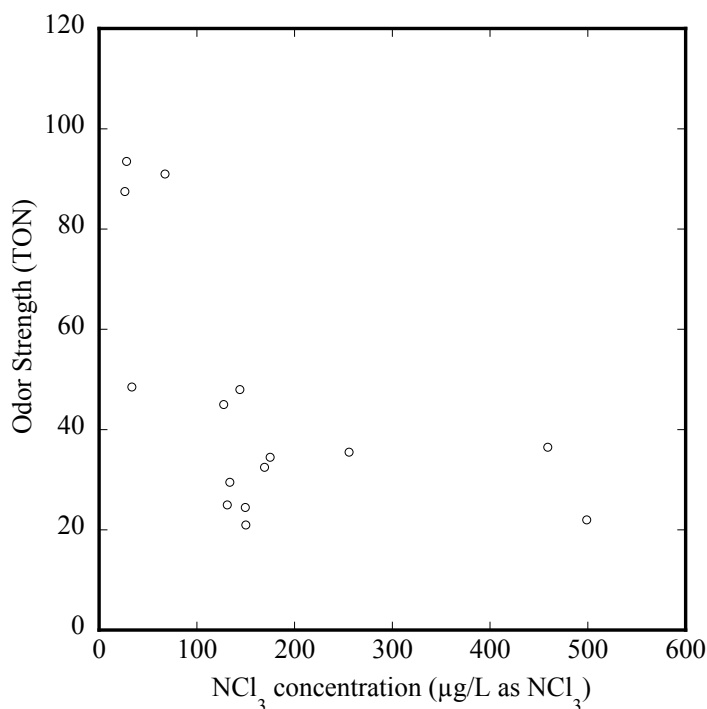
Figure 3.8 The relationship between odor strength and trichloramine (YRW1)

Because the increase in trichloramine concentration observed after ozonation and AOP does not correspond to the odor strength (Figure 3.8), it is plausible that trichloramine may not be a major odor compound in chlorinated YRW1. The reduced odor strength is possibly due to the oxidation of precursors of other odor compounds of which chemical identities are still unknown.

3.3.4 Effect of O_3 dose (at typical values, 1 mg/L and 2 mg/L) during ozonation and AOP on chlorinous odor control

Because a lower O_3 dose is preferable for controlling bromate ion formation (Krasner et al., 1995; von Gunten, 2003a; Huang et al., 2003), ozonation and AOP experiments were conducted with YRW2 with varying O_3 dose in a typical range, 1 and 2 mg/L. As the volume of Milli-Q water used to dilute the control sample was the same as the

volume of O_3 solution injected into the samples, changing O_3 dose from 2 mg/L to 1 mg/L resulted in two "Control" samples, as seen in Figure 3.9. The change in O_3 dose from 2 mg/L to 1 mg/L did not affect the odor strength following chlorination. The odor strengths of the control samples (chlorination alone) for O_3 doses of 1 mg/L and 2 mg/L were 138 and 95, respectively. The average of the remaining odor strengths for conventional ozonation and AOPs was 45. Because of some variation in the sensory test, it was difficult to conclude that the change of O_3 in a typical dose (2 mg/L or less) has an effect on the reduction of odor strength. A high dose of O_3 is, however, not cost effective. The results again confirm that the use of ozonation and AOP can decrease the chlorinous odor by approximately 50% compared with chlorination alone.

The results of •OH exposure for varying O_3 dose from 2 mg/L to 1 mg/L are different from the previous data set shown in Figure 3.5. AOP0.5 and AOP1 were approximately 15% better than the conventional ozonation in terms of •OH exposure (Figure 3.10). Because H_2O_2 could be either a promoter or a scavenger (Kosaka et al., 2001), it was considered that H_2O_2 was in large excess for AOP3, and that •OH was mostly scavenged by H_2O_2, leading to a lower oxidation capacity. The reduction of O_3 dose from 2 mg/L to 1 mg/L decreased •OH exposure by approximately 40% for all of the conditions. However, increasing the •OH exposure when operating under a typical O_3 dose did not improve the efficiency of odor removal. The average odor strength of sample after treated by a series of ozonation (or AOP)/chlorination was approximately 40. It is assumed that there is a limitation on odor removal through ozonation and AOP. A possible reason for this limitation on odor control is that the odor strength of the negative control (residual chlorine concentration at 1 mg/L in Milli-Q water) was approximately 20, which was high and was 50% of the odor strength of the sample following treatment with ozonation and AOP. Also, the remaining odor may be contributed by trichloramine (note that ammonium ion, which is a trichloramine precursor, can not be oxidized by O_3 and •OH).
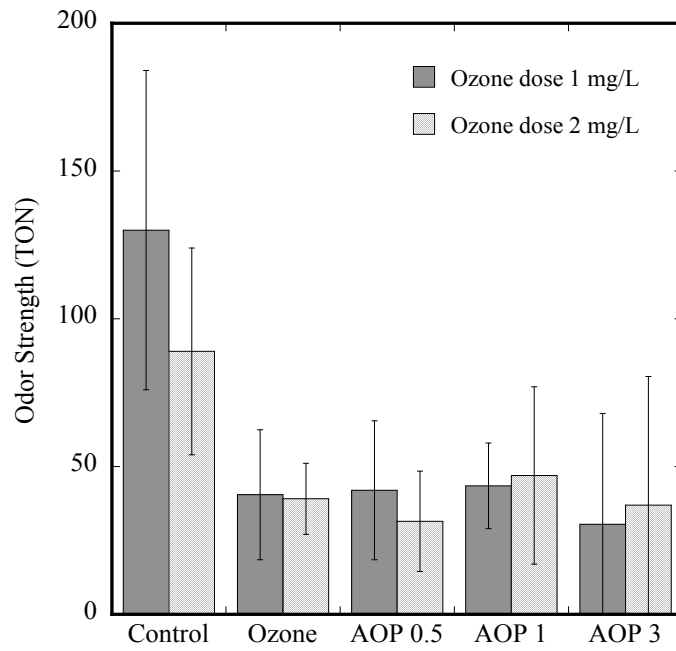
Figure 3.9 Odor strengths for O₃ doses of 1 mg/L, and 2 mg/L (YRW2)
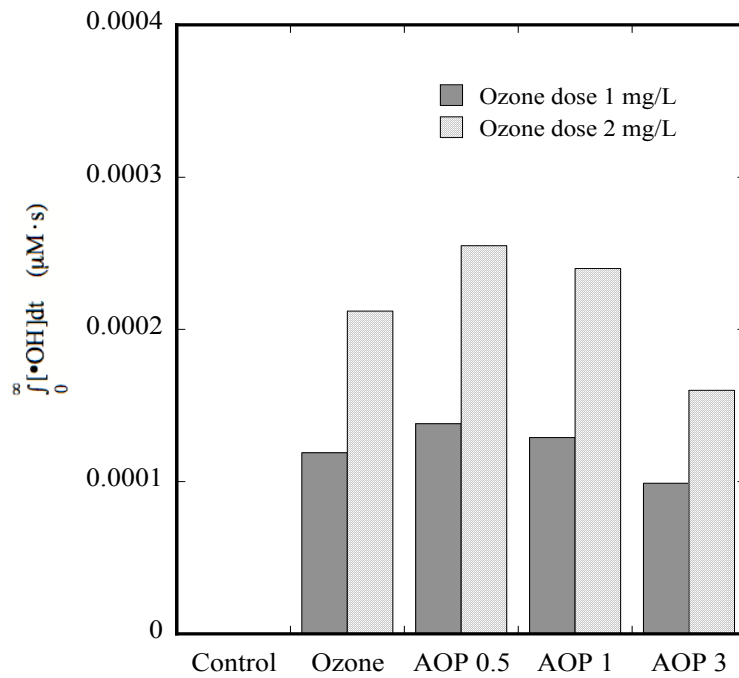
Figure 3.10 •OH exposures for O₃ doses of 1 mg/L, and 2 mg/L

(YRW2, pCBA$_{t=0}$ 0.5 μM)

Bromate ion formation during conventional ozonation and AOPs with O_3 doses of 2 mg/L and 1 mg/L is presented in Figure 3.11. Reducing the O_3 dose from 2 mg/L to 1 mg/L reduced bromate ion concentration by 60% for conventional ozonation, whereas for AOP0.5, AOP1, and AOP3, bromate ion concentration was suppressed to 3.5 µg/L, 3.3 µg/L and 1.9 µg/L, respectively. A lower O_3 dose resulted in a decrease in the oxidation efficiency for both •OH and O_3 that led to the reduction of HOBr formation. Furthermore, AOPs have been found to be effective in reducing other DBPs, such as THMs and HAAs (Chin and Bérubé, 2005). According to the reasons described above regarding the control of DBP and •OH formation, AOP0.5 or AOP1 operated with an O_3 dose of 1 mg/L is proposed for the simultaneous control of odor and DBPs in drinking water, as long as other requirements (e.g., the decomposition of micropollutants) are met (See chapter 4).
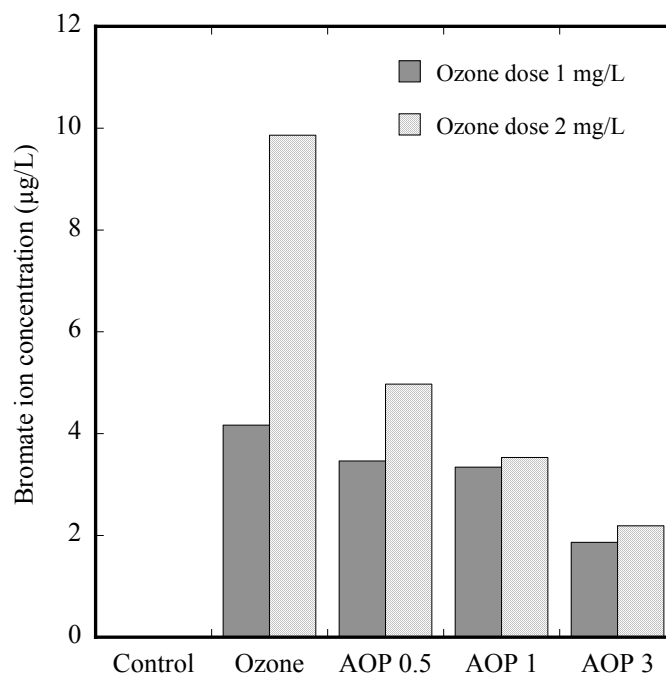
Figure 3.11 Bromate ion formation for O_3 doses of 1 mg/L, and 2 mg/L (YRW2)
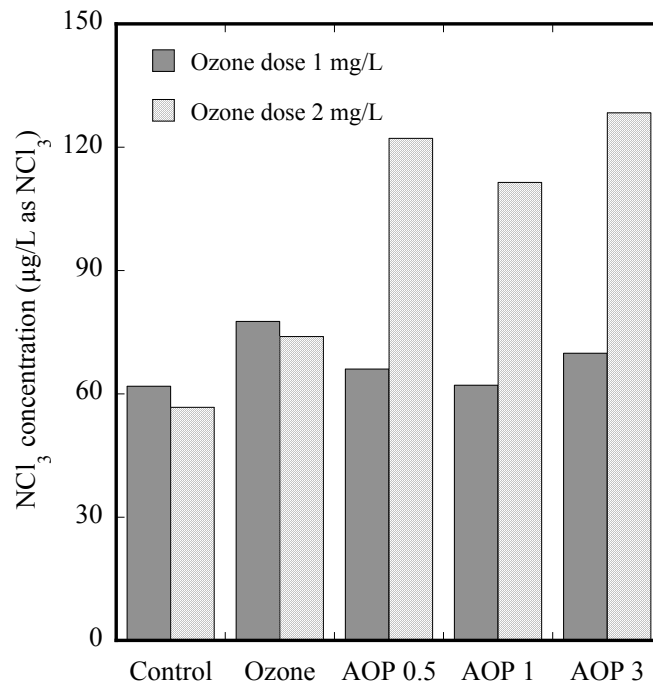
Figure 3.12 Trichloramine formation for O$_3$ doses of 1 mg/L, and 2 mg/L (YRW2)

Lowering the O$_3$ dose from 2 mg/L to 1 mg/L reduced the trichloramine formation for the AOPs, while no clear difference was observed in case of the conventional ozonation (Ozone) (Figure 3.12). An explanation similar to ones provided for previous experiments can be applied here. That is, the decrease of Cl/N ratio caused by the reduction of chlorine dose for quenching excess H$_2$O$_2$ when operated at an O$_3$ dose of 1 mg/L resulted in less trichloramine formation, whereas chlorine dose for chlorination of the control sample and ozonated sample (Ozone) did not significantly change. The higher trichloramine formation for O$_3$ dose of 2 mg/L was the same reason as the explanation above for Figure 3.7. A higher Cl/N ratio resulted in an increase in trichloramine formation. Still, it is important to note that the increase in trichloramine concentration in AOPs operated with an O$_3$ dose of 2 mg/L did not affect the odor following chlorination as shown in Figure 3.13.
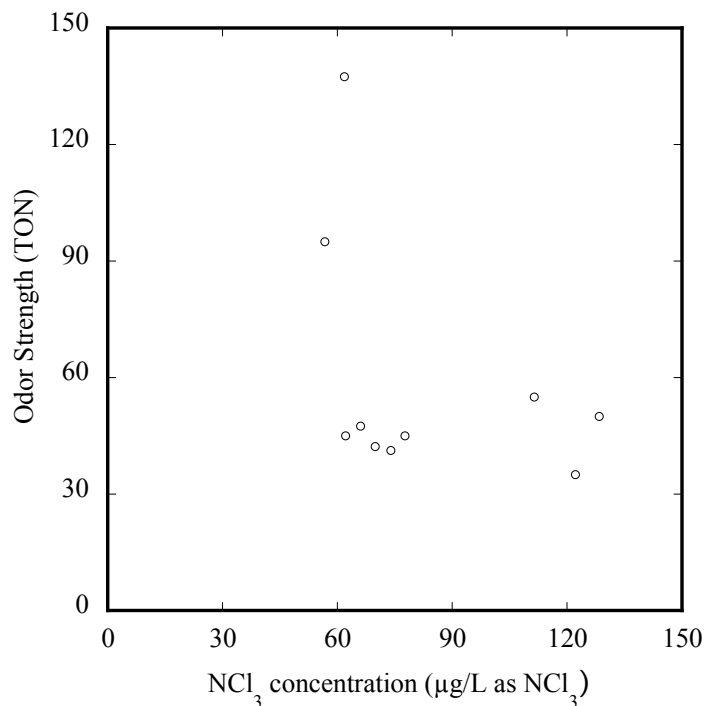
Figure 3.13 The relationship between odor strength and trichloramine (YRW2)

3.3.5 Effect of pH and extremely high O_3 dose in conventional ozonation on chlorinous odor control

To ozonate the test sample, the stock O_3 solution was injected into the samples, depending upon the target O_3 dose. The dilution of the samples was directly proportional to the O_3 doses. Thus, the 3 samples of "Control" seen in Figure 3.14 represent the control samples for different O_3 dose for fair comparison. The chlorinous odor strength, indicated by the odor strength of the three control samples, was approximately 100. That is, the dilution of the samples for ozonation had a negligible effect on the odor evaluation. After chlorination of ozonated samples, the odor strength decreased by more than 50% when compared to samples treated with chlorination alone. The increase in O_3 dose from 1 mg/L to 5 mg/L improved the efficiency of odor removal from 60% to 80%. It was deduced that the reduction in chlorinous odor intensity may result from the oxidation of precursors of chlorinous

odor by both O_3 and •OH, and the treatment efficiency mainly depended on the O_3 dose compared to pH. A comparison of odor removal under different pH conditions (acidic and neutral) displayed an ambiguous trend, but lowering the pH showed the benefit on the control of bromate ion (Figure 3.15).
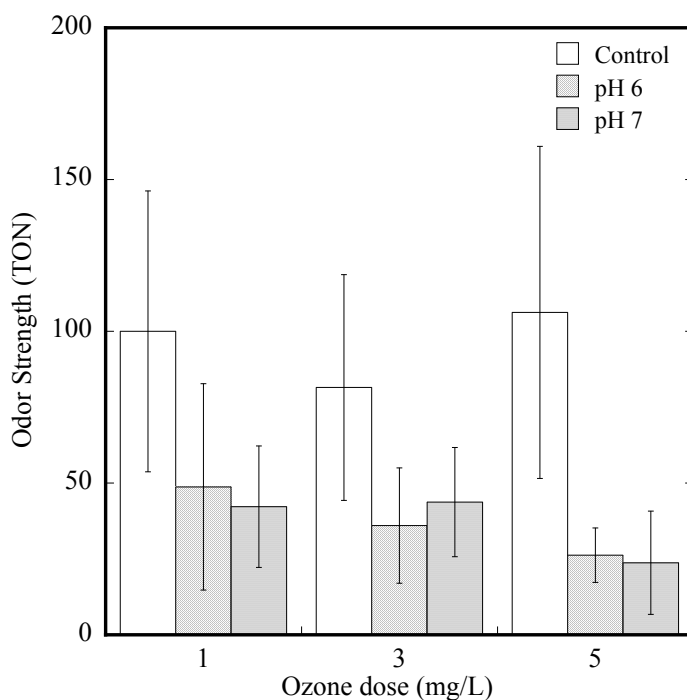
Figure 3.14 Odor strengths for a conventional ozonation with varying pH and O_3 dose (YRW3)

Figure 3.15 suggests that lowering pH decreased the bromate ion concentration by approximately 50%. This is because lowering pH can suppress the conversion of $BrO^-/HBrO$ to BrO_3^- (Pinkernell and von Gunten, 2001; von Gunten, 2003b). Ozonation with a high O_3 dose (more than 2 mg/L) could not control bromate ion formation, even when the pH was changed to an acidic pH during ozonation. Thus, lowering the pH for the control of bromate ion formation is suggested for ozonation only with a typical O_3 dose. Application of an extremely high O_3 dose may need other options (e.g., additional H_2O_2) for keeping bromate ion below the standard value.

Figure 3.15 also indicates that lowering the pH has little effect on the •OH depression, as indicated by pCBA removal, when compared to the neutral pH condition. A similar result was obtained by von Gunten (2003a). Although elevation of •OH and molecular O_3 itself by increasing O_3 dose improved the removal efficiency of chlorinous odor, the change of oxidation capability with regard to lowering pH from 7 to 6 did not increase odor strength.
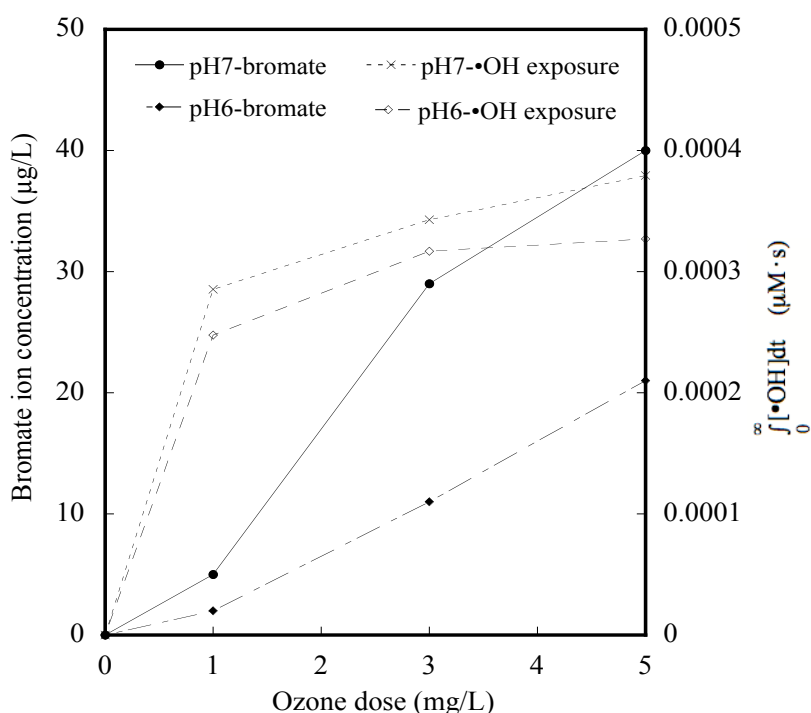
Figure 3.15 Bromate ion formation and •OH exposure (Ct-value) during ozonation (YRW3, pCBA$_{t=0}$ 0.5 µM)

Average trichloramine concentrations in the control samples with O_3 doses of 1 mg/L, 3 mg/L, and 5 mg/L were 72 µg/L, 67 µg/L, and 52 µg/L respectively (Figure 3.16). The decrease in trichloramine concentration observed in the control samples for O_3 doses of 3 mg/L and 5 mg/L resulted from the change of dilution corresponding to the ozone doses. Trichloramine concentrations of ozonated samples were higher than those of the control sample, and increased with increasing O_3 dose. Furthermore, higher concentrations of trichloramine were observed at neutral pH compared to

acidic pH. This was due to the formation of ammonium ion resulting from the oxidation of organic-nitrogen compounds by ozonation.
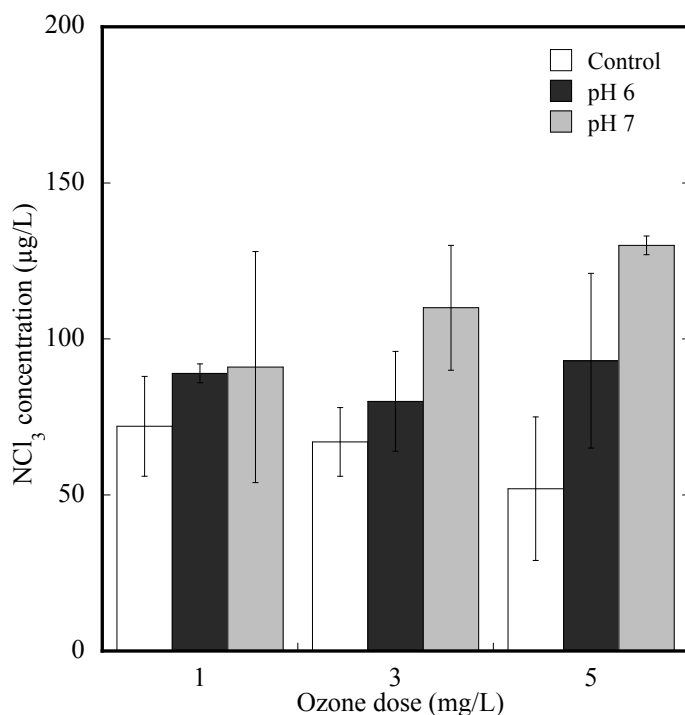
Figure 3.16 Trichloramine formation during ozonation with varying pH and O₃ dose (YRW3)

The relationship between odor strength and trichloramine concentration shown in Figure 3.17 indicates that the increase in trichloramine concentration does not lead to an increase in the odor strength. Thus, it was deduced that trichloramine was not a major odor compound in drinking water. The remaining odor can be explained by reasons similar to those mentioned above.

From three sets of experiments (involving YRW1, YRW2, and YRW3), the chlorine demands of ozonated samples were found to be slightly less than those of the control samples. Similar results were found by Glaze (1987). This decrease in chlorine demand was due to the oxidation of some organic compounds by residual O_3 and •OH. Chlorine demands of water treated by AOP were higher than those of the control

samples due to the remaining H_2O_2 levels, which depended on the O_3/H_2O_2 ratio used. In practice, the remaining H_2O_2 should be removed by other treatments (e.g., GAC, BAC) prior to chlorination, in order to decrease chlorine consumption.
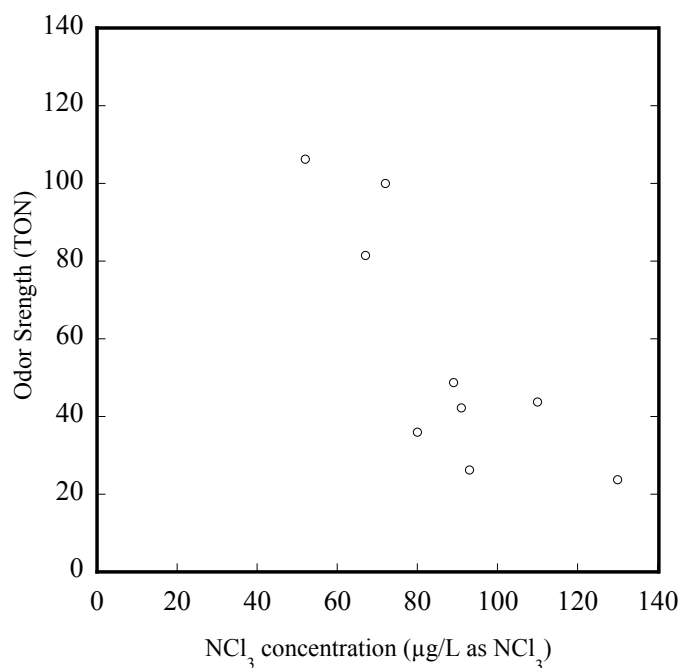
Figure 3.17 The relationship between odor strength and trichloramine (YRW3)

The suitable molar ratio of H_2O_2 to O_3 for controlling odor and bromate ion formation at the same time was difficult to determine because it depended on characteristics of source water quality (e.g., O_3 dose, pH, and bromide ion concentration). A higher ratio of H_2O_2 to O_3 could reduce not only bromate ion but also •OH formation, which may sacrifice oxidation capacity. The •OH formation must therefore be taken into consideration for the simultaneous control of drinking water odor and bromate ion formation. Generally, AOP0.5 and AOP1 were the best processes for •OH production and bromate ion control. As shown above, the operation system may require modification such as a lower pH or higher molar ratio of O_3/H_2O_2 due to variations in source water quality. Thus, it is necessary that the treatment system be flexible.

3.4 Conclusions

A bench-scale ozonation reactor operated in batch mode was used to evaluate the possibility of chlorinous odor reduction by an advanced oxidation process. The major findings were as follows:

- The use of ozonation and AOP (O_3/H_2O_2 process) decreased the odor strength (TON) by more than 50% compared to chlorination alone.

- No relationship between odor strength and trichloramine was observed. Thus, trichloramine was possibly a minor contributor to chlorinous odor.

- Changes in O_3 dose (in a typical range), pH, and ammonium ion and bromide ion concentrations during ozonation and AOP did not change the efficiency of odor removal compared with the odor removal efficiency by ozonation and AOP in normal condition of water. Increase O_3 dose of 1 mg/L to extremely high concentration (5 mg/L) improved chlorinous odor reduction by 20%.

- The removal efficiency of chlorinous odor in water treated by AOP was similar to that of the water treated by conventional ozonation, but AOP was better for not only controlling DBP formation (e.g., bromate ion, THMs, and HAAs) but also enhancing •OH formation. With the fact that musty odor compounds (e.g., 2-MIB, geosmin) are resistant to O_3, •OH may be required. Thus, AOP could be an alternative for the simultaneous control of chlorinous odor and DBP formation.

Chapter 4

Minimization of Chlorinous Odor and Bromate Ion Formation by Ozonation and Advanced Oxidation Process (O_3/H_2O_2 Process) with an Ozone Bubble Contactor

Abstract − This study attempted the simultaneous control of chlorinous odor and bromate ion formation in a more practical set up. Water collected after sand filtration was fed through an ozone column contactor running with O_3 doses of 1 and 4 mg/L. The molar ratios of hydrogen peroxide (H_2O_2) to ozone (O_3) were controlled as 0 (Ozone), 0.5 (AOP0.5), 1.0 (AOP1.0), and 2.0 (AOP2.0). Odor strength decreased approximately 50% by ozonation and AOP compared with chlorination alone. Increasing O_3 dose resulted in a higher •OH exposure, which slightly enhanced the odor reduction. Upon comparing the performance between batch-mode reactor (O_3 served by dissolved O_3) and ozone column reactor (O_3 provided by flowing O_3 gas) in terms of odor reduction, no discernable difference was observed. AOP0.5 produced the highest •OH exposure with an acceptable level of bromate ion, even when the O_3 dose was increased to 4 mg/L. This experiment confirmed that trichloramine is a minor odorous compound, and that AOP could be an alternative solution for the simultaneous control of chlorinous odor and bromate ion formation when concentrations of micropollutants (e.g., 2-MIB, geosmin) increased.

4.2 Introduction

Hydroxyl radical (•OH) is a very reactive and nonselective oxidant (Acero and von

Gunten, 2001). •OH formation is the key to the successful oxidation of ozone (O_3)-resistant micropollutants (e.g., geosmin, 2-MIB) (von Gunten, 2003a; Peter and von Gunten, 2007). For the bench scale experiments in chapter 3, •OH formation was investigated without taking in account the effect of mixing condition and the O_3 transferred from gas phase. In contrast, for practical ozonation, the effect of hydraulic characteristics on •OH formation has to be taken into consideration (von Gunten et al., 1999). Buffle et al. (2006) found that various mixing conditions during the reaction led to a different concentration of O_3 and •OH in the initial state (instantaneous occurrence after addition of O_3). Also, a change in O_3 decomposition at the initial phase may result in a different molar ratio of •OH to O_3 (R_{ct}) including the bromate ion formation (von Gunten and Oliveras, 1997). Furthermore, the different mechanisms of O_3 mass transfer (gas-to-liquid in practical ozonation; liquid-to-liquid in the experiments of previous chapter) may have significant effects on •OH and bromate ion formations. Therefore, the study of the control of chlorinous odor and bromate ion by ozonation and AOP in a more practical setup is necessary. To obtain a configuration similar to the real ozone contactor used in water treatment plants, an ozone column reactor is a simple option.

This chapter attempted the simultaneous control of chlorinous odor and bromate ion formation using an ozone bubble column in continuous mode. The performance of ozonation and AOP in controlling chlorinous odor and bromate ion under different •OH exposure with an ozone bubble contactor is discussed and compared to the result in chapter 3. The contribution of trichloramine to drinking water odor was also evaluated using data obtained in continuous mode. Finally, the optimum condition for controlling odor and bromate ion formation was investigated.

4.2 Materials and Methods

4.2.1 Source water

The water used in this chapter was obtained from a water treatment plant in the Kansai

area following treatment by sand filtration (RSF) (DOC, 1.0 ± 0.1 mg/L; pH, $7.1\pm$ 0.2; Br$^-$, 39 ± 4 μg/L).

4.2.2 Chemical preparation

All chemical preparations were as described in chapter 3.

4.2.3 Procedure

A schematic diagram of the ozone bubble contactor is shown in Figure 4.1. The glass column reactor (working volume, 9 L; height, 1.8 m; inner diameter, 8 cm) was operated continuously in counter-current mode with water flowing downward and gas flowing upward. The pressure and flow rate of oxygen gas were maintained at 0.2 Mpa and 0.25 L/min, respectively. O_3 was generated from pure oxygen using an ozone generator (AZH-3S, Hamamatsu Vegetable). Remaining O_3 in the gas phase was removed by activated carbon in a glass column prior to discharging it into the atmosphere. The RSF water was fed into the flow-through reactor at a flow rate of 0.32 L/min.

The molar ratios of H_2O_2 to O_3 were controlled at 0.0 (i.e., ozonation, hereinafter called Ozone), 0.5 (AOP0.5), 1.0 (AOP1.0), and 2.0 (AOP2.0). Each condition of the H_2O_2-to-O_3 ratio was run with an applied O_3 dose of 1 and 4 mg/L approximately (note that O_3 dose 1 mg/L is also for comparison with the data from chapter 3). Applied O_3 dose is the mass of O_3 added to unit volume of water entering a reactor vessel. H_2O_2 was injected into the ozone contactor under the water level to minimize the loss of H_2O_2 due to oxidation by O_3 gas. Chlorinated samples without ozonation/AOP called the control samples. Chlorine residual after 24 hours was kept at 1 mg/L. 0.5 μM of *p*-chlorobenzoic acid (pCBA) was used as a probe compound of •OH. The remaining H_2O_2 after ozonation and AOP was quenched by sodium hypochlorite (NaOCl).

In order to investigate the flow pattern inside the ozone column reactor, tracer test was run with 1000 µg/L bromide ion (Br⁻) solution and pure oxygen using a tank-in-series model. All experiments were duplicated for quality control, except the experiments that utilized pCBA and the tracer test.
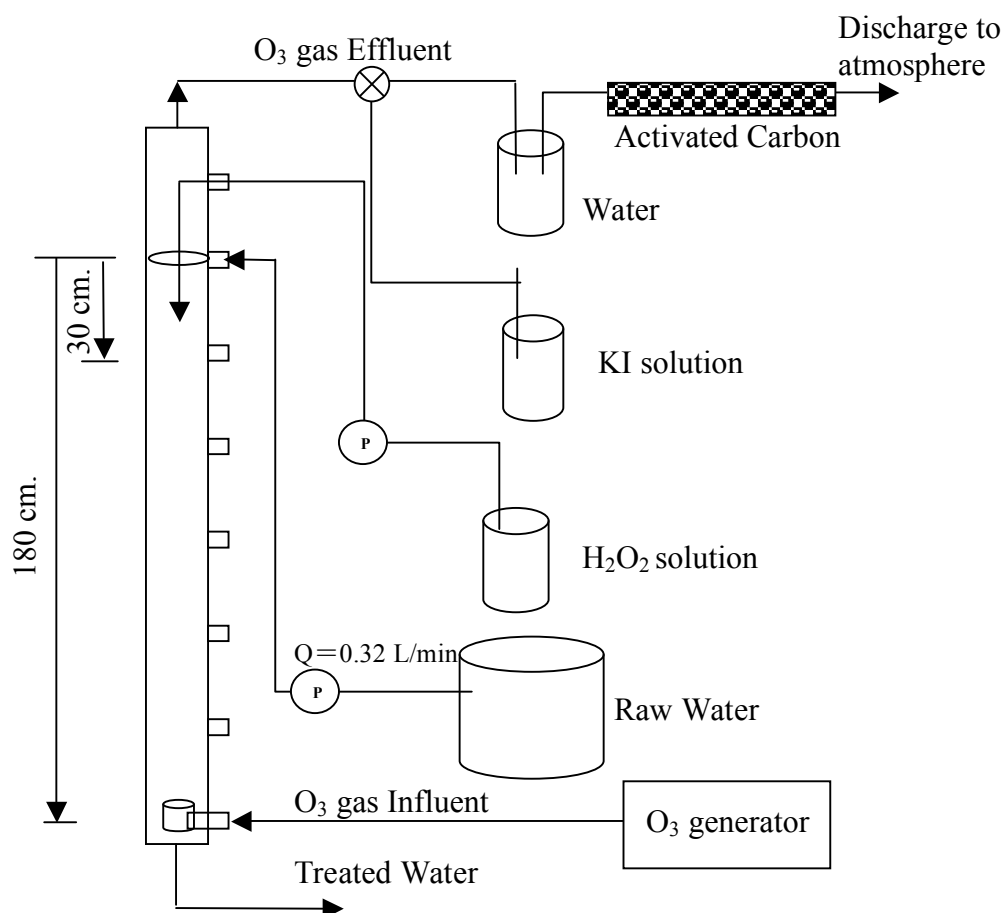
Figure 4.1 Schematic diagram of ozone bubble column

4.2.4 Analytical Methods

For ammonium ion analysis, a Shodex-IC-YS50 column protected with a guard column (Shodex-IC-YS-G) for separation was used with 2 mM of methanesulfonic acid solution as a mobile phase and a post-column fluorometric derivatization solution for the reaction of ammonia (post column reagent, o-phthaldialdehyde (OPA) solution; excitation light, UV at 364 nm; emission light, UV at 425 nm; injection

volume, 50 µL) (Kuo et al., 2005). Other analyses (pCBA, O_3 dose, bromate ion, trichloramine, sensory test) were as listed in chapter 3.

4.3 Results and Discussion

4.3.1 Characterization of flow pattern of the ozone column contactor

The hydraulic flow of the ozone contactor was characterized by a step input (continuous addition) of bromide ion, a positive step method of determining residence-time distribution. The model calculation using a tank in series model (two CSTRs (complete stirred tank reactors): volume of upper tank (V1), 2 L; volume of lower tank (V2), 7 L) showed a good fit with the observed data (Figure 4.2). The average concentrations of pCBA collected in the sampling ports were used to determine •OH exposure in each modeled tank. The design HRT (30 min) was similar to the data obtained from the tracer test (27.2 min). Therefore, the existing HRT (27.2 min) was used to calculate •OH.
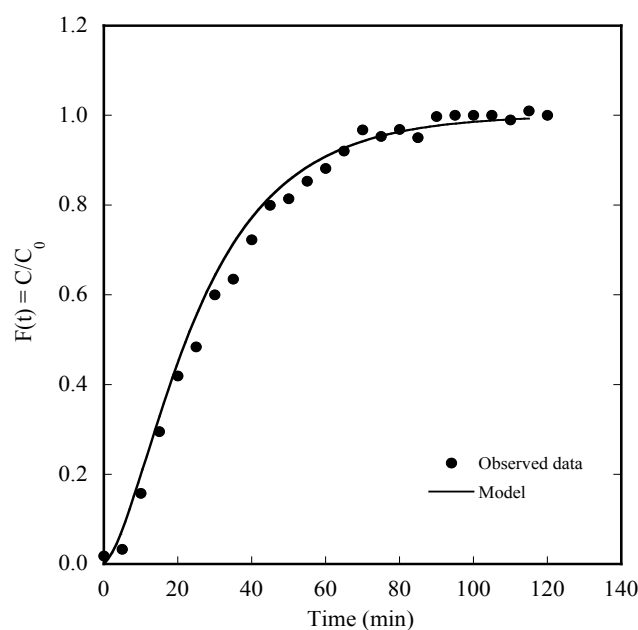
Figure 4.2 Cumulative residence-time distribution function, F(t), for the tracer test

4.3.2 Effect of ozonation and AOP on the control of chlorinous odor and bromate ion formation

Tables 4.1 and 4.2 show the dissolved O_3 concentrations in the ozone column reactor for applied O_3 doses of 1 mg/L and 4 mg/L, respectively. Dissolved O_3 concentration in the ozone column reactor was close to zero at an applied O_3 dose of 1 mg/L. At an applied O_3 dose of 1 mg/L, the percentage of O_3 consumption, which was calculated by dividing the O_3 consumption by the applied O_3 dose, increased by 13% when H_2O_2 was added, compared to the ozonation (Ozone) case. Raising the applied O_3 dose to 4 mg/L slightly increased the concentration of dissolved O_3, but the efficiency of O_3 consumption in ozonation dropped by 20% compared to that of the 1 mg/L applied O_3 dose trial. The addition of H_2O_2 improved the efficiency of O_3 consumption to more than 80%. This result can be explained by the faster decomposition of O_3 when activated by H_2O_2 (von Gunten, 2003a). Such information on O_3 adsorption efficiency is very useful for the improvement of existing ozone contactors in terms of reducing O_3 usage and increasing oxidation capability.

Odor strength (TON) in chlorinated water decreased by approximately 50% when ozonation or AOP was applied to raw water, compared to the control sample (Figure 4.3). This result implies that O_3 and/or •OH can oxidize precursors of chlorinous odor. Increasing the applied O_3 dose to 4 mg/L, an extremely high O_3 dose, slightly improved chlorinous odor removal (by 10-30%) in all samples except AOP2.0. However, no difference between ozonation and AOP in terms of odor removal was observed. The average odor strength for water treated with ozonation or AOP followed by chlorination was approximately 30. The same result was observed in chapter 3 when the O_3 dose was increased to an extreme level. When the average of the odor strength was taken using the only one data set at a time (4 data points, after the highest and lowest odor strength were dropped), the lowest average odor strength (20) was achieved in one of the two AOP0.5 trials operated with an applied O_3 dose of 4 mg/L. When the average of the odor strengths was taken using both data sets (8 data

60

points total), the lowest average odor strength (26) was observed in the AOP1.0 case. Therefore, the ratio of H_2O_2 to O_3 recommended for the achievement of chlorinous odor removal was in the range of 0.5 to 1.0.
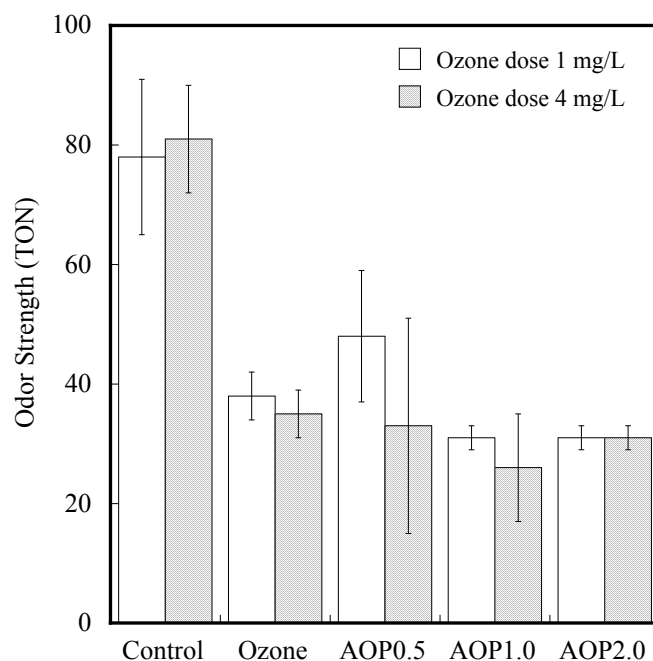
Figure 4.3 Odor strengths after chlorination for various oxidation conditions

The formation of bromate ion along the ozone column reactor with applied O_3 dose of 1 mg/L (a) and 4 mg/L (b) is shown in Figure 4.4. At an applied O_3 dose of 1 mg/L, no significant formation of bromate ion was observed (below 10 µg/L). Increasing the applied O_3 dose to an extreme level (4 mg/L) significantly elevated bromate ion concentration (to 18 µg/L). Bromate ion concentration decreased when H_2O_2 was added. AOP therefore succeeded in controlling bromate ion below the standard of drinking water quality, even when the applied O_3 dose was increased to an extreme level (4 mg/L). Similar results were reported by von Gunten and Oliveras (1998).

Table 4.1 Summary of dissolved O_3 concentrations for applied O_3 dose of 1 mg/L, mg/L

Conditions	Distance from the inlet (cm)							O_3 dose (mg/L)			% O_3 consumption
	0	30	60	90	120	150	180	Input	Output	Consumed	
Ozone	0	0.019	0.019	0.050	0.067	0.089	0.076	1.3	0.4	0.9	72
AOP0.5	0	0.013	0.013	0.016	0.016	0.035	0.020	1.3	0.2	1.1	85
AOP1.0	0	0.005	0.008	0.003	0.004	0.011	0.010	1.3	0.2	1.1	82
AOP2.0	0	0.005	0.008	0.008	0.007	0.006	0.004	1.3	0.2	1.1	84

Table 4.2 Summary of dissolved O_3 concentrations for applied O_3 dose of 4 mg/L, mg/L

Conditions	Distance from the inlet (cm)							O_3 dose (mg/L)			% O_3 consumption
	0	30	60	90	120	150	180	Input	Output	Consumed	
Ozone	0	0.502	0.485	0.617	0.640	0.717	0.634	4.0	1.9	2.1	52
AOP0.5	0	0.022	0.024	0.035	0.054	0.075	0.033	4.2	0.6	3.7	85
AOP1.0	0	0.005	0.016	0.015	0.013	0.014	0.014	4.1	0.6	3.6	86
AOP2.0	0	0.012	0.017	0.012	0.009	0.016	0.014	4.2	0.5	3.7	88
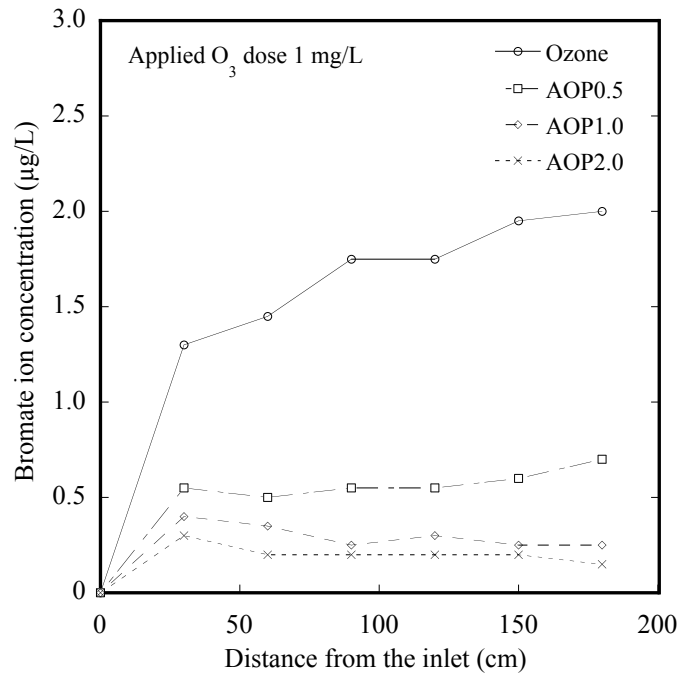
(a) Applied O$_3$ dose 1 mg/L
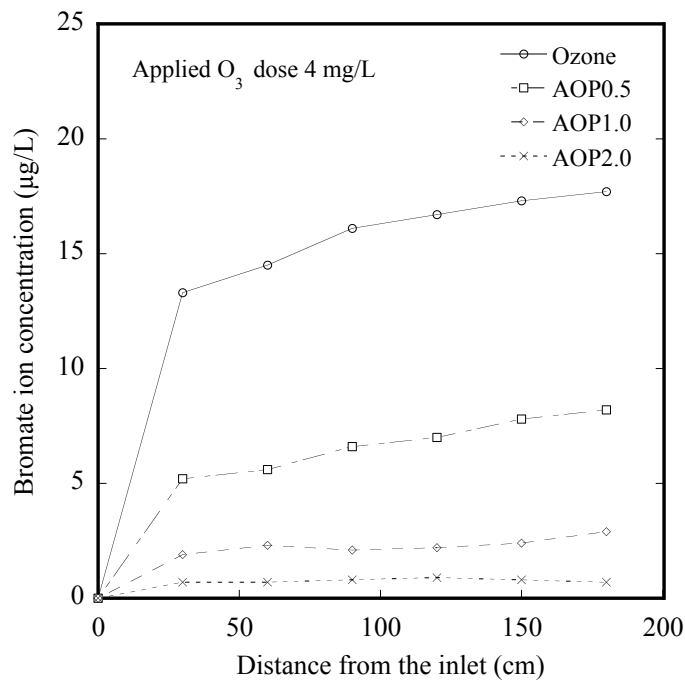
(b) Applied O$_3$ dose 4 mg/L

Figure 4.4 Bromate ion formations for various oxidation conditions operated with
(a) applied O$_3$ dose of 1 mg/L and (b) applied O$_3$ dose of 4 mg/L

4.3.3 Effect of •OH exposure on chlorinous odor control

Using the assumption about a CSTR that the fluid at the inlet is instantaneously perfectly mixed, the fluid within the reactor is homogeneous mixture, and the concentration of substance within the reactor is the same as the outlet concentration (Metcalf and Eddy, 2003). The column reactor is generally translated into a series of tank reactors in numeric solutions because it is easier to analyze at steady state. The equations used to calculate •OH exposure for the ozone column reactor are shown in eqs. 4.1- 4.5. The assumptions underlying the equations are as follows:

　　1. The volumetric flow rate into and out of the control volume is constant.

　　2. The liquid within each CSTR is completely mixed.

　　3. The control volume is considered at steady state.

The oxidation rate of pCBA (r);

$$r = \frac{dC}{dt} = -k_{•OH/pCBA}[•OH]C_{pCBA} \tag{4.1}$$

The mass balance of the system;

　　Accumulation rate = In – Out + Reaction rate　　　　(4.2)

$$V\frac{dC_{pCBA}}{dt} = Q(C_{pCBA_0} - C_{pCBA}) + rV \tag{4.3}$$

At steady state ($\frac{dC_{pCBA}}{dt} = 0$), substitute eq. (4.1) to (4.2);

$$[•OH] = \frac{Q(C_{pCBA_0} - C_{pCBA})}{k_{•OH/pCBA}VC_{pCBA}} \tag{4.4}$$

Thus, Ct-value can be obtained from;

$$Ct - value = \frac{Q(C_{pCBA_0} - C_{pCBA})}{k_{•OH/pCBA}VC_{pCBA}}T \tag{4.5}$$

where;　C　　　 = concentration of •OH, [•OH]; M

T = hydraulic retention time of pCBA, HRT; min

Q = flow rate; L/min

C_{pCBA} = final concentration of pCBA; μM

C_{pCBA0} = initial concentration of pCBA; μM

V = volume of a tank; L

$k_{\bullet OH/pCBA}$ = reaction rate of •OH with pCBA, $5 \times 10^{9} \text{ M}^{-1}\text{s}^{-1}$

Figure 4.5 shows the •OH exposure for various oxidation conditions. Increasing the applied O_3 dose to 4 mg/L elevated the •OH exposure by more than 50%. It also clearly indicates that AOP0.5 was the most effective process for •OH formation. Similar results have been reported by von Gunten (2003a). AOP0.5 enhanced the •OH exposure to 0.69×10^{-3} μM•s and 2.41×10^{-3} μM•s at applied O_3 doses of 1 and 4 mg/L, respectively. While addition of H_2O_2 increased •OH exposure in AOP0.5, a decrease in •OH exposure in the range of 20-30% was observed for AOP1 and AOP2, compared to AOP0.5. This decrease may have resulted from the presence of excess promoters of •OH formation (Kosaka et al., 2001). As H_2O_2 can be either a promoter or inhibitor of •OH, H_2O_2 seems to act as an inhibitor of •OH for AOP1.0 and AOP2.0. The •OH exposure also greatly depended in O_3 dose. The increase in applied O_3 dose from 1 mg/L to 4 mg/L elevated the •OH formation by 100-250 %.

It was also found that the •OH exposure in AOP0.5 was enhanced by more than 250% when the applied O_3 dose was raised from 1 mg/L to 4 mg/L, while the •OH exposure in the conventional ozonation samples increased by only about 100% when the O_3 dose was raised. This result may be due to the 30% increase in O_3 consumption at an applied O_3 dose of 4 mg/L for AOP0.5 compared to ozonation, whereas the O_3 consumption efficiency at an applied O_3 dose of 1 mg/L for AOP0.5 increased by only 10% compared to ozonation (Tables 4.1 and 4.2). However, a significant reduction in chlorinous odor was not achieved by using an applied O_3 dose of 4 mg/L compared to applied O_3 dose of 1 mg/L. Odor strength only slightly decreased at higher •OH exposures.
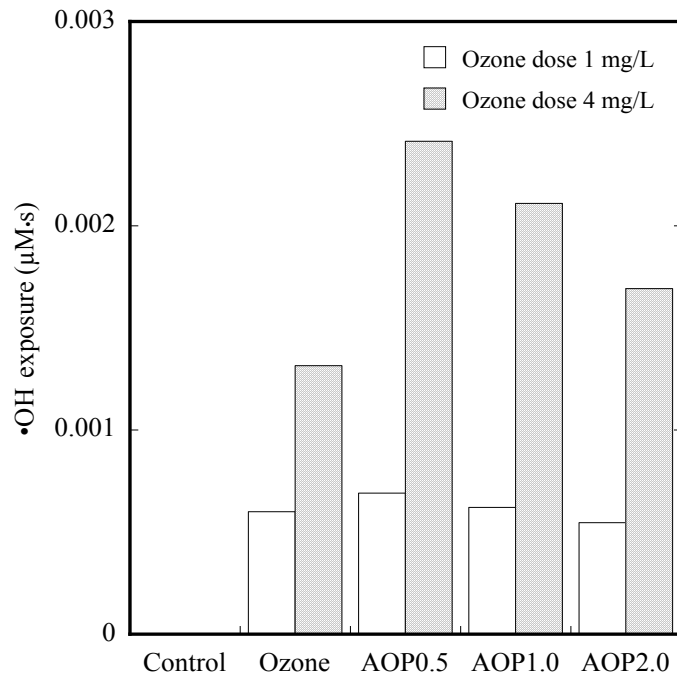
Figure 4.5 •OH exposure for various oxidation conditions
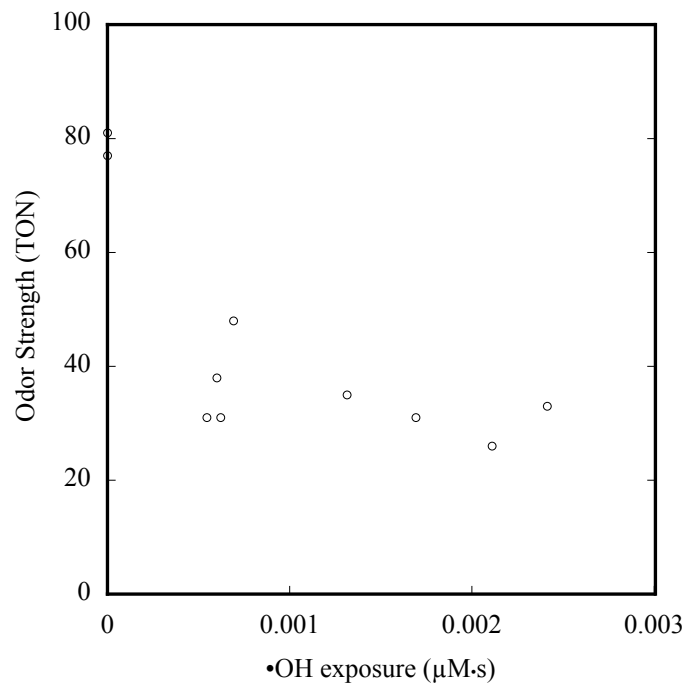
Figure 4.6 The relationship between odor strength and •OH exposure

The relationship between •OH exposure and odor strength is shown in Figure 4.6. An increase in •OH exposure appeared to induce a slight reduction in odor strength. •OH may be effective in the oxidation of organic odor precursors (e.g., amino acids) (Leitner et al., 2002). Because NH_4^+, a trichloramine precursor, is not oxidized by •OH and O_3, odor produced from trichloramine (odor contribution) may not be negligible. The effect of trichloramine on odor contribution is discussed later.

In addition to the •OH exposure, the removal efficiency of natural odor compounds (i.e., geosmin and 2-MIB) was estimated. The calculations were based on eqs 4.6 and 4.7.

From eq. 4.4;

$$[\bullet OH] = \frac{Q}{kV}\left(\frac{C_0}{C} - 1\right) \tag{4.6}$$

$$\frac{C}{C_0} = \frac{1}{1 + kT[\bullet OH]} \tag{4.7}$$

where; C = final concentration of odor compound; ng/L

C_0 = initial concentration of odor compound; ng/L

T = hydraulic retention time, HRT; min

Q = flow rate; L/min

V = volume of tank; L

k = reaction rate of •OH with odor compound ($k_{\bullet OH/geosmin}$ = 7.8 x 10^9 $M^{-1}s^{-1}$; $k_{\bullet OH/2\text{-MIB}}$ = 5.09 x 10^9 $M^{-1}s^{-1}$) (Peter and von Gunten, 2007).

The removal efficiencies of musty odor compounds by ozonation and AOPs are shown in Figure 4.7. The removal efficiency of geosmin was 87% for treatment with an applied O_3 dose of 1 mg/L. The removal efficiencies for AOP0.5, AOP1, and AOP2 were 91%, 89%, and 88%, respectively when operated with applied O_3 dose of 1 mg/L. Increasing the applied O_3 dose to 4 mg/L raised the geosmin removal efficiency to 95% for ozonation, while AOPs operated with an applied O_3 dose of 4

mg/L succeeded in removing approximately 99% of geosmin. AOP with higher O_3 dose increased the removal efficiency of geosmin by approximately 10% compared to AOP with applied O_3 dose of 1 mg/L.

For 2-MIB, the removal efficiency was 75% for ozonation operated with an applied O_3 dose of 1 mg/L. Addition of H_2O_2 enhanced the 2-MIB removal efficiencies by approximately 3%. Increasing the applied O_3 dose to 4 mg/L yielded a 90% removal efficiency of 2-MIB, while a 95% removal was achieved when AOP0.5 was applied. For musty odor removal by ozonation and AOP, conventional ozonation with an applied O_3 dose of 1 mg/L should be upgraded to an AOP in order to reduce natural odor compounds below their odor threshold concentration (geosmin, 4 ng/L; 2-MIB 15 ng/L) when the concentrations of geosmin and 2-MIB in source water are more than 31 and 60 ng/L, respectively (Peter and von Gunten, 2007). For Japanese standard of drinking water quality (MHLW, 2008), the levels of both geosmin and 2-MIB should be lower than 10 ng/L. Thus, AOP0.5 with an applied O_3 dose of 1 mg/L should be applied when the concentrations of geosmin and 2-MIB are more than 77 and 40 ng/L, respectively. Although ozonation with higher O_3 dose could oxidize the odor compounds below the regulation value, bromate ion was above the Japanese standard value as seen in Figure 4.4. AOP0.5 with a higher O_3 dose is needed when the concentrations of geosmin and 2-MIB are higher than 125 ng/L and 83 ng/L, respectively. These results imply that ozonation needed to be upgraded to an AOP in order to achieve the simultaneous control of odor and bromate ion formation.
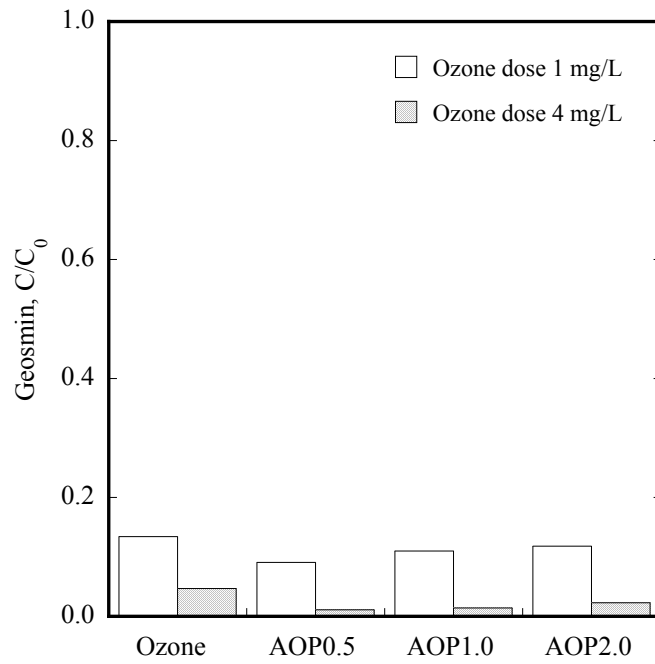
(a) Geosmin removal efficiency
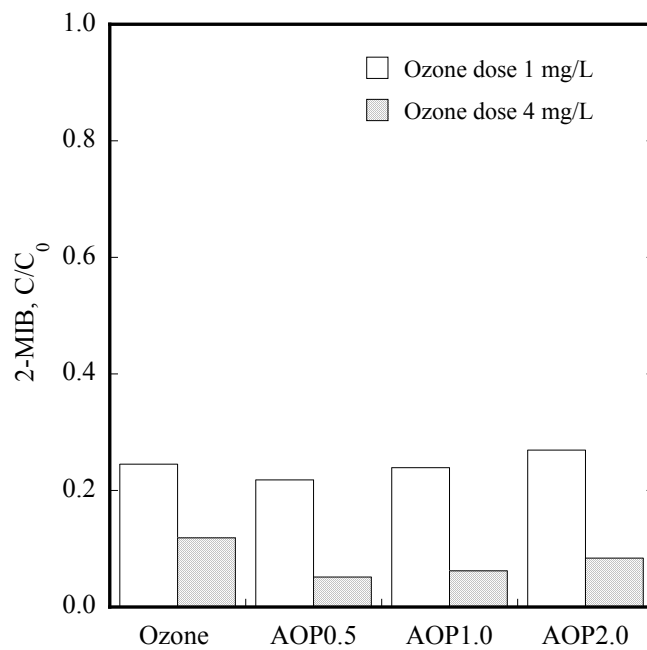
(b) 2-MIB removal efficiency

Figure 4.7 The estimation of removal efficiency of musty odor compounds by •OH
(a) Geosmin and (b) 2-MIB

69

4.3.4 Effect of trichloramine on odor in chlorinated water

Ammonium ion concentrations were measured in order to study the effect of O_3 and •OH on the oxidation byproduct formation when organic compounds were oxidized. The results are shown in Figure 4.8. Initial concentrations of ammonium ion (in Control) were lower than the ammonium ion concentrations in water treated by ozonation and AOP. Ammonium ion concentrations increased by a factor of 2 to 3 after ozonation and AOP. This result goes along with the assumption that ammonium ion is an ozonation byproduct that forms when nitrogenous organic compounds are oxidized (Shang et al., 1999; Berger et al., 1999; Leitner et al., 2002). The ammonium ion concentrations in samples treated with an applied O_3 dose of 1 mg/L were higher than the concentrations in samples treated with an applied O_3 dose of 4 mg/L. This disparity was attributed to the difference in the initial ammonium concentration, as observed in the control samples, and may have resulted because the sample used for the 1 mg/L and 4 mg/L applied O_3 trials were collected on different days.
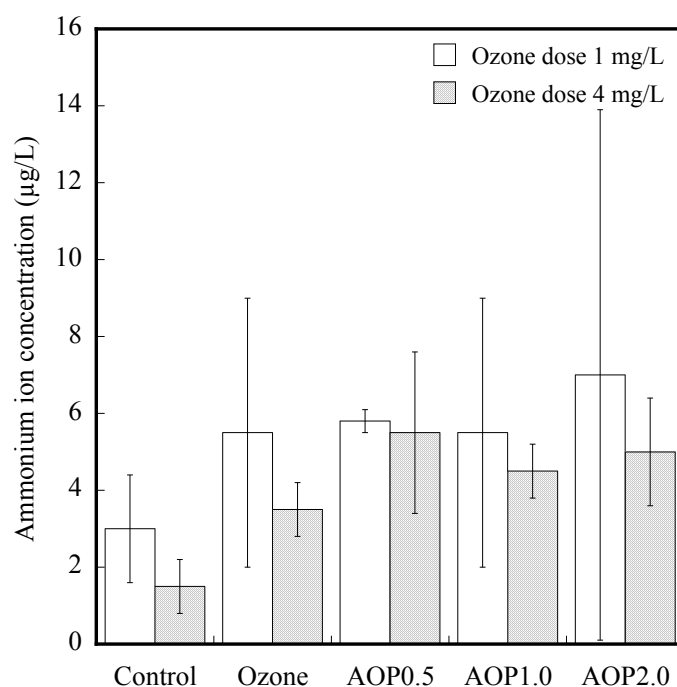
Figure 4.8 Ammonium ions for the various oxidation conditions

Figure 4.9 illustrates the relationship between trichloramine formation and ammonium ion concentration. As seen in the regression line (solid line, $R^2 = 0.858$) of Figure 4.9, trichloramine formation highly depends on the level of ammonium ion following ozonation and AOP. The relationship between trichloramine formation and ammonium ion for control samples showed the different trend with other samples. This implied that the trichloramine precursors in control samples were possibly different from sample treated by ozonation and AOP. The plausible reason is that trichloramine in water treated by ozonation and AOP is produced from the reaction of chlorine to ammonium ion, whereas in control samples, trichloramine forms from chlorination of organic compounds.
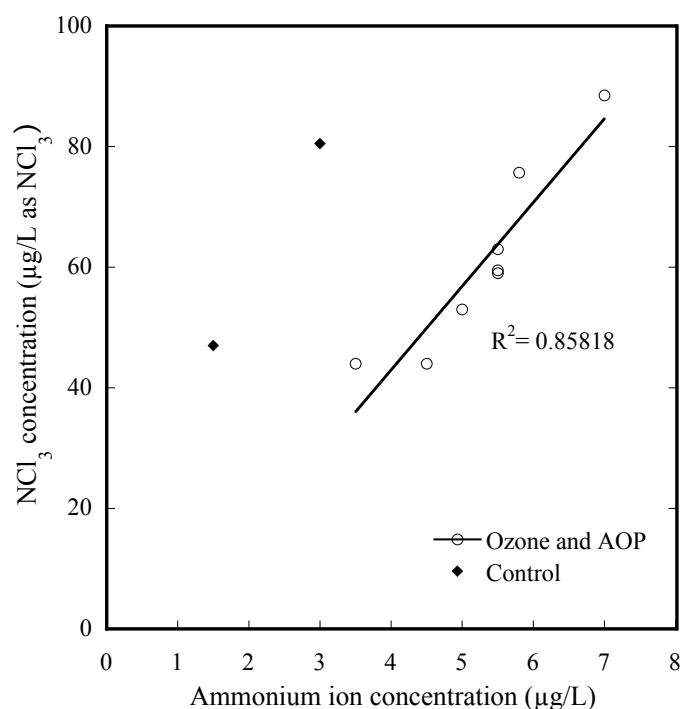
Figure 4.9 The relationship between trichloramine formation and ammonium ion

Figure 4.10 shows the formation of trichloramine under various oxidation conditions. Trichloramine formations in samples treated by an applied O_3 dose of 1 mg/L were higher than the concentration in samples treated by an applied O_3 dose of 4 mg/L because of the different initial concentrations of ammonium ion (Figure 4.8).

71

Although low concentrations of ammonium ion were observed in the control samples compared to samples treated by ozonation and AOP (Figure 4.8), the trichloramine concentrations in the control samples were sometimes higher than the concentration in samples treated by ozonation or AOP. This implies that the chlorination of organic compounds in RSF water (Control) produces trichloramine as a chlorination byproduct.
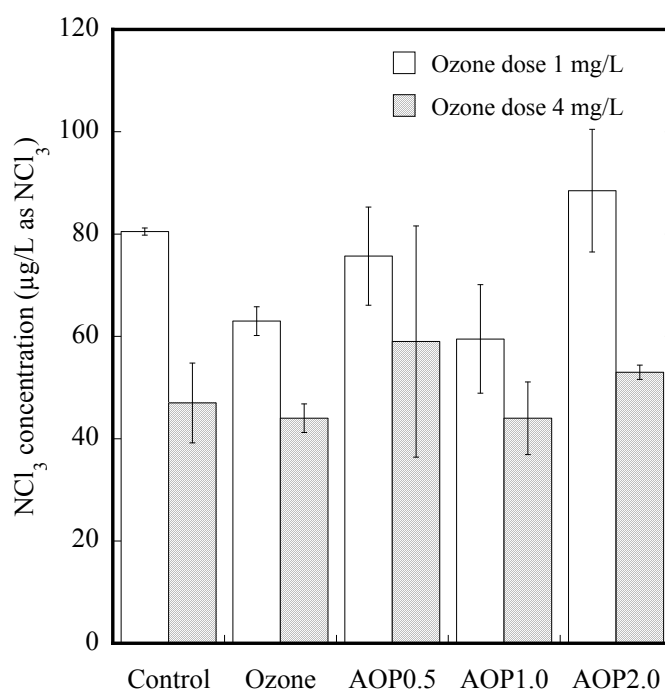
Figure 4.10 The formation of trichloramine under various oxidation conditions

No clear relationship between trichloramine concentration and odor strengths was found as shown in Figure 4.11. That is, trichloramine was not a major odorous contributor to chlorinous odor in tested samples. The odor reduction may be influenced from the decrease of nitrogenous organic compounds (e.g., amino acids) in which its odor threshold concentrations lower than trichloramine odor threshold values (Bruchet et al., 2004; Freuze et al., 2005).
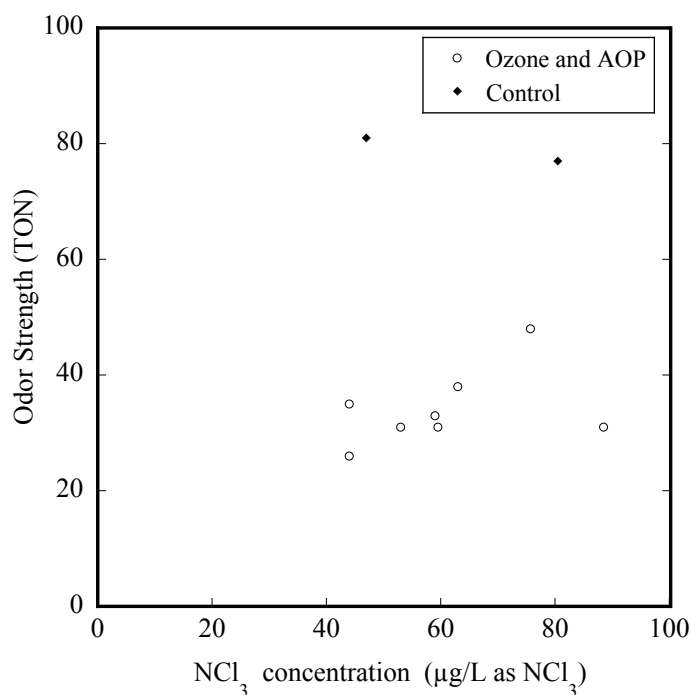
Figure 4.11 The contribution of trichloramine to odor in chlorinated water

A limitation for the control of chlorinous odor was present with ozonation and AOP, as seen in the lack of a clear reduction in chlorinous odor even when the •OH exposure was increased to 2.41×10^{-3} μM•s. To determine if the observed limitation in chlorinous odor removal was caused by trichloramine, trichloramine concentrations for each sample were converted to a corresponding odor strength based on the lowest odor threshold concentration at 3.4 μg/L as NCl_3 (Yanagibashi, 2008). The estimated odor contribution from trichloramine is the detected trichloramine concentration divided by odor threshold concentration of trichloramine (3.4 μg/L as NCl_3). To calculate the odor contribution of trichloramine, the calculation based on the assumption that the dilution decreases only individual concentration of odor compound, and total odor strength is equivalent to the summation of individual odor strength. The comparison between the observed odor strengths and estimated odor strength values is shown in Figure 4.12. The estimated values of odor strength calculated from the trichloramine concentration made up only 20 to 30% of the observed odor strength in the control sample. This result verified that trichloramine is

a minor odor compound in water treated by conventional treatment processes (RSF and chlorination). Major odor contributors in the control samples are suspected to be products from the chlorination of organic compounds (e.g., amino acids), which have very low odor threshold values (less than 1 µg/L) (Freuze et al., 2005). Trichloramine had larger impact on the remaining odor strength of water pretreated by ozonation and AOP. The estimated odor strengths were equivalent to 40 to 80% of the observed data for samples treated by ozonation and AOP. This implied that trichloramine possibly caused perceptible chlorinous odor in drinking water even water treated by ozonation or AOP. In fact, tap water consists of several odor compounds (Brosillon et al., 2009). Thus, the remaining odor in water treated by ozonation and AOP also possibly caused by other unidentified chlorinous odorants. Brosillon et al. (2009) found that *N*-chloroaldimines exhibited in tap water and its concentration was close to their threshold level (1 µg/L) even that water was treated by ozonation. Thus, future study needs to focus on a combination of ozonation or AOP with ion exchange to remove remaining compounds causing chlorinous odor such as ammonium ion.
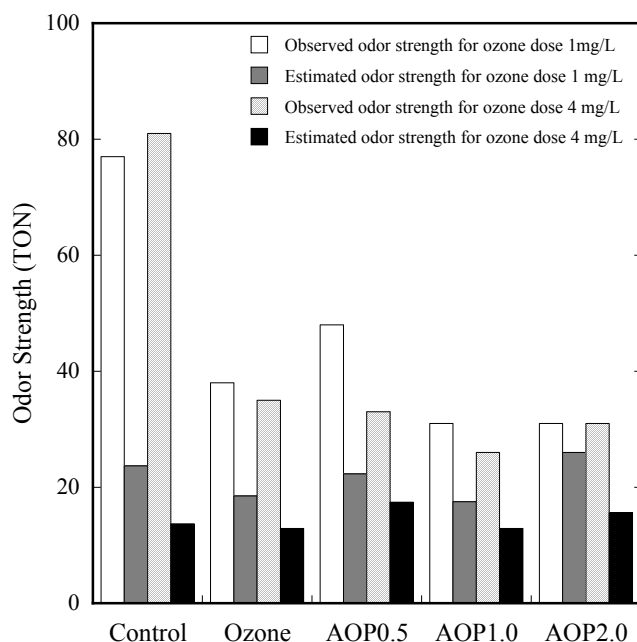
Figure 4.12 The comparison between odor strength estimated from trichloramine concentration compared with observed odor strength

4.3.5 The comparison of the performance between batch-mode reactor and ozone column contactor

The results (e.g., TON, bromate ion, •OH exposure) were compared to the results of the previous chapter (O_3 dose 1 mg/L without pH adjustment). In chapter 3, the experiments were conducted with the single injection of dissolved O_3 into test samples, whereas practical ozonation normally provides continuous injection of O_3 gas. Differences in •OH formation between the two reactors may have a great impact on odor control with regard to the different •OH formation when gas-liquid contactor is applied for controlling odor (Buffle et al., 2006). The •OH exposures for both experiments were shown in Table 4.3. •OH exposures in ozone column reactor were higher than in bench scale reactor. This implied that ozonation reaction in the steady state, exhibited in ozone column reactor, plays an important role on the formation of •OH exposure.

Table 4.3 The comparison of •OH exposures between batch-mode reactor and ozone bubble column (O_3 dose of 1 mg/L)

Conditions	•OH exposure ($\mu M \cdot s$)	
	Batch-mode reactor	Ozone bubble column
Ozone	0.00012	0.00060
AOP0.5	0.00014	0.00069
AOP1.0	0.00013	0.00062
AOP2.0	n/d	0.00055
AOP3.0	0.00010	n/d

Note: n/d   no data

Figure 4.13 summarizes the effects of •OH exposure on odor strength removal for both reactors, batch-mode reactor and ozone column reactor. Although batch-mode reactor had a lower •OH exposure than ozone column reactor, the remaining odor strength was similar (approximately 30-40). The remaining odor strengths were

suspected to be produced from unidentified chlorination products and trichloramine.
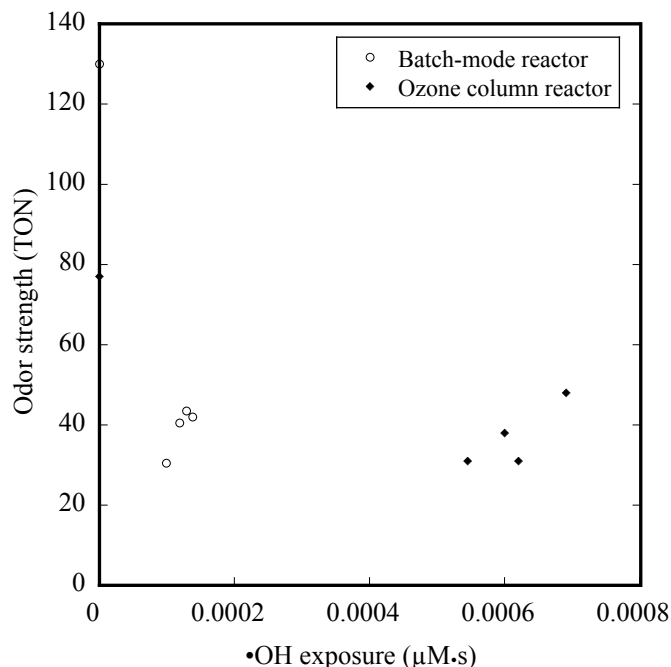
Figure 4.13 The relationship between the formation of •OH exposures and odor
strengths for batch-mode reactor and ozone column contactor

Table 4.4 shows the formation of bromate ion in both reactors, batch-mode reactor and ozone column contactor, when O_3 dose of 1 mg/L was applied. It is noted that the higher bromate ion concentration was observed when dissolved O_3 was used. It was suspected that bromate ion may quickly form at the initial phase of ozonation, where predominant oxidant is •OH (rapid decomposition of O_3) (Buffle et al., 2006). The mechanism of O_3 gas transferred into water as a form of dissolved O_3 in ozone column reactor is fast and complex (it probably changes to •OH immediately after contact to NOM), and that may result in a either short or long lifetime of dissolved O_3 in a test solution. Because the injection of dissolved O_3 solution greatly produced bromate ion than the used of O_3 gas even the values of •OH exposure in batch-mode reactor were less, the O_3 decomposition rate is suspected to play a major role of bromate ion formation (von Gunten, 2003b).

Table 4.4 The comparison of the bromate ion formation between batch-mode reactor (Br⁻ concentration in raw water = 37 µg/L) and ozone bubble column (Br⁻ concentration in raw water =41±2.8 µg/L) at O₃ dose of 1 mg/L

Conditions	Bromate ion concentration (µg/L)	
	Batch-mode reactor	Ozone bubble column
Ozone	4.17	2.00
AOP0.5	3.46	0.70
AOP1.0	3.34	0.25
AOP2.0	n/d	0.15
AOP3.0	1.87	n/d

Note: n/d no data

4.4 Conclusions

A series of ozonation and AOP experiments in continuous mode with an ozone column contactor was conducted in order to study the efficiency of odor removal at applied O_3 doses of 1 mg/L and 4 mg/L in a more practical setup. The results are highlighted below:

- Ozonation and advanced oxidation process (H_2O_2/O_3 process) with ozone column reactor could minimize chlorinous odor by more than 40-50% compared with chlorination alone.
- Odor strength of samples slightly decreased with increasing •OH exposure.
- AOP succeeded to suppress bromate ion below the Japanese regulation of drinking water quality even when the O_3 dose was increased to 4 mg/L.
- The oxidation of organic compounds by ozonation and AOP in Yodo river water produced ammonium ion as end-products.
- Trichloramine was a minor odorous contributor to chlorinous odor for water treated by conventional treatment.
- A limitation is present for the control of chlorinous odor in drinking water treated

with ozonation or AOP. The lowest odor strength was approximately 30.

- Upon comparing the performance of batch-mode reactor (reagent is dissolved O_3) with ozone column reactor (reagent is O_3 gas), there was no significant reduction in chlorinous odor.

- •OH exposures in ozone column contactor were much higher than occurrence in batch-mode reactor, whereas bromate ion concentrations were lower in continuous mode.

- Although the control efficiencies of chlorinous odor for ozonation and AOP in ozone column contactor were similar, AOP0.5 with O_3 dose of 1 mg/L can simultaneously control odor and bromate ion below Japanese standard values when the concentrations of geosmin and 2-MIB are more than 77 ng/L and 40 ng/L, respectively. AOP0.5 with O_3 dose of 4 mg/L is needed for odor control when the concentrations of geosmin and 2-MIB are higher than 125 ng/L and 83 ng/L, respectively.

Chapter 5

Characterization of Chlorinous Odor Precursors by a Comprehensive Fractionation Technique

Abstract – Waters treated by rapid sand filtration (RSF) and ozonation were characterized by a fractionation technique to study the primary fraction of NOM causing of chlorinous odor. The odor contribution, the dilution factors multiplied by the percentage of dissolved organic matter (DOM), in each fraction was determined by the triangle sensory test. The DOM of water treated by the filtration process mainly consisted of hydrophobic acid (HoA), transphilic (Trs), and hydrophilic acid (HiA) fractions, while only hydrophilic fraction was dominant in the ozonated water. Base fraction (Bas) was found to be the major organic precursor of chlorinous odor in water treated by RSF. Odor strength of ozonated water was mainly produced from the chlorination of HiA and hydrophilic neutral (HiN) fractions. Chlorination of base fraction required a high dose of chlorine. Ozonation had an effect on odor reduction by oxidizing and converting hydrophobic and base fractions to more hydrophilic fractions.

5.1 Introduction

Previous two chapters showed that ozonation could decrease chlorinous odor compared to chlorination alone, but its complete removal was difficult to achieve even with AOP. Since ozonation can oxidize and convert organic micropollutants into other forms (Owen et al., 1995), it may change the treatability of each treatment process depending on the characteristic of pollutants. In order to efficiently apply a treatment unit after ozonation for the control of chlorinous odor, all fractions of dissolved

organic matter (DOM) for waters after ozonation need to be characterized to find the remaining fraction causing chlorinous odor. Furthermore, in order to effectively apply ozonation for the control of chlorinous odor, the effects of ozonation on the fraction causing chlorinous odor need to be addressed.

One common way to characterize DOM is to fractionate it into several isolates by a series of ion-exchange operation with several types of resins as shown in chapter 2. This chapter aims to evaluate the contribution of each DOM and ozonated DOM fraction to chlorinous odor with this technique.

5.2 Materials and Methods

5.2.1 Water Sample

Water after treatment by rapid sand filtration at a water treatment plant in Osaka was stored at 4 ºC before fractionation. For the study of the contribution of DOM fractions to chlorinous odor, the filtrated water (hereinafter called to RSF1: dissolved organic carbon (DOC), 0.85 mg/L; ammonium ion (NH_4^+), 1 µg/L, bromide ion (Br^-), 22 µg/L) was sampled on December 1, 2009. The sensory tests were duplicated for all the fractions. To study the effect of ozonation on the DOM fraction responsible for chlorinous odor and remaining fractions in ozonated water, filtrated sample (hereinafter called to RSF2: DOC, 0.86 mg/L; NH_4^+, 2 µg/L, Br^-, 40 µg/L) and ozonated water (hereinafter called to OW: DOC, 0.85 mg/L; NH_4^+, 4 µg/L, Br^-, 7 µg/L), were collected on March 4, 2010. OW was sampled after treated by a conventional ozonation (O_3 dose, 1.75 mg/L; water flow rate, 0.32 L/min; reaction time, 30 min; water temperature, 9.5 ºC) with the same ozone bubble column used in the chapter 4.

5.2.2 Chemical and materials

All chemicals used are described in chapter 3.

For the fractionation, resin adsorption chromatography technique (Leenheer, 2004; Jo, 2008) was employed in this study. Superlite^{TM} DAX-8 resin (40-60 mesh), Dowex$^{®}$-Marathon$^{®}$- MSC strong cation-exchange resin (20-50 mesh), Amberlite$^{®}$ XAD-4 (20-60 mesh), and Dowex$^{®}$-Marathon$^{®}$- MSA strong anion-exchange resin (20-50 mesh) were used for DOM separation. Organic compounds were separated into 7 fractions including hydrophobic acid (HoA), hydrophobic neutral (HoN), hydrophobic base (HoB), hydrophilic base (HiB), hydrophilic acid (HiA), hydrophilic neutral (HiN), and transphilic (Trs). Original water, treated by either RSF or ozonation, called as "Control."

5.2.3 Procedure

A series of different synthetic resins (e.g., DAX-8, MSC, XAD-4, MSA) were employed for fractionation of DOM mixtures into 7 classes: HoA, HoB, HoN, Trs, HiA, HiB, and HiN. The procedure of fractionation was divided into 3 major steps: cleaning process, fractionation, and desorption process.

5.2.3.1 Cleaning process

- DAX-8 and XAD-4

I.   Resins were rinsed with 1 mol/L NaOH daily for 5 successive days.
II. The resins were sequentially washed by soxhlet extraction for 24 hr each with methanol, acetonitrile, and methanol before stored in methanol.
III. The methanol was removed from the resins with pure water (hereinafter called Elix water), produced by Elix 10 kit Millipore system (Tokyo, Japan), by using a slurry technique in a large beaker.

IV. The resins were packed as methanol-water slurry into a glass column. 0.5 L (wet volume) of DAX-8 resin and 0.2 L (wet volume) of XAD-4 resin were used. Both resins were rinsed with Elix water until free of methanol (DOC concentration: less than 0.2 mg/L). It was required approximately 200 bed volumes (BV) of water to achieve this DOC level.

V. The packed columns were rinsed several times with 10 BV of 0.1 mol/L NaOH and 0.1 mol/L HCl in turn, until the DOC concentration of the effluent reach 0.2 mg/L or less.

VI. When the resins were reused, the procedure 4 and 5 were repeated.

- MSC

I. Approximately 0.5 L (wet volume) of the resin was packed into a glass column, and then rinsed with Elix water until the DOC concentration of the effluent was less than 0.2 mg/L.

II. 3 ~ 6 BV of 1 mol/L HCl was fed for the regeneration of the resin.

III. Elix water was fed to the column until the pH of the effluent reach 5 or above.

IV. Elix water was fed until the DOC concentration of the effluent was less than 0.2 mg/L.

- MSA

I. Approximately 0.5 L (wet volume) of the resin was packed into a glass column, and then rinsed with Elix water until the DOC concentration of the effluent was less than 0.2 mg/L.

II. 5 ~ 7 BV of 1 mol/L NaOH was fed for the regeneration of the resin.

III. Elix water was fed until the pH of the effluent was below 9.

IV. Elix water was fed until the DOC concentration of the effluent was less than 0.2 mg/L.
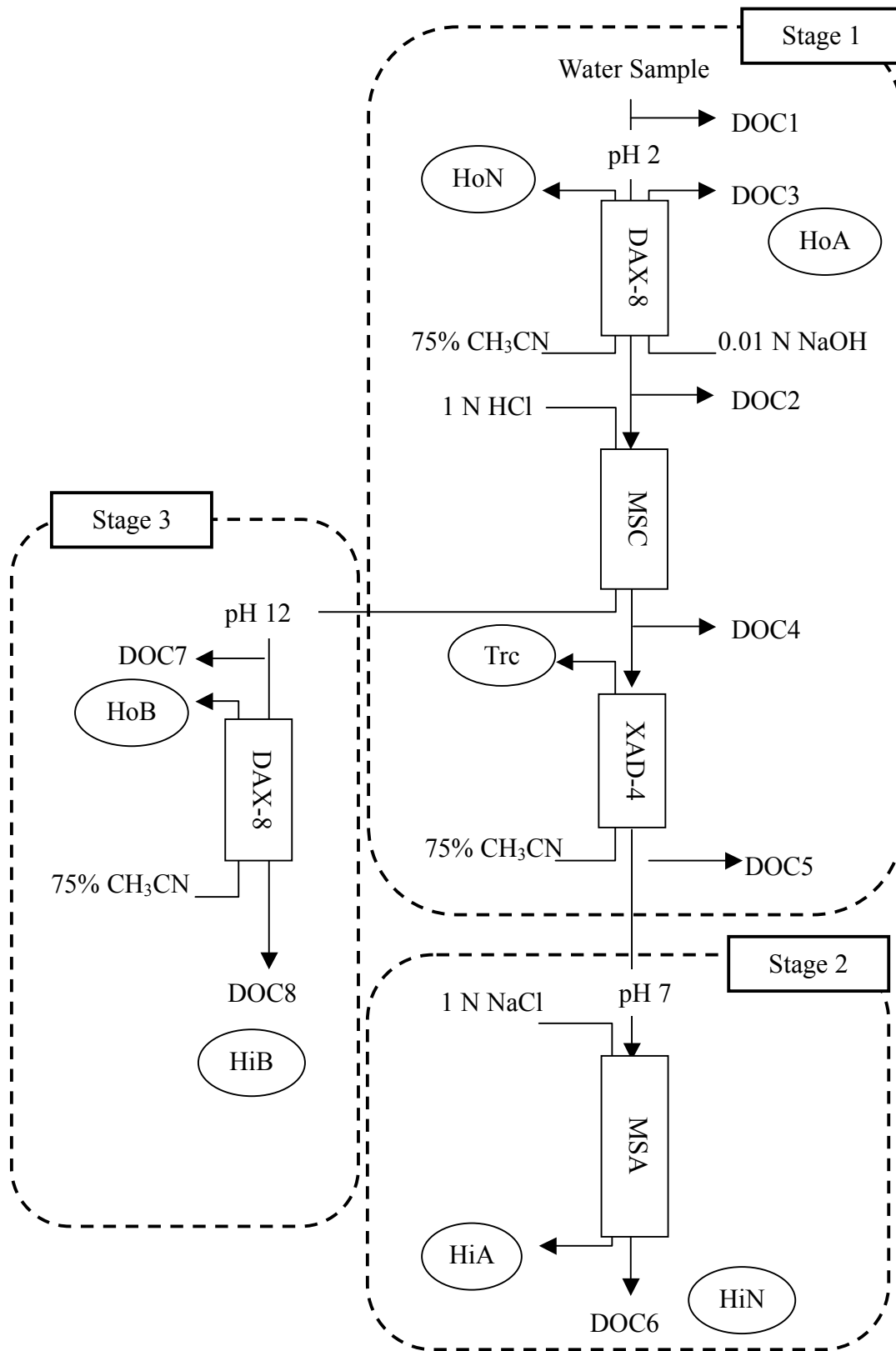
Figure 5.1. The schematic diagram of the procedure for DOM fractionations

5.2.3.2 Fractionation

Figure 5.1 shows the schematic diagram of the procedure for DOM fractionation. The fractionation procedure consists of three stages:

- Stage 1.

The columns of DAX-8, MSC, and XAD-4 were fixed to a stand in this order and connected in series. All the joints and tubings were made of Teflon. Elix water was fed at a flow rate of 15 BV/hr (125 mL/min) before 0.01 mol/L HCl was fed at a flow rate of 15 BV/hr replacing the solutions in the column and tubings. Water sample was adjusted to pH 2 with hydrochloric acid (HCl) before feeding to the columns at the flow rate of 15 BV/hr. The DOC concentrations of samples passed through DAX-8, MSC, and XAD-4 were called as DOC2, DOC4, and DOC5, respectively. The samples passing through the series of columns were collected, and its DOC was analyzed. The effluent from the XAD-4 resin was stored at 4 ºC before the stage 2.

- Stage 2.

The water sample passed through XAD-4 (DOM5) was neutralized to pH 7 with NaOH (products used for nitrogen analysis). If the DOC after neutralization (DOC5') was increased, the difference of the DOC concentration between DOC5' and DOC5 was defined as blank. Then, the sample was passed through the MSA column at a flow rate of 200 mL/min. The effluent, HiN fraction, was collected, and its DOC concentration was measured and named as DOC6 before stored at 4 ºC.

- Stage 3.

DAX-8 after washing was packed into a column and fixed to the stand. NaOH was added to 3 L of desorption solution (DOC7), collected after the desorption process

from MSC resins, to adjust the pH to 12. The sample was fed to the column of DAX-8 resin at a flow rate of 25 BV/hr (40 mL/min) by the use of a milli-pump (SPC Cont, Waters). The DOC of the effluent was obtained as DOC8. For the desoption of the HoB fraction, approximately 5 BV (0.75 L) of 0.01 mol/L NaOH was fed at a flow rate of 25 BV/hr (40 mL/min) for washing the resin. The resin was reversed upside-down and fixed to the stand before 10 BV (1.5 L) of 75% of acetonitrile (CH_3CN) was fed at a flow rate of 5 BV/hr (16 mL/min). The obtained effluent represented the HoB fraction. CH_3CN was evaporated by a vacuum-rotary evaporator (Rotary evaporator RE 71, Yamato).

5.2.3.3 Desorption process

- DAX-8

I. Approximately 5 BV (2.5 L) of 0.01 mol/L of HCl was fed through a column at a flow rate of 15 BV/hr (125 ml/min) for washing the resin.

II. The resin was reversed upside-down and fixed to the stand.

III. 20 ~ 60 BV (10-30 L) of 0.01 mol/L NaOH was fed through a column at a flow rate of 5 BV/hr (~ 40 mL/min). The effluent (DOC = DOC3) was the HoA fraction. The DOC concentration (DOC3') of 0.01 mol/L of NaOH was measured in advance. The subtraction of DOC3' from DOC3 was defined as blank.

IV. Elix water was fed through the column at a flow rate of 5 BV/hr (40 mL/min) until the pH of the effluent was below 9.

V. Approximately 10 BV (5 L) of 75% of CH_3CN was fed through the column at a flow rate of 5 BV/hr (40 mL/ min). The desorped solution from the DAX-8 resin was the HoN fraction.

VI. CH_3CN was evaporated by the vacuum-rotary evaporator.

- MSC

I. Approximately 5 BV (2.5 L) of Elix water was fed at a flow rate of 15 BV/hr (125

mL/min) for washing the resin.

II. 6 BV (3 L) of 1 mol/L NaCl was fed at a flow rate of 125 mL/min. The DOC of effluent was noted as DOC7.

- XAD-4

I. Approximately 5 BV (1 L) of 0.01 mol/L HCl was fed through a column at a flow rate of 125 mL/min for washing the resin.

II. The resin was reversed upside-down and fixed to the stand.

III. 10 BV (2 L) of 75 % of CH_3CN was fed at a flow rate of 40 mL/min. The effluent was the Trs fraction.

IV. CH_3CN was removed by the vacuum-rotary evaporator.

- MSA

I. Approximately 5 BV (2.5 L) of Elix water was fed at the flow rate of 200 mL/min for washing the resin.

II. 6 BV (3 L) of 1 mol/L NaCl was fed at a flow rate of 200 mL/min. The effluent was the HiA fraction.

5.2.3.4 DOC calculation of each fraction

The DOC concentrations of the fraction obtained were calculated as follows:

DOC of DOM = DOC1   (5.1)

DOC of HoA = DOC3 × volume of eluted sample/original sample   (5.2)

DOC of HoN = DOC1 – DOC2 – HoA   (5.3)

DOC of HoB = DOC7 – DOC8   (5.4)

DOC of HiB   = DOC8 × volume of eluted sample/original sample   (5.5)

DOC of Trs   = DOC4- DOC5   (5.6)

DOC of HiA   = DOC5 – DOC6   (5.7)

DOC of HiN = DOC6 $\qquad$ (5.8)

5.2.3.5 Concentration

The isolates were concentrated by the use of vacuum-rotary evaporator (rotary evaporator RE71, Yamato). Then, the concentrate was filtrated by passing through GA-100 glass fiber filter (ADVANTEC, Toyo Koshi Kaisha, Ltd.). Then, the pH of the concentrated solutions was neutralized in order to minimize decomposition of organic compounds before stored at 4 ºC.

5.2.3.6 Chlorination procedure

The concentrations of DOC for all the fractions including the original samples were adjusted to approximately 1 mg/L. The solution pH was adjusted to 7 with HCl and NaOH before chlorination. The concentration of residual chlorine after 1 day was controlled at 1 mg/L. Then, the chlorinated samples were measured the TON value and trichloramine concentration.

5.2.4 Analytical Methods

The DOC of the samples was analyzed with a TOC-5000A analyzer (Shimadzu). The specific UV-absorbance (SUVA) has been shown to be a good indicator for aromatic content of aquatic NOM, especially UV-absorbance at 254 nm, UV_{254} (the most suggested to represent aromatic organic structure). UV-254 values were measured on a Multispec-1500 spectrophotometer (Shimadzu) using a 1 cm cell. SUVA values were calculated as the ratio of the UV-254 to a DOC concentration of particular samples. Other analyses (e.g., TON, ammonium ion, O_3 gas) can be seen in chapter 3 and 4. After fractionation of RSF1 waters, all the analyses were duplicated (set1 and set2) for quality control.

5.3 Results and Discussion

This chapter aimed to characterize the contribution of DOM fractions to chlorinous odor after chlorination, and the fraction contributing to chlorinous odor after ozonation and chlorination.
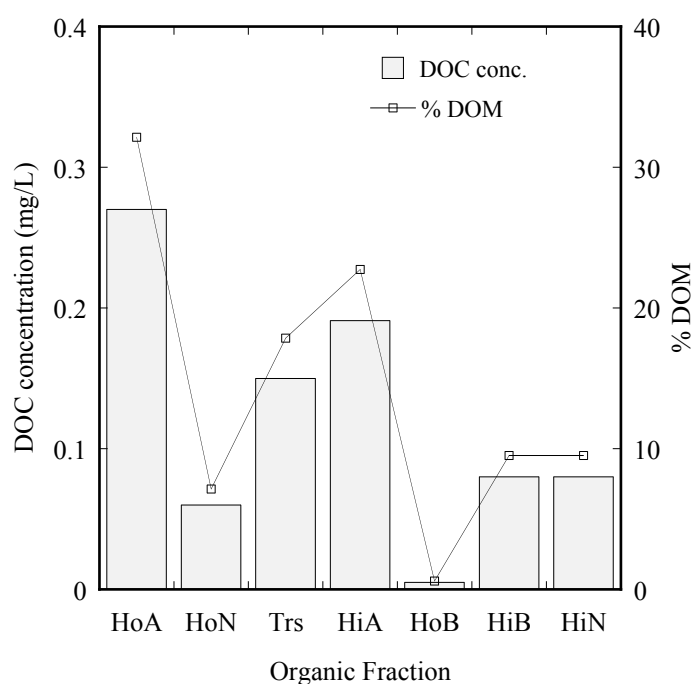
Figure 5.2. The DOC concentrations and the percentage of DOM fractions in RSF1 compared to the total DOM concentration (0.84 mg/L)

The DOC concentrations and the percentage of the DOM fractions of RSF1 compared to the DOC of RSF1 itself (0.84 mg/L) were shown in Figure 5.2. HoA, HiA, and Trs fractions were the three major fractions of DOM (31%, 23%, and 18%, respectively). The concentrations were 0.267, 0.191, and 0.150 mg/L for HoA, HiA, and Trs, respectively. In contrast, the concentration (0.005 mg/L) of the HoB fraction was found to be negligible (less than 1% of DOM fractions). Similar results were reported from other studies that the HoB fraction in surface water was negligible (Imai et al., 2001; Jo, 2008).

88

5.3.1 The contribution of DOM fractions to chlorinous odor

Figure 5.3 shows the average values of odor strength and the contribution to odor strength of organic fractions. HiB fraction, which presumably consists of amino acids, presented the strongest average odor strength (140) among the DOM fractions for the fixed DOM concentration (1 mg/L). HiN fraction also presented relatively strong odor strength (TON = 71), compared to the TON value of the control sample (TON = 63). The other fractions showed less odor strength than the control sample. Thus, both HiB and HiN fractions were the major DOM fractions responsible for chlorinous odor.
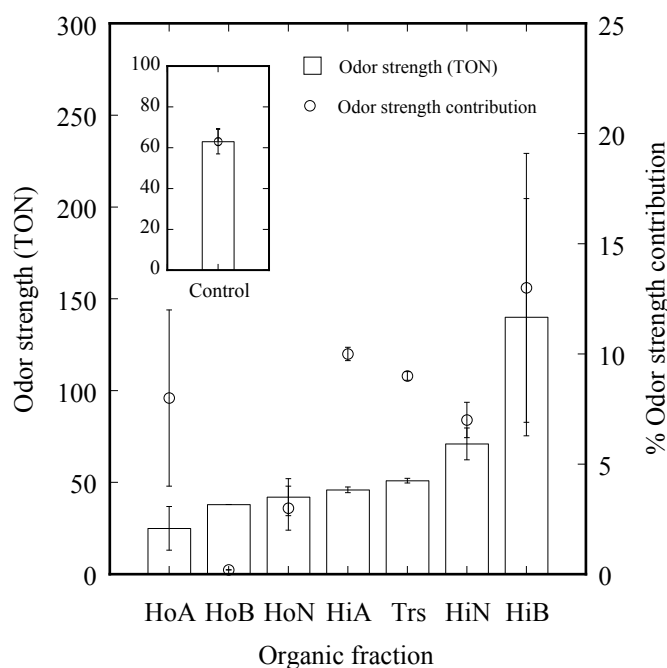
Figure 5.3. Odor strengths and percentage contributions of odor strength for each organic fraction in RSF1

While both HiB and HiN fractions were the main precursors of chlorinous odor based on the normalized DOC concentration, the HiB fraction was the main reason of chlorinous odor formation in RSF1 because of the highest percentage of odor strength contribution (13.3%) (note that odor strength contribution, calculated by the dilution factors multiplied by the percentage of DOM, is the percentage of odor produced from

chlorination of organic fractions in water source). Although the odor strength for a unit DOC was not significantly higher than other fraction, the HiA fraction was the second major contributor of chlorinous odor (TON = 10) when TON value (46) was multiplied by its DOC percentage (22.7%). The contribution of other fractions to odor was less than 10. The main cause of high contribution to odor strength in hydrophilic fractions (HiB and HiA fractions) is that a conventional treatment process (e.g., RSF) usually known as a process used for removing a hydrophobic organic fraction, whereas hydrophilic fraction cannot be significantly eliminated (Croué et al., 1993). Thus, many precursors of chlorinous odor like amino acids that are in hydrophilic fraction still exist in the water before chlorination, and its products after reacting to chlorine causes of chlorinous odor (Freuze et al, 2004; Freuze et al, 2005).

Tables 5.1 and 5.2 show the chemical properties of RSF1 for sample sets 1 and 2, respectively. Because of the extremely low percentage of HoB fraction in the water, the parameters (e.g., trichloramine, odor strength) for the HoB fraction were analyzed once and data were shown in sample set 1. Even though the HoB fraction produced an extremely high concentration of trichloramine (251 µg/L as NCl_3), it had the lowest percentage of odor contribution (less than 1%), indicating that it is not a significant fraction in odor formation. This is an evidence that trichloramine was not a major contributor of chlorinous odor. Interestingly, the chlorination of HoB fraction produced very high concentration of trichloramine although it contained low concentration of ammonium ion (3 µg/L). On the other hand, trichloramine concentrations were extremely low for HiB fraction (non detectable) even though HiB fraction contained the highest concentration of ammonium ion (60 and 119 µg/L for data sets 1 and 2, respectively) among the DOM fractions. This may be explained by the assumption that organic compounds in both HiB and HoB fractions are highly reactive to chlorine (faster than ammonium ion in case of organic compounds in HiB fraction), but their chlorination byproducts are different. The chlorination of HoB fraction may greatly produce inorganic chlorinated byproducts (e.g., trichloramines), whereas the chlorination of HiB fraction results in the formation of chlorinated organic byproducts.

Because bromide ion that is oxidized by chloramines or chlorines can lead to chlorine consumption (Gazda et al., 1995; Chang et al., 2001), high bromide ion concentration can cause the stability of trichloramine. Bromide ion concentrations before chlorination were presented in Tables 5.1 and 5.2. The concentrations of bromide ion for each fraction were rather low (less than 50 µg/L). With the previous finding in chapter 3 that the elevation of bromide ion to 100 µg/L did not affect the odor strength. Furthermore, the reaction of bromide ion to trichloramine was much slower than the oxidation of bromide ion by chlorine (Gazda et al., 1995). In addition, chlorine reactivity with ammonium ion is faster than bromide ion by 300 times (Deborde and von Gunten, 2008). Thus, the effects of bromide ion on the reaction between chlorine and ammonium ion were negligible.

To estimate chlorine demand of organic compounds in each fraction, the consumption of chlorine by ammonium ion is considered. The formula to calculate chlorine consumption by ammonium ion based on the assumption that nitrogen gas (N_2) is the major end-product as shown in eq. 5.9 with the molar ratio of 1.5:1. Chlorine demand by organic compounds in each fraction (excluding chlorine demand by ammonium ions) is summarized in Table 5.3.

$$2NH_4^+ + 3HOCl \longrightarrow N_2 + 3H_2O + 5H^+ + 3Cl^- \hspace{2cm} (5.9)$$

Among organic fractions, HiB fraction presented the highest chlorine demand utilized by organic compounds (2.09 and 1.94 mg/L as Cl_2 for the data sets 1 and 2, respectively). This is in agreement with a previous study that amino sugars and amino groups in Bas fraction (HiB+HoB) produce significant chlorine demand (Leenheer, 2004). The second largest consumer of chlorine was HoA fraction. The chlorine demands consumed by organics in HoA fraction were 1.87 and 1.94 mg/L as Cl_2 for data sets 1 and 2, respectively. This may result from high SUVA values in HoA fraction (0.027 and 0.025 $cm^{-1} \cdot mg^{-1}$ for data sets 1 and 2, respectively) as seen in Tables 5.1 and 5.2. Since SUVA is known as a good surrogate of the aromatic content of NOM and aromatic content is unsaturated and high reactive component (Nikolaou et al., 2001; Chang et al., 2002; Fabris et al., 2008), these compounds can accelerate

the chlorination reaction causing of high chlorine demand. Another fractions (e.g., HoN, Trs, HiA) presented low SUVA (less than 0.010 cm$^{-1}\cdot$mg^{-1}) and chlorine consumption by organic compounds (1.50 mg/L approximately) lower than HoA fraction. In a similar study, Weiss et al. (2004) also observed a higher SUVA value in hydrophobic fraction than hydrophilic fraction.

In Table 5.4, odor strengths of the DOM fractions are compared with the contributions of trichloramine to odor strength. The estimated odor strength contribution from trichloramine is the detected trichloramine concentration divided by odor threshold concentration of trichloramine (3.4 μg/L as NCl$_3$). Because of no contribution of trichloramine to odor in HiB and HiA fractions, it clearly indicated that organic compounds in HiB and HiA fractions were the major components causing chlorinous odor as mention above. The estimated odor strengths in original RSF water (22 and 39 for data sets 1 and 2, respectively) were lower than observed odor strengths (67 and 58 for data sets 1 and 2, respectively). This could be explained by that the major odor was not contributed by trichloramine, and its causes of chlorinous odor in RSF water are possibly included unidentified odor compounds and condition of chlorination (note that odor strength of negative control; residual chlorine concentration at 1 mg/L in Milli-Q water, was approximately 20). As mention in chapter 4, the assumption for the estimation of odor strength contributed by trichloramine is that the dilution decreases only individual concentration of odor compound, and total odor strength is equivalent to the summation of individual odor strength. In fact, the concentrations of each compound change when the water is diluted. Also, each odor chlorination byproduct may produce different odor, which it may interfere with the evaluation of trichloramine. Thus, the calculation of estimated odor strength from trichloramine included some discrepancy. That is why some fractions in sample set 1 (i.e., HoA, Trs, HoB) had estimated odor strengths that were higher than observed odor strengths.

Chlorination of HiB fraction presented the highest odor strength, whereas trichloramine was not detected. The reason of strong odor formation from the chlorination of HiB fraction may be explained by the formation of organic odorants (e.g., *N*-chloroadimines, aldehydes) from the chlorination of organic compounds (e.g.,

amino acids) (Freuze et al., 2004; Freuze et al, 2005). In addition, high chlorine demand to oxidize organic compounds in HiB fraction has an impact on increase of chlorine flavor (Krasner and Barret, 1984).

Table 5.1 Chemical properties for sample set 1 of RSF1

Parameters	Control	HoA	HoN	Trs	HiA	HoB	HiB	HiN
Chlorine demand (mg/L)	1.90	1.95	1.47	1.42	1.85	1.37	2.55	1.75
Residual chlorine (mg/L)	0.97	0.87	0.84	0.97	0.87	0.97	0.82	0.97
Adjusted DOC (mg/L)	0.85	0.98	1.03	1.02	0.92	1.01	0.91	0.88
NH_4^+ (µg/L)	3	10	11	9	51	3	60	40
pH	7.5	7.35	7.55	7.36	7.35	7.10	7.2	7.64
UV_{254} (cm^{-1})	0.020	0.026	0.009	0.000	0.007	0.001	0.007	0.004
SUVA ($cm^{-1} \cdot mg^{-1}$)	0.024	0.027	0.009	0.000	0.008	0.001	0.008	0.005
Br^- (µg/L)	20	35	n/d	4	n/d	n/d	n/d	23
NCl_3 (µg/L as NCl_3)	74	81	84	210	n/d	251	n/d	n/d

Note: n/d Not detected

Table 5.2 Chemical properties for sample set 2 of RSF1

Parameter	Control	HoA	HoN	Trs	HiA	HoB	HiB	HiN
Chlorine demand (mg/L)	1.90	2.03	1.48	1.42	2.00	ND.	2.84	2.05
Residual chlorine (mg/L)	0.92	0.72	1.02	1.07	0.82	ND.	1.02	0.99
Adjusted DOC (mg/L)	0.86	1.02	0.98	1.02	0.94	ND.	0.86	0.81
NH_4^+ (µg/L)	9	12	n/d	23	97	ND.	119	47
pH	7.5	7.6	7.6	7.4	7.4	ND.	7.0	7.6
UV_{254} (cm^{-1})	0.021	0.026	0.010	0.002	0.011	ND.	0.009	0.003
SUVA (cm^{-1}•mg^{-1})	0.024	0.025	0.010	0.001	0.011	ND.	0.010	0.003
Br$^-$ (µg/L)	24	47	7	n/d	n/d	ND.	n/d	39
NCl_3 (µg/L as NCl_3)	131	33	82	128	n/d	ND.	n/d	44

Note: n/d   Not detected
ND. No data

Table 5.3 Chlorine demands of organics in each fraction for RSF1

Sample	Parameters	Control	HiN	HoA	HiA	HiB	HoN	Trs	HoB
	Total chlorine demand (mg/L)	1.9	1.75	1.95	1.85	2.55	1.47	1.42	1.37
Set 1	Chlorine consumption by ammonium ions (mg/L)	0.02	0.30	0.08	0.39	0.46	0.08	0.07	0.02
	Chlorine consumption by organics (mg/L)	1.88	1.45	1.87	1.46	2.09	1.39	1.35	1.35
	Total chlorine demand (mg/L)	1.9	2.05	2.03	2.00	2.84	1.48	1.42	ND.
Set 2	Chlorine consumption by ammonium ions (mg/L)	0.07	0.36	0.09	0.74	0.90	n/d	0.17	ND.
	Chlorine consumption by organics (mg/L)	1.83	1.69	1.94	1.26	1.94	1.48	1.25	ND.

Note: ND. No data

Table 5.4 Observed odor strengths compared to the contribution of trichloramine in each fraction for RSF1

Sample	Parameters	Control	HiN	HoA	HiA	HiB	HoN	Trs	HoB
Set 1	Observed odor strength (observed TON)	67	77	17	45	95	35	52	38
	Odor strength contributed from trichloramine	22	n/d	23	n/d	n/d	25	61	74
Set 2	Observed odor strength (observed TON)	58	65	34	47	186	49	50	ND.
	Odor strength contributed from trichloramine	39	13	10	n/d	n/d	24	38	ND.

Note: n/d   Not detected
ND.   No data

5.3.2 The effect of ozonation on the DOM fractions contributing to chlorinous odor

Water was collected at the outlet of RSF process and ozonation to study not only the influence of ozonation on the organic fraction causing chlorinous odor, but also the remaining fractions responsible for chlorinous odor after ozonation. The DOC concentrations of each fraction and the percentages of DOM for water before and after ozonation were summarized in Figure 5.4. DOM concentrations of RSF2 and OW were 0.858 and 0.849 mg/L, respectively. Thus, the DOM concentration of the control sample was unaffected by ozonation. Because the concentration of HoB fraction was negligible, base fraction (hereinafter called to Bas) was used for representing the combination of HoB and HiB in order to save time during the fractionation process. To obtain the DOC concentration of Bas fraction in DOC7, DOC4 was subtracted from DOC2. As seen in previous discussion that chlorination of HiB fraction produced strongest chlorinous odor, the concentration of Bas fraction was supposed to represent the major contributor of chlorinous odor in RSF2 water.
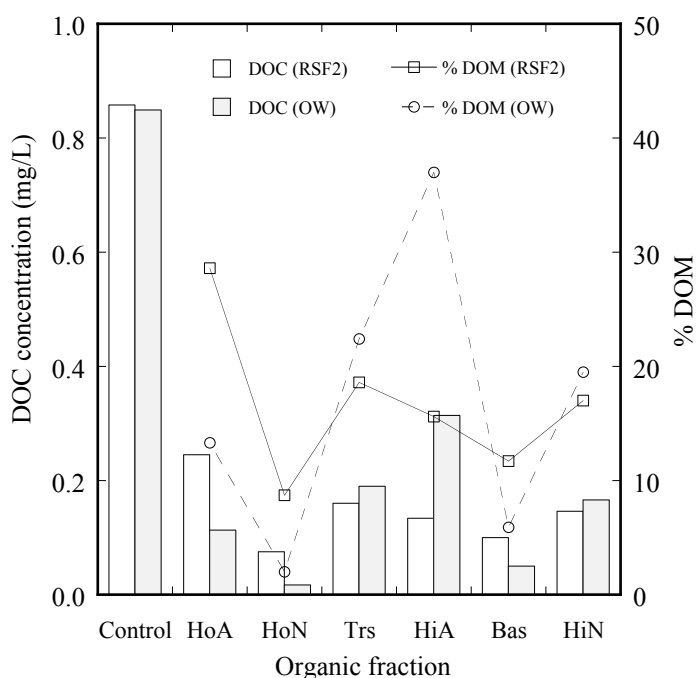
Figure 5.4. The DOC concentrations and the percentages of DOM fractions for RSF2 and OW

Ozonation changed the property of DOM significantly. The concentration of Bas fractions in RSF2 was 0.10 mg/L. After ozonation, DOC of Bas fraction was reduced by 50% as shown in Table 5.5. Similar trend was also found in the oxidation of hydrophobic fraction (HoA + HoN). After ozonation, the DOC concentration of HoA and HoN fractions decreased by more than 50%, whereas DOC concentrations of HiA, HiN and Trs fractions were increased after ozonation by 57%, 12%, and 16%, respectively. This can be explained with the hypothesis that O_3 and •OH oxidize organic compounds in the hydrophobic fraction, and the products become more hydrophilic compounds (e.g., carboxylic acids, and alcohols). This assumption is supported by the information of ozonation that O_3 and •OH can react quickly with double bonds, aromatic compounds and deprotonated amines (von Gunten, 2003a). Huang et al. (2005) also reported that the concentration of aromatics, amines and amino acids (exhibit in Base fraction) could be decreased by ozonation, whereas the increase of alcohols and aliphatic carboxylic acids were observed. Chang et al. (2002) found that ozonation could decrease aromatic C=C double bonds, whereas the structures of single bond (e.g., O-H, C-H) was present in ozonated water. Therefore, hydrophilic fraction became dominant in the ozonated water, accounting for more than 60% of DOM. Because the formation of harmful DBPs (e.g., THMs and HAAs) depends on types of organic fraction, changes of organic fractions after ozonation can potentially produce other DBPs (Marhaba et al., 2000). Although ozonation has been found to reduce the overall disinfection byproducts formation potential (DBPFP), which includes THMs and HAAs (Chiang et al., 2002), major organic fractions contributing to chlorinous odor can be changed after ozonation.

Table 5.5 The organic fractions for RSF2 and OW

Organic fraction	DOC (mg/L)		Removal Efficiency (%)
	RSF2	OW	
Control	0.858	0.849	1
HoA	0.245	0.113	54
HoN	0.075	0.017	77
Trs	0.160	0.190	-16
HiA	0.134	0.314	-57
Bas	0.100	0.050	50
HiN	0.146	0.166	-12
Summation of fractions	0.860	0.850	-

Figure 5.5 shows the odor strength for the fractions of water before and after ozonation. Odor strengths of several hydrophilic fractions (HiA, HiN and Trs) increased in the range of 30-50% after ozonation, while the odor strength of Bas fraction decreased approximately 60%. Furthermore, the TON value of HoA fraction decreased from 57 to 20 when RSF2 was ozonated. This may result from ozonation changes the structure of organic compounds in each fraction, and unidentified ozonation byproduct presents a different intensity of odor after chlorination. Although odor strength of hydrophilic fractions increased after ozonation, TON value of the control sample for OW decreased by 50% compared to RSF2. It was suspected that precursors of strong odor compounds in Bas or HoA fractions were oxidized by ozonation and the products from ozonation of organics in HoA and Bas fractions were in Trs, HiA, and HiN fractions in which its odor strength (TON) was less than the original odor compounds in HoA and Bas fractions.

Because the DOC concentration of HiA fraction after ozonation greatly increased (by 57%), the percentage of odor strength contribution for HiA fraction (21%) was higher than Bas fraction (3%). Thus, HiA found to be the major fraction causing chlorinous odor instead of the Bas fraction when the difference in DOC percentage

was considered (i.e., odor strength of each fraction was multiplied). Chlorination of HiN fraction in OW increased the percentage of odor strength contribution from 6 to 14. That is, HiN was the second major contributor to chlorinous odor. This was possibly explained by the change in chemical structure after ozonation.
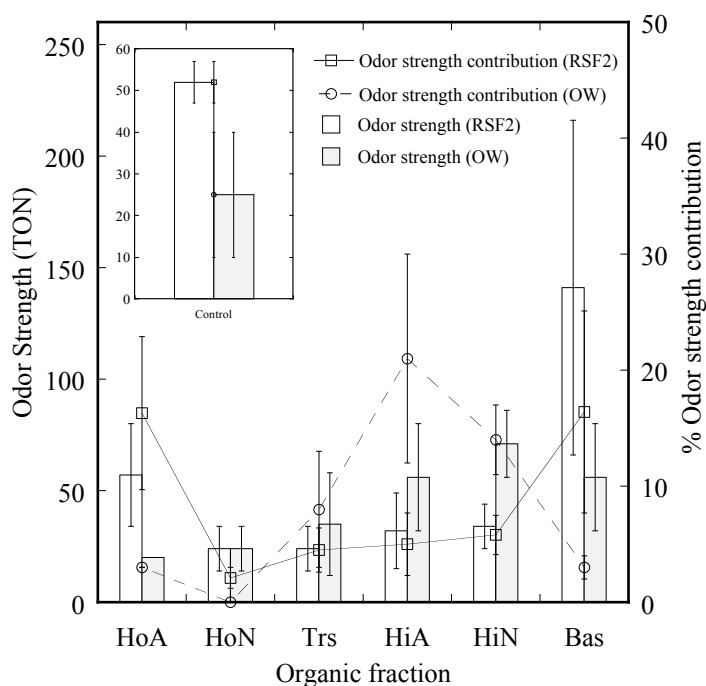
Figure 5.5. The odor strengths (TONs) and percentage contributions of odor strength for organic fractions of RSF2 and OW

Tables 5.6 and 5.7 show the chemical properties of RSF2 and OW. High concentrations of ammonium ion in Bas fraction for RSF2 and OW (approximately 120 µg/L) were observed, while trichloramine was not detected in Bas fraction. According to the previous assumption that the formation of trichloramine in Bas fraction is mainly from the chlorination of HoB fraction and the reaction of chlorine to HiB fraction is much faster than to ammonium ion in HoB fraction, Bas fraction of RSF2 mostly consisted of HiB fraction, and the concentration of HoB fraction was negligible. Thus, the chlorination of HiB fraction in Bas fraction was a predominant reaction for the formation of odor byproducts in RSF2.

The SUVA value for the control sample of RSF2 was reduced by the ozonation (0.010 to 0.001 cm^{-1}•mg^{-1}) as shown in Tables 5.6 and 5.7. Similar results were reported by Chang et al. (2002) and Chiang et al. (2002). This suggests that ozonation can effectively lower the SUVA value, which usually represents the quantity of unsaturated bonds in organic matters (Chang et al., 2002 and references therein). With the fact that unsaturated bonds in organic is reactive to chlorine. Thus, the reduction of SUVA can lead to the lower chlorine consumption.

The chlorine demand of organic compounds (without ammonium ion effects) in each fraction was shown in Table 5.8. It indicated that ozonation changed chlorine demand. Chlorine demand decreased by 22% in the control sample of RSF2 compared to OW. Similar results were found by Glaze (1987). Reduction of chlorine demand for HiA and Trs fractions after ozonation were 41 and 12%, respectively. Because ozonation can change the chemical structure of organic compound by reaction to double bonds, activated aromatic compounds, deprotonated amines (von Gunten, 2003a), this may affect chlorine reactivity of organic compounds. After ozonation, chlorine demand of HoA fraction also decreased by 10%. This can be explained by the great reduction of DOC concentration for HoA fraction after treated by ozonation (more than 50%). The chlorine demands for other fractions compared to OW changed only slightly (less than 10%).

Table 5.9 presents the comparison between observed odor strengths and the contribution of trichloramine to odor strengths. It indicated that the estimated odor strength from trichloramine in the control sample of RSF2 was 25% of observed odor strength, while it was 80% of observed odor strength for control sample of OW. This indicated that trichloramine was minor odor compound in chlorinated water treated by conventional treatment, but it still caused chlorinous odor even water treated by ozonation. After ozonation, the main organic fractions causing chlorinous odor of the DOM isolates (with trichloramine effects) were HiA, HiN and Bas fractions with the odor strengths of 46, 55, and 56, respectively.

Table 5.6 Chemical properties for RSF2

Parameter	Control	HoA	HoN	Trs	HiA	HiN	Bas
Chlorine demand (mg/L)	2.00	1.98	1.32	2.39	1.74	1.70	3.06
Residual chlorine (mg/L)	0.99	0.87	0.89	0.97	0.78	1.17	1.12
Adjusted DOC (mg/L)	0.86	1.11	0.99	1.09	1.00	0.81	1.02
NH_4^+ (µg/L)	2	92	19	52	51	105	121
pH	7.1	7.0	6.8	6.9	7.5	7.0	7.2
UV_{254} (cm^{-1})	0.009	0.009	0.003	0.010	0.005	0.000	0.012
SUVA ($cm^{-1} \cdot mg^{-1}$)	0.010	0.008	0.003	0.009	0.005	0.000	0.012
Br^- (µg/L)	40	19	n/d	n/d	n/d	47	n/d
NCl_3 (µg/L as NCl_3)	43	38	70	111	34	41	n/d

Note: n/d Not detected

Table 5.7 Chemical properties for OW

Parameter	Control	HoA	HoN	Trs	HiA	HiN	Bas
Chlorine demand (mg/L)	1.57	1.32	1.34	1.84	1.32	1.16	2.94
Residual chlorine (mg/L)	1.28	0.94	1.08	1.14	0.77	0.76	1.22
Adjusted DOC (mg/L)	1.10	1.02	0.96	0.98	1.09	0.87	1.06
NH_4^+ (µg/L)	4	22	2	10	69	33	117
pH	7.3	7.1	7.1	6.9	7.2	7.1	6.9
UV_{254} (cm^{-1})	0.001	0.006	0.003	0.006	0.002	0.000	0.014
SUVA ($cm^{-1} \cdot mg^{-1}$)	0.001	0.006	0.003	0.006	0.002	0.000	0.013
Br^- (µg/L)	7	32	6	n/d	n/d	86	n/d
NCl_3 (µg/L as NCl_3)	68	39	36	66	34	53	n/d

Note: n/d   Not detected

Table 5.8 Chlorine demands of organics in each fraction for RSF2 and OW

Sample	Parameters	Control	HiN	HoA	HiA	Bas	HoN	Trs
RSF2	Total chlorine demand (mg/L)	2.00	1.70	1.98	1.74	3.06	1.32	2.39
	Chlorine consumption by ammonium ions (mg/L)	0.02	0.80	0.70	0.39	0.92	0.14	0.40
	Chlorine consumption by organics (mg/L)	1.98	0.09	1.28	1.35	2.14	1.18	1.99
OW	Total chlorine demand (mg/L)	1.57	1.16	1.32	1.32	2.94	1.34	1.84
	Chlorine consumption by ammonium ions (mg/L)	0.03	0.25	0.17	0.52	0.89	0.02	0.08
	Chlorine consumption by organics (mg/L)	1.54	0.91	1.15	0.80	2.05	1.32	1.76

Table 5.9 Observed odor strengths compared to the contribution of trichloramine in each fraction for RSF2 and OW

Sample	Parameters	Control	HiN	HoA	HiA	Bas	HoN	Trs
RSF2	Observed odor strength (Observed TON)	52	34	57	32	141	24	24
	Odor strength contributed from trichloramine	13	12	11	10	n/d	20	33
OW	Observed odor strength (Observed TON)	25	71	20	56	56	24	35
	Odor strength contributed from trichloramine	20	16	11	10	n/d	11	19

Note: n/d Not detected

As mentioned above that ozonation lowered SUVA values corresponding to the decrease of chlorine demand, the decrease of chlorinous odor possibly resulted from the reduction of Cl/N. Ozonation can also decrease chlorinous odor by converting chlorinous DBP precursors (e.g., amino acids) to non-chlorinous odor precursors (e.g., nitrate ion) (Berger et al., 1998; Leitner et al., 2002 and references therein). However, HiA and HiN fractions, main fractions causing chlorinous odor after ozonation, consist of organic compounds, and ammonium ions released after ozonation may not be negligible (discussed in chapter 4), it was suggested that ozonated water should be treated by a series process of granular activated carbon (GAC) or biological activated carbon (BAC) with an ion-exchange prior to chlorination in order to minimize the organic odor precursors and trichloramine precursor (NH_4^+).

5.4 Conclusions

This chapter aims to characterize the DOM fractions causing chlorinous odor by the use of resin adsorption chromatography technique (fractionation). The results were summarized as follows:

- HoA, HiA, and Trs fractions were major organic fractions in source water treated by RSF.
- Base fraction, including HoB and HiB fractions, was the major contributor to chlorinous odor in river water treated by RSF.
- Among organic fractions, HoB fraction was a major precursor of trichloramine.
- Ozonation decreased chlorinous odor by the oxidation of hydrophobic and base fractions, and oxidized organic fractions became more hydrophilic.
- Hydrophilic fractions (HiA, HiN, and Trs) were the major fractions in ozonated water.
- HiA and HiN fractions were predominant precursors of chlorinous odor

in ozonated water.

Chapter 6

Conclusions

This research has addressed several issues on the control of chlorinous odor by the oxidation with O_3 and $\cdot OH$. The aim of this research is to accomplish safe and odorless drinking water by advanced oxidation process (AOP). The major findings in each chapter are summarized below:

In chapter 3, a bench scale of ozonation reactor was used with batch-mode operation and various operating parameters in order to investigate the possibility of application of O_3 and $\cdot OH$ for the control of chlorinous odor and bromate ion at the same time. The major findings are summarized here:

- Ozonation and AOP (O_3/H_2O_2 process) decrease chlorinous odor in drinking water by more than 50% compared to chlorination alone.

- Odor strength reduction is clearly unaffected by pH, and bromide ion and ammonium ion concentrations.

- Increase of O_3 in a typical value (1-2 mg/L) does not have an effect on the improvement of odor strength removal, whereas an extremely high O_3 dose slightly increase the efficiency of TON removal.

- Trichloramine has no relationship with odor strength. Thus, trichloramine is a minor odorous contributor.

In chapter 4, several conditions for ozonation obtained from previous chapter were performed with a pilot scale of ozone bubble contactor to attempt the simultaneous control of chlorinous odor and bromate ion formation in a more practical set up. The

major findings from this chapter are:

- Ozonation and AOP (O_3/H_2O_2 process) can decrease odor strength by more than 50% compared to chlorination alone.

- H_2O_2 addition enhances •OH exposure, and the increasing •OH exposure has an effect on odor strength removal.

- The oxidation of nitrogenous organic compounds by ozonation and AOP in Yodo river water produces ammonium ion as end-byproducts.

- Trichloramine is a minor odorous contributor to chlorinous odor for water treated by conventional treatment, but its odor contribution can cause a limitation of odor control by ozonation and AOP (note that ammonium ion, a trichloramine precursor, cannot be oxidized by O_3 and •OH).

- Comparing odor control by ozonation and AOP in batch-mode reactor with ozonation and AOP in ozone bubble contactor, no significant reduction in chlorinous odor is observed although •OH exposure in ozone bubble reactor is higher. Bromate ion formation in ozone column reactor is lower than in batch-mode reactor.

- Based on the removal of musty odor compounds (e.g., geosmin and 2-methylisoborneol (2-MIB)) by ozonation and AOP, the operation of AOP0.5 with an O_3 dose of 1 mg/L can be a viable option for simultaneous control of odor compounds and bromate ion below their Japanese standard values when the concentrations of musty odor compounds in natural water increase to 77 ng/L and 40 ng/L for geosmin and 2-MIB, respectively. When the concentrations of geosmin and 2-MIB are higher than 125 ng/L and 83 ng/L, respectively, AOP0.5 with a higher O_3 dose is needed.

In chapter 5, the fractionation technique was applied to investigate the major precursors of chlorinous odor, and the O_3-resistant organic compound causing

chlorinous odor. The major findings from this chapter are highlighted below:

- NOM of source water treated by RSF is mainly composed of hydrophobic acid (HoA), hydrophilic acid (HiA), and transphilic (Trs) fractions.

- Base fraction (Bas), including hydrophilic base (HiB) and hydrophobic base (HoB), is a major fraction of chlorinous odor precursors when water treated by conventional treatment processes.

- Chlorination of HoB fraction produces a high concentration of trichloramine.

- Ozonation has an effect on odor strength removal by oxidation of hydrophobic and Bas fractions, and oxidized organic fractions become more hydrophilic.

- The major organic precursors of chlorinous odor in ozonated water are hydrophilic fractions (HiA and HiN).

Chapter 7

Future Research

This research has revealed our knowledge on the simultaneous control of chlorinous odor and bromate ion concentration by advanced oxidation process (O_3/H_2O_2 process). Also, the predominant organic fraction corresponding to precursors of chlorinous odor has been shown for water with and without ozonation. To produce odorless drinking water with ozonation, severally challenging research should be included from this study:

1. With the information that high •OH exposure can improve the odor reduction, increase in O_3 dose to extremely high dose such as 10 mg/L may improve the efficiency of chlorinous odor control.

2. In this study, hydrophilic organic fraction was shown to be the predominant after ozonation. Also, trichloramine formation may not be negligible because ammonium ions are resistant to O_3 and •OH. Thus, this useful information should be further examined by the series treatment of granular activated carbon (GAC) or biological activated carbon (BAC) and ion exchange after ozonation and AOP in order to eliminate or biodegrade the remaining odor precursors.

3. Other separation technique such as molecular weight (MW) separation, carbon-13 nuclear magnetic resonance (^{13}C NMR) should be applied to identify the major precursor of chlorinous odor in each organic fraction.

4. According to this research was applied ozonation and AOP to oxidize odor precursors before chlorination. Other treatment process such as membrane filtration should be also evaluated.

5. The contribution of other odorous organic DBP (i.e., N-chloaldimines, odorous aldehydes) should be evaluated for the control of chlorinous odor.

References

Acero, J.L., and von Gunten, U. : Characterization of oxidation processes: ozonation and the AOP O_3/H_2O_2, J.-Am. Water Works Assoc., Vol. 93, pp. 90-100, 2001.

Acero, J.L., and von Gunten, U. : Influence of carbonate on ozone/hydrogen peroxide based advanced oxidation process for drinking water treatment, Ozone Sci. Eng., Vol. 21, pp. 305-328, 2000.

American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF). *Standard Methods for the Examination of Water and Wastewater*, 21st Edition, American Public Health Association, Washington DC, 2005.

Ates, N., Kitis, M., and Yetis, U. : Formation of chlorination by-products in waters with low SUVA-correlations with SUVA and differential UV spectroscopy, Water Res., Vol. 41, pp. 4139-4148, 2007.

Bao, M. L., Barbieri, K., Burrini, D., Griffini, O., and Pantani, F. : Determination of trace levels of taste and odor compounds in water by microextraction and gas chromatography-ion-trap detection-mass spectrometry, Water Res., Vol. 31, pp. 1719-1727, 1997.

Bartels, J.H.M., Burlingame, G.A., and Suffet, I.H. : Flavor profile analysis: taste and odor control of the future, J.-Am. Water Works Assoc., Vol. 83, pp. 50-55, 1986.

Bader, H., Sturzenegger, V., and Hoigné, J.: Photometric method for the determination of low concentration of hydrogen peroxide by the peroxidase catalyzed oxidation of N, N-diethyl-p-phenylenediamine (DPD), Water Res., Vol. 22, pp. 1109-1115, 1988.

Berger, P., Leitner, K.V.N., Doré, M., and Legube, B. : Ozone and hydroxyl radicals induced oxidation of glycine, Water Res., Vol. 33, pp. 433-441, 1999.

Bernard, A., Carbonnelle, S., Michel, O., Higuet, S., de Burbure, C., Buchet, J.P., Hermans, C., Dumont, X., and Doyle, I. : Lung hyperpermeability and asthma prevalence in schoolchild: unexpected associations with the attendance at indoor chlorinated swimming pools, , Occup. Environ. Med., Vol. 60, pp. 385-394, 2003.

Bhandari, B. and Grant, M. : User satisfaction and sustainability of drinking water schemes in rural communities of Nepal, Sustainability: Sci., Practice, & Policy, Vol. 3, pp. 12-20, 2007.

Boyer, T.H. and Singer, P.C. : Stoichiometry of removal of natural organic matter by ion exchange, Environ. Sci. Technol., Vol. 42, pp. 608-613, 2008.

Brosillon, S., Lemasle, M., Renault, E., Tozza, D., Heim, V., and Laphanche, A. : Analysis and occurrence of odorous disinfection by-products from chlorination of amino acids in three different drinking water treatment plants and corresponding distribution networks, Chemosphere, Vol. 77, pp. 1035-1042, 2009.

Bruchet, A., Costentin, E., Legrand, M.F., and Mallevialle, J. : Influence of the chlorination of natural nitrogenous organic compounds on taste and odors in finished drinking water, Water Sci. Technol., Vol. 25, pp. 323-334, 1992.

Bruchet, A., Duguet, J.P., and Suffet, I.H. (Mel). : Review: Role of oxidants and disinfectants on the removal, masking and generation of tastes and odours, Environ. Sci & Bio/Tech., Vol. 3, pp. 33-41, 2004.

Buchanan, W., Roddick, F., Porter, N., and Drikas, M. : Fractionation of UV and VUV pretreated natural organic matter from drinking water, Environ. Sci. Technol., Vol. 39, pp. 4647-4654, 2005.

Buffle, M.O., Schumacher, J., Salhi, E., Jekel, M., and von Gunten, U. : Measurement of the initial phase of ozone decomposition in water and wastewater by means of a continuous quench-flow system : Application to disinfection and pharmaceutical oxidation, Water Res., Vol. 40, pp. 1884-1894, 2006.

Cabinet Office, Government of Japan. <in Japanese> : National survey on water, 2009.

Camel, V., and Bermond, A. : Review paper: the use of ozone and associated oxidation processes in drinking water treatment, Water Res., Vol. 32, pp. 3208-3222, 1998.

Chang, E.E., Lin, Y.P., and Chiang, P.C. : Effects on bromide on the formation of THMs and HAAs, Chemosphere, Vol. 43, pp. 1029-1034, 2001.

Chang, C.N., Ma, Y.S., and Zing, F.F. : Reducing the formation of disinfection by products by pre-ozonation, Chemosphere, Vol. 46, pp. 21-30, 2002.

Chiang, P.C., Chang, E.E., and Liang, C.H. : NOM characteristics and treatabilities of ozonation precesses, Chemosphere, Vol. 46, pp. 929-936, 2002.

Chiang, P.C., Ko, Y.W., Liang, C.H., and Chang, E.E. : Modeling an ozone bubble column for predicting its disinfection efficiency and control of DBP formation, Chemosphere, Vol. 39, pp. 55-70, 1999.

Chin, A., and Bérubé, P.R. Removal of disinfection by-product precursors with ozone-UV advances oxidation process, Water Res., Vol. 39, pp. 2136-2144, 2005.

Croué, J.P., Lefebvre, E., Martin, B., and Legube, B. : Removal of dissolved hydrophobic and hydrophilic organic substances during coagulation/flocculation of surface waters, Water Sci. Technol., Vol. 27, pp. 143-152, 1993.

Croué, J.P., Violleau, D., Bodaire, C., and Legube, B. : Removal of hydrophobic and

hydrophilic constituents by anion exchange resin, Water Sci. Technol., Vol. 40, pp. 207-214, 1999.

Mizkan company (Culture for human life with Aqua). <in Japanese> : Dissatisfaction factors of drinking water quality, 2009.

Deborde, M., and von Gunten. : Reactions of chlorine with inorganic and organic compounds during water treatment-kinetics and mechanisms: a critical review, Water Res., Vol. 42, pp. 13-51, 2008.

Dietrich, A.M. : Aesthetic issues for drinking water, J. Water Health, Vol. 4, pp. 11-16, 2006.

Donnermair, M.M., and Blatchley III, E.R. : Disinfection efficacy of organic chloramines, Water Res., Vol. 37, pp. 1557-1570, 2003.

Dotson, A., and Westerhoff, P. : Occurrence and removal of amino acids during drinking water treatment, J. Am. Water Works Assoc., Vol. 101, pp. 101-115, 2009.

Echigo, S., Zhang, X.R., Lei, H., Smith, M.E. and Minear, R.A. : Evaluation of control strategies for disinfection byproducts for small water supplies using ozone as an alternative disinfection process, Water Sci. Technol.: Water Suppl., Vol. 9, pp., 431-437, 2009.

Elovitz, M.S., and von Gunten, U. : Hydroxyl radical/Ozone ratios during ozonation processes. I. The R_{ct} concept, Ozone Sci. Eng., Vol. 21, pp. 239-260, 1999.

Fabris, R., Chow, C.W.K., Drikas, M., and Eikebrokk, B. : Comparison of NOM character in selected Australian and Norwegian drinking water, Water Res., Vol. 42, pp. 4188-4196, 2008.

Freuze, I., Brosillon, S., Arlot, J., Laplanche, A., Tozza, D., and Cavard, J. : Impact of

UV-irradiation on the formation of odorous chloroaldimines in drinking water, Chemosphere, Vol. 63, pp. 1660-1666, 2006.

Freuze, I., Brosillon, S., Herman, D., Laplanche, A., Démocrate, C., and Cavard, J. : Odorous products of the chlorination of phenylalanine in water formation, evolution, and quantification, Environ. Sci. Technol., Vol. 38, pp. 4134-4139, 2004.
.
Freuze, I., Brosillon, S., Laplanche, A., Tozza, D., and Cavard, J. : Effect of chlorination on the formation of odorous disinfection by-products, Water Res., Vol. 39, pp. 2636-2642, 2005.

Froese, K.L., Wolanski, A., and Hrudey, S.E. : Factors governing odorous aldehyde formation s disinfection by-products in drinking water, Water Res., Vol. 33, pp. 1355-1364, 1999.

Gazda, M., Kumar, K., and Margerum, D. W. : Non-metal redox kinetics: oxidation of bromide ion by nitrogen trichloride, Inorg. Chem., Vol. 34, pp. 3536-3542, 1995.

Glaze, W.H. : Drinking-water treatment with ozone, Environ. Sci. Technol., Vol. 21, pp. 224-230, 1987.

Gottschalk, C., Libra, J.A., and Saupe, A. : Ozonation of water and waste water, Wiley-VCH Verlag GmbH, Federal republic of Germany, Weinheim D-69469, pp. 176, 2000.

Hargesheimer, E.E., and Watson, S.B. : Drinking water treatment options for taste and odor control, Water Res., Vol. 30, pp. 1423-1430, 1996.

Hisamoto, Y. : Evaluation of chlorinous odor formation potential from dissolved organic nitrogen compounds, Bachelor thesis, Kyoto University, Japan, 2009.

Hrudey, S.E., Gac, A., and Daignault, S.A. : Potent odor causing chemicals arising

from drinking water disinfection, Water Sci. Technol., Vol. 20, pp. 55-61, 1988.

Hrudey, S.E. : Review: chlorination disinfection by-products, public health risk tradeoffs and me, Water Res., Vol. 43, pp. 2057-2092, 2009.

Huang, W.J., Fang, G.C., and Wang, C.C. : The formation and fate of disinfection by-products from ozonation of polluted raw water, Sci. Total Environ., Vol. 345, pp. 261-272, 2005.

Huang, W.J., Tsai, Y.Y., and Chu, C.H. : Evaluation of disinfection by-products formation during ozonation of bromide-containing ground water, J. Environ. Sci. Health., Vol. 38, pp. 2919-2931, 2003.

IARC : Some chemicals that cause tumours of the kidney or urinary bladder in rodents and some other substances. Lyon, International Agency for Research on Cancer, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Vol. 73, pp. 481–496, 1999.

Imai, A., Fukushima, T., Matsushige, K., Inoue, T., and Ishibashi, T. <in Japanese> : Fractionation of dissolved organic carbon from the waters of Lake Biwa and its inflowing rivers, Jpn. J. Limnol., Vol. 59, pp. 53-68, 1998.

Imai, A., Fukushima, T., Matsushige, K., and Kim, Y.H. : Fractionation and characterization of dissolved organic matter in a shallow eutrophic lake, its inflowing rivers, and other organic matter sources, Water Res., Vol. 35, pp. 4019-4028, 2001.

Imai, A., Matsushige, K., and Nagai, T. : Trihalomethane formation potential of dissolved organic matter in a shallow eutrophic lake, Water Res., Vol. 37, pp. 4284-4294, 2003.

Itoh, S., Shiro, S., Hirayama, N., Echigo, S., and Ohkouchi, Y. <in Japanese> : Factors related to citizens satisfaction with tap water and analysis of improvement needs in

water supply system, Environ. Sanit. Eng. Res., Vol. 20, pp. 27-34, 2006.

Jafvert, C.T., and Valentine, R. L. : Reaction scheme for the chlorination of ammoniacal water, Environ. Sci. Technol., Vol. 26, pp. 577-586, 1992.

Jo, I. <in Japanese>: Contribution of hydrophilic and basic fraction of dissolved organic matter to the transformation potential of haloacetic acids by an comprehension fractionation technique, Master thesis, Kyoto University, Japan, 2008.

Jung, HS., and Madjid, M. : A study on the relationship between biodegradability enhancement and oxidation of 1,4-dioxane using ozone and hydrogen peroxide, Water Res., Vol. 38, 2596-2604, 2004.

Kajino, M. and Sakamoto, K. : The relationship between musty-odor-causing organisms and water quality in lake Biwa, Water Sci Technol., Vol. 31, pp. 153-158, 1995.

Karpel Vel Leitner, N., Berger, P., and Legube, B. : Oxidation of amino groups by hydroxyl radicals in relation to the oxidation degree of α-carbon, Environ. Sci. Technol., Vol. 36, pp. 3083-3089, 2002.

Kim, J.H., von Gunten, U., and Mariñas, B.J. : Simultaneous prediction of Cryptosporidium parvum Oocyst inactivation and bromate formation during ozonation of synthetics waters, Environ. Sci. Technol., Vol. 38, pp. 2232-2241, 2004.

Kirmeyer, G.J., Foust, G.W., Pierson, G.L., Simmler, J.J., and Lechevallier, M.W. : Optimizing chloramines treatment. Prepared for the American Water Works Association Research Foundation, 1993.

Kosaka, K., Seki, K., Kimura, N., Furubayashi, H., and Asami, M. <in Japanese> : Development of an analytical method for trichloramine in drinking water by

HS-GC/MS, Proc. 60th JWWA Annual Meeting, pp. 402-403, 2009.

Kosaka, K., Yamada, H., Shishida, K., Echigo, S., Minear, R.A., Tsuno, H., and Matsui, S. : Evaluation of the treatment performance of a multistage ozone/hydrogen peroxide process by decomposition by-products, Water Res., Vol. 35, pp. 3587-3594, 2001.

Krasner, S.W., and Barrett, S.E. : Aroma and flavor characteristics of free chlorine and chloramines, Proc. AWWA WQTC, AWWA, Denvor, Colo., pp. 381- 398, 1984.

Krasner, S.W., Gramith, J.T., Coffey, B.M., Yates, R.S. : Impact of water quality and operational parameters on the formation and control of bromate during ozonation, Water Suppl., Vol., 13, pp. 145-156, 1995.

Kuo, C.T., Wang, P.Y., Wu, C.H. : Fluorometric determination of ammonium ion by ion chromatrography using post column derivatization with *o*-phthaldialdehyde, J. Chromatogr., A., Vol. 1085, pp. 91-97, 2005.

Lee, K.H. : Formation of ketoacids and AOC during ozonation in drinking water, Environ. Eng. Res., Vol. 11, pp. 293-302, 2006.

Leenheer, J.A. : Comprehensive assessment of precursors, diagenesis, and reactivity to water treatment of dissolved and colloidal organic matter, Water Sci. Technol.: Water Suppl., Vol. 4, pp. 1-9, 2004.

Leitner, N.K.V., Berger, P., and Legube, B. : Oxidaion of amino groups by hydroxyl radicals in relation to the oxidation degree of the α-Carbon, Environ. Sci. Technol., Vol. 36, pp. 3083-3089, 2002.

MaGuire, M.J. : Off-flavour as the consumer's measure of drinking water safety, Water Sci. Technol., Vol. 31, pp. 1-8, 1995.

Marhaba, T.F., and Van, D. : The variation of mass and disinfection by-product formation potential of dissolved organic matter fractions along a conventional surface water treatment plant, J. Hazard. Mater., A74, Vol. 74, pp. 133-147, 2000.

Massin, N., Bohadana, A.B., Wild, P., Héry, M., Toamain, J.P., and Hubert, G. : Respiratory symptoms and bronchial responsiveness in lifeguards exposed to nitrogen trichloride in indoor swimming pools, Occup. Environ. Med., Vol. 55, pp. 258-263, 1998.

Matsui, Y., Ando, N., Sasaki, H., Matsushita, T., and Ohno, K. : Branched pore kinetic model analysis of geosmin adsorption on super-powdered activated carbon, Water Res., Vol. 43, pp. 3095-3103, 2009.

Metcalf & Eddy, Tchobanoglous, G., Burton, F. L., and Stensel, H. D. : Wastewater Engineering, Treatment and Reuse, 4th Edn, McGraw Hill Education, pp. 1329, 2003.

Ministry of Health, Labor and Welfare (MHLW), Japan : The revision of drinking water quality standard, (in Japanese), 2008.

Nakai, J.S., Poon, R., Lacavalier, P., Chu, I., Yagminas, A., and Valli, V. E. : Effect of subchronic exposure of rats to dichloramine and trichloramine in drinking water, Regul. Toxicol. Pharmacol., Vol. 31, pp. 200-209, 2000.

Neumann, M.B., von Gunten, U., and Gujer, W. : Sources of parameter uncertainty in predicting treatment performance: the case of preozonation in drinking water engineering, Environ. Sci. Technol., Vol. 41, pp. 3991-3996, 2007.

Nikolaou, A.D., Kostopoulou, M.N., and Lekkas, T.D. : Organic by-products of drinking water chlorination, Global Nest: the Int. J., Vol. 1, pp. 143-156, 1999.

Nikolaou, A.D., and Lekkas, T.D. : The role of natural organic matter during

formation of chlorination by-products: a review, Acta hydrochim. Hydrobiol., Vol. 29, pp. 63-77, 2001.

Owen, D.M., Amy, G.L., Chowdhury, Z.K., Paode, R., Mccoy, G., and Viscosil, K. : NOM characterization and treatability, J.-Am. Water Works Assoc., Vol. 87, pp. 46-63, 1995.

Peter, A., and von Gunten, U. : Oxidation kinetics of selected taste and odor compounds during ozonation of drinking water, Environ. Sci. Technol., Vol. 41, pp. 626-631, 2007.

Pinkernell, U., and von Gunten, U. : Bromate minimization during ozonation: Mechanistic considerations, Environ. Sci. Technol., Vol. 35, pp. 2525-2531, 2001.

Pomes, M.L., Larive, C.K., Thurman, E.M., Green, W.R., Orem, W.H., Rostad, C.E., Copten, T.B., Cutak, B.J., and Dixon, A.M. : Sources and haloacetic acid/trihalomethane formation potentials of aquatic humic substances in the Wakamura River and Clinton Lake near Lawrence, Kansas, Environ. Sci. Technol., Vol. 34, pp. 4278-4286, 2000.

Satoh, N., Echigo, S., Itoh, S., and K. Kosaka <in Japanese>, Control of bleach odor compounds by ion exchange treatment, Environ. Sanitary Eng. Res., Vol. 23, pp. 112-115, 2009.

Schurter, L.M., Bachelor, P.P., and Margerum, D.W. : Nonmetal redox kinetics: Mono-, Di-, and Trichloramine reactions with cyanide ion, Environ. Sci. Technol., Vol. 29, pp. 1127-1134, 1995.

Shang, C., and Blatchley III, E.R. : Differentiation and quantification of free chlorine and inorganic chloramines in aqueous solution by MIMS, Environ. Sci. Technol., Vol. 33, pp. 2218-2223, 1999.

Suffet, I.H., Corado, A., Chou, D., McGuire, M.J., and Butterworth, S. : AWWA taste and odor survey, J.-Am. Water Works Assoc., Vol. 88, pp. 168-180, 1996.

Suffet, I.H.(Mel), Schweitzer, L., and Khiari, D. : Olfactory and chemical analysis of taste and odor episodes in drinking water supplies, Environ. Sci. & Bio/Technol., Vol. 3, pp. 3-13, 2004.

Terauchi, N., Ohtani, T., Yamanaka, K., Tsuji, T., Sudou, T., and Ito, K. : Studies on a biological filter for musty odor removal in drinking water treatment processes, Water Sci. Technol., Vol. 31, pp. 229-235, 1995.

Ueno, H., Moto, T. Sayato, Y., and Nakamuro, K. : Disinfection by-products in the chlorination of organic nitrogen compounds: by-products from Kynurenine, Chemosphere, Vol. 33, pp. 1425-1433, 1996.

von Gunten, U. : Review: Ozonation of drinking water: Part I. Oxidation kinetics and product formation, Water Res., Vol. 37, pp. 1443-1467, 2003a.

von Gunten, U. : Review: Ozonation of drinking water: Part II. Disinfection and by-products formation in presence of bromide, iodide or chlorine, Water Res., Vol. 37, pp. 1469-1487, 2003b.

von Gunten, U., Elovitz, M., and Kaiser., H.-P. : Calibration of full-scale ozonation systems with conservative and reactive traces, J. Water SRT-Aqua, Vol. 48, pp. 250-256, 1999.

von Gunten, U., and Oliveras, Y. : Kinetics of the reaction between hydrogen peroxide and hypobromous acid: Implication on water treatment and natural systems, Water Res., Vol. 31, pp. 900-906, 1997.

von Gunten, U., and Oliveras, Y. : Advanced oxidation of bromide-containing waters: bromate formation mechanism, Environ. Sci. Technol., Vol. 32, pp. 63-70, 1998.

Weaver, W.A., Li, J., Wen, Y., Johnston, J., Blatchey, M.R., and Blatchey II, E.R. : Volatile disinfection by-product analysis from chlorinated indoor swimming pools, Water Res., Vol. 43, pp. 3308-3318, 2009.

Weiss, W.J., Bouwer, E.J., Ball, W.P., ÓMelia, C.R., Aboytes, R. and Speth, T.F. : Riverbank filtration: Effect of ground passage on NOM character, J. Water Suppl.: Res. Technol., Vol. 53, pp. 61-83, 2004.

Welte, B., and Montiel, A. : Study of the possible origins of chlorinous taste and odour episodes in a distribution network, Water Sci. Technol., Vol. 40, pp. 257-263, 1999.

Wert, E.C., Rosario-Ortiz, F.L., and Snyder, S.A. : Effect of ozone exposure on the oxidation of trace organic contaminants in wastewater, Water Res., Vol. 43, pp. 1005-1014, 2009.

Williams, D.T., LeBel, G.L., and Benoit, F.M. : Disinfection by-products in Canadian drinking water, Chemosphere, Vol. 34, pp. 299-316, 1997.

Wolfe, R.L., Ward, N.R., and Olson, B.H. : Inorganic chloramines as drinking water disinfectants: a review, J.-Am. Water Works Assoc., Vol. 76, pp. 74-88, 1984.

World Health Organization (WHO): Guidelines for safe recreational water environments, Vol. 2: swimming pools and similar environments, 2006.

World Health Organization (WHO): Guidelines for drinking-water quality, third edition incorporating the first and second agenda, Vol. 1, Recommendations, 2008.

Yanagibashi, Y. <in Japanese> : A study on inhalation exposure of chemicals in drinking water, Ph.D. Dissertation, Kyoto University, Japan, 2008.

Yee, L.F., Abdullah, M.P., Abdullah, A. Ishak, B., and Abidin, K.N.Z. :

Hydrophobicity characteristics of natural organic matter and the formation of THM, Malaysian J. Anal. Sci., Vol. 13, pp. 94-99, 2009.

Yiin, B.S., and Margerum, D.W. : Non-metal redox kinetics: reaction of trichloramine with ammonia and with dichloramine, Inorg. Chem., Vol. 29, pp. 2135-2141, 1990.

Zazouli, M.A., Nasseri, S., Mahvi, A.H., Mesdaghinia, A.R., Younecian, M., and Gholami, M. : Determination of hydrophobic and hydrophilic fractions of natural organic matter in raw water of Jalalieh and Tehranspars water treatment plants (Tehran), J. Appl. Sci., Vol. 7, pp. 2651-2655, 2007.

Zhang, X., Echigo, S., Lei, H., Smith, M.E., Minear, R.A., and Talley, J.W. : Effects of temperature and chemical addition on the formation of bromoorganic DBPs during ozonation, Water Res., Vol. 39, pp. 423-435, 2005.