Oxidation of Disinfection Byproducts and Algae-related Odorants by UV/H$_2$O$_2$

Chang Hyun Jo

Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy In Civil and Environmental Engineering

Dr. Andrea M. Dietrich, committee chair
Dr. John T. Novak, committee member
Dr. John C. Little, committee member
Dr. Marc A. Edwards, committee member
Dr. James M. Tanko, committee member
Dr. Susan E. Duncan, committee member

August 26, 2008
Blacksburg, Virginia

UV/H$_2$O$_2$, Odorant, Disinfection byproduct, Advanced oxidation process

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ABSTRACT

This research involved an investigation of the application and reaction mechanisms of UV/H$_2$O$_2$ for the simultaneous removal of regulated halogenated disinfection byproducts (DBPs) and odorous aldehydic algal byproducts in the presence of geosmin and 2-methylisoborneol, which are earthy-musty odorants that commonly occur in drinking water. UV/H$_2$O$_2$ is an expensive advanced oxidation process that is used to successfully control geosmin and 2-methylisoborneol. The aqueous oxidation of odorous aldehydes and halogenated DPBs were compared to that of the earthy-musty odorants and the changes to the sensory properties of the drinking water were examined. Geosmin, 2-methylisoborneol, heptadienal, decadienal, and nonadienal, hexanal, and the two most prevalent classes of DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) were oxidized by UV photolysis alone and the UV/H$_2$O$_2$ process with 6 mg/L H$_2$O$_2$ and realistic ng/l to μg/L concentrations of the test compounds.

The di-, and tri-brominated THMs and HAAs were substantially (80-99%) removed by direct UV photolysis mechanism at the same UV/H$_2$O$_2$ dose required for removing 95% of geosmin and 65% of 2-methylisoborneol with faster reaction rates for the more bromine substituted compounds. The C-Br bond cleavage is the first step of brominated HAAs degradation by UV photolysis, and followed by either of two second steps: reaction with oxygen producing peroxyl radical or interaction with water molecule causing O-H insertion/H-Br elimination.

Trichloromethane and mono-, di-, and tri-chlorinated HAAs were not substantially removed under the same conditions used for the brominated compounds. The principal removal mechanism was by the reaction with hydroxyl radical for the UV/H$_2$O$_2$ process. The second order reaction rate constants were on the order of 10^6 - 10^8 M^{-1} s^{-1} with faster reaction rates

for the less chlorine substituted compounds. Based on the reaction rates, hydrogen and halogen ion balance, and isotope effect, both hydrogen abstraction and electron transfer reaction were involved in the first steps of the chlorinated HAA degradation.

Three odorous aldehydes - heptadienal, decadienal, and nonadienal - were removed faster than geosmin or 2-methylisoborneol, and direct UV photolysis was the principal reaction mechanism for the removal of these unsaturated aldehydes. Hexanal was poorly removed. In sensory tests, new odors such as sweet or chalky odors were produced while the concentration and initial odor intensity of these fishy/grassy-smelling aldehydes were reduced with increasing exposure time to UV/H_2O_2. Carbonyl compounds were detected as products of the UV photolysis of nonadienal. These carbonyls were not removed by further UV irradiation, which was thought to be partially related with production of new odors.

The results indicate that the UV/H_2O_2 is effective to control both odorous compounds and brominated DBPs. This process can be seasonally applied to control both contaminants especially, in the warm summer when both odorants and DBPs have their higher concentrations. Removal of brominated DBPs can be a significant addition to water utilities that have difficulty in meeting regulatory levels for these highly toxic compounds. The result on the removal of odorous aldehydes indicate that new types of odors were produced from the oxidation of odorous aldehydes suggesting sensory test coupled with chemical analysis should be considered in designing oxidation process to control recalcitrant odorants.

Table of Contents

List of Tables

List of Figures

Acknowledgement

There was a turtle in America.

What the turtle did was to keep going slowly without a long break because he couldn't run or fly. Many good people helped and supported the turtle. With their help, the turtle is about to finish his race.

My wife, Sun Young and my son, Hyun Jae gave me a good reason I had to keep going. I also want to express a deep appreciation to my parents. While I was in Blacksburg, I came to better realize how much family means to me.

First of all, I'd like to greatly thank my advisor, Dr. Dietrich and her family. She was like my aunt in America. She always shows me the way when I am lost, and supports me.

I also thank my committee members (Dr. Novak, Dr. Little, Dr. Edwards, Dr. Duncan, Dr. Tanko), department head, Dr. Knocke, and other professors for their good guidance. It was lucky for me to learn from them. Especially, I thank Dr. Tanko for helping me enter the radical chemistry world.

My friends in our research group (Pinar, Andy, Jose, Ryan, Dave, Heather, Tim, and Monique) supported and encouraged me a lot. I was happy to be with them. I also thank Betty, Beth, Jody, Julie, and other friends in my department for their kind help.

My Korean friends, if there were not their help, I would have had much more difficult times adapting myself to the life in America.

My friend, Bruce, Nicki, and Angelo, I thank you guys for your friendship. That means a lot to me.

Last, I specially thank my company, Kwater for supporting me. I always thought how I was lucky to have a chance to study abroad even if it was a big challenge to me.

The more I study science, the more I realize that humans just mimic what the mother nature does. While I am studying, I also realized happiness lies rather in how we are related with each other than what we have or what we accomplished. I wish I had spent more time getting closer to my good friends in Blacksburg.

I know this dissertation is just a minimum requirement for Ph.D and a first step to the expertness. I might walk faster in my country than in America. However, I will remember that I was a turtle in a foreign country.

Chapter 1. Introduction

Drinking water treatment has evolved to fulfill demands for safe and clean water. At the early 20th century, sanitary water treatment systems were required to inactivate pathogens and supply a sufficient amount of water. Since then, many treatment techniques have been introduced to the water industry in order to supply safe drinking water that is free of chemical contaminants as well as biological contaminants, many of which were released into source water as a result of civilization. However, there still have been concerns about the quality of drinking water.

Most of the concerns about drinking water result from health issues. Disinfection byproducts (DBPs) are one of the major health issues in the drinking water industry due to their carcinogenicity and genotoxicity (Richardson, Plewa et al. 2007). Many utilities are suffering from the disinfection byproducts problem, which is also frequently in conflict with obtaining disinfection credit required to inactivate pathogens such as *Giardia* and *Cryptosporidium*.

Currently, consumers require more than safe water, and more interest is being shown to aesthetic issues such as taste and odor (Khiari 2004; Liang, Wang et al. 2007; Peter and Von Gunten 2007). This trend indicates that consumers demand "more pleasant" or "more tasty" water. Geosmin (*trans*-1,10-dimethyl-*trans*-9-decalol) and 2-MIB (2-methylisoborneol) are typical earthy-musty smelling odorants found in surface water and subsequently, drinking water. These compounds cause seasonal odor episodes, and are difficult to remove by conventional water treatment processes, and easy for consumers to detect even at low concentrations due to their low odor threshold levels (4-10 ng/L). Another widespread algae-related odor problem is the fishy/grassy odor that is frequently produced from aldehyde compounds. Aesthetic issues also frequently involve concerns about health issues, causing consumer complaints because consumers tend to relate aesthetic issues to health risks. Consequently, meeting the demands for taste and safety is the current agenda of the water industry in 21st century (Figure 1-1). This research is a study on a treatment method, UV/H_2O_2 advanced oxidation, which is being evaluated for removing odorous compounds and disinfection byproducts and is known to be effective for disinfection.
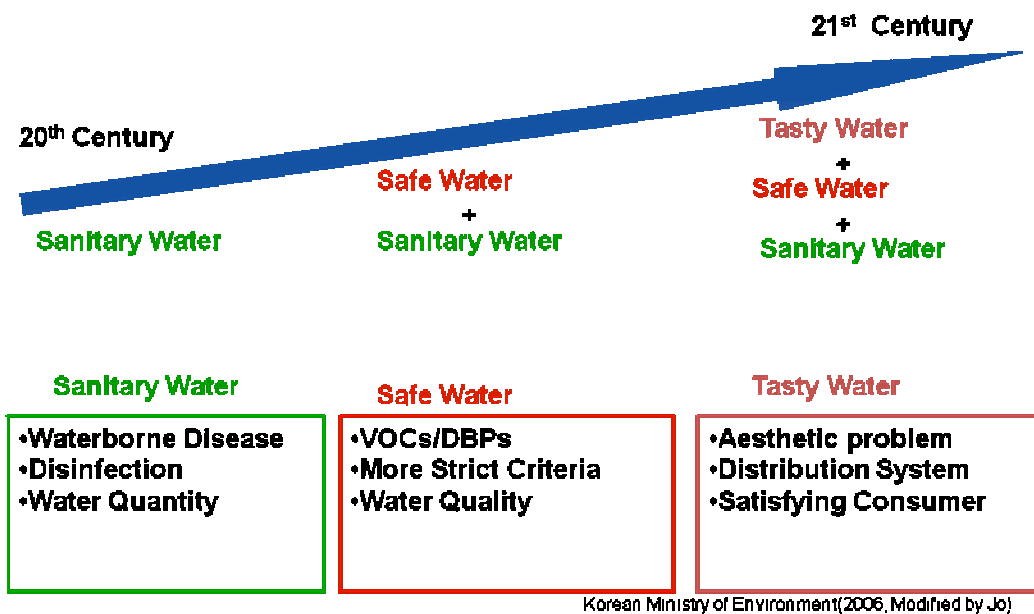
Figure 1-1. Paradigm shift in drinking water quality

A variety of treatment processes have been developed and used to control taste and odor compounds and DBPs, including activated carbon, ozonation, and advanced oxidation process (AOP). AOP oxidizes contaminants with hydroxyl radical (·OH). AOP, like other technologies developed by humans, basically mimics natural phenomena such as the oxidation in the surface water or atmosphere by sunlight (Oppenlander 2003). AOP has an advantage that it efficiently removes organic contaminants without production of residual solids. Additionally, AOP, when it is combined with UV, is an alternative disinfection method for pathogen inactivation (EPA 1999).
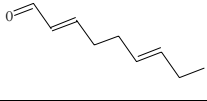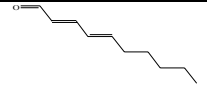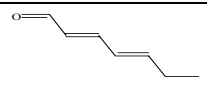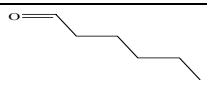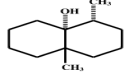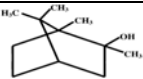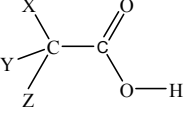
UV/H_2O_2 is an AOP that has been applied to drinking water since the 1990s. In this process, hydroxyl radicals are generated by the direct photolysis of H_2O_2 under UV irradiation (Liao and Gurol 1995; Stefan, Hoy et al. 1996; Stefan and Bolton 1998; Stefan, Mack et al. 2000; Rosenfeldt, Melcher et al. 2005; Rudra, Thacker et al. 2005; Xu, Gao et al. 2007). This process has been known to efficiently remove organic contaminants, including recalcitrant odorous compounds such as geosmin and 2-MIB, mainly by the hydroxyl radical reaction and partially by direct UV photolysis (Beltran, Ovejero et al. 1993; Stefan, Hoy et al. 1996; Stefan and Bolton 1998; Cater, Stefan et al. 2000; Stefan, Mack et al. 2000; Rosenfeldt, Melcher et al. 2005; Rudra, Thacker et al. 2005; Paradis and Hoffman 2006; Rosenfeldt and Linden 2007). AOPs are also thought to effectively remove other algae-related odorants such as odorous aldehydes based on the measured second order reaction rate constant with

hydroxyl radical (Peter and Von Gunten 2007). However, less AOP research was performed on the removal of other algae-related odorants than geosmin and 2-MIB. Furthermore, it was reported that some algal metabolites were transformed into new types of odor by oxidation (Dietrich, Hoen et al. 1995), and the fruity smelling aldehydes were produced from the ozonation of drinking water (Anselme, Suffet et al. 1988; AWWARF 1995; Bruchet and Duguet 2004). Therefore, further research is required to investigate how effectively algae-related odorants can be removed, how odor descriptors change, and what types of new odors are produced.

Recently, UV/H_2O_2 was applied to full scale water treatment plants (WTPs) to control earthy-musty odors (geosmin and 2-MIB), N-nitrosodimethylamine (NDMA), and 1,4-dioxane (Cotton and Collins 2006). Full scale UV/H_2O_2 systems utilize low intensity UV for disinfection and high intensity UV for both disinfection and advanced oxidation (Cotton and Collins 2006). The UV/H_2O_2 process is known to have several advantages compared to other AOPs; simple operation procedure, small foot print, no regulated DBPs formation, and dual mode (low intensity UV for disinfection, high intensity UV and H_2O_2 for advance oxidation) (Legrini, Oliveros et al. 1993; Cotton and Collins 2006).

However, UV/H_2O_2, like other AOPs, typically cost much more than conventional treatment. Total cost for applying UV/H_2O_2 to an existing 40 MGD utility with typical water quality and taste/odor episode was estimated as $0.05-0.07/kgal in a field study (Royce and Stefan 2005)[AMD1]. Due to the economical and practical aspects, AOP could be best applied to address a seriously concerning contaminant or multiple contaminants. This research will investigate DBP removal and its mechanism when UV/H_2O_2 is applied to control earthy-musty odorous compounds. Additionally, the removal of algae-related odorous aldehydes by UV/H_2O_2 and its effect on the sensory was studied. Geosmin and 2-MIB, and four types of odorous aldehydes were used in this research as well as two most prevalent DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) (Krasner, Weinberg et al. 2006) as shown in Table 1-1. The objectives of this research were to investigate: 1) types of DBPs that can be removed by UV/H_2O_2 dose for recalcitrant earthy-musty odor control, 2) mechanisms involved in this DBP removal, 3) how effectively fishy/grassy smelling aldehydes are removed, and 4) how odorous aldehydes are transformed after the advanced oxidation. This research could be an addition to the AOP design that controls both taste/odor and DBP problem.

Table 1-1. Odorants and DBPs selected for this research

Compounds		Structure	Guideline in drinking water	Effect in drinking water
Odorants	trans-2,cis-6-nonadienal		-	Cucumber/Fishy Odor
	trans-2,trans-4-decadienal		-	Fishy/Oily/Cucumber Odor
	trans-2,trans-4-heptadienal		-	Grassy/Oily/Fishy Odor
	Hexanal		-	Grassy/Sweet Odor
	Geosmin		10 ng/L [a]	Earthy odor
	2-MIB		10 ng/L [a]	Musty odor
Disinfection Byproducts	Trihalomethanes (THMs)	X, Y, Z= Cl, Br, I	80 μg/L [b]	Carcinogenic [c]
	Haloacetic acids (HAAs)	X, Y, Z= H,Cl, Br, I	60 μg/L [b]	Genotoxic and carcinogenic [c]

[a] Guideline in Korea and secondary standard in Japan

[b] Maximum contaminant level in U.S

[c] (Richardson, Plewa et al. 2007)

Chapter 2. Review of Literature

1. General concepts of UV application for drinking water

UV Irradiation

The UV spectrum can be classified as Vacuum UV (VUV, 100-200 nm), UV-C (200-280nm), UV-B (280-315 nm), and UV-A (315-400 nm) based on wavelength. It is well established that UV inactivates microorganisms by transforming DNA. In terms of germicidal effects, the optimum UV range is between 245 and 285 nm because DNA does not absorb UV above the wavelength of 300 nm (AWWA 1999; EPA 1999; Crittenden, Trussell et al. 2005). UV is transmitted through water to be absorbed into or reflected off of the materials. No residual is produced from the UV radiation, which is an advantage in terms of DBP formation. However, a secondary chemical disinfectant is required to maintain a residual in the distribution system (AWWA 1999; EPA 1999). UV demand of water, the absorption of energy per unit depth or absorbance, can be measured by a spectrophotometer set at a wavelength of 254 nm. UV dose (fluence) can be represented as follows (EPA 1999):

$$D = I \cdot t$$

D = UV dose (mJ/cm^2 or mW·s/cm^2)

I = Intensity (mW/cm^2)

t = Exposure time (s)

Measurement of UV dose (fluence)

UV dose can be determined with the iodide/iodate actinometer by measuring triiodide ion (I_3^-) produced from the UV photolysis of iodide ion (I^-) at the wavelength of 352 nm. Iodate ion (IO_3^-) plays a role of electron scavenger by inhibiting the reverse reaction of UV photolysis ($I^- + e^- \rightarrow I^-$). Reactions in this actinometry are as follows (Rahn 2004; Rahn, Bolton et al. 2006):

$$I^- + h\nu \rightarrow I\cdot + e^-$$
$$2I\cdot + 2\ I^- \rightarrow 2I_2\cdot^-$$
$$2I_2\cdot^- \rightarrow I^- + I_3^-$$

$$IO_3^- + e^- + 2H_2O \rightarrow IO^- + H_2O_2 + \cdot OH + OH^- \text{ (electron scavenging)}$$
$$\cdot OH + I^- \rightarrow I \cdot + OH^-$$
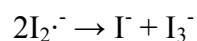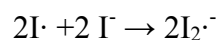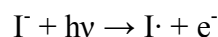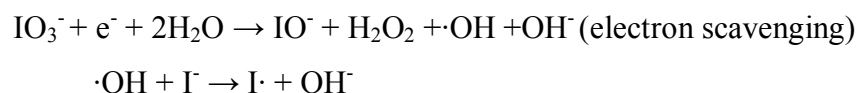
UV irradiance or incident intensity at a surface is typically measured by 'collimated beam' system that measures the intensity of collimated UV at the surface of the sample water (Rosenfeldt, Melcher et al. 2005).

UV lamp

Three types of UV lamps are used in the water industry: (1) low-pressure, low-intensity lamp, (2) low-pressure, high-intensity (high output) lamp, (3) medium-pressure, high intensity lamp (Crittenden, Trussell et al. 2005). Both low-pressure and medium-pressure lamps can be used for disinfection application. Low-pressure lamps have their maximum energy output at a wavelength of 253.7nm, while the spectrum of medium pressure lamps have energy output at wavelengths ranging from 180 to 1370 nm (EPA 1999; Crittenden, Trussell et al. 2005). Fewer medium pressure lamps are required for an equivalent dosage than low pressure lamps due to higher intensity. Several low-pressure lamps are recommended compared to one medium pressure lamp for small systems because of reliability of multiple lamps and cleaning cycle (EPA 1999).

UV dose required for pathogen inactivation

The UV dose required for effective inactivation is determined by site-specific data related to the water quality and log removal requirements (EPA 1999). A UV dose of 36 mJ/cm^2 was required for 3-log inactivation of viruses (AWWA 1991; EPA 1999). Much higher dosages are required for larger protozoa such as *Cryptosporidium* and *Giardia* inactivation (White 1992; EPA 1999). To achieve 2-log inactivation of *Giardia lamblia* cysts, at least 121 mJ/cm^2 was required (Carlson 1982; EPA 1999). Since AOPs have been proven to be equal or more effective than ozone for pathogen inactivation, UV used with ozone and H$_2$O$_2$ enhances the disinfection effectiveness (EPA 1999).

2. Fundamentals of AOPs

Comparison of typical AOPs

Muller and Jekel compared three AOPs (UV/H_2O_2, O_3/H_2O_2, O_3/UV) in the pilot and full scale study on the atrazine removal. Based on the comparison of electrical energy per order (E_{EO}), O_3/H_2O_2 was reported to be the most economical process (Muller, Gottschalk et al. 2001; Muller and Jekel 2001). Characteristics of AOPs were compared in Table 2-1.

Table 2-1. Characteristics of AOPs   (National Water Research Institute 2000)

AOP	Major reaction	Advantages	Disadvantages
UV/H_2O_2	$H_2O_2 + h\nu \rightarrow 2 \cdot OH$	- No bromate formation - Can serve a disinfectant - Full scale drinking water treatments exist - No off-gas treatment required - No mass transfer between Liquid and gas phase	- Interference of turbidity - Interference of UV absorbing compounds
O_3/H_2O_2	$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+$ $O_3 + HO_2^- \rightarrow \cdot OH + O_2^- + O_2$	- The most economical process based on E_{EO} - Efficient in MTBE treatment - Established technology for remediation	- Potential for bromate formation (controllable by O_3/H_2O_2 ratio and pH) - May require excessive H_2O_2 treatment - May require off-gas treatment
O_3/UV	$O_3 + H_2O + h\nu \rightarrow O_2 + H_2O_2$ $H_2O_2 + h\nu \rightarrow 2 \cdot OH$	- More efficient at generating $\cdot OH$	- Energy and cost intensive process - May require off-gas treatment

Ozonation

Basic reactions in ozonation

Ozone itself is a selective oxidant but it oxidizes organic compounds through hydroxyl

radical produced from the reaction of ozone and natural organic matter (NOM) or auto-decomposition as below (AWWA 1999; Ho, Newcombe et al. 2002; Ho, Croue et al. 2004; Westerhoff, Nalinakumari et al. 2006). Higher pH is recommended for ozonation to produce more hydroxyl radical because ozone is dominant at lower pHs.

$$O_3 + NOM \rightarrow \cdot OH + \text{other products}$$
$$O_3 + OH^- \rightarrow \cdot HO_2 + \cdot O_2^-$$
$$\cdot HO_2 \leftrightarrow H^+ + \cdot O_2^- \ (pKa = 4.8)$$
$$O_3 + \cdot O_2^- + H_2O \rightarrow \cdot OH + OH^- + 2O_2$$
$$O_3 + \cdot OH \rightarrow \cdot HO_2 + O_2$$
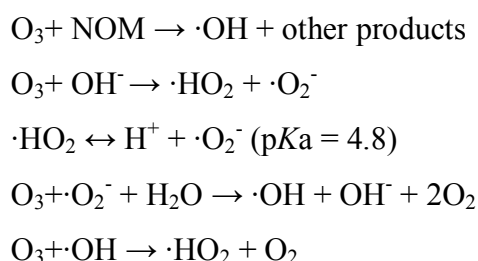
R_{ct} in ozonation process

In the ozonation process, compounds are oxidized by hydroxyl radical rather than ozone itself because hydroxyl radical is highly reactive and nonspecific while ozone itself is a selective oxidant to many organic compounds (Michael and Von Gunten 1999). R_{ct} is the parameter for determining hydroxyl radical concentration based on ozone concentration. In this concept, a change in concentration of a $\cdot OH$-probe compound, para-chlorobenzoic acid (pCBA) is measured and equated to a hydroxyl radical concentration that is difficult to directly measure. R_{ct} is specific to given water quality, and can be calculated from the pCBA removal and dissolved ozone concentrations. Dissolved ozone concentration can be measured by Indigo method where decreased indigo trisulfonic acid concentration by ozone is measured by the decreased light absorption at 600 nm (Bader and Hoign 1981). R_{ct} is useful for determining the steady state hydroxyl radical concentration by measured ozone concentration.

$$\frac{-d[pCBA]_t}{dt} = k_{\cdot OH/pCBA}[pCBA]_0[\cdot OH]$$

$$\ln\left(\frac{[pCBA]_t}{[pCBA]_0}\right) = -k_{\cdot OH/pCBA}\int[\cdot OH]dt$$

$$R_{ct} = \int[\cdot OH]dt \Big/ \int[O_3]dt$$

$$\ln\left(\frac{[pCBA]_t}{[pCBA]_0}\right) = -k_{\cdot OH/pCBA}R_{ct}\int[O_3]dt$$

Because R_{ct} is constant for given water quality and independent of the reaction time, hydroxyl radical concentration can be represented as follows:

$$[\cdot OH] = R_{ct}[O_3]$$

3. Fundamentals of UV/H$_2$O$_2$

UV/H$_2$O$_2$ process

The UV/H$_2$O$_2$ process is a homogeneous AOP in which hydroxyl radicals are generated by the direct photolysis of H$_2$O$_2$ under UV irradiation and radical chain reactions (Liao and Gurol 1995; Stefan, Hoy et al. 1996; Stefan and Bolton 1998; Stefan, Mack et al. 2000; Rosenfeldt, Melcher et al. 2005; Rudra, Thacker et al. 2005; Xu, Gao et al. 2007).

$$H_2O_2 + h\nu \rightarrow 2OH\cdot \qquad \text{Light absorption/initiation}$$
$$\cdot OH + H_2O_2 \rightarrow HO_2\cdot + H_2O \qquad \text{Propagation}$$
$$HO_2\cdot + H_2O_2 \rightarrow \cdot OH + H_2O + O_2$$
$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad \text{Termination}$$
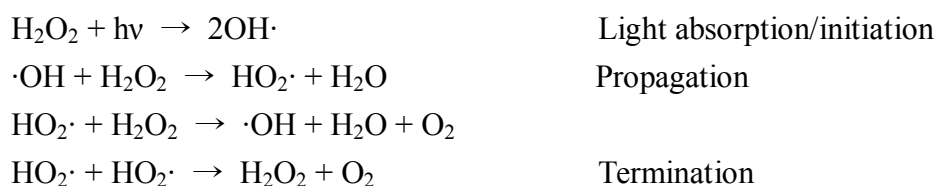
The quantum yield for this reaction, which is the number of moles of H$_2$O$_2$ decreased per mole of photon absorbed, has been reported as 1.0 for the overall quantum yield (Φ_T), and as 0.5 for the primary quantum yield (Φ_P). (Liao and Gurol 1995; Oppenlander 2003). In the case of the hydroxyl radical reaction, a steady state radical concentration is assumed due to relatively higher H$_2$O$_2$ concentration (mg/L level) than contaminants concentration (ng/L~µg/L level) (Sharpless and Linden 2003; Rosenfeldt, Melcher et al. 2005; Pereira, Weinberg et al. 2007; Xu, Gao et al. 2007).

Advantages and limits of UV/H$_2$O$_2$ process

The UV/H$_2$O$_2$ process has a number of advantages compared to other AOPs: commercial availability of the oxidant, thermal stability, on-site storage, infinite solubility in water, no mass transfer problems between two phases, minimal capital investment, simple operation procedure, small foot print, no regulated DBPs formation, dual mode (low intensity UV for disinfection, high intensity UV and H$_2$O$_2$ for advance oxidation) (Legrini, Oliveros et al. 1993; Cotton and Collins 2006).

However, H$_2$O$_2$ has a relatively small absorption cross section, the ability to absorb a photon of a particular wavelength; this limits the rate of hydroxyl radical formation. Therefore, in order to obtain higher rate of hydroxyl radical formation, Xe-doped Hg arc lamp that has a strong emission at 210-240 nm wavelength is used. At this range of wavelength, H$_2$O$_2$ has a higher molecular extinction coefficient. As in all AOPs, hydroxyl radical is trapped by scavengers, such as bicarbonate and carbonate in water, which is the

main disadvantage of UV/H_2O_2 process (Legrini, Oliveros et al. 1993).

Oxidation by hydroxyl radical

Hydroxyl radical is a very strong oxidants based on reduction potential shown in Table 2-2.

Table 2-2. Reduction potential of oxidants (AWWA 1999)

Species	Reduction potential, E^0_{red} (V)
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Permanganate	1.68
Chlorine dioxide	1.57
Chlorine	1.36
Molecular Oxygen	1.23

Hydroxyl radical oxidizes organic compounds generally by hydrogen abstraction generating organic radicals. The organic radical yields peroxyl radical by the reaction with oxygen. These organic and peroxyl radicals initiate oxidative chain reactions leading to mineralization where the final products are carbon dioxide, water, and inorganic salts. Another mechanism is electron transfer to hydroxyl radicals leading to hydroxyl ion (Legrini, Oliveros et al. 1993).

$HO\cdot + RH \rightarrow R\cdot + H_2O$ hydrogen abstraction

$R\cdot + O_2 \rightarrow RO_2\cdot$ peroxyl radical production

$HO\cdot + RX \rightarrow RX^{\cdot +} + HO^-$ electron transfer to hydroxyl radical
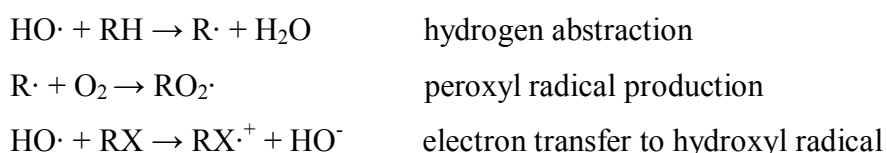
The rate and efficiency of the oxidation process performed by hydroxyl radical depends on the energy required to homolyze a given chemical bond, and the concentration of dissolved oxygen (Legrini, Oliveros et al. 1993). Based on the characteristics of water, other types of radicals can react with organic pollutants. Superoxide radical ($HO_2\cdot$), carbonate radical($CO_3\cdot^-$/$HCO_3\cdot$), or phosphate radicals ($HPO_4\cdot^-$) can oxidize organic contaminants (Crittenden, Hu et al. 1999).

$R_{OH,UV}$ parameter in UV/H_2O_2 process

Recently, the $R_{OH,UV}$ concept, which is similar to R_{ct} concept in ozonation, was indroduced

to characterize the water-specific effectiveness of the UV/H$_2$O$_2$. R$_{OH,UV}$ is defined as the hydroxyl radical exposure per UV fluence, and affected by scavenging and UV absorbance of water matrix (Rosenfeldt and Linden 2007). From the R$_{OH,UV}$ and UV fluence, hydroxyl radical concentration produced from the UV/H$_2$O$_2$ reaction can be determined.

$$\frac{d[pCBA]}{dt} = -(k_d' + k_i')[pCBA]$$

$$k_i' = \text{pseudo first order rate constant of hydroxyl radical reaction} = k_{\cdot OH/pCBA}[\cdot OH]$$

$$k_d' = \text{pseudo first order rate constant of direct UV photolysis}$$

$$\ln\left(\frac{[pCBA]_0}{[pCBA]}\right) = k_d't + k_{\cdot OH,pCBA}\int_0^t [\cdot OH]dt$$

$$\frac{\ln\left(\frac{[pCBA]_0}{[pCBA]}\right)}{t} = k_T' = k_d' + \frac{k_{\cdot OH,pCBA}\int_0^t[\cdot OH]dt}{t}$$

$$k_T' = \text{apparent pseudo first order rate constant of overall reaction}$$

Both sides are divided by average UV fluence rate E$_0$ (mW/cm^2) to convert a time-based rate constant into a fluence-based constant yielding following equation.

$$k_T'^D - k_d'^D = \frac{k_{\cdot OH,pCBA}\int_0^t[\cdot OH]dt}{E_0 \cdot t}$$

$$R_{OH,UV} = \frac{\int_0^t[\cdot OH]dt}{E_0 \cdot t} = \frac{k_T'^D - k_d'^D}{k_{\cdot OH,pCBA}}$$

$$k_T'^D = \text{fluence based apparent pseudo first order rate constant of overall reaction}$$

$$k_d'^D = \text{fluence based pseudo first order rate constant of direct UV photolysis}$$

<u>Direct UV photolysis</u>

Photoxidation generally takes place in two ways. First is by the excitation of an organic substrate followed by the electron transfer from the excited state to the ground state molecular oxygen (eq. 1 and 2). Second is by the homolysis where radicals are formed followed by the subsequent reaction with oxygen (eq. 3 and 4) (Legrini, Oliveros et al. 1993). In order to absorb UV, a compound has to possess a UV absorbing chromophore at 253.7nm for low pressure UV lamp or at wider range of wavelength for medium pressure UV lamp.

$$\text{C} \xrightarrow{h\nu} \text{C*} \qquad\qquad (1)$$

$$\text{C*} + \text{O}_2 \rightarrow \text{C}^{\cdot +} + \text{O}_2{}^{\cdot -} \qquad (2)$$

$$h\nu$$

$$R\text{-}X \rightarrow R\cdot + X\cdot \qquad (3)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (4)$$
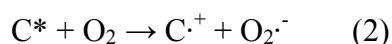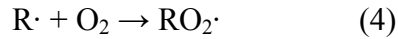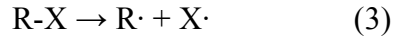
In many UV/H_2O_2 studies, direct UV photolysis, without H_2O_2, also has been shown to contribute to removal of organic compounds. However, removal rates depended on the type of compounds. Geosmin and 2-MIB were removed 40% and 20% respectively at the UV irradiance of 1,700 mJ/cm^2 (Rosenfeldt, Melcher et al. 2005). Diazinon decreased 20% at the UV irradiance of 600 mJ/cm^2 (Shemer and Linden 2006). Microcystin decreased 50% at the UV irradiance of about 3,000mJ/cm^2 (Qiao, Li et al. 2005). In regard to UV photolysis of DBPs, it was reported that brominated THMs were photolysed and the quantum yield of the photolysis was 0.43 (Nicole, De Laat et al. 1991). In the same research, more bromine substituted THMs were shown to be photolysed faster. In a study of chlorinated swimming pool water, tribromomethane and chlorodibromomethane levels were reported to decrease significantly with UV irradiation of 145mJ/cm^2 (Cassan, Mercier et al. 2006). For the direct UV photolysis and hydroxyl radical reactions of organic compounds such as geosmin/2-MIB, diethyl phthalate, and pharmaceutical compounds in UV/H_2O_2, pseudo-first order reaction rate models at a wavelength (λ) were proposed as follows (Sharpless and Linden 2003; Rosenfeldt, Melcher et al. 2005; Pereira, Weinberg et al. 2007; Xu, Gao et al. 2007):

$$-\frac{d[C]}{dt} = k'_d[C]$$

k'_d = the measured pseudo-first order rate constant of direct photolysis (s^{-1})

$$= k_{s,c}(\lambda)\,\Phi c(\lambda)$$

$k_{s,c}(\lambda)$ = specific rate of UV absorption by the compound (Es·mol^{-1}s^{-1})

$$= \frac{E_p^0(\lambda)\varepsilon(\lambda)[1-10^{-a(\lambda)z}]}{a(\lambda)z}$$

$\Phi_C(\lambda)$ = quantum yield of compound (mol Es^{-1})

$E_p^0(\lambda)$ = incident photon irradiance (mEscm^{-2}s^{-1})

$\varepsilon(\lambda)$ = molar extinction coefficient of compound at a specific wavelength (M^{-1}cm^{-1})

$a(\lambda)$ = solution absorbance at a specific wavelength (cm^{-1})

z = solution depth (cm)

Kinetics in UV/H_2O_2 process

For the direct UV photolysis and hydroxyl radical reactions of organic compounds such as geosmin/2-MIB, diethyl phthalate, and pharmaceutical compounds in UV/H_2O_2, pseudo-first

order reaction models at a wavelength (λ) were proposed as follows (Sharpless and Linden 2003; Rosenfeldt, Melcher et al. 2005; Pereira, Weinberg et al. 2007; Xu, Gao et al. 2007):

$$-\frac{d[C]}{dt} = k'[C]$$

Where, $k' = k'_d + k'_i$

k' = the observed pseudo-first order rate constant (s^{-1})

k'_d = the measured pseudo-first order rate constant of direct photolysis (s^{-1})

$\quad = k_S(\lambda)\, \Phi_c(\lambda)$

$\quad\quad k_{S,C}(\lambda)$ = specific rate of UV absorption by the compound ($Es \cdot mol^{-1}s^{-1}$)

$$= \frac{E_p^0(\lambda)\varepsilon(\lambda)[1-10^{-a(\lambda)z}]}{a(\lambda)z}$$

$\quad\quad \Phi_C(\lambda)$ = quantum yield of compound ($mol \cdot Es^{-1}$)

$\quad\quad E_p^0(\lambda)$ = incident photon irradiance ($mEs \cdot cm^{-2}s^{-1}$)

$\quad\quad \varepsilon(\lambda)$ = molar extinction coefficient of compound at a specific wavelength ($M^{-1}cm^{-1}$)

$\quad\quad a(\lambda)$ = solution absorbance at a specific wavelength (cm^{-1})

$\quad\quad z$ = solution depth (cm)

$\quad k'_i$ = the measured pseudo-first order rate constant of the reaction with $\cdot OH$

$k'_i = k_{C/OH}[OH]_{ss}$

$\quad\quad k_{C/OH}$ = Second order reaction rate constant of compound and $\cdot OH$

$\quad\quad [OH]_{ss}$ = steady state $\cdot OH$ concentration

In case of the hydroxyl radical reaction, a steady state hydroxyl radical concentration is assumed due to relatively higher H_2O_2 concentration (2-30 mg/L) (Sharpless and Linden 2003; Rosenfeldt, Melcher et al. 2005; Cotton and Collins 2006; Pereira, Weinberg et al. 2007; Xu, Gao et al. 2007).

$$[OH]_{ss} = \frac{\sum k_{S,H_2O_2}(\lambda)\Phi_{OH}(\lambda)[H_2O_2]}{\sum\limits_i k_{S,OH}[S]_i}$$

$\quad k_{S,H_2O_2}(\lambda)$ = specific rate of UV absorption by H_2O_2 ($Es\ mol^{-1}s^{-1}$)

$\quad \Phi_{OH}(\lambda)$ = quantum yield for $\cdot OH$ formation ($\approx 1 mol\ Es^{-1}$)

$\quad k_{S,OH}$ = second order reaction rate constant of scavenging species and $\cdot OH$ ($M^{-1}s^{-1}$)

$\quad [S]_i$ = concentration of scavenging species (M)

13

Factors affecting photochemical AOP performance

UV transmittance (UVT) affects dose, which is related to hydroxyl radical formation. Carbonate and bicarbonate are the most common inorganic hydroxyl radical scavenger in natural water (Crittenden, Hu et al. 1999; Cotton and Collins 2006). Although these two scavengers produce carbonate radicals ($\cdot CO_3^-/\cdot HCO_3$) as shown below, which can react with organic contaminants, these reactions are not significant (Crittenden, Hu et al. 1999).

$$CO_3^{2-} + \cdot OH \rightarrow \cdot CO_3^- + OH^-$$

$$HCO_3^- + \cdot OH \rightarrow \cdot HCO_3 + OH^-$$
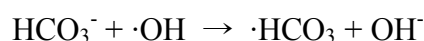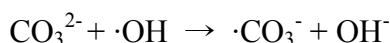
Bromide and chloride ions are also known to scavenge hydroxyl radical with the reaction rate constants of 10^{10} $M^{-1}s^{-1}$ and 2×10^7 $M^{-1}s^{-1}$, respectively as shown below (von Gunten and Hoigne 1994; Nakatani, Hashimoto et al. 2007). Chloride (Cl^-) was shown to substantially contribute to scavenging of hydroxyl radical in typical drinking water based on the rate constant for the reaction with hydroxyl radical (2×10^7 $M^{-1}s^{-1}$) and its typical concentration (Nakatani, Hashimoto et al. 2007).

$$Br^- + \cdot OH \rightarrow BrOH^-$$

$$Cl^- + \cdot OH \rightarrow ClOH^-$$
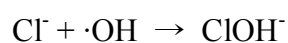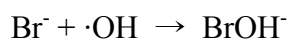
Natural organic matters (NOM), such as humic or fulvic substance, lower the efficiency of AOPs by absorbing UV and scavenging hydroxyl radicals (Crittenden, Hu et al. 1999). NOM with higher UV absorbing properties consumed ozone and produced hydroxyl radical at a higher rate in the ozonation process (Ho, Croue et al. 2004). In general, maximum UV/H_2O_2 performance can be obtained in slightly acidic condition. UV/H_2O_2 performance decreases with suspended solids, nitrate and iron concentrations (TrojanUV 2003). The optimum H_2O_2 dose in UV/H_2O_2 process is required to be determined because an excessive dose can reduce the oxidation rate (Wang, Hsieh et al. 2000) by scavenging hydroxyl radical and producing less reactive hydroperoxyl radical as below (Legrini, Oliveros et al. 1993).

$$HO\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot$$
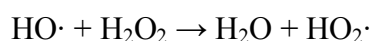
Quenching of the peroxide residual is required after it passes through the UV reactor in full scale process. In pilot or full scale plant, chlorine is used to quench H_2O_2 (Royce and Stefan 2005). Since oxidation potential of H_2O_2 (1.77V) is greater than Cl_2 (1.36V) or OCl^- (0.89V), H_2O_2 can be quenched by free chlorine as follows (Batterman, Zhang et al. 2000; Liu, Andrews et al. 2003):

$$Cl_2 + H_2O_2 \rightarrow 2Cl^- + 2H^+ + O_2$$
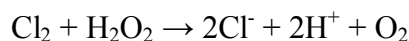
E_{EO} (Electrical Energy per Order) (Bolton and Stefan 2002; TrojanUV 2003; Rosenfeldt, Melcher et al. 2005)

E_{EO} (Electrical Energy per Order) is the metric for measuring efficiency of the UV oxidation process, and has been used in industrial applications. E_{EO} is defined as the electrical energy required for reducing the contaminant concentration by one order of magnitude (1-log or 90%) per cubic meter or 1000 gallons of water as follows:

$$E_{EO}\left(\frac{kWh}{kgal \cdot order}\right) = \frac{measured\ reactor\ power\ draw\ (kW)}{flow\ rate\ (gpm) \times 0.06 \times log\left(\frac{C_0}{C}\right)}$$

0.06 = conversion factor of time and volume $\left(\frac{min \cdot kgal}{h \cdot gal}\right)$

C_0= intial (influent) concentration

C = final (effluent) concentration

E_{EO} is specific for the reactor type, contaminants, and water quality. The less E_{EO} means that the lower power is required by the system. Parameters affecting E_{EO} are 1) reactor design , 2) lamp type, 3) water quality such as UV transmittance (UVT) and scavengers concentration, 4) lamp age, 5) flow rate, 6) hydrogen peroxide concentration, and 7) contaminant characteristics such as quantum yield, molar extinction coefficient, and hydroxyl radical reaction rate. Industries are using this E_{EO} as a comprehensive parameter of UV oxidation performance because UV dose should be normalized by other chemical dose such as hydrogen peroxide dose, and there is a nonlinear relationship between power draw and UV dose. For the removal of geosmin and 2-MIB by medium pressure (MP) UV and hydrogen peroxide, E_{EOS} of 0.5 to 1.2 was reported by researchers (Cotton and Collins 2006).

Application to full scale WTPs

Recently, UV/H_2O_2 has been applied in several full scale water treatment plants (WTPs) to mainly control earthy-musty odor (geosmin and 2-MIB), N-nitrosodimethylamine (NDMA), and 1,4-dioxane (Cotton and Collins 2006). In 2004, PWN water supply company in Holland applied UV/H_2O_2 for disinfection and reducing organic pollutants with removing breakpoint chlorination. O_3/H_2O_2 was also proved to be a good process for this case but was not selected due to high bromated levels formed by the process (Martijn, Kruithof et al. 2006). The optimum dose range of hydrogen peroxide for removing geosmin and 2-MIB was reported to

be 6-10 mg/L in pilot and bench scale research (Cotton and Collins 2006; Paradis and Hoffman 2006).

The cost of UV/H$_2$O$_2$

Based on E$_{EO}$ and electricity cost ($0.075 per kWh), a UV/H$_2O_2$ treatment cost of $0.35 per 1,000 gallons to remove the geosmin and 2-MIB by one order of magnitude was reported (Rosenfeldt, Melcher et al. 2005). Conceptual level capital, operation and management cost were estimated in a research. When design flow rate is 50 MGD ($\approx$190,000 m^3/d), taste and odor removal is 90%, hydrogen peroxide dose is 10 mg/L, and UVT is 90%, total capital cost and annual operation/management cost were calculated to be about $17,000,000 and $1,000,000, respectively (Cotton and Collins 2006). Total cost including installment capital and operation and management cost for a 40 MGD utility with typical water quality and taste/odor episode was estimated as $0.05-0.07/kgal in a field study while ozonation cost was estimated as $0.06-0.09/kgal (Royce and Stefan 2005).

4. DBP(FP) removal by AOPs

Disinfection byproduct formation potential (DBPFP) removal by AOPs

One of approaches to control DBPs in drinking water is to reduce DBP precursor, such as NOM in the raw water by coagulation/flocculation or oxidation. The NOM removal in coagulation/flocculation is quite low, between 10~50%. Therefore, AOP has been proposed as an alternative for the control of DBP precursors (Wang, Hsieh et al. 2000; Chin and Berube 2005). AOP has been reported to reduce total organic carbon (TOC) and trihalomethane formation potential (THMFP) of raw water by removing aromatic structures and double bonds of NOM (Collivignarelli 2004). However little research has been performed on the AOP effect on the haloacetic acid formation potential (HAAFP) (Chin and Berube 2005). Ozone/UV was found to reduce THMFP and HAAFP by 80 and 70% respectively at an ozone dose of 0.62 mgO$_3$/mL and a UV dose of 1,610 mJ/cm^2. Interestingly, Ozone had very little impact on TOC concentration but rapidly reduced UV$_{254}$ absorbance and reduced DBPFP, which means ozone did not mineralize the NOM in the raw water but altered the chemical structure of DBP precursors such that they did not form DBP (Chin and Berube 2005).

THMFP was found to decrease by either UV radiation or Vacuum UV(VUV) radiation, but HAAFP decreased not by sole UV radiation but by VUV (Buchanan, Roddick et al. 2006).

DBP removal by AOPs

There have been only a few studies on DBPs removal by AOP, and reports are conflicting. 92~100% of 200 μg/L of chloroform, bromodichloromethane, dibromochloromethane and bromoform were removed with 0.1% of H_2O_2 and 90 min of 3.2 mW/cm^2 UV irradiation (UV dose 17,280mJ/cm^2) (Rudra, Thacker et al. 2005). However, in another study, THMs increased at lower levels of UV/H_2O_2 doses and decreased with higher level of UV/H_2O_2 doses (Cassan, Mercier et al. 2006). In the other study, haloacetic acids (HAAs) decreased with UV/H_2O_2 in two samples and increased in one sample (Paradis and Hoffman 2006). It was reported that more bromine substituted THMs have slightly higher reaction rate constants with hydroxyl radical (Mezyk, Helgeson et al. 2006). More bromine substituted THMs were also shown to be better photolysed by UV (Nicole, De Laat et al. 1991).

DBP formation by AOPs

UV can produce similar DBPs to those formed by ozone or advanced oxidation process (AOP) because UV radiation can result in the formation of ozone or radicals in water. UV radiation was found to produce low levels of formaldehyde in surface water studies. Formaldehyde concentration ranged up to 14 μg/L in UV treatment of raw water, whereas 1 to 2 μg/L levels were found in a UV treatment of conventionally treated water. However, the overall effect of UV on DBPs was reported to be insignificant (EPA 1999).

The uniform formation conditions (UFC) test is the method to assess the effect of UV or UV/H_2O_2 on DBP formation from subsequent chlorination or chloramination. H_2O_2 can react with chlorine and DBP reagent affecting DBP formation and the measurement of chlorine residuals due to higher oxidation potential than chlorine. Quenching H_2O_2 by bovine catalase of 0.05-0.2 mg/L was proposed as a simple method that has no effect on DBP formation (Muller and Jekel 2001; Liu, Andrews et al. 2003). In pilot or full scale plant, chlorine is used to quench H_2O_2 (Royce and Stefan 2005).

Regarding DBP formation, UV/H_2O_2 has been reported to produce no harmful by-products (Cotton and Collins 2006). Concentration of bromate (BrO_3^-), a DBP from the reaction of Br^- and ozone, from the ozonation coupled with UV was reported to be 40~50% lower than in ozonation alone (Collivignarelli and Sorlini 2004).

5. Taste/odor and AOP

General concepts related with taste/odor

Drinking water taste and odor wheel

Suffet et al. updated the drinking water taste and odor wheel that consists of primary taste and odor categories, common expressions of taste and odors from each categories, and typical chemicals that cause the specific taste and odor (Suffet, Khiari et al. 1999) (Figure 2-1).

Figure 2-1. The drinking water taste and odor wheel (Suffet, Khiari et al. 1999)

Sensory tests

Sensory tests evaluate the sensory characteristics of a sample and can be divided into two categories: analytical and affective. Analytical tests use trained panelists and measure characteristics of sample such as taste/odor attributes and intensity. Affective tests typically use large numbers of untrained subjects and measure preference or acceptance to investigate the consumer's ability to detect a difference, reasons for detected difference, and attitudes about the differences. Analytical tests can be divided into two categories: discriminative tests and descriptive test. Discriminative tests determine if human perception is different between samples. Generally, five panelists are recommended as a minimum number to reduce the dominance by a single panelist. Triangle test, duo-trio test, and the 2-of-5 test are well known

discriminative tests. Descriptive tests are used for identifying the sensory characteristics, correlating sensory test results to instrumental analysis. Four to fifteen trained panelists are recommended. Attribute rating, flavor profile analysis (FPA), quantitative descriptive analysis (QDA) are well known descriptive tests *(Lawless and Heymann 1999; Meilgaard, Civille et al. 1999)*.

Flavor profile analysis (FPA)

Five to eight panelists individually evaluate one sample at a time for both aroma and flavor and record the attributes, aftertastes and intensities based on seven-point scale (none, threshold, very slight, slight, slight-moderate, moderate, moderate-strong, strong). Discussion among the panelists is allowed to reach a consensus on descriptors and intensity (Krasner, McGuire et al. 1985; Meilgaard, Civille et al. 1999).

Weber-Fechner plot

Weber found that the amount of compounds added for the detectable change in intensity increases in proportion to the initial concentration (Meilgaard, Civille et al. 1999).

$$\frac{\Delta C}{C} = k \ (Weber's \ law)$$

Fechner derived an equation from the fact that plot of intensity perceived by panelists shows logarithmic curve.

$$R = k \log C \ (Fechner's \ law)$$

Weber-Fechner plot is a dose-response curve based on Weber-Fechner law shown below and can be drawn from log concentration and taste/odor intensity (Rashash, Dietrich et al. 1997).

$$S = a \log C + b \ (Weber - Fechner \ law)$$

Where S is the average odor intensity, C is the concentration, a and b are the constants for slope and intercept, respectively.

Earthy-musty odorants (Geosmin and 2-MIB)

Geosmin and 2-MIB are one of the most widespread odorants found in fresh water. Geosmin and 2-MIB have been identified in fresh water as earthy-musty odorants, and reported to be produced from algae or actinomycetes (Rashash, Dietrich et al. 1995; Suffet, Khiari et al. 1999; Jüttner and Watson 2007). These compounds cause seasonal earthy-musty odor episode and are difficult to remove below threshold level by conventional water treatment due to the

poor removal efficiency and the low threshold level.

Other algae-related odorants

There is a "fishy/rancid" category in the drinking water taste and odor wheel. Fishy odors were reported to occur naturally from the algae. 2-trans-4-cis-7-cis-decatrienal, trans-2, cis-4-decadienal, n-heptenal, and trans,trans-2,4-heptadienal are typical fishy odorants in fresh water, and 1-pentene-3-one was associated with rancid odors. Trans-2, cis-6-nonadienal, cucumber-smelling aldehyde was reported to be produced from algae, and added in "Fragrant: vegetable/fruity/flowery" category in the drinking water taste and odor wheel. (Rashash, Dietrich et al. 1995; Suffet, Khiari et al. 1999; Watson, Satchwill et al. 2001). Aldehydes were reported to play an important role in the production of off-flavor and have a synergic effect with ketones or carboxylic acids (Andersson, Forsgren et al. 2005).

Oxidation of earthy-musty odorants (geosmin and 2-MIB)

Taste and odor episodes typically occur seasonally or periodically, mostly in warm summer season, and it is difficult to predict when they occur and how long they last. Therefore, sometimes it is not economical to install permanent treatment system such as granular activated carbon (GAC) filter to control taste and odor. Especially for the utilities that use UV for disinfection, adding H_2O_2 prior to UV step on an "as-needed" basis could be economic and practical (Paradis and Hoffman 2006).

Glaze et al. investigated several types of AOPs as an alternative process for the removal of 2-MIB and geosmin. H_2O_2 or UV in addition to ozonation showed higher removal efficiency (Glaze W. H. 1990). Complete removal of geosmin and 2-MIB was achieved with a combination of 1.5~3 mg/L ozone (2~3 min contact time) and 500~600 mJ/cm^2 UV radiation. (Collivignarelli 2004). Addition of H_2O_2 in UV photolysis oxidized greater than 70% of 2-MIB and geosmin while direct UV photolysis removed 10% and 25-50% of the 2-MIB and geosmin at the UV dose of 1,000 mJ/cm^2, respectively (Rosenfeldt 2005). In a pilot scale study, optimal hydrogen peroxide dose of 6-10 mg/L was reported in terms of removal efficiency, chlorine residual decay, and DBP formation (Paradis and Hoffman 2006).

Initially it was thought that UV could not perform both disinfection and advanced oxidation in a system because of different levels of UV dose required. Recently, UV systems labeled as "dual purpose" were developed and applied to full scale water treatment plants (WTPs).

These dual systems combine low intensity UV for disinfection and high intensity UV for both disinfection and advanced oxidation of odorants (Cotton and Collins 2006). UV/H_2O_2 has been applied to 9 full scale WTPs to control geosmin and MIB, N-nitrosodimethylamine (NDMA), 1,4-dioxane, and PCE (Sarathy 2006). A pilot scale study in Canada reported that site specific evaluation including impact on secondary disinfectant level and DBP formation is required when the feasibility of UV/H_2O_2 on taste and odor control is investigated (Paradis and Hoffman 2006).

Oxidation of algae-related odorants

Nonadienal had a greater reaction rate constant with hydroxyl radical than geosmin and 2-MIB while other odorants such as 2-isopropyl-3-methoxypyrazine (IPMP), 2,4,6 trichloroanisole (TCA), and 2,6-di-tert-butyl-4-methylphenol (BHT) has similar or less reaction rate constants compared to geosmin and 2-MIB (Peter and Von Gunten 2007). In research on oxidation of algal metabolites, algal-related compounds were able to be degraded by chlorine and permanganate. However, oxidation of certain algal metabolite caused the formation of other odors (Dietrich, Hoen et al. 1995). Qualitative descriptors were reported to change with odorant concentration change (Rashash, Dietrich et al. 1997).

Derivatization method for detecting carbonyl group

Carbonyls are frequently related with odors found in fresh water (Rashash, Dietrich et al. 1997; Suffet, Khiari et al. 1999; Watson, Satchwill et al. 2001; Satchwill, Watson et al. 2007), and can be more easily determined by derivatization method. One method is the derivatization with 2.4-dinitrophenylhydrazine (DNPH) followed by liquid-liquid extraction. Another common method is the derivatization with pentafluorobenzyl-hydroxylamine hydrochloride (PFBHA) followed by liquid-liquid extraction. Solid phase microextraction (SPME) can be combined with these derivatization method for both liquid and headspace. (Bao, Pantani et al. 1998).

6. Kinetics of geosmin/ 2-MIB and DBPs with hydroxyl radical

Second order rate constant of hydroxyl radical reaction in aqueous phase

Researchers have measured the second order reaction rate constants of odorants and DBPs with hydroxyl radical as shown in Table 2-3. (Glaze, Schep et al. 1990; Mezyk, Helgeson et al. 2006; Westerhoff, Nalinakumari et al. 2006; Cole, Cooper et al. 2007; Peter and Von Gunten 2007). Reaction rate constants of geosmin, 2-MIB, and nonadienal are greater by three orders of magnitude than those of THMs and chlorinated HAAs as shown. According to the reaction rate constants, it is thought that DBPs can not be practically reduced by hydroxyl radical reaction compared to odorants.

Table 2-3. Second order rate constants of DBPs and odorants with hydroxyl radical

Compounds		Reaction rate constant with ·OH ($M^{-1}s^{-1}$)
THMs	Trichloromethane	$0.7 \sim 5.4 \times 10^{7}$ [a]
	Bromodichloromethane	7.1×10^{7} [a]
	Chlorodibromomethane	8.3×10^{7} [a]
	Tribromomethane	1.5×10^{8} [a]
HAAs	Chloroacetic acid (MCAA)	8.3×10^{7} [b] 4.0×10^{8} [c] 4.3×10^{7} [d]
	Dichloroacetic acid (DCAA)	1.0×10^{8} [b]
	Trichloroacetic acid (TCAA)	6.0×10^{7} [b]
Odorants	Geosmin	1.4×10^{10} [e]
		7.8×10^{9} [f]
	2-MIB	8.2×10^{9} [e]
		5.1×10^{9} [f]
	Nonadienal	10.5×10^{9} [f]

[a] Mezyk et al. 2006,
[b] Maruthamuthu 1995,
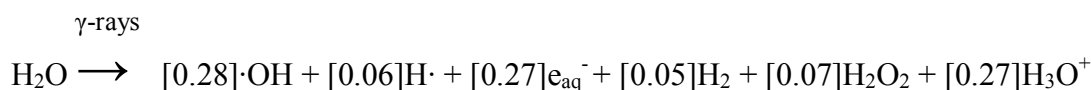[c] Yokohata et al. 1969
[d] Adams et al. 1965
[e] Glaze et al. 1990,
[f] Peter and Von Gunten 2007

7. Reaction mechanism of DBPs and Geosmin/2-MIB in UV/H$_2$O$_2$

Methods for investigating radical reaction mechanism

Electron Pulse Radiolysis (EPR) involves exposing γ-rays to an aqueous solution. The EPR of water generates highly reactive electrons, radical ions, and neutral radical species according to the following equation (Makogon, Fliount et al. 1998; Cole, Cooper et al. 2007). The coefficients of species in the radiolysis are chemical yields, G which have a unit of μmol/10J.

$$H_2O \xrightarrow{\text{γ-rays}} [0.28]\cdot OH + [0.06]H\cdot + [0.27]e_{aq}^- + [0.05]H_2 + [0.07]H_2O_2 + [0.27]H_3O^+$$

Laser flash photolysis, electron spin resonance (ESR) spectrometry, and spin trapping are methods for investigating radical reaction mechanism. In the trapping method, a reactive radical is trapped to form a more stable radical from which the structure of an initial radical can be determined (Paul, Small et al. 1978; Kochany and Bolton 1992; Parsons 2000). For organic pollutants, the reaction mechanism was investigated by analyzing intermediates and final products using GC/MS, and by measuring total organic carbon (TOC) to make a carbon balance in the process of the mineralization (Stefan, Hoy et al. 1996; Stefan and Bolton 1998; Stefan, Mack et al. 2000). Bromide and chloride ion concentrations and pH change were measured to investigate the mechanism in the reaction of halogenated compounds with hydroxyl radical (Lay 1989; Milano, Bernatescallon et al. 1990; Crittenden, Hu et al. 1999; Cole, Cooper et al. 2007) and in the reduction of haloacetic acid (Zhang, Arnold et al. 2004).

Geosmin/MIB oxidation by hydroxyl radical

No mechanism has been elucidated for the reaction of geosmin and 2-MIB with hydroxyl radical. In a research of UV/H$_2$O$_2$, geosmin and 2-MIB was reported to be removed mainly by hydroxyl radical reaction and partially by direct UV photolysis (Rosenfeldt, Melcher et al. 2005). Hydroxyl radical was reported not to be directly responsible for the degradation of geosmin and 2-MIB in ultrasonication even though ultrasonication causes the oxidation by hydroxyl radical as well as pyrolysis. In this research, degradation pathways were proposed by identifying pyrolitic cyclo alkene intermediates using GC/MS analysis (Song and O'Shea

2007).

UV photolysis of Halogenated methanes

In regard to reaction mechanisms of DBP degradation by UV photolysis or advanced oxidation process, only a few mechanisms of DBP degradation were studied. The UV photolysis mechanism of tribromomethane ($CHBr_3$) and carbon tetrabromide (CBr_4) in aqueous phase was proposed as a water-catalyzed dehalogenation. According to the proposed mechanism, O-H was inserted and H-Br was eliminated by water-catalyzed reaction producing three HBr and CO, and four HBr and CO_2 as final products for tribromomethane and carbon tetrabromide, respectively (Li, Kwok et al. 2004; Zhao, Lin et al. 2005). In these studies, UV absorption spectra were measured from 190 to 280 nm wavelength to make a mas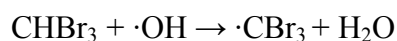s balance of bromide and hydrogen ion. Bromide concentration was measured from the increased UV absorbance at 190nm. Decreased concentration of tribromomethane was measured from the decreased UV absorbance at 215nm. Final products were detected by ^{13}C NMR, infrared spectrum and Raman shift. The reaction pathway was proposed as below. Reaction mechanisms of other THMs have not been elucidated.

$$CHBr_3 + h\nu \rightarrow \cdot CHBr_2 + \cdot Br$$

$$\cdot CHBr_2 + \cdot Br \rightarrow BrCHBr\text{-}Br \text{ (isobromoform)}$$

$$BrCHBr\text{-}Br + n(H_2O) \rightarrow CHBr_2OH + HBr + (n\text{-}1)\, H_2O$$

$$CHBr_2OH + n(H_2O) \rightarrow HBrCO + HBr + n(H_2O)$$

$$HBrCO + n(H_2O) \rightarrow CO + HBr + n(H_2O)$$

Overall $CHBr_3 + h\nu + n(H_2O) \rightarrow CO + 3HBr + (n\text{-}1)H_2O$
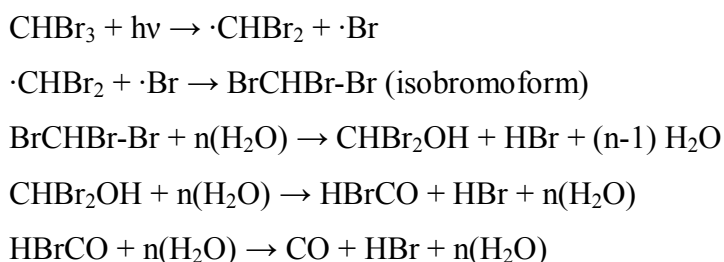
Hydroxyl radical reaction of halogenated methane

The first step of the reaction mechanism of tribromomethane and hydroxyl radical in the gas phase was proposed to be hydrogen abstraction. The $\cdot CBr_3$ radical produced from the reaction was proposed to be degraded in two pathways, which are reaction with hydroxyl radical, and more likely, with oxygen (Fliount, Makogon et al. 1997; McGivern, Francisco et al. 2002; McGivern, Kim et al. 2004).

In gas phase :

$$CHBr_3 + \cdot OH \rightarrow \cdot CBr_3 + H_2O$$

Pathway Ⅰ

$$\cdot CBr_3 + \cdot OH \quad \rightarrow CBr_3OH$$

$$CBr_3OH + H_2O \rightarrow 3H^+ + 3Br^- + CO_2$$

Pathway Ⅱ

$$\cdot CBr_3 + O_2 \rightarrow CBr_3OO\cdot \rightarrow \rightarrow \rightarrow 3\ Br^- + CO_2\ (preferred)$$
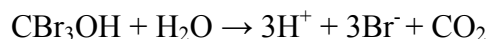
Water catalysis was reported in the hydroxyl radical reaction of acetaldehyde where the reaction rate was enhanced in the presence of water. This increased reaction rate was explained by the reduction of an intrinsic reaction barrier resulting from the water aggregation (Vohringer-Martinez, Hansmann et al. 2007).

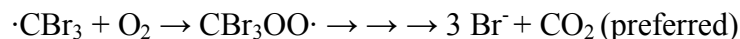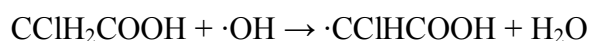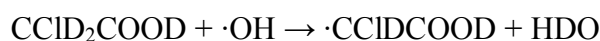## Polar effects and deuterium isotope effect in hydroxyl radical reaction

Reactivity of an atom or radical had a more direct relationship with stabilization of the transition states by the polar effect rather than exothermicity. The factor of transition state energy difference to enthalpy change between normal and deuterated reactants (α) could be used as a measure of reactivity of an atom or radical, and could be interpreted as a percentage of C-H bond breakage (Russell 1957). Kinetic-isotope effect(KIE) is the ratio of reaction rate constant between original compound and deuterated compound as presented below, and can be used to elucidate the reaction mechanism such as hydrogen abstraction (Russell 1957; Farkas, Szilagyi et al. 2003). KIE varies with the types of compounds ranging from 1.0 to 11.9, and KIE of 5.7 was reported for the hydroxyl radical reaction of acetone where hydrogen abstraction was attributed to 50% reaction. However, KIE can give the information only on the rate-controlling step of the reaction, and in itself, is not sufficient for elucidating the reaction mechanism because the contribution of hydrogen abstraction compared to other pathway also has to be known (Farkas, Szilagyi et al. 2003).

$$k_H$$

$$CClH_2COOH + \cdot OH \rightarrow \cdot CClHCOOH + H_2O$$

$$\rightarrow other\ products$$

$$k_D$$

$$CClD_2COOD + \cdot OH \rightarrow \cdot CClDCOOD + HDO$$

$$\rightarrow other\ products$$

$$k_H\ /k_D = Deuterium\ isotope\ effect$$
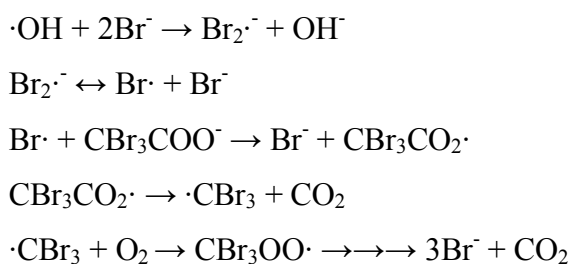
Peroxy radical reaction

In the presence of oxygen, radical species produced from carbon-halogen bond cleavage, hydrogen abstraction, and electron transfer reaction react with oxygen and form the peroxyl radical (Spangenberg, M?ler et al. 1996; Lifongo, Bowden et al. 2004; Zalazar, Labas et al. 2007). In the Russell mechanism, peroxyl radicals mutually react with each other and generate a ketone and a alcohol, while two ketones and hydrogen peroxide are produced in the Bennett mechanism (Russell 1957; Bennett and Howard 1973).

Halogenated acetic acid

For the hydroxyl radical reaction of trichloroacetic acid (TCAA), photo-Kolbe reaction was proposed as a reasonable mechanism because hydrogen abstraction was impossible. This Kolbe reaction was thought to be more effective for less halogenated HAAs due to higher electron density at the carboxyl function (Mao, Schoeneich et al. 1991).

$$CCl_2HCOO\cdot \rightarrow \cdot CHCl_2 + CO_2 \text{ (Kolbe mechanism)}$$
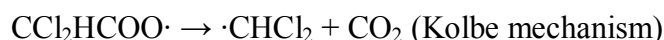
In research on radical-meditated degradation of tribromoacetic acid (TBAA), hydroxyl radical was likely to indirectly oxidize TBAA by oxidation of bromide (Fliount, Makogon et al. 1997).

$$\cdot OH + 2Br^- \rightarrow Br_2\cdot^- + OH^-$$
$$Br_2\cdot^- \leftrightarrow Br\cdot + Br^-$$
$$Br\cdot + CBr_3COO^- \rightarrow Br^- + CBr_3CO_2\cdot$$
$$CBr_3CO_2\cdot \rightarrow \cdot CBr_3 + CO_2$$
$$\cdot CBr_3 + O_2 \rightarrow CBr_3OO\cdot \rightarrow\rightarrow\rightarrow 3Br^- + CO_2$$

Hydrogen abstraction and electron transfer reaction were proposed to be the first step in the degradation mechanism of dichloroacetic acid (DCAA) by UV/H_2O_2, and HCl and CO_2 were proposed as final products (Zalazar, Labas et al. 2007). In this study, chloride and total organic carbon concentration were measured and plotted with calculated values. Two moles of chloride and hydrogen ion were shown to be produced from each mole of DCAA, and complete mineralization was achieved based on the molar decrease in TOC. Reaction

mechanism was proposed as follows:

Pathway Ⅰ

$CCl_2HCOO^- + \cdot OH \rightarrow \cdot CCl_2COO^- + H_2O$

$\cdot CCl_2COO^- + O_2 \rightarrow \cdot OOCCl_2COO^-$

$\cdot OOCCl_2COO- \rightarrow COCl_2 + CO_2 + 1/2O_2$

$COCl_2 + H_2O \rightarrow CO_2 + 2HCl$

Pathway Ⅱ

$CCl_2HCOO^- + \cdot OH \rightarrow CCl_2HCOO \cdot + HO^-$

$CCl_2HCOO \cdot \rightarrow \cdot CHCl_2 + CO_2$ (Kolbe mechanism)

$\cdot CHCl_2 + O_2 \rightarrow Cl_2HCOO \cdot$

$Cl_2HCOO \cdot \rightarrow COCl_2 + 1/2H_2O_2$

$COCl_2 + H_2O \rightarrow CO_2 + 2HCl$
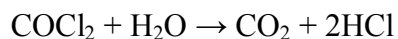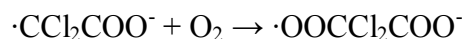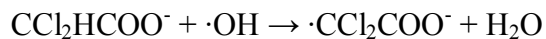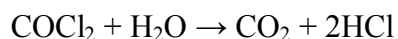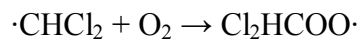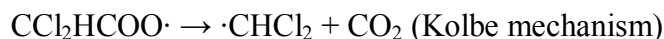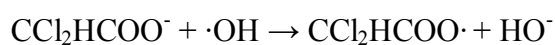
In research on TCAA degradation in the gas phase, photochemical disproportionation was proposed as below (Spangenberg, M?ler et al. 1996):

$$CCl_3COOH + h\nu + H_2O + 1/2\ O_2 \rightarrow 3HCl + 2CO_2$$

$$CCl_3COOH + h\nu + H_2O \rightarrow 3HCl + CO + CO_2 \text{ (In acidic solution)}$$
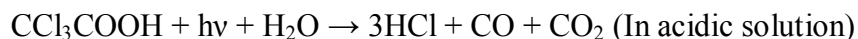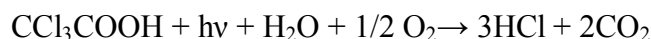
A trace amount of trichloromethane was observed from the degradation of TCAA in the same research, which was explained by the following reaction:

$$CCl_3COOH \rightarrow CHCl_3 + CO_2$$
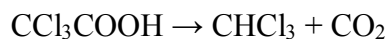
Chemiseddine and Boehm (1990) obtained a Cl^-/CO_2 ratio of about 2:1 from the photocatalytical degradation of TCAA. In this research, the slow reaction rate of TCAA to MCAA was explained by the absence of α-C-H bond where hydrogen could be abstracted by hydroxyl radical. Anglada (2004) reported that hydroxyl radical predominantly extracted acidic hydrogen of formic acid by electron transfer mechanism while hydrogen abstraction from carbon contributed at higher temperatures.

In the case of photodegradation of HAAs, the rates were proportional to the number of halogen atoms (i.e. TCAA>DCAA>MCAA). The final products from the photodegradation of HAAs were HCl and CO_2, which indicates complete mineralization. The main process for the photodegradation of HAAs is proposed as the C-X bond cleavage where electronegativity

of halogen atoms plays an important role to the bond strength. However, at higher temperatures, reaction rate increased because of thermal decarboxylation. Apparent reaction rate of photocatalytic dehalogenation of HAAs were in the order TCAA > TBAA > DCAA > DBAA > MCAA > MBAA (Lifongo, Bowden et al. 2004).

Li et al. proposed decarboxylation for the hydroxyl radical reaction in the photocatalytic degradation of MCAA and DCAA, while TCAA was shown to have a different mechanism (Li, Xie et al. 2006).

$$TiO_2 + h\nu \rightarrow e_{cb}^- + h_{vb}^+$$
$$h_{vb}^+ + OH^- \rightarrow \cdot OH$$

MCAA

$$CH_2ClCOO^- + \cdot OH \rightarrow CO_2 + \cdot CH_2Cl + OH^-$$
$$\cdot CH_2Cl + H_2O \rightarrow CH_2Cl\text{-}OH + H\cdot$$
$$CH_2Cl\text{-}OH + H_2O \rightarrow CH_2(OH)_2 + HCl$$

DCAA

$$CHCl_2COO^- + \cdot OH \rightarrow CO_2 + \cdot CHCl_2 + OH^-$$
$$\cdot CHCl_2 + H_2O \rightarrow CHCl_2\text{-}OH + H\cdot$$
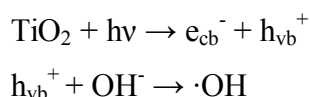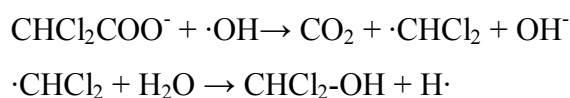
In the sonolysis of TCAA, two mechanisms were proposed; free radical reaction and thermal degradation (Wu, Wei et al. 2001).
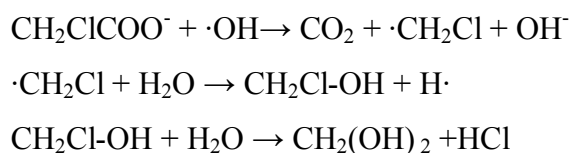
$$CCl_3COO^- \xrightarrow{\text{))), } \cdot OH} CCl_3COO\cdot \rightarrow \rightarrow Cl^- + CO_2 + CO + H_2O$$

$$CCl_3COO^- \xrightarrow{\text{))), } \Delta} \text{other intermediates} \rightarrow \rightarrow Cl^- + CO_2 + CO + H_2O$$
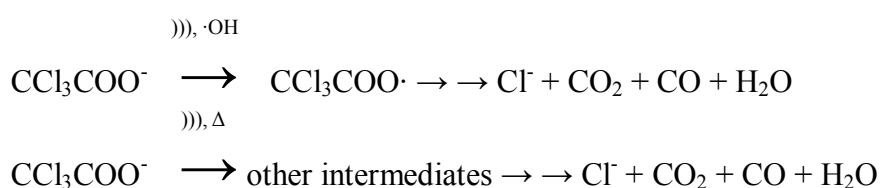
Halogenated organic compounds

Oxidation of 1,1,1-trichloroethane and halomethane with hydroxyl radical was proposed to be initiated by hydrogen abstraction (Makogon, Fliount et al. 1998; Louis, Gonzalez et al. 2000; Louis, Gonzalez et al. 2000; Louis, Gonzalez et al. 2001) and hydrogen-abstracted-radical was proposed to react with oxygen producing another intermediate peroxyl radical (Makogon, Fliount et al. 1998).

In aqueous phase :

$$CHXYZ + \cdot OH \rightarrow \cdot CXYZ + H_2O \quad\quad (X, Y, Z = H, Cl, Br, or F)$$

$$CCl_3CH_3 + \cdot OH \rightarrow CCl_3 \cdot CH_2 + H_2O$$
$$CCl_3 \cdot CH_2 + O_2 \rightarrow CCl_3CH_2OO \cdot$$
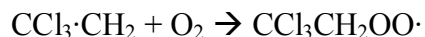
The primary mechanism for the reaction of acetic acid and hydroxyl radical in the atmosphere was suggested as the abstraction of the acidic (carboxyl group) hydrogen (Butkovskaya, Kukui et al. 2004; Vimal and Stevens 2006) and reaction pathway was postulated as follows;

$$CH_3COOH + \cdot OH \rightarrow CH_3COO \cdot + H_2O \rightarrow \cdot CH_3 + CO_2 + H_2O$$

Chemical properties of C-H bond in halogenated DBPs

According to the studies on the gas phase reaction of hydroxyl radical and halogenated methane and acid, both chlorinated and brominated compounds have similar activation energies and reaction enthalpy changes (Louis, Gonzalez et al. 2000; Lagoa, Diogo et al. 2001). In addition, in the transition state of the gas phase reaction between halogenated methane and hydroxyl radical, C-H bond lengths, bond angles and ratios between the elongation of the C-H bond and O-H bond of brominated and chlorinated methane are very close to each other (Louis, Gonzalez et al. 2000). C-H and C-Cl bond lengths in transition state were shown to slightly increase with the increasing number of chlorine atoms, and reaction of trichloromethane and hydroxyl radical was more favorable than monochloromethane (Louis, Gonzalez et al. 2000; Louis, Gonzalez et al. 2004). C-Cl bond is stronger than C-Br bond in halomethanes (80.1 and 70.4 kcal/mol respectively) and in haloacetic acid (McGivern, Derecskei-Kovacs et al. 2000; McGivern, Derecskei-Kovacs et al. 2000).

Chapter 3. Simultaneous Removal of DBPs and Odorants by UV/H$_2$O$_2$ Advanced Oxidation Process

Abstract

Many utilities experience both taste/odor episodes and higher disinfection byproduct level mostly in summer. This research investigated if UV/H$_2$O$_2$, when applied for the removal of odorants geosmin and 2-methyl isoborneol, could simultaneously remove trihalomethane and haloacetic acid disinfection byproducts. These results demonstrate that brominated trihalomethanes and haloacetic acid were substantially removed by direct UV photolysis in UV/H$_2$O$_2$ at the same dose for removing geosmin and 2-MIB. Tribromomethane and dibromochloromethane were removed by 99% and 80% respectively at the UV dose of 1,200 mJ/cm^2 and 6 mg/L H$_2$O$_2$, where geosmin and 2-MIB were removed by 95% and 65% respectively. Tribromoacetic acid (TBAA) and dibromoacetic acid (DBAA) were removed by 99% and 90% respectively under the same condition. Brominated DBPs were removed by direct photolysis, presumably via photo-induced C-Br bond cleavage. Concentrations of trichloromethane and chlorinated HAAs were not substantially reduced under the same conditions. Reduction of brominated DBPs can be a significant addition to water utilities that have difficulty in meeting regulated DBPs level especially in the region with higher bromine concentration. These results indicate that the UV/H$_2$O$_2$ can be seasonally applied to control both taste/odor and brominated DBPs.

Introduction

Advanced oxidation process (AOP) in water treatment involves the hydroxyl radical (•OH). AOP essentially mimics photo-initiated oxidation processes in natural systems, such as sun light on surface water or in the atmosphere (Oppenlander 2003). AOP has been proven to efficiently remove organic contaminants without production of residual solids, which is an advantage compared to the activated carbon adsorption process. Ultraviolet (UV) irradiation is well established for disinfection of water. UV/H_2O_2 process is a homogeneous AOP in which hydroxyl radicals are generated by the direct photolysis of H_2O_2 under UV irradiation (Liao and Gurol 1995; Stefan, Hoy et al. 1996; Stefan and Bolton 1998; Stefan, Mack et al. 2000; Rosenfeldt, Melcher et al. 2005; Rudra, Thacker et al. 2005; Xu, Gao et al. 2007). This process results in highly efficient removal of organic contaminants, including recalcitrant odorous compounds such as geosmin and 2-MIB, mainly by the reaction with hydroxyl radicals and partially by direct UV photolysis (Beltran, Ovejero et al. 1993; Stefan, Hoy et al. 1996; Stefan and Bolton 1998; Cater, Stefan et al. 2000; Stefan, Mack et al. 2000; Rosenfeldt, Melcher et al. 2005; Rudra, Thacker et al. 2005; Paradis and Hoffman 2006; Rosenfeldt and Linden 2007). Recently, UV systems labeled as "dual purpose" were developed and applied to full scale water treatment plants (WTPs). These dual systems combine low intensity UV for disinfection and high intensity UV for both disinfection and advanced oxidation of odorants (Cotton and Collins 2006). The operation of these systems involves UV transmittance (UVT) and alkalinity constraints because these increase the demand for hydroxyl radical (Ho, Croue et al. 2004; Cotton and Collins 2006). The optimum H_2O_2 dose in the UV/H_2O_2 process should be empirically determined because excess H_2O_2 can be an hydroxyl radical scavenger (Wang, Hsieh et al. 2000).

Disinfection byproducts (DBPs) and taste/odor compounds are two of the major problems in drinking water quality. DBPs form from the reaction of DBP precursors and disinfectant. Natural organic matter (NOM) such as humic or fulvic acid, is a typical DBP precursor. AOP has been proposed as an alternative method to reduce disinfection byproduct formation potential (DBPFP) by reducing total organic carbon (TOC), and aromatic structures or double bonds of NOM (Kusakabe, Aso et al. 1990; Wang, Hsieh et al. 2000; Murray and Parsons 2004). Trihalomethanes (THMs) and haloacetic acids (HAAs) represent regulated DBPs in drinking water. Chlorinated compounds such as trichloromethane or trichloroacetic acid are the most prevalent DBPs. However, THMs can be locally composed of more than 40% of

brominated THMs, and HAAs can be composed of 10-25% of brominated HAAs (Hyun, Kim et al. 2005; Buchanan, Roddick et al. 2006). Brominated HAAs were reported to constitute at least 10% of the total HAA concentration in waters containing 0.1mg/L bromide (Cowman and Singer 1996). In addition, brominated DBPs are more toxic than their chlorinated analogues (Echigo, Itoh et al. 2004; Richardson, Plewa et al. 2007) and can be problematic in regions where aqueous bromide concentrations are relatively higher.

Geosmin and 2-MIB are typical earthy-musty odor compounds found in surface water and drinking water resulting in seasonal odor episodes, and mostly related to cyanobacteria or actinomycetes (Jüttner and Watson 2007). These compounds are difficult to remove by conventional water treatment processes and have low odor threshold levels (4-10 ng/L); thus activated carbon or AOPs are required to control them.

Advanced technologies are expected to control multiple contaminants in full scale WTPs. If an advanced process can reduce both DBPs and odorous compounds significantly, it would be immensely beneficial to many WTPs. Many studies reported AOPs can control DBP precursors and consequently reduce DBP level in finished water (Wang, Hsieh et al. 2000; Chin and Berube 2005; Buchanan, Roddick et al. 2006). However, many WTPs are utilizing pre-chlorination to control taste/odor or iron/manganese or ammonia nitrogen or to obtain required CT value, which occurs prior to coagulation and produces a variety of DBPs while AOPs typically occur after filtration to increase UV transmission. Therefore, in case of pre-chlorination, DBPs are already formed before filtration. There have been only a few studies on the removal of DBPs by UV/H_2O_2, and these reports are contradictory. Rudra et al. (2005) reported over 90% removal of THMs at high UV and H_2O_2 dose (17,000 mJ/cm^2 and 0.1% respectively). In another study, THMs increased at lower levels of UV/H_2O_2 doses and decreased with higher level of UV/H_2O_2 doses, and HAAs decreased for two samples and increased for one sample (Paradis and Hoffman 2006).

Researchers have measured second order rate constants for the reaction of odorous compounds and DBPs with hydroxyl radical (Mezyk, Helgeson et al. 2006; Westerhoff, Nalinakumari et al. 2006; Cole, Cooper et al. 2007; Peter and Von Gunten 2007). owever, few studies have been reported on the possibility and mechanisms of DBPs removal by UV/H_2O_2 process in aqueous phase.

There are two mechanisms associated with UV/H_2O_2 oxidation treatment. One involves photolysis of H_2O_2, yielding the hydroxyl radical which subsequently reacts with the contaminant, generally by abstracting a hydrogen, or by adding to an unsaturated site. The

other mechanism involves direct photolysis of the contaminant itself, often resulting in bond homolysis and radical generation. These radicals subsequently are oxidized by reaction with H_2O_2, O_2, etc. Direct UV photolysis has shown to be either a partial or substantial contributor for the removal of organic compounds based on the types of compounds when UV/H_2O_2 is applied. Geosmin and 2-MIB decreased by 40% and 20% respectively with a UV dose of 1,700 mJ/cm^2 (Rosenfeldt, Melcher et al. 2005), diazinon decreased by 20% at a UV dose of 600 mJ/cm^2 (Shemer and Linden 2006), and microcystin decreased by 50% at a UV dose of approximate 3,000 mJ/cm^2 by direct UV photolysis (Qiao, Li et al. 2005). In regard to UV photolysis of THMs, it was reported that only the brominated THMs were photolysed and quantum yield of the photolysis was 0.43 (Nicole, De Laat et al. 1991). In the same research, polybrominated THMs were shown to be photolysed faster. In other research, tribromomethane and chlorodibromomethane levels in chlorinated swimming pool water were reported to decrease significantly with UV irradiation of 145 mJ/cm^2 (Cassan, Mercier et al. 2006). Polyhalomethanes such as tribromomethane ($CHBr_3$) and carbon tetrabromide (CBr_4) were reported to be photolysed by a proposed water-catalyzed O-H insertion/HBr elimination (Li, Kwok et al. 2004; Zhao, Lin et al. 2005).

For the direct UV photolysis and hydroxyl radical reactions of organic compounds such as geosmin/2-MIB, diethyl phthalate, and pharmaceutical compounds in UV/H_2O_2, pseudo-first order reaction models at a wavelength (λ) were proposed as follows (Sharpless and Linden 2003; Rosenfeldt, Melcher et al. 2005; Pereira, Weinberg et al. 2007; Xu, Gao et al. 2007):

$$-\frac{d[C]}{dt} = k'[C]$$

Where, $k' = k'_d + k'_i$

k' = the observed pseudo-first order rate constant (s^{-1})

k'_d = the measured pseudo-first order rate constant of direct photolysis (s^{-1})

$\quad = k_S(\lambda)\ \Phi c(\lambda)$

$\quad\quad \Phi_C(\lambda)$ = quantum yield for the photolysis of compound (mol Es^{-1})

$\quad k_S(\lambda)$ = specific rate of UV absorption by compound (Es $mol^{-1}s^{-1}$)

$$\quad = \frac{E_p^0(\lambda)\varepsilon(\lambda)[1-10^{-a(\lambda)z}]}{a(\lambda)z}$$

$\quad\quad E_p^0(\lambda)$ = incident photon irradiance (mEs$cm^{-2}s^{-1}$)

$\quad\quad \varepsilon(\lambda)$ = molar extinction coefficient of compound at a specific wavelength ($M^{-1}cm^{-1}$)

$a(\lambda)$ = solution absorbance at a specific wavelength (cm^{-1})

z = solution depth (cm)

k'_i = the measured pseudo-first order rate constant of the reaction with ·OH

$k'_i = k_{C/OH}[OH]_{ss}$

$k_{C/OH}$ = Second order reaction rate constant of compound and ·OH (M^{-1}s^{-1})

$[OH]_{ss}$ = steady state ·OH concentration (M)

In case of the hydroxyl radical reaction, a steady state radical concentration is assumed due to relatively higher H$_2$O$_2$ concentration (0-30 mg/L) (Sharpless and Linden 2003; Rosenfeldt, Melcher et al. 2005; Pereira, Weinberg et al. 2007; Xu, Gao et al. 2007).

$$[OH]_{ss} = \frac{\sum k_{S,H_2O_2}(\lambda)\Phi_{OH}(\lambda)[H_2O_2]}{\sum_i k_{S,OH}[S]_i}$$

$k_{S,H_2O_2}(\lambda)$ = specific rate of UV absorption by H$_2$O$_2$ (Es mol^{-1}s^{-1})

$\Phi_{OH}(\lambda)$ = quantum yield for ·OH formation ($\approx$ 1mol Es^{-1})

$k_{S,OH}$ = second order reaction rate constant of scavenging species and ·OH (M^{-1}s^{-1})

$[S]_i$ = concentration of scavenging species (M)

Second order reaction rate constants of hydroxyl radical with geosmin and 2-MIB are 0.78 x 10^9 ~ 1.4 x 10^{10} M^{-1}s^{-1}, which are greater by three orders of magnitude than for the reaction of hydroxyl radical with THMs (0.7 x 10^7 ~1.5 x 10^8 M^{-1}s^{-1}) or chlorinated HAAs (6 x 10^7 ~1.0 x 10^8 M^{-1}s^{-1}). The reaction rate constant of tribromomethane is greater than trichloromethane by a factor of 10 (Glaze, Schep et al. 1990; Maruthamuthu, Padmaja et al. 1995; Mezyk, Helgeson et al. 2006; Westerhoff, Nalinakumari et al. 2006; Cole, Cooper et al. 2007; Peter and Von Gunten 2007).

This research investigated simultaneous removal of odorants and DBPs under conditions similar to when UV/H$_2$O$_2$ is applied for removing recalcitrant odorants. The objectives of this research were to investigate the types of DBPs that can be removed while exposed to UV/H$_2$O$_2$ doses designed for geosmin/2-MIB control at typical concentrations found in drinking water, and to evaluate the role of UV photolysis and hydroxyl radical reaction involved in this removal.

Methods and Materials

1. Apparatus

  Experiments were performed with a Rayonet RPR-100 photochemical reactor equipped with 253.7 nm wavelength UV lamps of 7.2 mW/cm^2 total intensity, and quartz reaction vessels. UV dose was confirmed with the iodide/iodate actinometer (Rahn 2004; Rahn, Bolton et al. 2006). Samples were completely mixed and headspace free while being irradiated with UV (Figure 3-1).
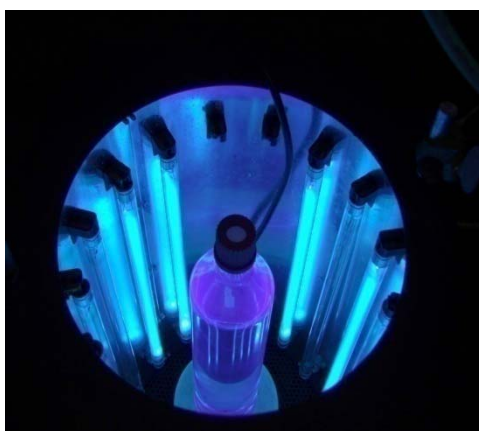

Figure 3-1. UV irradiation system and quartz reactor

2. Reagents and Sample Preparation

  Samples were prepared in de-ionized water using individual compounds; geosmin (200 mg/L, Supelco), and 2-MIB (100 mg/L, Supelco), trichloromethane (≥99%, Fisher scientific), tribromomethane (≥99%, Acros organics), chloroacetic acid (MCAA) (≥99%, Aldrich), dichloroacetic acid (DCAA) (≥99%, Signa-Aldrich), trichloroacetic acid (TCAA) (≥99%, Alfa Aesar), bromoacetic acid (MBAA) (≥99%, Sigma-Aldrich, dibromoacetic acid (DBAA) (≥99%, Fluka), tribromoacetic acid (TBAA) (≥99%, Acros organics). Hydrogen peroxide (30%, Fisher) was diluted to desired concentrations of 6 mg/L which was selected based on typical concentration range in pilot scale study (Paradis and Hoffman 2006), and added into the samples immediately before UV irradiation. THMs standard (5,000 mg/L, Ultra Scientific) was used in THM mixture samples for comparing the removal rates in UV/H$_2$O$_2$. HAA$_9$ standard mixture could not used because it was dissolved in tert-methyl butyl ether (MTBE) that has a great scavenging effect with hydroxyl radical (second order rate constant,

k=3.9 x $10^9 M^{-1}s^{-1}$) (Chang and Young 2000). Typical concentrations of compounds used in the research are shown in Table 3-1.

Table 3-1. Typical concentrations of compounds in the research

Compounds	Typical concentrations in the research	
	μg/L	μM
Odorants		
geosmin	0.04-0.2	0.0002-0.0005
2-MIB	0.1-0.3	0.0006-0.002
THMs		
Trichloromethane	60-500	0.5-4.2
Bromodichloromethane	90	0.5
Dibromochloromethane	80	0.4
Tribromomethane	80-550	0.3-2.2
Tetrahalo methanes		
Carbon tetrachloride	350	2.3
Carbon tetrabromide	1,000	3.0
HAAs		
Chloroacetic acid (MCAA)	270	2.9
Dichloroacetic acid (DCAA)	190	1.5
Trichloroacetic acid (TCAA)	180	1.1
Bromoacetic acid (MBAA)	200	1.4
Dibromoacetic acid (DBAA)	190	0.9
Tribromoacetic acid (TBAA)	160	0.5
Hydrogen Peroxide	6,000	176.5

3. Analysis

Geosmin and 2-MIB were measured by solid-phase microextraction (SPME, Supelco) with GC/MS (Agilent 5973) as in other studies (Watson, Brownlee et al. 1999; Watson, Brownlee et al. 2000; Song and O'Shea 2007). Compounds partitioned from sample water were sorbed on SPME fiber (65μm, PDMS/DVB) for 10 min at 60℃. The SPME fiber was injected into the GC at 220℃ and desorbed for 2 min. A Rtx-5Sil column (30m, 0.25mm ID) with a temperature program of 60℃ to 180℃ by 15℃/min was used. Approximate retention times of 2-MIB and geosmin were 5.4 min and 7.9 min respectively; m/z value of 112, 125, 182 for geosmin and 95, 108, 168 for 2-MIB were detected in selective ion mode. THMs were

measured based on Standard Method 6232.D by purge/trap (Tekmar 3000) and GC (Tremetrics 9001) with DB-624 column (J & W). GC temperature was initially maintained at 45℃ for 3min, and then increased by 11℃/min up to 200℃. HAAs were determined by liquid-liquid extraction method (EPA 552.2 method) and GC (HP 5890) ECD detector. Injector temperature was 210℃ and initial oven temperature was set to 35℃ and increased up to 140℃. UV absorption was measured by UV/Vis spectrophotometer (Beckman, DU640). H_2O_2 concentration was determined by triiodide (I_3^-) titration method (Klassen, Marchington et al. 1994). Linear regression was performed to determine the difference between reaction rates of compounds under UV photolysis and hydroxyl radical reaction ($\alpha=0.05$).

Results

1. UV absorbance

Direct UV photolysis has been known to partially reduce organic compounds in UV/H_2O_2 process, although hydroxyl radicals are thought to play the key role (Liao and Gurol 1995; Stefan, Hoy et al. 1996; Stefan and Bolton 1998; Stefan, Mack et al. 2000; Sharpless and Linden 2003; Rosenfeldt, Melcher et al. 2005; Rudra, Thacker et al. 2005; Pereira, Weinberg et al. 2007; Peter and Von Gunten 2007; Xu, Gao et al. 2007). To investigate the relative role of hydroxyl radical production versus UV photolysis of the organic contaminants in UV/H_2O_2 process, molar extinction coefficients were measured (Figure 3-2). Brominated compounds and geosmin and 2-MIB had at least two order of magnitude higher molar extinction coefficients than chlorinated compounds, and one order of magnitude than H_2O_2. At typical concentrations used in this research, H_2O_2 of mg/L concentration and brominated DBPs of μg/L concentration were shown to absorb UV appreciably. Geosmin and 2-MIB of ng/L concentration barely absorb UV. UV absorbance result suggests that one mechanism via which brominated DBPs can be reduced is by UV photolysis. H_2O_2 of 6 mg/L absorbed the UV the most at the wavelength of 253.7 nm, which indicates that hydroxyl radicals can be produced from UV photolysis of H_2O_2 under these conditions.
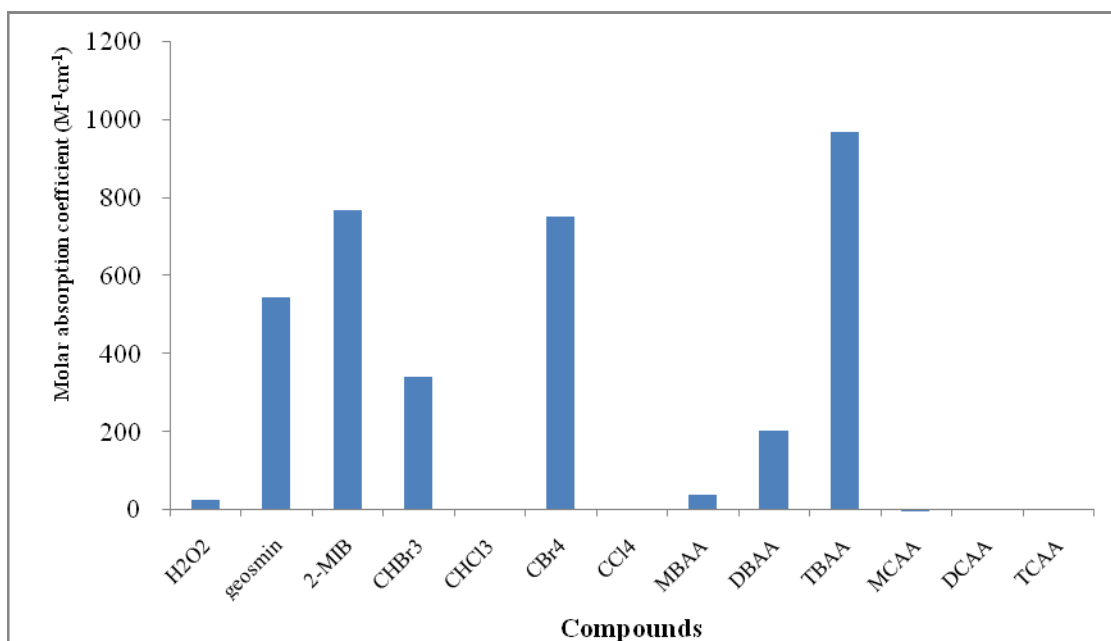
Figure 3-2. Molar absorption coefficients measured at 254 nm in this research

2. Removal of odorants and DBPs at typical concentrations found in drinking water

Geosmin/2-MIB and DBPs were prepared in a mixed sample. The reaction rates were compared under the same UV/H_2O_2 condition to investigate types of DBPs whose concentrations were reduced at the UV/H_2O_2 dose effective for removing geosmin/2-MIB. These results demonstrate that for both THMs and HAAs, brominated DBPs concentrations were not only reduced faster than chlorinated DBPs, but they could be completely or partially removed at the UV/ H_2O_2 dose for removing geosmin/2-MIB.

2.1 Geosmin and 2-MIB

Geosmin and 2-MIB results showed 90 and 65 % removal, respectively, with a UV dose of 1,200 mJ/cm^2 and 6 mg/L H_2O_2. Under identical conditions, but in the absence of H_2O_2, only about 20% were removed with UV photolysis (Figure 3-3). As suggested by other research (Rosenfeldt, Melcher et al. 2005), geosmin and 2-MIB concentrations are mainly reduced by reaction with hydroxyl radical (formed by photolysis of H_2O_2) rather than by direct photolysis of these compounds.
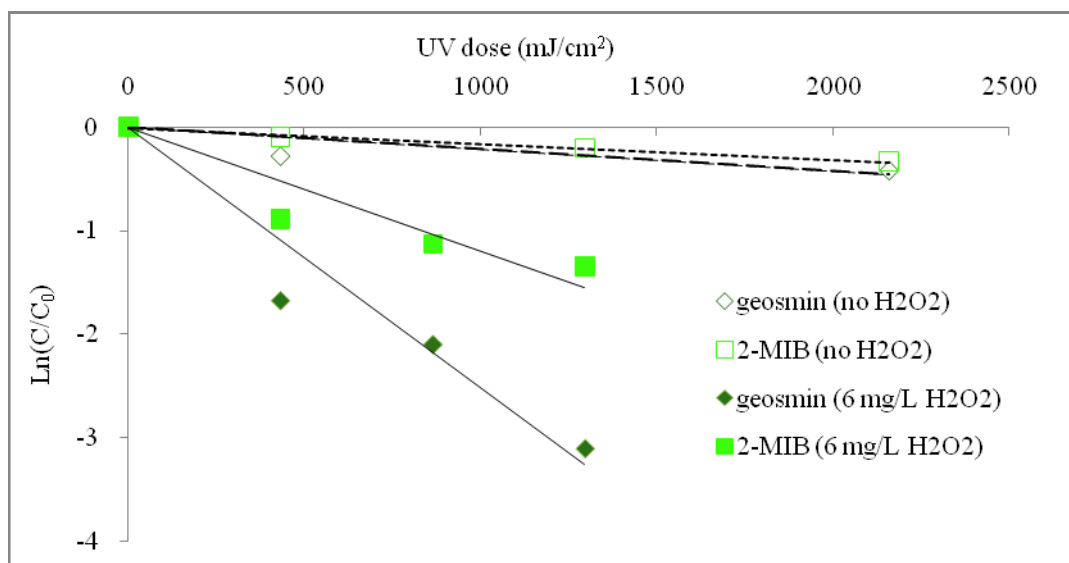
Figure 3-3. Comparison of removal rate between UV photolysis and UV/H_2O_2 for geosmin and 2-MIB

Initial concentration (C_0) : geosmin (no H_2O_2) = 39.9 ng/L, geosmin (H_2O_2 6mg/L) = 183.4 ng/L, 2-MIB (no H_2O_2) = 108.0 ng/L, 2-MIB (6mg/L H_2O_2) = 306.4 ng/L

2.2 Geosmin/MIB and THMs

THMs removal compared to geosmin/2-MIB by UV/H_2O_2

Brominated THMs were shown to be simultaneously removed at the UV/H_2O_2 dose for removing geosmin/2-MIB. Tribromomethane and dibromochloromethane were removed by 99% and 80% respectively at the UV dose of 1,200 mJ/cm^2 and 6 mg/L H_2O_2, where geosmin and 2-MIB were removed by 95% and 65% respectively. The THMs with higher numbers of bromine atoms were removed faster than trichloromethane, which for all practical purposes, was not removed by UV/ H_2O_2 (Figure 3-4). Tribromomethane was removed faster than either geosmin/2-MIB or other THMs.
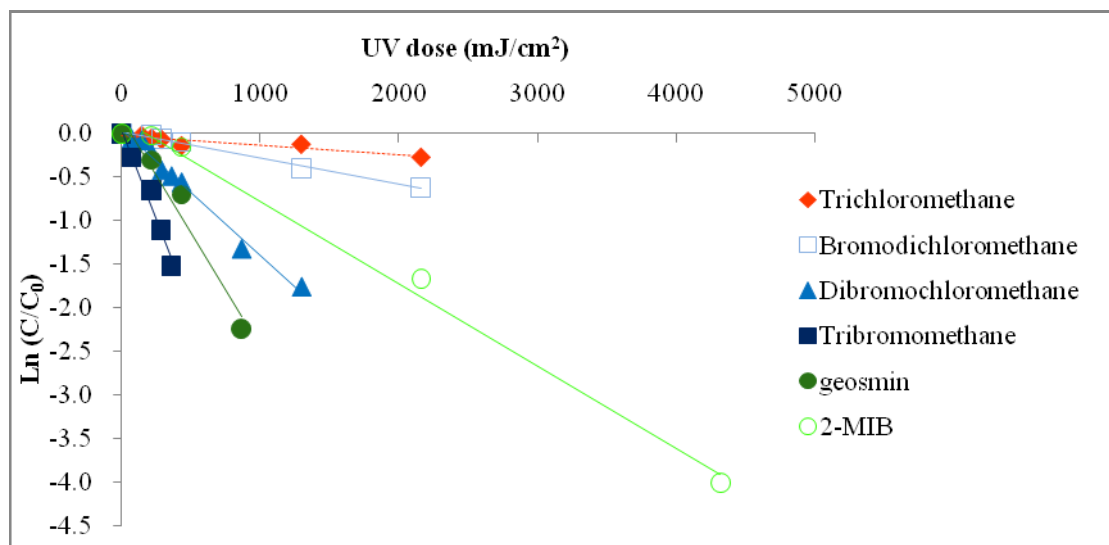
Figure 3-4. Removal of geosmin/2-MIB and THMs with UV/H_2O_2

Initial concentration (C_0) : geosmin = 43.3 ng/L, 2-MIB = 100.0 ng/L, trichloromethane = 63.2 μg/L, bromodichloromethane = 93.5 μg/L, dibromochloromethane = 75.7 μg/L, tribromomethane = 81.9 μg/L, H_2O_2 = 6 mg/L

Direct UV photolysis of brominated THMs

To investigate the contribution of direct UV photolysis on the removal of compounds, a mixture of THMs was reacted with UV in the absence of H_2O_2. Brominated THMs were removed by direct UV photolysis and removal rates were in direct proportion with the number of bromine atoms in their molecule. For three brominated THMs, there was no significant difference between the removal rates of UV photolysis and UV/H_2O_2 treatment as a result of linear regression analysis (α=0.05, for bromodichloro methane p=0.56, dibromochloromethane p=0.17, tribromomethane p=0.51) (Figure 3-5) indicating that brominated THMs are removed, not by reaction with hydroxyl radical, but rather by direct UV photolysis, with C-Br bond cleavage as the likely first step of the process (Li, Kwok et al. 2004; Zhao, Lin et al. 2005).
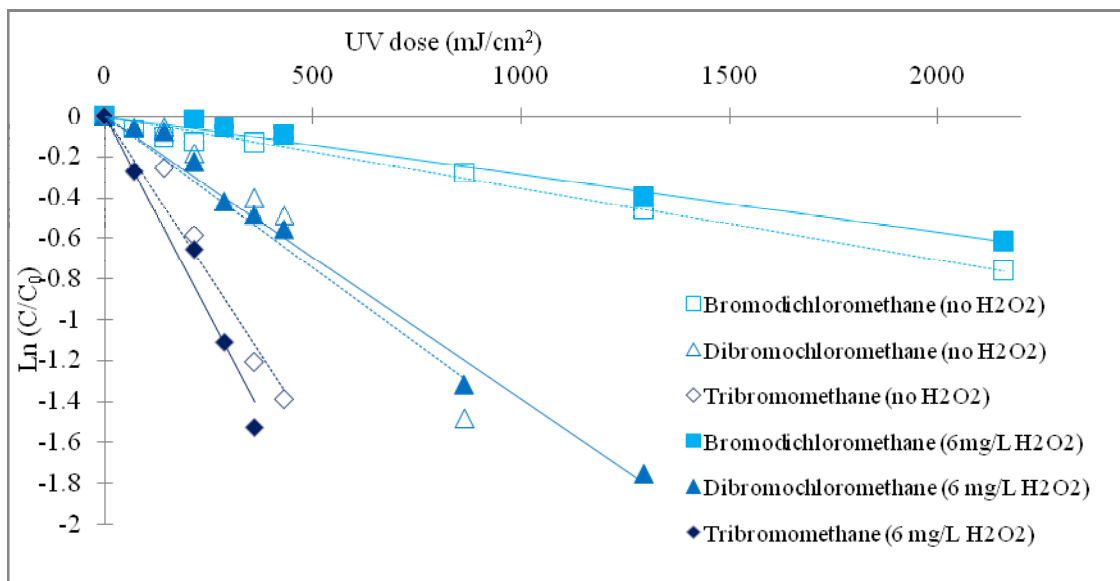
Figure 3-5. Comparison of removal rates between UV photolysis and UV/H_2O_2 for brominated THMs

Initial concentration (C_0) : trichloromethane = 63.2 μg/L, bromodichloromethane = 93.5 μg/L, dibromochloromethane = 75.7 μg/L, tribromomethane = 81.9 μg/L, H_2O_2 = 6 mg/L

Removal mechanism of THMs

To investigate the role of hydrogen abstraction and its effects on THMs removal, reaction of carbon tetrachloride (CCl_4) and carbon tetrabromide (CBr_4), were compared to each other, and to trichloromethane or tribromomethane respectively. Because they do not possess abstractable hydrogens, carbon tetrachloride and carbon tetrabromide cannot react with hydroxyl radical and can only be removed by direct photolysis. Based on these result, the tri and tetra brominated methanes were removed faster than their chlorinated analogues as shown in Figure 3-6. Furthermore, CX_4 (X = Cl or Br) were removed at a greater rate than CHX_3, even though the latter posesses a hydrogen atom that can be abstracted by hydroxyl radical. These results confirm that the different removal rates in UV/H_2O_2 between chlorinated and brominated THMs results from the different UV photolysis rates and not from the hydrogen abstraction by hydroxyl radicals.
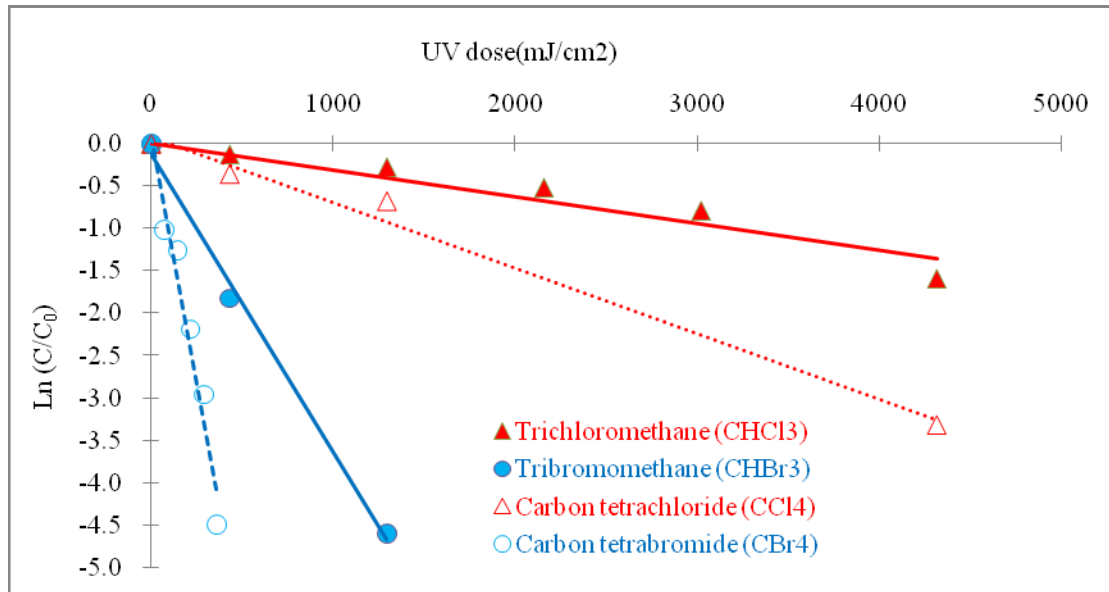
Figure 3-6. Removal rates of halogenated methanes measured for individual compounds

Initial concentration (C_0) : trichloromethane = 513.6 μg/L, tribromomethane = 523.3 μg/L, carbon tetrachloride = 343.3 μg/L, carbon tetrabromide 926.3 μg/L, H_2O_2 = 6 mg/L

2.3 Geosmin/2-MIB and HAAs

HAAs removal compared to geosmin/2-MIB by UV/H_2O_2

Treatment with UV/H_2O_2 removed brominated HAAs faster than chlorinated HAAs (Figure 3-7). Tribromoacetic acid (TBAA) and dibromoacetic acid (DBAA) were removed by 99% and 90% respectively at the UV dose of 1,200 mJ/cm^2 and 6 mg/L H_2O_2, where geosmin and 2-MIB were removed by 95% and 65% respectively. Chlorinated HAAs with no bromine atoms were barely removed by a UV dose range 0 ~ 4,300 mJ/cm^2 and 6 mg/L of H_2O_2 that would effectively remove geosmin and 2-MIB. Brominated HAAs removal rates increased in proportion to the number of bromine atoms in the molecule. Consequently, tribromoacetic acid (TBAA) had the highest removal rate among all HAAs and geosmin/2-MIB. During water treatment, TBAA and DBAA can be substantially removed at the UV dose for removing geosmin/2-MIB in UV/H_2O_2 process while MBAA was not efficiently reduced.
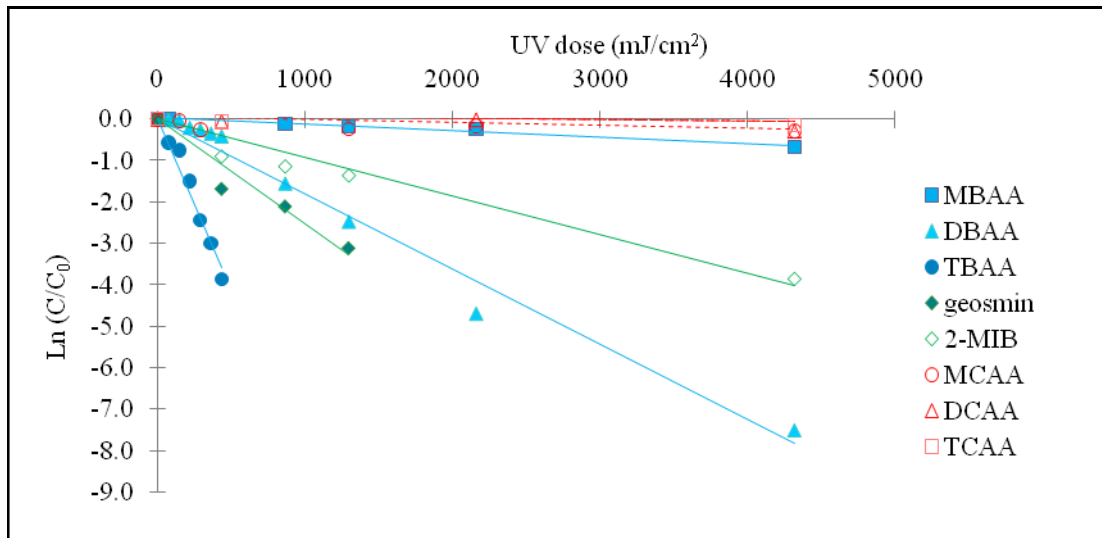
Figure 3-7. Removal of Geosmin/2-MIB and HAAs with UV/H_2O_2

Initial concentration (C_0) : geosmin = 183.4 ng/L, 2-MIB = 306.4 ng/L, bromoacetic acid = 202.4 μg/L, dibromoacetic acid = 190.4 μg/L, tribromoacetic acid = 161.2 μg/L, chloroacetic acid = 270.7 μg/L, dichloroacetic acid = 190.6 μg/L, trichloroacetic acid = 175.9 μg/L, H_2O_2 = 6 mg/L

UV photolysis of brominated HAAs

Three brominated HAAs were reacted with only UV to investigate the contribution of UV photolysis on the higher removal of brominated HAAs in UV/H_2O_2 process. As shown in Figure 3-8, no significant difference of removal rate were observed for TBAA between UV photolysis and UV/H_2O_2 process (α=0.05, p=0.3), and slightly better removals were observed with UV photolysis for MBAA and DBAA (α=0.05, p<0.002) from the linear regression analysis. Thus, brominated HAAs are removed mainly by UV photolysis in UV/H_2O_2 process.
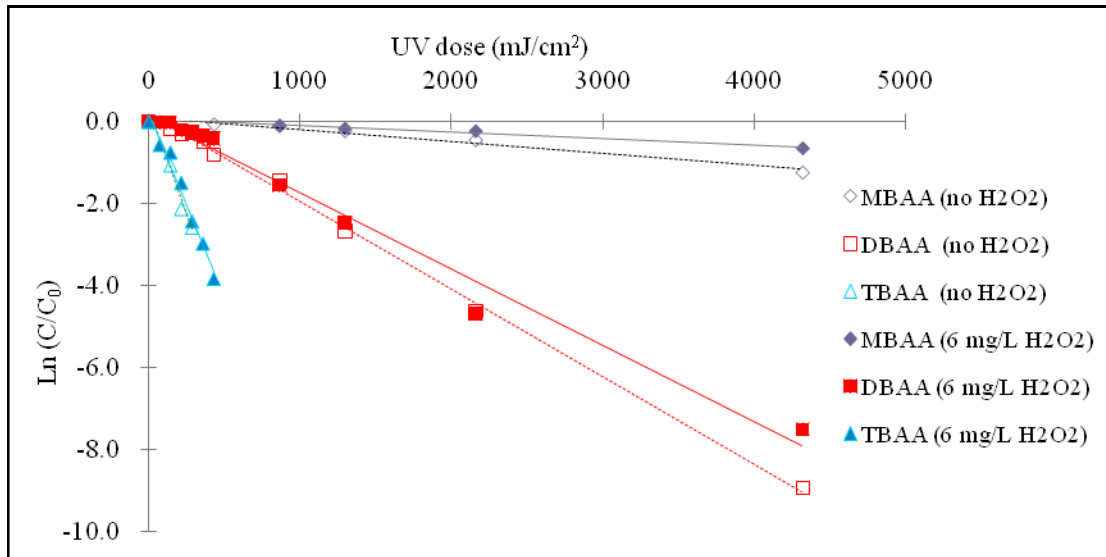
Figure 3-8. Comparison of removal rates between UV photolysis and UV/H_2O_2 for brominated HAAs

Initial concentration (C_0) : bromoacetic acid = 202.4 μg/L, dibromoacetic acid = 190.4 μg/L, tribromoacetic acid = 161.2 μg/L, H_2O_2 = 6 mg/L

2.4 Removal efficiency of DBPs in the presence of inorganic ions

In order to investigate the removal efficiency of DBPs in the presence of inorganic ions, percent removals of selected DBPs in reference water which contains 50mg/L of alkalinity were compared. After 5 min UV irradiation, relative % removal of MCAA, dibromochloromethane (DBCM), and chlorodibromoacetic acid (CDBAA) in reference water were shown to be similar to de-ionized water (Table 3-2). This result indicates that relative removal efficiency of DBPs compared to geosmin and 2-MIB would not change with the different water matrix.

Table 3-2. Comparison of % removal in de-ionized water and reference water

Compound	Relative % removal to 2-MIB	
	De-ionized water	Reference water
Chloroaectic acid (MCAA)	31	28
Dibromochloromethane (DBCM)	266	216
Chlorodibromoacetic acid (CDBAA)	250	223

44

Discussion

This research confirms that geosmin and 2-MIB were mainly reduced by the reaction with hydroxyl radical (Rosenfeldt et al. 2005). Under UV/H_2O_2 conditions that provide substantial removal of these odorants, brominated DBPs were also shown to be substantially removed. However, chlorinated DBPs were not substantially removed under these conditions. For halogenated DBPs such as THMs and HAAs, a possible first reaction step in UV/H_2O_2 could be the hydrogen abstraction by hydroxyl radical or carbon-halogen bond cleavage by direct UV photolysis. Bond dissociation energies (BDE) of the C-H bond in trichloromethane ($CHCl_3$) and tribromomethane ($CHBr_3$) are very close; 100.0 and 99.9 kcal/mol, respectively (McGivern, Derecskei-Kovacs et al. 2000). Thus BDE of C-H bond cannot explain the faster removal of brominated DBPs. Carbon-bromine cleavage due to UV photolysis is the likely mechanism of faster removal of brominated DBPs. This is supported by the higher strengths of C-Cl bond than C-Br bonds in trichloromethane and tribromomethane, 80.1 and 70.4 kcal/mol respectively (McGivern, Derecskei-Kovacs et al. 2000), and higher molar absorption coefficients of brominated DBPs (Figure 3-2).

Brominated DBPs were removed faster in proportion to the number of bromine atoms in their structure. Tribromomethane and tribromoacetic acid (TBAA) were reduced the fastest among the THMs and HAAs respectively. This can be explained by the fact that the C-Br bond is the chromophore in these molecules; note that the molar extinction coefficient for these compounds increases with increasing number of bromines. Regarding UV photolysis of tribromomethane, water-catalyzed mechanism was proposed, in which isotribromomethane recombinated from tribromomethane reacts with water molecule resulting O-H insertion and HBr elimination (Li, Kwok et al. 2004). Consequently, in this research, brominated THMs and HAAs were shown to be reduced by mainly UV photolysis in UV/H_2O_2 process.

Conclusion

Many water treatment plants (WTPs) experience earthy-musty odor episodes during the warm summer and fall months due to proliferation of cyanobacteria and production of geosmin and 2-MIB. DBPs are typically at their highest level in the warm weather of summer as well. Brominated DBPs are known to be more toxic than chlorinated DBP analogues, and constitute about 10-40% of total DBPs produced. Therefore, UV/H_2O_2 process, when

implemented for odor control, can have the additional benefit of DBP reduction, especially in the region where source water bromide concentration leads to brominated DBPs. This simultaneous reduction of DBPs when applying UV/H_2O_2 to control earthy-musty odorants has a substantial implication that UV/H_2O_2 can be seasonally used for controlling both earthy-musty odorants and brominated DBPs.

Chapter 4. Reaction Mechanism of Haloacetic acid Degradation in UV/H$_2$O$_2$ Advanced Oxidation Process

Abstract

Haloacetic acids (HAAs) are class of the regulated disinfection byproducts (DBPs) in drinking water. In previous research, brominated HAAs were shown to be reduced faster than chlorinated DBPs by direct UV photolysis while chlorinated DBPs were reduced by hydroxyl radical reaction in UV/H$_2$O$_2$. In this research, the removal mechanisms of HAAs in UV/H$_2$O$_2$ process were investigated using low pressure UV lamps of 253.7nm wavelength and 7.2 mW/cm^2 total intensity and 100mL quartz reactor.

More bromine substituted HAAs had higher apparent pseudo-first order rate constant of UV photolysis while less chlorine substituted HAAs had higher second order rate constants of hydroxyl radical reaction. The moles of H$^+$ and Br$^-$ or Cl$^-$ produced from the UV photolysis of brominated HAAs and hydroxyl radical reaction of chlorinated HAAs were proportional to the number of halogen atoms in HAAs. Two carbons in a HAA molecule were completely mineralized with molar decrease of chlorinated HAAs while partial mineralization was observed for brominated HAAs. Based on the postulated reaction mechanism, molar increase ratio of hydrogen ion to halogen ion produced from both brominated and chlorinated HAAs were 0, 0.5, 0.7 for mono-, di-, tri-halogenated HAAs, respectively, which was similar to measured ratio of chlorinated HAAs. For MBAA and DBAA, molar increase ratio of H$^+$ to Br$^-$ produced from the UV photolysis of brominated HAAs were close to 1 due to incomplete mineralization.

The C-Br bond cleavage is thought to be the first step of brominated HAAs degradation by UV photolysis, followed by the reaction with oxygen or with water molecule. Faster removal rates of brominated HAAs were associated with increased number of bromine atoms. Hydrogen abstraction and electron transfer reaction are two possible first steps of the degradation of chlorinated HAAs by hydroxyl radical. The stability of the transition state in hydrogen abstraction and different electron density in electron transfer reaction can explain faster removal of less chlorine substituted HAAs. The different reaction rates and removal mechanisms of brominated and chlorinated HAAs indicate that UV/H$_2$O$_2$ oxidation will not uniformly remove all HAA compounds.

Introduction

Advanced oxidation process (AOP) involving hydroxyl radical (·OH) are applied to remove organic contaminants from water. UV/H_2O_2 process is an AOP that produces hydroxyl radical via the photolysis of H_2O_2; this process can efficiently remove organic contaminants from water (Beltran, Ovejero et al. 1993; Stefan, Hoy et al. 1996; Stefan and Bolton 1998; Cater, Stefan et al. 2000; Stefan, Mack et al. 2000; Rosenfeldt, Melcher et al. 2005; Rudra, Thacker et al. 2005; Paradis and Hoffman 2006; Rosenfeldt and Linden 2007). Recently, UV/H_2O_2 has been applied in several full scale water treatment plants (WTPs) to control earthy-musty odors from geosmin (*trans*-1,10-dimethyl-*trans*-9-decalol) and 2-MIB (2-methylisoborneol), the disinfection byproduct, N-nitrosodimethylamine (NDMA), and the industrial chemical, 1,4-dioxane (Cotton and Collins 2006).

The reaction mechanisms of UV/H_2O_2 consists of both direct UV photolysis and hydroxyl radical reaction. Hydroxyl radical produced from the UV photolysis of hydrogen peroxide plays a key role in UV/H_2O_2 process by oxidizing contaminants via radical chain reactions. In case of compounds that have substantial UV absorbances, direct UV photolysis can mainly or partially contribute to the removal of organic compounds in the UV/H_2O_2 process. In selected research, UV irradiation without adding hydrogen peroxide has been shown to partially remove geosmin, 2-MIB, diazinon, and mycrocystin (Qiao, Li et al. 2005; Rosenfeldt, Melcher et al. 2005; Shemer and Linden 2006).

Many utilities are challenged by production of regulated disinfection byproducts (DBPs), and their control frequently conflicts with fulfilling disinfection capacity required to inactivated microorganisms such as *Giardia* and *Cryptosporidium*. Haloacetic acids (HAA) are one of the typically regulated DBPs in drinking water; compared to THMs, they have not been extensively studied (Buchanan, Roddick et al. 2006). Selected HAAs are known to be more harmful to humans than THMs (Singer 2002). Although chlorinated HAAs are the most prevalent, brominated HAAs are present in many source waters around the world (Richardson, Thruston et al. 2003), and brominated HAAs were reported to typically consist of 9-13% of total HAAs in U.S (Krasner, McGuire et al. 1989) and can locally consist of up to 25% of total HAAs (Hyun, Kim et al. 2005; Buchanan, Roddick et al. 2006). Total HAA in waters containing 0.1 mg/L bromide were reported to comprise at least 10% of brominated HAAs (Cowman and Singer 1996). Brominated DBPs are known to be more toxic than their chlorinated analogues (Echigo, Itoh et al. 2004; Richardson, Plewa et al. 2007) and can be

locally problematic in regions with higher aqueous bromide concentrations such as the coastal areas or coal mining regions (von Gunten and Hoigne 1994; Richardson, Thruston et al. 2003).

In regard to DBP, the AOP is known to reduce disinfection byproduct formation potential (DBPFP) by breaking or changing the structures of precursors (Kusakabe, Aso et al. 1990; Wang, Hsieh et al. 2000; Murray and Parsons 2004). The effect of UV/H_2O_2 on the formation of THMs and HAAs were water specific in a bench-scale study (Paradis and Hoffman 2006). However, to obtain higher UV transmittance, the AOP is generally used after filtration in full scale treatment system. In addition, pre-chlorination is commonly used before coagulation in WTPs, which means DBPs are already formed before AOPs are implemented.

However, there have not been sufficient studies on the removal of DBPs by AOPs and the mechanisms. THMs were reported to be reduced at high UV intensity and H_2O_2 dose (17,000 mJ/cm^2 and 0.1% respectively) (Rudra et al. 2005). It was reported that more bromine substituted THMs have slightly greater reaction rate constants with hydroxyl radical than chlorine substituted THMs (Mezyk, Helgeson et al. 2006). More bromine substituted THMs were also shown to be better photolysed by UV (Nicole, De Laat et al. 1991). In a recent study with UV/H_2O_2, brominated and chlorinated DBPs were shown to have different removal mechanisms. Brominated DBPs were shown to be reduced faster than chlorinated DBPs due to direct UV photolysis while chlorinated DBPs were reduced by hydroxyl radical reaction. Consequently, UV/H_2O_2 was shown to significantly remove brominated DBPs at the dose effective for removing geosmin and 2-MIB (Jo, Dietrich et al. 2008). Based on those results, UV/H_2O_2 was thought to be one desirable oxidation process for the water of high bromine concentration because ozonation causes bromate formation in high bromide source waters.

In regard to reaction mechanisms of DBP degradation by UV photolysis or advanced oxidation process, only a few mechanisms have been proposed. The UV photolysis mechanism of tribromomethane ($CHBr_3$) in aqueous solution was proposed to be a water-catalyzed dehalogenation where HBr and CO_2 were the final products (Li, Kwok et al. 2004). Reaction mechanisms for other THMs have not been reported. In the case of haloacetic acids, two pathways of dichloroacetic acid degradation with hydroxyl radical were proposed, where two moles of chloride, hydrogen ion, and carbon dioxide were produced from a molar decrease of dichloroacetate via hydrogen abstraction and electron transfer reaction (Zalazar, Labas et al. 2007). Reaction mechanisms for haloacetic acids other than dichloroacetic acid

have not been reported. Reaction rate constants of halogen substituted acetic acids with UV photolysis or hydroxyl radical reaction could be an important clue in investigating the degradation mechanism of haloacetic acid in UV/H_2O_2 process and improving water treatment and drinking water quality. UV photolysis reaction rates of brominated THMs and HAAs were shown to increase with bromine substitution (Nicole, De Laat et al. 1991; Jo, Dietrich et al. 2008). Reaction rate constants for chlorinated HAAs with hydroxyl radical need to be further investigated. Reaction rate constants of chlorine substituted acetic acids with several radical species exhibited an increasing trend of rate constants with fewer chlorine substitutions. However, dichloroacetic acid had a greater rate constant with hydroxyl radical than chloroacetic acid (Maruthamuthu, Padmaja et al. 1995). Therefore, it is needed to further study on the reaction rate constant and mechanism of HAAs.

In this research, UV photolysis mechanism of brominated DBPs and hydroxyl radical reaction mechanism of chlorinated DBPs in UV/H_2O_2 process were further studied. The understanding of DBPs removal mechanism and kinetics of UV/H_2O_2 will be a useful addition to the water treatment system design. The objectives of this research were 1) to measure apparent pseudo-first order rate constants of UV photolysis of brominated HAAs and second order reaction rate constants of chlorinated HAAs with hydroxyl radical, and 2) to investigate the reaction mechanism of UV photolysis of brominated HAAs and hydroxyl radical reaction of chlorinated HAAs in UV/H_2O_2 advanced oxidation process.

Methods and Materials

Apparatus

UV lamps of 253.7 nm wavelength with 7.2 mW/cm^2 total intensity (Rayonet RPR-100) were used for UV irradiation system in the center of which a 100mL quartz vial was set as a reactor. UV dose calculated by UV lamp intensity was verified with UV dose determined from the iodide/iodate actinometer (Rahn 2004; Rahn, Bolton et al. 2006). Samples were completely mixed by stirring while being irradiated with UV. A temperature of $22.5 \pm 1.0\,℃$ was maintained by an electric fan set blowing through dry ice and the UV system.

Reagents and Sample Preparation

Six pure individual HAAs were diluted to desired concentrations in de-ionized water. Higher concentrations than typical concentrations found in drinking water, by three order of magnitude, were used to measure reaction rate constants and investigate reaction mechanisms (Table 4-1). The HAAs tested consist of three chlorinated and three brominated compounds. Chlorinated HAAs were chloroacetic acid (MCAA) (≥99%, Aldrich), dichloroacetic acid (DCAA) (≥99%, Sigma-Aldrich), and trichloroacetic acid (TCAA) (≥99%, Alfa Aesar). Brominated HAAs were bromoacetic acid (MBAA) (≥99%, Sigma-Aldrich), dibromoacetic acid (DBAA) (≥99%, Fluka), and tribromoacetic acid (TBAA) (≥99%, Acros Organics). Hydrogen peroxide (30%, Fisher) was diluted to desired concentrations of 6 - 12 mg/L, and added into the samples immediately before UV irradiation. Tribromomethane (≥99%, Acros Organics) and trichloromethane (≥99.9%, Fisher Scientific) are used as reference compounds at concentrations of 82 μg/L and 120 μg/L for brominated HAAs and chlorinated HAAs, respectively. Deuterated MCAA (MCAA-d3, 98% deuterium, Signma-Aldrich) was used to investigate the isotope effect.

Table 4-1. concentrations of HAA compounds examined

HAAs	Concentration				pKa*
	reaction rate constant experiment		mass balance experiment		
	μg/L	μM	mg/L	mM	
Chloroacetic acid (MCAA)	108	1.14	20	0.21	2.80
Dichloroacetic acid (DCAA)	105	0.81	20	0.16	1.48
Trichloroacetic acid (TCAA)	98	0.60	20	0.12	0.70
Bromoacetic acid (MBAA)	202	1.45	10	0.07	1.10
Dibromoacetic acid (DBAA)	190	0.87	10	0.05	0.60
Tribromoacetic acid (TBAA)	161	0.54	10	0.03	-

* (Nikolaou, Golfinopoulos et al. 2002)

Analysis

HAAs were determined by liquid-liquid extraction method (EPA method 552.2) with a HP 5890 gas chromatograph (Avondale, PA, USA) and ECD detector (U.S. EPA 1995). Injector temperature was 210℃ and initial oven temperature was set to 35℃ and ramped to 140℃. UV absorbances were measured at a wavelength of 253.7 nm to calculate molar extinction

coefficients on a UV/Vis spectrophotometer (Beckman DU640). Bromide ion (Br$^-$) and chloride ion (Cl$^-$) concentrations were measured by ion chromatography (Dionex DX-120) based on EPA method 300.0 B. Brominated HAA concentration and bromide ion concentration were also analyzed by UV absorbance where the parent brominated HAAs and bromide ion concentrations were measured at a wavelength of 254 nm and 194 nm, respectively (Li, Kwok et al. 2004; Zhao, Lin et al. 2005). In order to quantify mineralization, TOC reduction was measured using a TOC analyzer (Sievers 800). Water pH was measured by pH meter (Fisher Accumet 910) to quantify the increased concentration of hydrogen ion released from the reaction. H_2O_2 concentration was determined by iodide (I_3^-) method (Klassen, Marchington et al. 1994; Rosenfeldt, Melcher et al. 2005). Tribromomethane and trichloromethane were measured based on Standard Method 6232.D by purge/trap (Tekmar 3000) and GC (Tremetrics 9001) with DB-624 column (J & W) (AWWA, APHA et al. 2005).

Experimental Procedure

An appropriate concentration of aqueous HAA, with or without H_2O_2 was added to a 100 mL quartz reactor that was filled with the solution headspace free. The solution was de-ionized water with an equilibrium amount of O_2 from contact with room air. The initial pH of de-ionized water was in the range of pH 6.60 to 6.98. The reactor containing the HAA was irradiated for a predetermined time period that ranged from 10 seconds and 30 minutes. After irradiation, samples were removed for analysis of HAA, bromide and chloride ion, TOC, and pH. All samples were analyzed within 24 hours.

Results

From the previous research, brominated HAAs were shown to be removed by UV photolysis, not by hydroxyl radical reaction in UV/H_2O_2. On the other hand, chlorinated HAAs were shown to be removed by hydroxyl radical reaction (Jo, Dietrich et al. 2008). In this research, removal mechanism of HAA was investigated by measuring reaction rate constants and making balances of hydrogen ion, halogen ion, and carbon.

Apparent reaction rate constant of brominated HAAs

Apparent pseudo-first order reaction rate constants of UV photolysis of brominated HAAs were derived by measuring slopes in the plot of log removal ($\ln[C/C_0]$) versus time (Figure 4-

1). Reaction rate constants of UV photolysis of three brominated HAAs were compared to each other and tribromomethane, which was shown to decrease the fastest among the brominated and chlorinated THMs in previous studies (Nicole, De Laat et al. 1991). Like THMs, more bromine substituted HAAs were removed faster in UV photolysis. Tribromoacetic acid was shown to have twice the reaction rate constant of tribromomethane. Dibromoacetic acid had a slightly lower reaction rate constant than tribromomethane (Table 4-2). This faster removal of more bromine substituted HAAs results from more C-Br chromophores in their molecule in previous research (Jo et al. 2008). The relative ratios of measured apparent reaction rate constants of brominated HAAs were 1:8:34, which was greater than the expected ratio (1:2:3). This greater difference in reaction rates of brominated HAAs can be explained by the ratio of molar extinction coefficients which was 1:5:24 as shown in Figure 4-2.
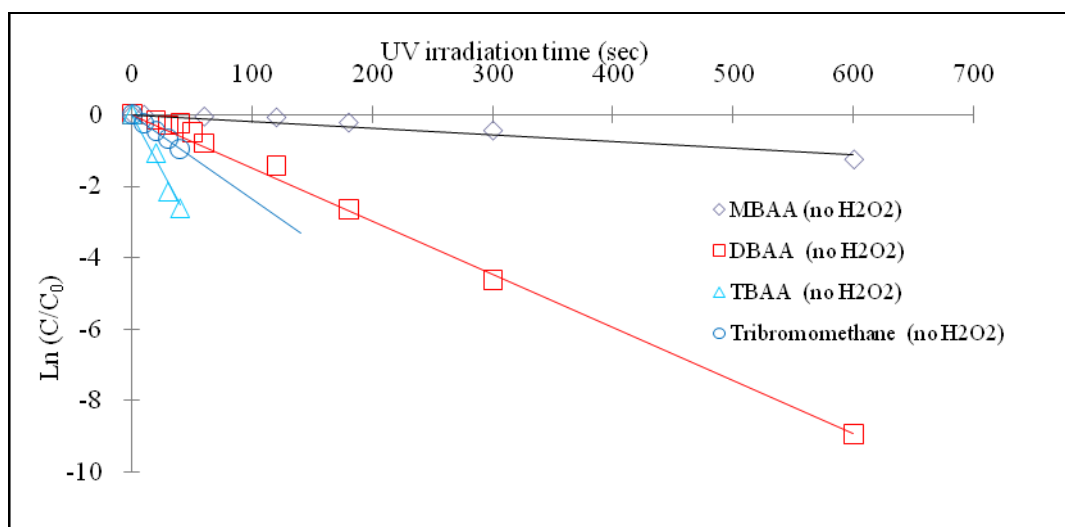

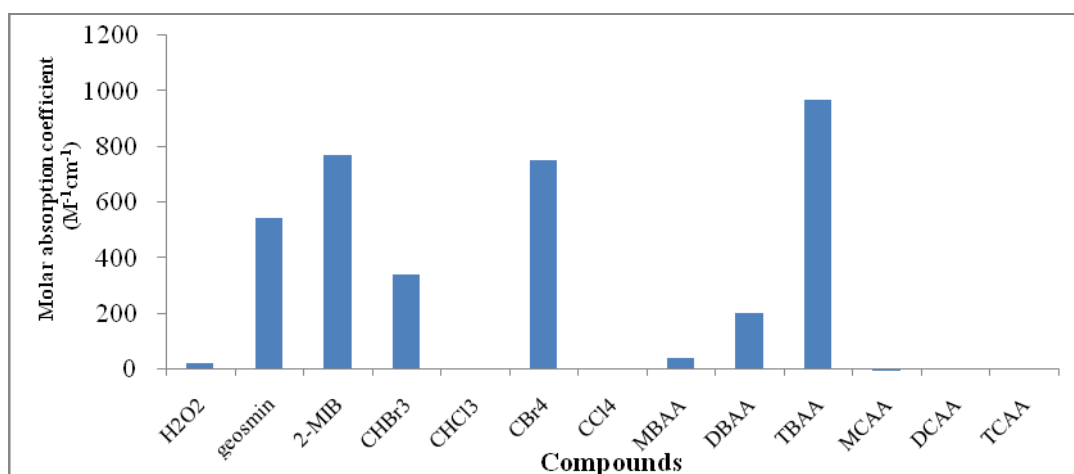Figure 4-1. Removal rate of brominated HAAs and tribromomethane by UV photolysis

Figure 4-2. Molar absorption coefficients measured at 254 nm in this research

53

Table 4-2. Apparent pseudo-first order reaction rate constants for UV photolysis of three brominated HAAs and tribromomethane

Compound	Apparent k measured (s^{-1})	Relative rate constant versus MBAA
Bromoacetic acid (MBAA)	1.9×10^{-3}	1
Dibromoacetic acid (DBAA)	1.5×10^{-2}	8
Tribromoacetic acid (TBAA)	6.3×10^{-2}	34
Tribromomethane	2.4×10^{-2}	13

Reaction mechanism of brominated HAAs in UV/H$_2$O$_2$ process

To investigate the mechanisms, molar increases of bromide and hydrogen ion concentration were plotted with molar decrease of HAA. Molar TOC removal was plotted with molar HAA removal to determine whether complete mineralization takes place or stable intermediates are present. This approach was based on previous studies on the reaction rate and mechanism of trihalomethane and DCAA (Nicole, De Laat et al. 1991; Li, Kwok et al. 2004; Zalazar, Labas et al. 2007).

[H$^+$] and [Br$^-$] balance

[H$^+$] and [Br$^-$] produced from the UV photolysis of three brominated HAAs were measured and plotted (Figure 4-3). The ratio of molar increase in [Br$^-$] from MBAA to molar increase in [Br$^-$] from DBAA and TBAA was 1:1.7:2.9 which was close to the theoretical ratio, 1:2:3. Ratios of [H$^+$] to [Br$^-$] were almost 1:1 for each of the three compounds even though less [H$^+$] was consistently produced than [Br$^-$] for three brominated HAAs. The experiment was repeated three times and results were similar (data not shown).

This result indicates that the moles of H$^+$ and Br$^-$ produced from the UV photolysis of molar brominated HAAs was in proportion to the number of bromine atoms in HAAs. Bromide ion production is thought to result from the C-Br bond cleavage because the C-Br bond is the chromophore, and molar extinction coefficient increases with the number of C-Br bonds. Hydrogen ion is thought to be released from photo-assisted hydrolysis of the molecule.
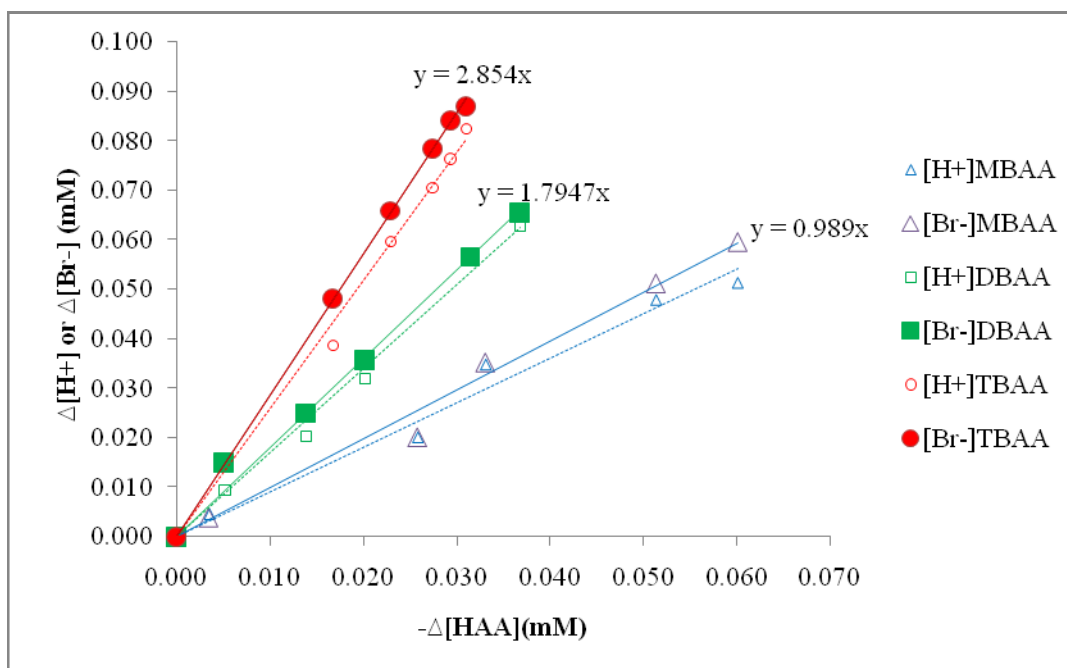
Figure 4-3. Molar increase of [H⁺] and [Br⁻] with molar decrease of brominated HAAs exposed to UV photolysis at 253.7 nm wavelength (Regression equations are provided for bromide ion)

Carbon balance

To investigate mineralization, a carbon balance was made by measuring total organic carbon (TOC). Two moles of TOC were completely removed with a molar decrease of TBAA. However, only 10% and 30% of TOC were removed for MBAA and DBAA, respectively (Figure 4-4). This result indicates that the two carbons in a TBAA molecule were completely mineralized while two carbons in MBAA and DBAA molecules were partially mineralized under the condition used in this research and subsequently, stable intermediate(s) would be present in the UV photolysis of MBAA and DBAA .
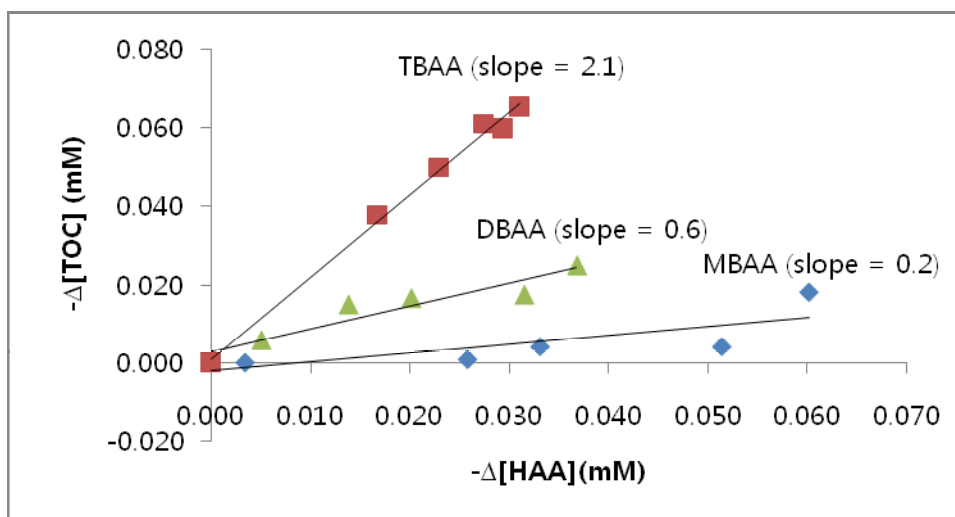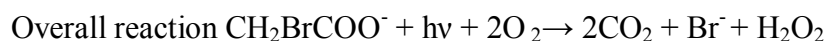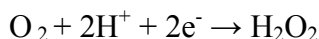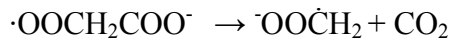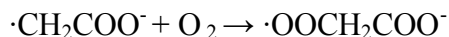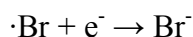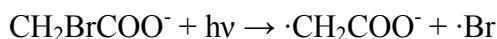
Figure 4-4. Molar decrease of TOC with molar decrease of HAA concentration for three brominated HAAs

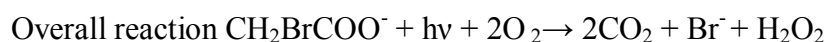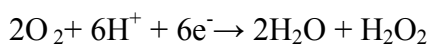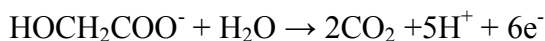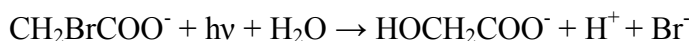*Postulated UV photolysis mechanism of brominated HAAs*

Based on the results above, UV photolysis mechanisms of brominated HAAs were examined. Result of $[H^+]$ and $[Br^-]$ balance indicates that H^+ and Br^- would be produced according to the number of bromine atoms in HAA molecules. Carbon balances indicate that there were partial mineralizations for MBAA and DBAA. In the case of mineralization, two moles of carbon dioxide would be produced as a final product. In contrast, incomplete mineralization would produce stable intermediates resulting in different pathways. C-Br bond cleavage was thought to be the first step in this UV photolysis because C-Br bond is the chromophore in the HAA molecule.

In the case of mineralization, two mechanisms are possible. From the first step, two radicals can be produced ($\cdot CX_nH_{n-3}COO^-$ and $\cdot Br$). The second step can be a reaction with oxygen. With a presence of oxygen, the $\cdot CX_nH_{n-2}COO^-$ radical is likely to react with oxygen producing peroxyl radical, $\cdot OOCX_nH_{n-2}COO^-$ as frequently seen in other radical reactions (Fliount, Makogon et al. 1997; Makogon, Fliount et al. 1998; Zalazar, Labas et al. 2007) (pathway 1). Another possible explanation is O-H insertion/H-Br elimination resulting from the interaction with water molecule (pathway 2). Based on these results, when complete mineralization takes place, the reaction mechanisms of brominated HAAs were postulated as follows:
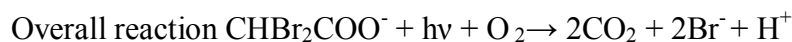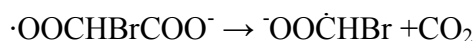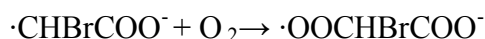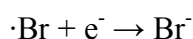
MBAA-pathway 1

$CH_2BrCOO^- + h\nu \rightarrow \cdot CH_2COO^- + \cdot Br$

$\cdot Br + e^- \rightarrow Br^-$

$\cdot CH_2COO^- + O_2 \rightarrow \cdot OOCH_2COO^-$

$\cdot OOCH_2COO^- \rightarrow {}^-OO\dot{C}H_2 + CO_2$

${}^-OO\dot{C}H_2 \rightarrow CO_2 + 2H^+ + 3e^-$

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

Overall reaction $CH_2BrCOO^- + h\nu + 2O_2 \rightarrow 2CO_2 + Br^- + H_2O_2$

MBAA-pathway 2

$CH_2BrCOO^- + h\nu + H_2O \rightarrow HOCH_2COO^- + H^+ + Br^-$

$HOCH_2COO^- + H_2O \rightarrow 2CO_2 + 5H^+ + 6e^-$

$2O_2 + 6H^+ + 6e^- \rightarrow 2H_2O + H_2O_2$

Overall reaction $CH_2BrCOO^- + h\nu + 2O_2 \rightarrow 2CO_2 + Br^- + H_2O_2$

DBAA-pathway 1

$CHBr_2COO^- + h\nu \rightarrow \cdot CHBrCOO^- + \cdot Br$

$\cdot Br + e^- \rightarrow Br^-$

$\cdot CHBrCOO^- + O_2 \rightarrow \cdot OOCHBrCOO^-$

$\cdot OOCHBrCOO^- \rightarrow {}^-OO\dot{C}HBr + CO_2$

${}^-OO\dot{C}HBr \rightarrow CO_2 + Br^- + H^+ + e^-$

Overall reaction $CHBr_2COO^- + h\nu + O_2 \rightarrow 2CO_2 + 2Br^- + H^+$

DBAA-pathway 2

$CHBr_2COO^- + h\nu + H_2O \rightarrow HOCHBrCOO^- + H^+ + Br^-$

$HOCHBrCOO^- + H_2O \rightarrow 2CO_2 + Br^- + 4H^+ + 4e^-$

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Overall reaction $CHBr_2COO^- + h\nu + O_2 \rightarrow 2CO_2 + 2Br^- + H^+$

TBAA-pathway 1

$CBr_3COO^- + h\nu \rightarrow \cdot CBr_2COO^- + \cdot Br$

$\cdot Br + e^- \rightarrow Br^-$

$\cdot CBr_2COO^- + O_2 \rightarrow \cdot OOCBr_2COO^-$

$\cdot OOCBr_2COO^- \rightarrow {}^-OOĊBr_2 + CO_2$

${}^-OOĊBr_2 + 2H_2O \rightarrow CO_2 + 2Br^- + 2H^+ + H_2O_2 + e^-$

Overall reaction $CBr_3COO^- + h\nu + 2H_2O + O_2 \rightarrow 2CO_2 + 3Br^- + 2H^+ + H_2O_2$

TBAA-pathway 2

$CBr_3COO^- + h\nu + H_2O \rightarrow HOCBr_2COO^- + H^+ + Br^-$

$HOCBr_2COO^- + H_2O \rightarrow 2CO_2 + 2Br^- + 3H^+ + 2e^-$

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

Overall reaction $CBr_3COO^- + h\nu + 2H_2O + O_2 \rightarrow 2CO_2 + 3Br^- + 2H^+ + H_2O_2$

Based on these postulated reaction mechanisms, less hydrogen ion than bromide ion would be produced, and no hydrogen ion increase would be observed from the reaction of MBAA. However, almost same amounts of H^+ compared to Br^- were produced from the three brominated HAAs (Figure 4-3). This can be explained by the incomplete mineralization which were observed in the carbon balance of MBAA and DBAA (Figure 4-4). In the case of incomplete mineralization, organic intermediate and hydrogen ion can be produced. One possible explanation is the formation of oxalate. Oxalate formation causes incomplete mineralization because oxalate is detected as an organic compound in the TOC measurement. With the oxalate production, hydrogen ion would be produced from the following reaction:

$$CH_2BrCOO^- + h\nu + O_2 \rightarrow HC_2O_4^- + Br^- + H^+$$

$$CHBr_2COO^- + h\nu + O_2 + 2H_2O \rightarrow HC_2O_4^- + 2Br^- + 2H^+ + H_2O_2$$
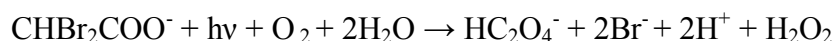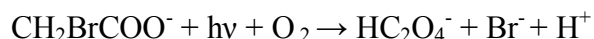
To investigate this assumption, percentage of mineralization and oxalate formation was calculated respectively from the measured $\Delta TOC/\Delta HAA$, and measured $\Delta[H^+]/\Delta HAA$ was compared to calculated $\Delta[H^+]/\Delta HAA$ that was determined by mineralization percentage and theoretical ratio of $\Delta[H^+]/\Delta HAA$ (Table 4-5). Measured $\Delta[H^+]/\Delta HAA$ for the brominated

HAAs were similar to calculated $\Delta[H^+]/\Delta HAA$ for MBAA and DBAA. Therefore, production of oxalate was thought to be a possible explanation of the increased H^+ production observed in the UV photolysis of these two brominated HAAs compared to the amount of H^+ expected from the mineralization mechanism.

Table 4-3. Comparison of measured and calculated $\Delta[H^+]/\Delta HAA$ based on percent mineralization

Parameter		MBAA	DBAA	TBAA
$\Delta TOC/\Delta HAA$	Measured	0.2	0.6	2.1
	Expected*	2.0	2.0	2.0
$\Delta[H^+]/\Delta HAA$	Measured	**0.9**	**1.7**	2.6
	Expected*	0.0	1.0	2.0
$\Delta[Br^-]/\Delta HAA$	Measured	1.0	1.8	2.9
	Expected*	1.0	2.0	3.0
% incomplete mineralization** ($HC_2O_4^-$ formation)		88.5	79.1	0.0
$\Delta[H^+]/\Delta HAA$ for incomplete mineralizaiton		1.0	2.0	3.0
% mineralization** (CO_2 formation)		11.5	20.9	100.0
$\Delta[H^+]/\Delta[HAA]$ for complete mineralization		0.0	1.0	2.0
Calculated $\Delta[H^+]/\Delta HAA$ ***		**0.9**	**1.8**	2.0

*based on complete mineralization
**calculated from measured $\Delta TOC/\Delta HAA$ (when $\Delta TOC/\Delta HAA = 2$, complete mineralization = 100%)
***calculated from the sum of (percentage times theoretical $\Delta[H^+]/\Delta[HAA]$) for incomplete and complete mineralization

Reaction rate constants of Chlorinated HAAs and Hydroxyl Radicals

Second order reaction rate constants of chlorinated HAAs and hydroxyl radicals were measured by competition kinetics using trichloromethane as a reference compound (Figure 4-5). UV at 253.7 nm wavelength and 6 mg/L H_2O_2 were used as a hydroxyl radical source. Second order reaction rate constants of chlorinated HAAs with hydroxyl radicals can be used to explain the chlorine substitution effect on the hydroxyl radical reaction rate. In addition,

those reaction rate constants provide some clue about the reaction mechanism such as the role of hydrogen abstraction. Reaction rate constants measured in this research were similar to those for chlorinated HAAs reported by other researchers (Adams, Boag et al. 1965; Yokohata, Ohmura et al. 1969; Maruthamuthu, Padmaja et al. 1995). However, based on the results, less chlorine substituted HAAs had higher reaction rate constant (Figure 4-5 and Table 4-4). This is the opposite to the faster removal of more bromine substituted HAAs that was shown to be degraded by C-Br bond cleavage resulting from UV photolysis. Considering two possible pathways, hydrogen abstraction and electron transfer reaction, as shown in the equation (1) and (2), higher reaction rate constants of less chlorine substituted HAAs can be explained by two mechanisms.

$$CClH_2COO^- + \cdot OH \rightarrow \cdot CClHCOO^- + H_2O \quad \text{Hydrogen abstraction} \quad (1)$$
$$CH_2ClCOO^- + \cdot OH \rightarrow CH_2ClCOO\cdot + HO^- \quad \text{Electron transfer} \quad (2)$$
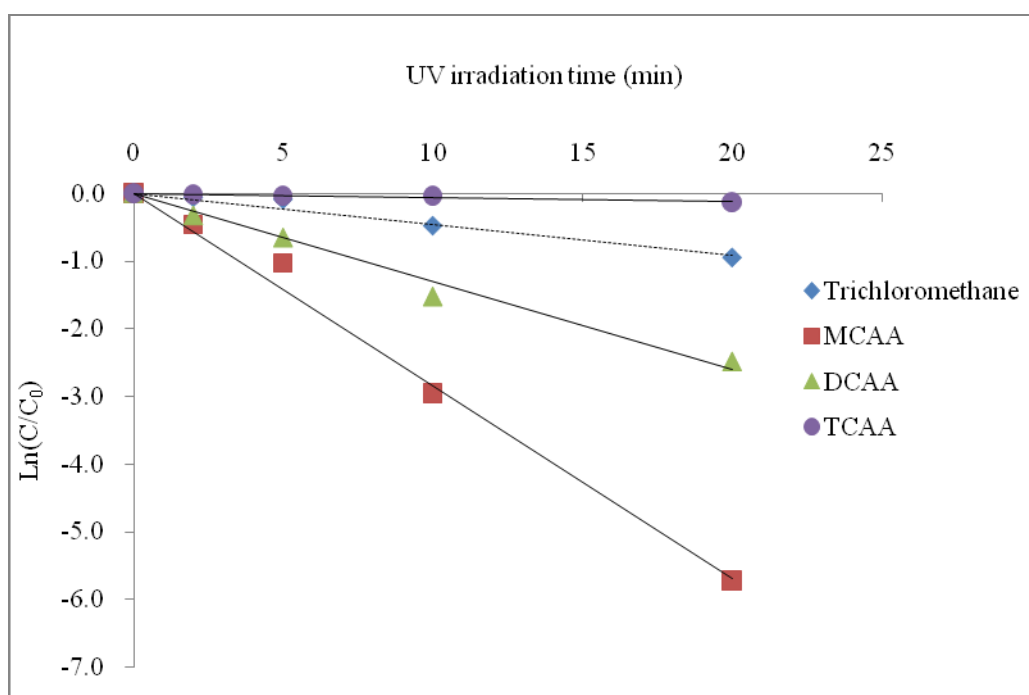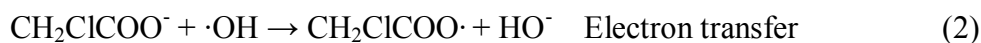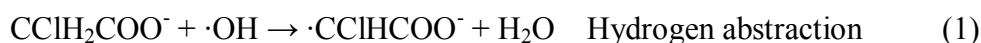

Figure 4-5. Removal rates of three chlorinated HAAs compared to trichloromethane

Table 4-4. Second order reaction rate constants of chlorinated HAAs

Compound	Measured k in this research ($M^{-1}s^{-1}$)	Relative rate constant versus TCAA	Reported k in literature ($M^{-1}s^{-1}$)
MCAA	3.3×10^8	46	$8.3 \times 10^{7\,a}$ $4.0 \times 10^{8\,b}$ $4.3 \times 10^{7\,c}$
DCAA	1.5×10^8	21	$1.0 \times 10^{8\,a}$
TCAA	7.2×10^6	1	$6.0 \times 10^{7\,a\,*}$

[a] (Maruthamuthu, Padmaja et al. 1995)

[b] (Yokohata, Ohmura et al. 1969)

[c] (Adams, Boag et al. 1965)

[*] This value was reported as an upper limit due to impurity issue in the research

Faster removal of MCAA and DCAA than TCAA implies that hydrogen abstraction is a likely the first step in this reaction, because there are two, one, and zero abstractable hydrogen atoms in their molecules, respectively. The rate of TCAA removal is also less than trichloromethane, which has an abstractable hydrogen atom. Deuterated MCAA was compared to MCAA for the reaction rate with hydroxyl radical to assess the isotope effect. Reaction of deuterated MCAA with hydroxyl radical was slower than MCAA, and the isotope effect (k_H/k_D) was 2.9 indicating that hydrogen abstraction takes place as a rate-limiting step (Figure 4-6).
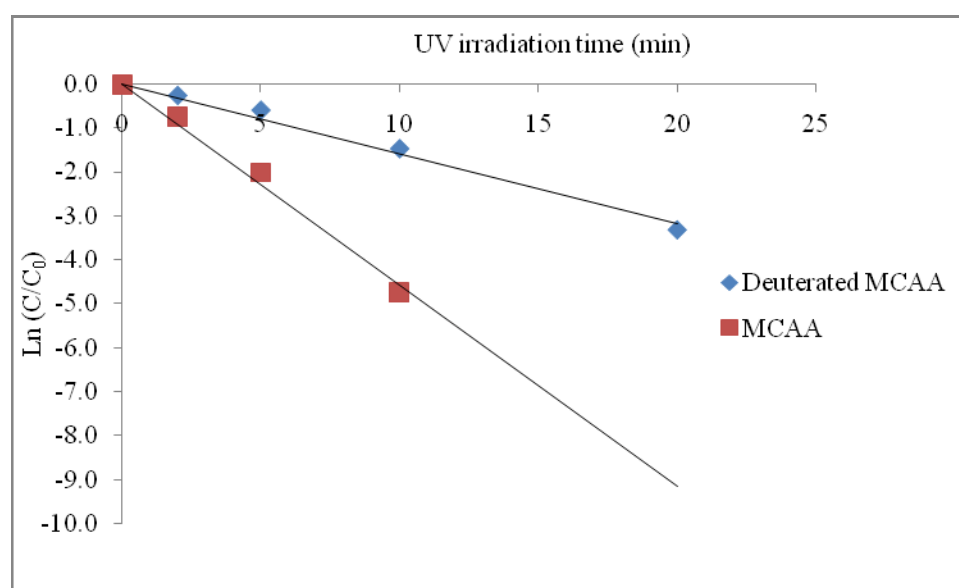

Figure 4-6. Comparison of reaction rates with UV/H_2O_2 between deuterated MCAA and MCAA

Faster removal of MCAA than DCAA can be explained by the stability of the transition state in the hydrogen abstraction step. In the transition state, the hydroxyl radical has a partial negative charge having an interaction with an abstractable hydrogen atom. On the other hand, the abstractable hydrogen atom has a partial positive charge which makes its transition state more unstable when the carbon atom also has a less electron density induced by electronegativity of substituted chlorine causing partial positive charge (Figure 4-6 and 4-7). Therefore, hydrogen abstraction of MCAA that has only one chlorine atom is more favorable than DCAA because halogen substituted carbon has more electron density in the transition state of MCAA due to less electron withdrawing of a single chlorine atom.
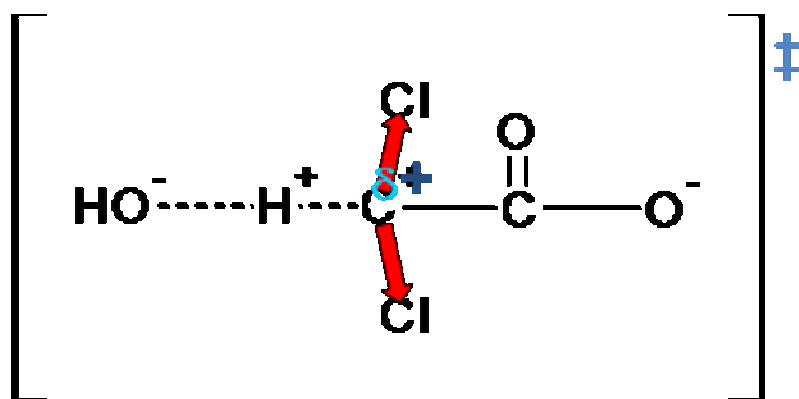
Figure 4-7. Transition state for hydrogen abstraction of DCAA; both chlorine atoms withdraw electron density from the carbon atom and destabilize the transition state
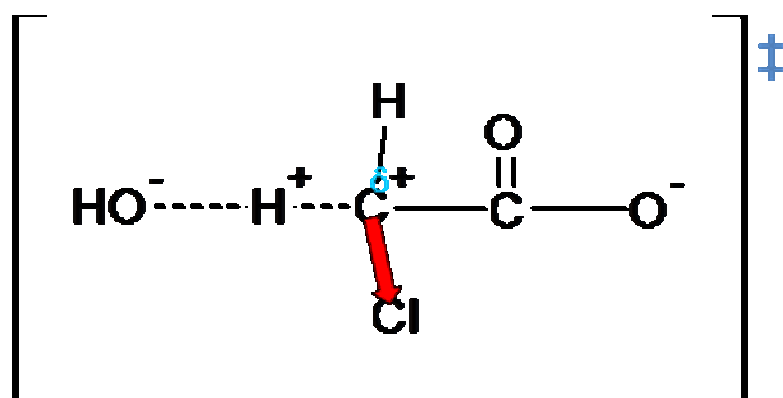
Figure 4-8. Transition state for hydrogen abstraction of MCAA

In the case of an electron transfer reaction, another explanation for the faster removal of MCAA is by the stability of the acetate ion and electron density around the carboxylic carbon. Compared to TCAA, MCAA has fewer chlorine atoms in the molecule, which makes the chloroacetate ion less stable due to less partial positive charge on the carbon atom with the

lower electronegativity of chlorine (Figure 4-9). Subsequently, in an electron transfer reaction, chloroacetate has higher electron density around the carboxylic oxygen, which makes electron transfer from carboxyl group to hydroxyl radical easier causing faster removal. This is consistent with the fact that MCAA has the highest pK_a among the three chlorinated HAAs (Table 4-1).
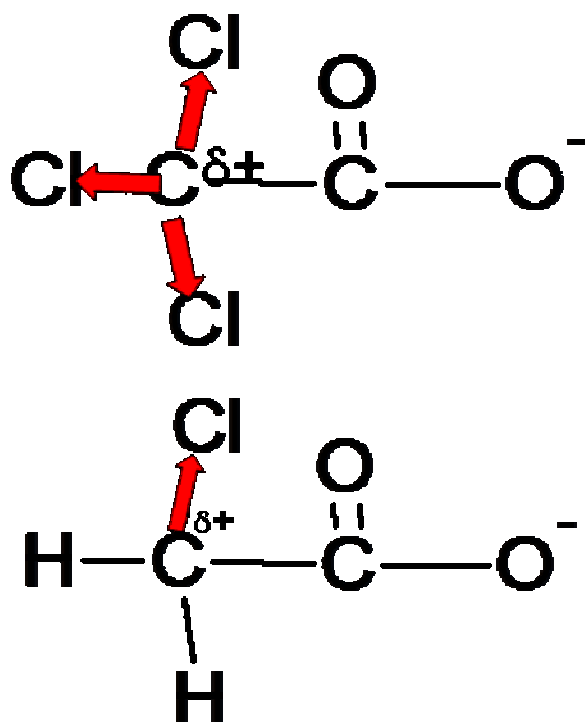
Figure 4-9. Partial positive charge on the chlorinated carbon atom of acetate ion; the partial positive charge on the carbon of chloroacetate is less than in trichloroacetate ion

Reaction mechanism of chlorinated HAAs in UV/H₂O₂ process

[H⁺] and [Cl-] balance

Chloride ion was produced in proportion to the number of chlorine atoms in a chlorinated HAA molecule. The ratio for molar increase of chloride ion to decrease of chlorinated HAA was 1:2.5:3.1 for MCAA, DCAA, and TCAA, respectively (Figure 4-10). Less hydrogen ion was released from the reaction than chloride ion. From the reaction of MCAA, hydrogen ion was barely produced. For DCAA and TCAA, ratios of increased molar hydrogen ion concentration to chloride ion were 0.4 and 0.5, respectively.
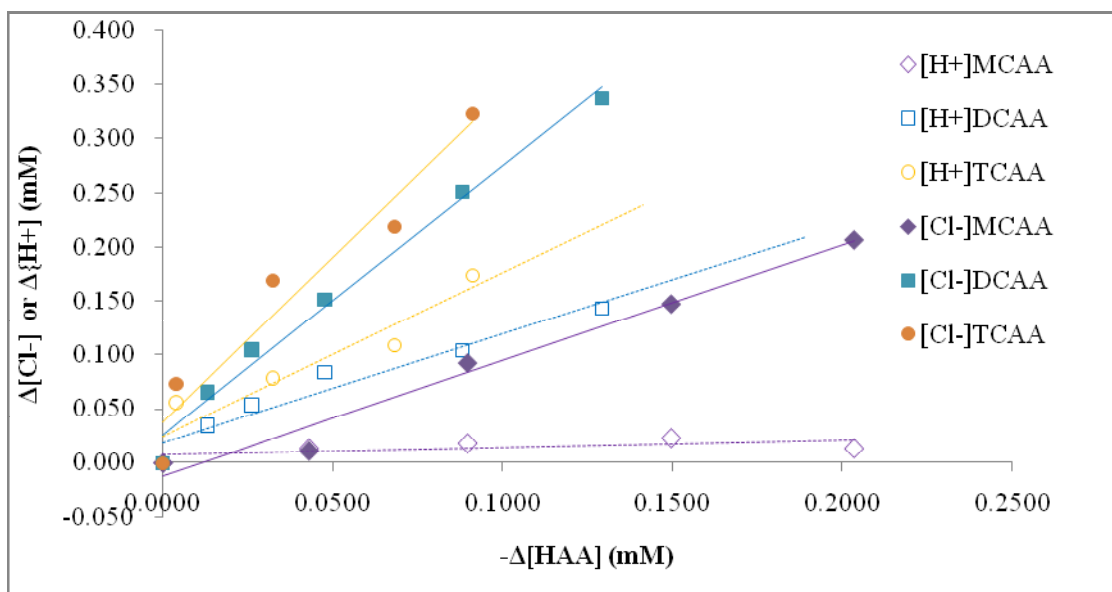
Figure 4-10. Molar increase of [H$^+$] and [Cl$^-$] compared to molar decrease of corresponding chlorinated HAA

Carbon balance

Molar decrease ratio of TOC to three chlorinated HAAs were close to expected ratio of 2:1 based on total mineralization (Figure 4-11). According to this carbon balance, two carbons in a HAA molecule were completely mineralized and no stable intermediates were present in the reaction of chlorinated HAAs with hydroxyl radical.
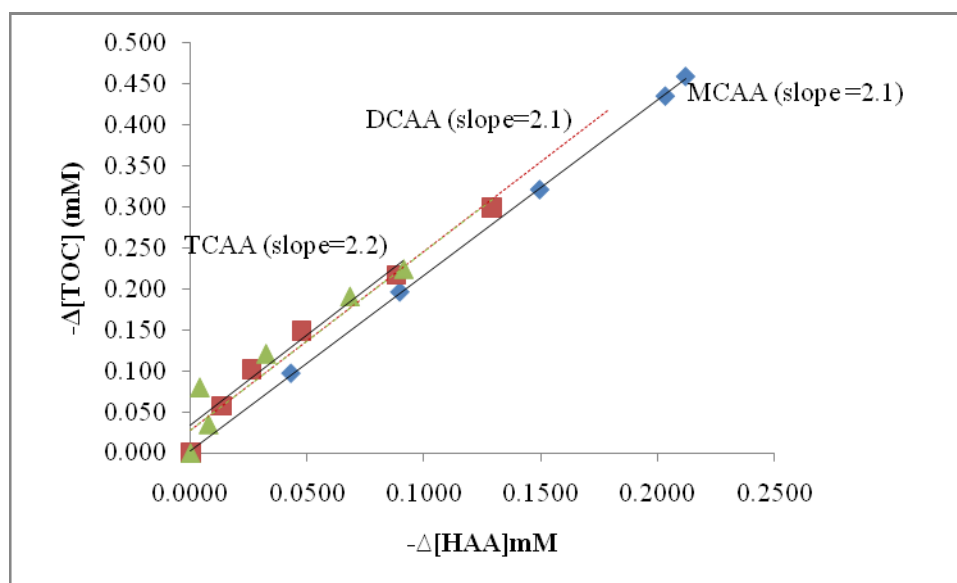
Figure 4-11. Molar decrease of TOC with molar decrease of three chlorinated HAAs

Two pathways are possible for the first step of the reaction mechanism; hydrogen abstraction and electron transfer reaction. According to the faster removal rate of less chlorine substituted HAAs and observed isotope effect, hydrogen abstraction is indicated to be a reaction mechanism except for TCAA which has no abstractable hydrogen atom. Electron transfer which was the only pathway for TCAA was also able to explain the faster removal of less chlorine substituted HAAs and lead to same overall reaction. These results were consistent with the previous research where both hydrogen abstraction and electron transfer were proposed as the first step of the hydroxyl radical reaction of DBAA (Zalazar, Labas et al. 2007). Base on the results, hydroxyl radical reaction mechanisms of chlorinated HAAs were postulated as follows:

MCAA   mechanism 1 - Hydrogen abstraction

$1/2H_2O_2 \rightarrow \cdot OH$

$CClH_2COO^- + \cdot OH \rightarrow \cdot CClHCOO^- + H_2O$

$\cdot CClHCOO^- + O_2 \rightarrow \cdot OOCClHCOO^-$

$\cdot OOCClHCOO^- \rightarrow 2CO_2 + H^+ + Cl^- + e^-$

$H^+ + e^- + 1/2O_2 \rightarrow 1/2H_2O_2$

Overall reaction $CClH_2COO^- + 3/2O_2 \rightarrow 2CO_2 + Cl^- + H_2O$

MCAA   mechanism 2 – Electron transfer

$1/2H_2O_2 \rightarrow \cdot OH$

$CH_2ClCOO^- + \cdot OH \rightarrow CH_2ClCOO\cdot + HO^-$

$CH_2ClCOO\cdot \rightarrow \cdot CH_2Cl + CO_2$

$\cdot CH_2Cl + O_2 \rightarrow H_2ClCOO\cdot$

$H_2ClCOO\cdot + \rightarrow CO_2 + 2H^+ + Cl^- + e^-$

$H^+ + e^- + 1/2O_2 \rightarrow 1/2H_2O_2$

Overall reaction $CH_2ClCOO^- + O_2 \rightarrow 2CO_2 + Cl^- + H_2O$

DCAA   mechanism 1 – Hydrogen abstraction

$1/2H_2O_2 \rightarrow \cdot OH$

$CCl_2HCOO^- + \cdot OH \rightarrow \cdot CCl_2COO^- + H_2O$

$\cdot CCl_2COO^- + O_2 \rightarrow \cdot OOCCl_2COO^-$

$\cdot OOCCl_2COO^- + 2H_2O \rightarrow 2CO_2 + 2Cl^- + 2H^+ + H_2O_2 + e^-$

$H^+ + e^- + 1/2O_2 \rightarrow 1/2H_2O_2$

Overall reaction $CCl_2HCOO^- + 3/2O_2 + H_2O \rightarrow 2CO_2 + 2Cl^- + H^+ + H_2O_2$

DCAA   mechanism 2 – Electron transfer

$1/2H_2O_2 \rightarrow \cdot OH$

$CHCl_2COO^- + \cdot OH \rightarrow CHCl_2COO\cdot + HO^-$

$CHCl_2COO\cdot \rightarrow \cdot CHCl_2 + CO_2$

$\cdot CHCl_2 + O_2 \rightarrow Cl_2HCOO\cdot$

$Cl_2HCOO\cdot + 2H_2O \rightarrow CO_2 + 2Cl^- + 3H^+ + H_2O_2 + e^-$

$H^+ + e^- + 1/2O_2 \rightarrow 1/2H_2O_2$

Overall reaction $CCl_2HCOO^- + 3/2O_2 + H_2O \rightarrow 2CO_2 + 2Cl^- + H^+ + H_2O_2$

TCAA   mechanism – Electron transfer

$1/2H_2O_2 \rightarrow \cdot OH$

$CCl_3COO^- + \cdot OH \rightarrow CCl_3COO\cdot + HO^-$

$CCl_3COO\cdot \rightarrow \cdot CCl_3 + CO_2$

$\cdot CCl_3 + 3/2H_2O_2 \rightarrow CO_2 + 3Cl^- + 3H^+ + 1/2O_2$

Overall reaction $CCl_3COO^- + 2H_2O_2 \rightarrow 2CO_2 + 3Cl^- + 2H^+ + H_2O + 1/2O_2$
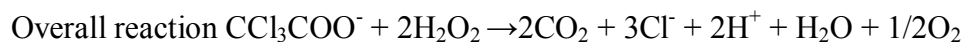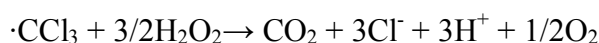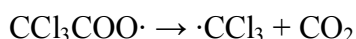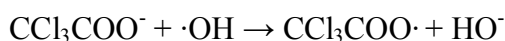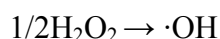
Based on postulated reaction mechanisms, no hydrogen ion would be produced from the reaction of MBAA, and ratios hydrogen ion to chloride and are 0.5 and 0.7 for DCAA and TCAA, respectively. This was consistent with the result where hydrogen ion barely increased for MCAA, and higher ratio of hydrogen ion to chloride was observed from TCAA than DCAA. In regard to the hydrogen ion balance, measured parameters were similar to expected ones calculated from postulated reaction mechanisms (Figure 4-10). Consequently, postulated

mechanisms well explain the observed production of hydrogen and chloride ion.

Table 4-5. Comparison of measured and expected parameters of chlorinated HAAs

Parameter		MCAA	DCAA	TCAA
$\Delta TOC/\Delta HAA$	Measured	2.1	2.1	2.2
	Expected*	2.0	2.0	2.0
$\Delta[H^+]/\Delta HAA$	Measured	**0.1**	**1.0**	**1.5**
	Expected*	**0.0**	**1.0**	**2.0**
$\Delta[H^+]/\Delta[Cl^-]$	Measured	**0.1**	**0.4**	**0.5**
	Expected*	**0.0**	**0.5**	**0.7**

*Theoretical ratio based on postulated mechanism

Discussion

UV photolysis mechanism of brominated HAA

Although both brominated and chlorinated HAAs can be photodegraded in water (Lifongo, Bowden et al. 2004), due to the difference in UV absorption, brominated compounds were shown to be removed by either direct UV photolysis or hydroxyl radical reaction, while chlorinated compounds were shown to only react with radical species (Fliount, Makogon et al. 1997; McGivern, Kim et al. 2004; Jo, Dietrich et al. 2008). According to the results, slightly more bromide and less hydrogen ion were produced from the UV photolysis in proportion with the number of bromine atoms in the brominated HAA molecules even though less hydrogen ion production was expected based on postulated mineralization mechanism. Based on observed incomplete mineralization of MBAA and DBAA, oxalate was proposed as a possible reaction intermediate. Oxalate formation via incomplete mineralization was able to explain more hydrogen ion production than the postulated complete mineralization mechanism, which however, needs to be further studied. In aqueous phase, homolysis of C-Br bonds of molar tribromomethane was reported to release three moles of bromide from the compound and three moles of hydrogen ion from the water while the other part of water molecule (O-H) react with the compound (Li, Kwok et al. 2004). This H-Br removal/O-H insertion mechanism could be one possible mechanism of UV photolysis of brominated HAAs. However, in many radical reactions of halogenated compounds, peroxyl radical formation was reported to occur after C-X bond cleavage (Fliount, Makogon et al. 1997;

67

Makogon, Fliount et al. 1998; Li, Stefan et al. 2004; McGivern, Kim et al. 2004). Therefore, the reaction with oxygen is more likely the second step. To elucidate the role of oxygen in this removal, oxygen was removed from the solution by purging nitrogen or helium gas before the UV irradiation. However, because realistic environmental μg/L concentrations of HAAs were used in this research, the dissolved oxygen concentration could not be lowered below the level that prevents peroxyl radical formation.

Hydroxyl radical reaction mechanism of chlorinated HAAs

  Although hydrogen abstraction is thought to be one pathway according to the observed isotope effect, electron transfer reaction is likely to be another important pathway in hydroxyl radical reaction of chlorinated HAAs based on stability and electron density on carboxylic oxygen of less chlorine substituted HAA. This is consistent with other studies where electron transfer was proposed as one of two pathways of the hydroxyl radical reaction of DCAA (Legrini, Oliveros et al. 1993; Zalazar, Labas et al. 2007). Faster removal of MCAA observed in this research is also consistent with other study that reported Kolbe reaction following electron transfer step was more effective for less halogenated HAAs due to higher electron density at the carboxyl function (Mao, Schoeneich et al. 1991).

$$CCl_2COO\cdot \rightarrow \cdot CHCl_2 + CO_2 \text{ (Kolbe mechanism)}$$
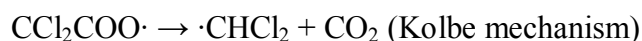
  Another consideration is the reaction of chloride and hydroxyl radical during the hydroxyl radical reaction of chlorinated HAAs ($Cl^- + \cdot OH \rightarrow Cl_2^{-\cdot} + OH^-$). Maruthamuthu et al. reported MCAA is removed faster likely because chloride reacts with hydroxyl radical producing $Cl_2^{-\cdot}$, which reacts faster with MCAA than DCAA (Maruthamuthu, Padmaja et al. 1995). Nevertheless, increased chloride ion concentrations measured in this research were equal to or greater than expected, which indicates that the reaction of chloride ion and hydroxyl radical has a minimal effect on pH change.

Future work

  In some of the reaction mechanisms postulated in this research, hydrogen peroxide was proposed as a final product. Concentration change of hydrogen peroxide needs to be measured to confirm this mechanism in the future work. In the case of incomplete mineralization of brominated HAAs, oxalate formation was proposed. To confirm oxalate formation as an incomplete mineralization, oxalate concentration also needs to be measured before and after UV photolysis in the future work.

Conclusion

Bromine substituted HAAs were photolysed producing hydrogen ion and bromide. TBAA was completely mineralized under the condition used in this research while MBAA and DBAA were partially mineralized. The C-Br bond cleavage is thought to be the first step followed by the second step, the reaction with oxygen. Interaction with a water molecule is possibly another second step. For MBAA and DBAA, more hydrogen ion was produced than postulated mineralization mechanism, which was explained by the production of oxalate via incomplete mineralization. More bromine substituted HAAs have greater reaction rates in direct UV photolysis. These results can be explained by the more C-Br bond and higher molar extinction coefficients.

Chlorine substituted HAAs were mineralized by hydroxyl radical reaction in UV/H_2O_2 process producing chloride and hydrogen ion. Molar increase ratios of chloride to decreased chlorinated HAAs were proportional to the number of chlorine in the molecules. However, unlike brominated HAAs, less chlorine substituted HAAs had greater second order reaction rate constants. Both hydrogen abstraction and electron transfer reaction were thought to be two first steps, and were able to explain the removal rate, hydrogen and chloride ion balance, and carbon balance of chlorinated HAA.

Acknowledgement

Chapter 5. Removal and Transformation of Odorous Aldehydes by UV/H₂O₂

Abstract

Removal of odorous aldehydes by UV/H$_2$O$_2$ was compared to that of geosmin and 2-MIB by the same process. Odor transformation was investigated by sensory test and byproducts were monitored by a carbonyl derivatization method. Heptadienal, decadienal, and nonadienal were removed faster than geosmin and 2-MIB. The primary mechanism was the direct UV photolysis in the UV/H$_2$O$_2$ process. In sensory tests, new odors such as chalky or sweet odors were produced while the initial odor intensity of fishy/grassy-smelling aldehydes was reduced with increasing exposure time to UV/H$_2$O$_2$. New carbonyl compounds were detected from the UV photolysis of nonadienal and were not removed by further UV irradiation, which was thought to be related with production of new odors. Results indicate that new types of odor were produced from the oxidation of odorous aldehydes, and consequently, sensory tests coupled with chemical analysis should be considered in designing oxidation process to control recalcitrant odorants.

Keywords : Odor, aldehyde, UV photolysis, UV/H₂O₂, AOP

Introduction

Recently, more interest has been focused on drinking water aesthetic issues. This trend indicates that consumers demand "more pleasant" or "more tasty" drinking water as well as safe water (Devesa, Fabrellas et al. 2004; Khiari 2004; Burlingame and Mackey 2007; Liang, Wang et al. 2007). Consumer comparison of tap water to bottled water may intensify this trend. Various efforts have been made to remove recalcitrant odorants in drinking water to prevent complaints and meet consumer standards about drinking water quality. Many researchers reported that advanced oxidation processes (AOPs), which involve hydroxyl radical, efficiently reduce earthy/musty odorants (geosmin and 2-MIB) in drinking water (Rosenfeldt, Melcher et al. 2005; Paradis and Hoffman 2006; Westerhoff, Nalinakumari et al. 2006; Jo, Dietrich et al. 2008). Odorous aldehydes such as nonadienal and heptadienal are mostly produced from algae and can cause off-flavor in drinking water, especially in the case

70

of insufficient chlorination (Burlingame, Muldowney et al. 1992; Andersson, Forsgren et al. 2005). Nonadienal had a greater reaction rate constant with hydroxyl radical than geosmin and 2-MIB (Peter and Von Gunten 2007). However, it was reported that some algal metabolites were transformed into new types of odor by oxidation (Dietrich, Hoen et al. 1995), and fruity smelling aldehyde were produced from the ozonation of drinking water (Anselme, Suffet et al. 1988; AWWARF 1995; Bruchet and Duguet 2004). Low molecular weight aldehydes, which are possible product of oxidation of unsaturated aldehyde, were considered to be related with off-flavor events (Fabrellas, Matia et al. 2004).
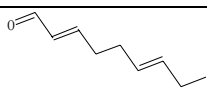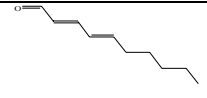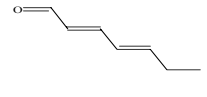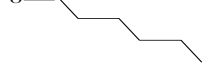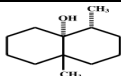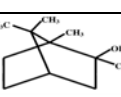
In this research, removal of odorous aldehydes by UV/H_2O_2 were compared to geosmin and 2-MIB, and odor transformation was investigated by sensory test and pentafluorobenzyl-hydroxylamine hydrochloride (PFBHA) derivatization method to detect carbonyls. The UV/H_2O_2 process performs by direct UV photolysis and hydroxyl radical reaction (Cotton and Collins 2006). Hydroxyl radical produced from the UV photolysis of hydrogen peroxide plays a key role for many reactions. However, for the compounds that greatly absorb UV, direct UV photolysis may be the main mechanism in the removal of the compounds by UV/H_2O_2 process (Nicole, De Laat et al. 1991; Qiao, Li et al. 2005; Jo, Dietrich et al. 2008). The objectives of the research were: 1) to compare removal rates of fishy/grassy smelling aldehydes to geosmin/2-MIB in UV/H_2O_2 process, 2) to elucidate the main mechanism of odorous aldehyde removal in UV/H_2O_2 process, 3) to investigate how odor intensities and descriptors change during the reaction with UV/H_2O_2, and 4) to detect intermediates and final products.

Materials and Methods

Four types of aldehydes were selected from the typical algae-related fishy/grassy odorants as well as geosmin and 2-MIB. Compounds used in this research were: *trans-2,cis-6*-nonadienal (Aldrich, 92%, CAS no. 552-48-2), hexanal (Aldrich, 98%, CAS no. 66-25-1), *trans-2,trans-4*-decadienal (TCI, 98%, CAS no. 25152-84-5), *trans-2,trans-4*-heptadienal (TCI, 90%, CAS no. 4313-03-5), geosmin (Sigma, 98%, CAS no. 16423-19-1), 2-MIB (Supelco, 99.9%, CAS no. 2371-42-8). Initial concentrations were selected based on threshold and detection limit (Watson, Satchwill et al. 2001; Satchwill, Watson et al. 2007). Structures and odor properties of these compounds are shown in Table 5-1. Experiments were performed with a 253.7 nm wavelength UV lamp of 7.2 mW/cm^2 intensity (Rayonet RPR-100) with quartz reactors. H_2O_2 concentration of 6 mg/L was used considering the optimal

range of H_2O_2 dosage in previous research (Cotton and Collins 2006; Paradis and Hoffman 2006). Samples were prepared in de-ionized water (Nanopure) and completely mixed and headspace free while being irradiated with UV. Odorants were dosed at μg/L concentrations and measured by solid-phase microextraction (SPME, Supelco) with scan mode of GC/MS (Agilent 5973) (Watson, Brownlee et al. 1999; Watson, Brownlee et al. 2000).` UV absorbances were measured at a wavelength of 253.7 nm by UV/Vis spectrophotometer (Beckman DU640). H_2O_2 concentration was determined by iodide (I_3^-) method (Klassen, Marchington et al. 1994; Rosenfeldt, Melcher et al. 2005). UV dose was verified with the iodide/iodate actinometer (Rahn 2004; Rahn, Bolton et al. 2006). Flavor Profile Analysis (FPA) was performed by four trained panelists according to the Standard Method 2170 to assess the odor intensity and investigate the change of odor descriptor (AWWA, APHA et al. 2005). In FPA, panelists smelled 8 samples per session including odor free sample, and discussed on the odor descriptors and intensities. One or two sessions were held for one compound coupled with chemical analysis. PFBHA derivatization method was used with SPME and GC/MS to detect low molecular weight carbonyl groups (aldehydes and ketones) produced from the oxidation of nonadienal (Weinberg and Glaze 1997; Bao, Pantani et al. 1998), where higher concentration (10 mg/L) of nonadienal were reacted by UV/H_2O_2 and subsequently derivatized with PFBHA.

Table 5-1. Odorants selected for this research

Compounds	Structure	Odor	Odor threshold (ng/L)	Guideline in drinking water
trans-2,cis-6-nonadienal		Cucumber/Fishy	80 [a]	-
trans-2,trans-4-decadienal		Fishy/Oily/Cucumber	300 [b]	-
trans-2,trans-4-heptadienal		Grassy/Oily/Fishy	25,000 [b]	-
Hexanal		Grassy/Sweet	4,500 [c]	-
Geosmin		Earthy	6-10 [d]	10 ng/L [e]
2-MIB		Musty	2-20 [d]	10 ng/L [e]

[a] (Young, Horth et al. 1996)

[b] (Watson, Satchwill et al. 2001)
[c] (Rychlik, Schieberle et al. 1998)
[d] (Rashash, Dietrich et al. 1997; Oestman, Schweitzer et al. 2004)
[e] Guideline in Korea and secondary standard in Japan (KNIER 2000; KMOE 2006)

Results

UV absorbance

In order to assess the contribution of direct UV photolysis, molar extinction coefficients which indicate the UV absorbance of a compound were measured as shown in Figure 5-1. Three unsaturated aldehyde compounds absorbed greater amount of UV compared to geosmin and 2-MIB. The order of molar extinction coefficient from greatest to least was heptadienal, decadienal, and nonadienal. Based on the measured molar extinction coefficients, it was expected that three unsaturated aldehyde compounds would be reduced much faster than geosmin and 2-MIB by UV photolysis. In contrast, UV absorbance of hexanal and decanal were almost zero, which indicates that removal of these compounds, if any, would be by hydroxyl radical reaction in the UV/H_2O_2 process.
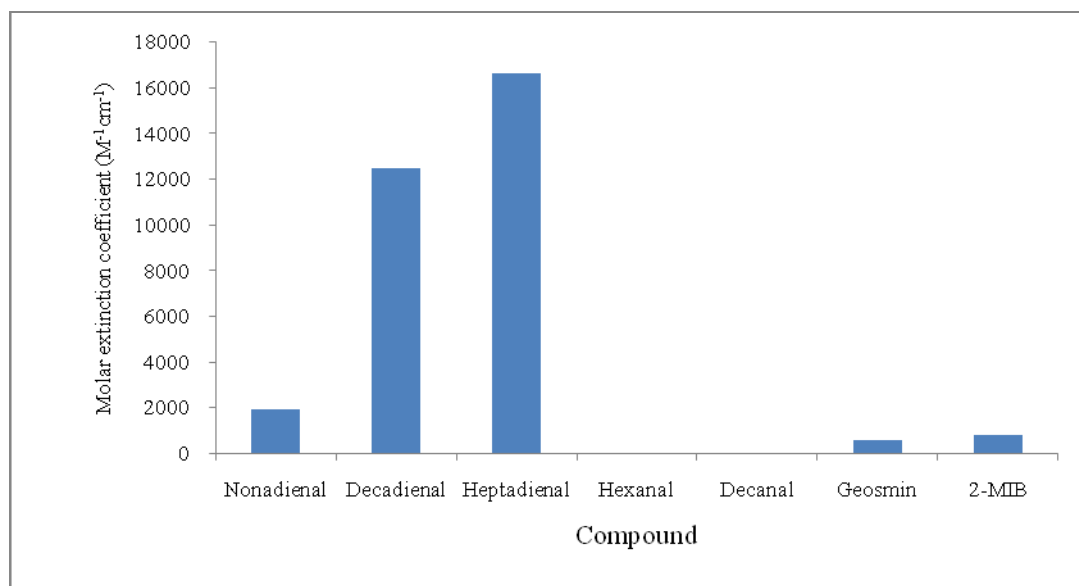
Figure 5-1. Molar extinction coefficient measured in this research ($M^{-1}cm^{-1}$)

Removal rate by UV/H$_2$O$_2$

Compared to geosmin and 2-MIB, the three "dienal" compounds were removed faster. Heptadienal was reduced faster than either nonadienal or decadienal, which is thought to be related to its higher UV absorbance. Nonadienal and decadienal had similar removal rates to each other. Hexanal was not better removed than geosmin.
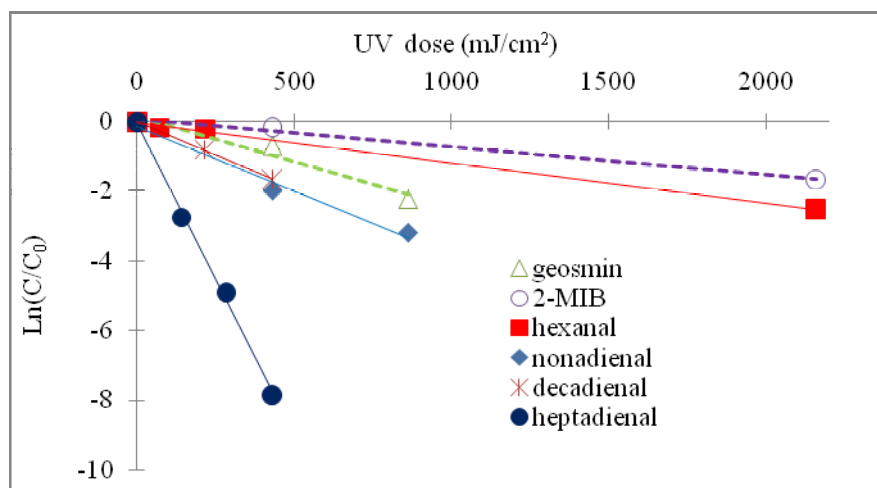
Figure 5-2. Log removal of odorants with UV dose (6 mg/L H$_2$O$_2$)

Sensory test

Sensory tests revealed that the initial odor intensity of odorous aldehydes was reduced with increasing exposure time to UV/H$_2$O$_2$. However, new types of odors were detected when the initial fishy/grassy odors were mostly or completely removed. Fishy/cucumber odor of nonadienal changed into sweet/chalky odor (Figure 5-3) as concentration of nonadienal was reduced by UV/H$_2$O$_2$. This sweet/chalky odor was thought to be produced from the oxidation of nonadienal. Oily/fishy/cucumber odor of decadienal changed into sweet/stale odor (Figure 4). Grassy/oily/fishy odor of heptadienal changed into sweet/concrete/wet cardboard odor (Figure 5-5). Grassy/sweet/pumpkin odor of hexanal changed into cement/waxy/metallic/oily odor (Figure 5-6). Consequently, in the oxidation of odorous "dienal" compounds by UV/H$_2$O$_2$, new types of odors were produced as the concentration of the original compounds and initial odors were reduced. These results indicate that the oxidation of odorous aldehyde by UV/H$_2$O$_2$ produce byproducts that have different types of odor.

74
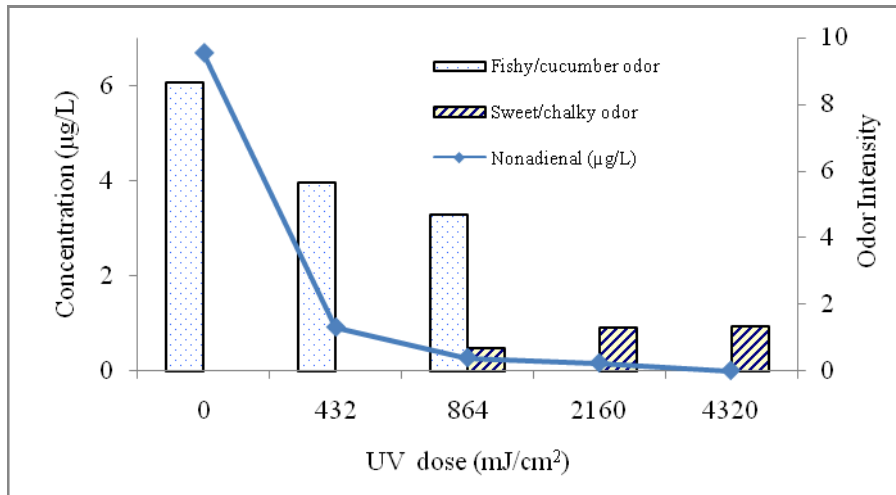
Figure 5-3. Nonadienal concentration and odors as a function of UV dose (6 mg/L H_2O_2)
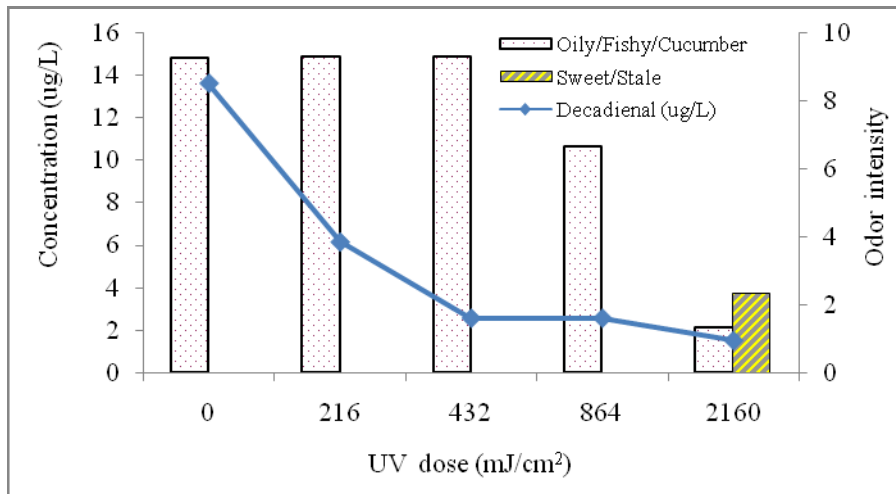
Figure 5-4. Decadienal concentration and odors as a function of UV dose (6 mg/L H_2O_2)
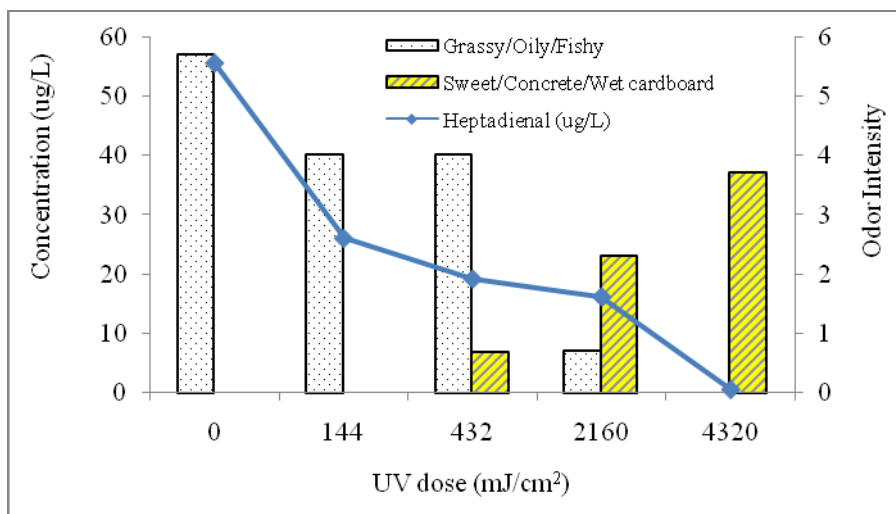
Figure 5-5. Heptadienal concentration and odors as a function of UV dose (6 mg/L H_2O_2)
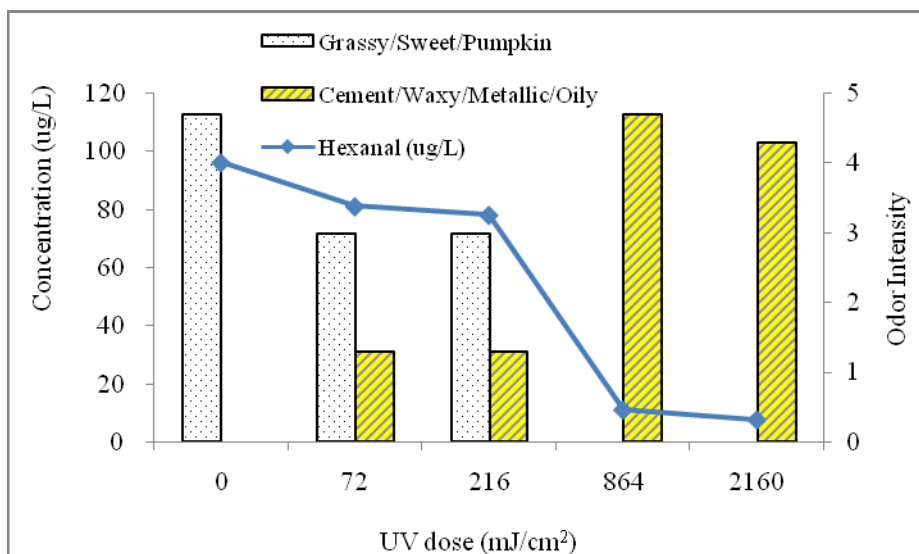
Figure 5-6. Hexanal concentration and odors as a function of UV dose (6 mg/L H_2O_2)

Result for PFBHA derivatization of nonadienal

In order to investigate the reaction mechanism and detect the intermediates or final products, a higher concentration (10 mg/L) of nonadienal was reacted by UV/H_2O_2 and then derivatized with PFBHA. Based on the derivatized chromatograms, there was no difference between UV photolysis and UV/H_2O_2 process (Figure 5-7). This result indicates that nonadienal was removed mainly by UV photolysis in UV/H_2O_2 process because UV photolysis is faster than radical reaction and the addition of hydrogen peroxide did not alter the reaction that produced carbonyls.
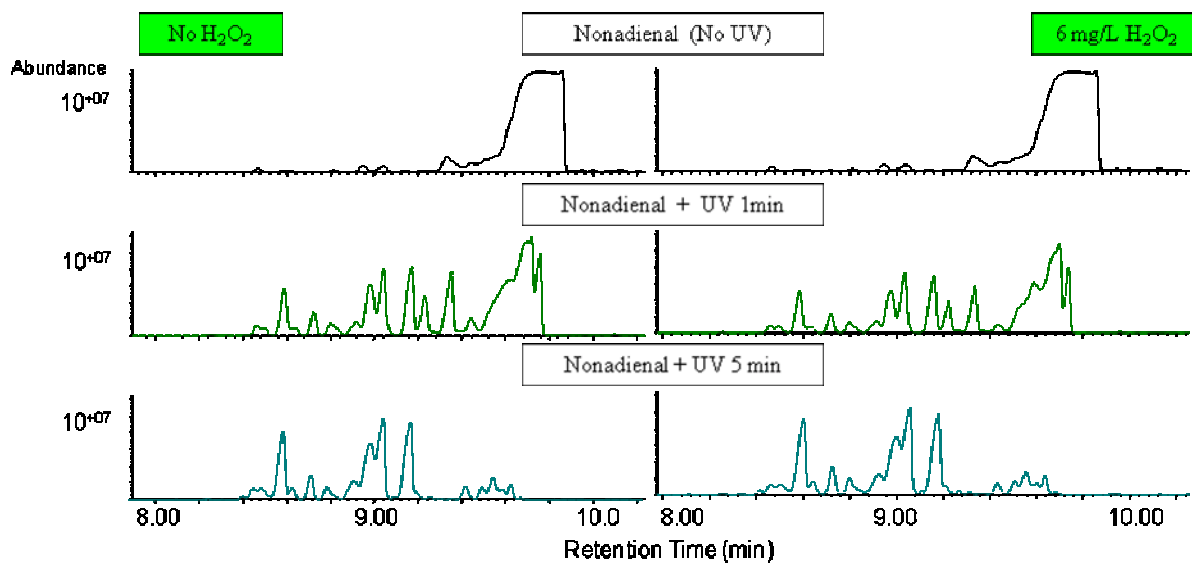
Figure 5-7. Comparison of PFBHA derivatized chromatograms for UV photolysis and UV/H$_2$O$_2$ treatment of nonadienal

Figure 5-8 shows that carbonyl groups derivatized by PFBHA (oximes) were produced from the UV irradiation of nonadienal. This result indicates that nonadienal was degraded into smaller ketone or aldehyde molecules by UV photolysis. Most of these new carbonyl groups produced from the reaction were not removed by further UV irradiation indicating that these ketone or aldehyde compounds are highly stable to UV irradiation. However, these ketones or aldyhydes were not able to be identified in this research. Further study is required to identify these carbonyl products and to detect other alcoholic or carboxyl products that may be produced.
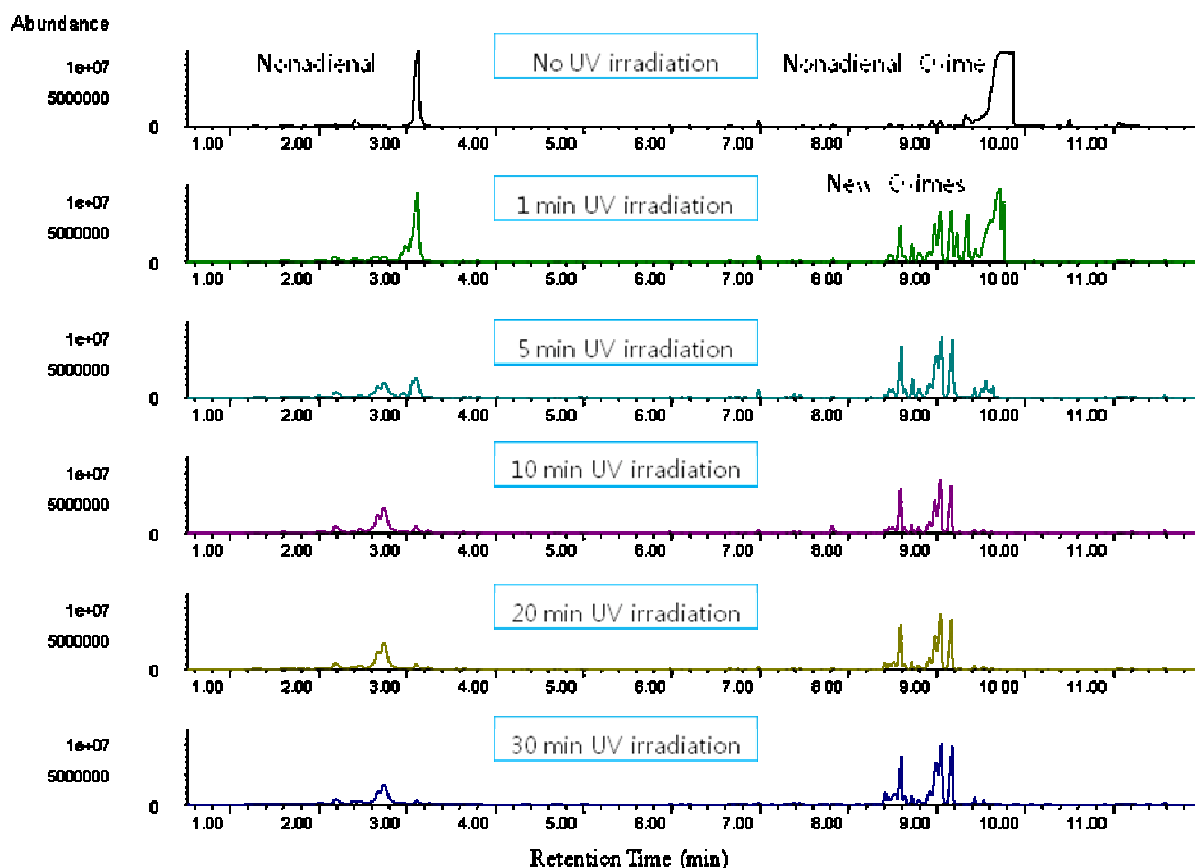
Figure 5-8. GC/MS chromatograms of PFBHA derivatized nonadienal

Discussion

According to the measured molar extinction coefficients and derivatization results, nonadienal was removed by direct UV photolysis, and a similar mechanism would be expected for decadienal and heptadienal. While UV photolysis removes fishy/grassy smelling "dienal" compounds, new types of odors were produced after the oxidation of original compounds. These transformed odors may be related to carbonyl groups produced from the UV photolysis of nonadienal, based on the result that these carbonyl groups were not removed by further UV photolysis. These results are comparable to the results of other research that reported the fruity smelling aldehydes production from the ozonation (Anselme, Suffet et al. 1988; AWWARF 1995; Bruchet and Duguet 2004). The C_4-C_{12} normal aldehydes typically have odor threshold concentrations of $< 1\mu g/L$, and are known to be problematic in drinking water (Fabrellas, Matia et al. 2004). Consequently, carbonyls produced from the reaction can be one of the causes for the new odors. However, these carbonyl groups produced by UV photolysis could not be identified and no conclusive evidence was found on

the relationship between carbonyl groups produced and new types of odors detected in the sensory test in this research. Further investigation is required to identify the reaction products, which may include functional groups other than carbonyls, such as carboxyl or alcohol groups.

Conclusion

The UV/H_2O_2 process was able to effectively reduce odorous aldehydes concentrations compared to removal of geosmin and 2-MIB. The result indicates that direct UV photolysis is the main mechanism involved in this removal. Although the concentration of odorous aldehydes were reduced by UV/H_2O_2, new types of odors were produced from these reactions, which was confirmed by sensory test. Carbonyl groups were detected from the UV photolysis of nonadienal and were not removed by further UV irradiation. These carbonyl groups were thought to be related with production of new types of odors such as chalky or sweet odor. Results indicate that new types of odor can be produced from the oxidation of odorants, and consequently sensory and chemical analysis should be considered in designing oxidation process to control recalcitrant odorants.

Acknowledgement

References

Adams, G. E., J. W. Boag, et al. (1965). <u>Absolute Rate constants for the Reaction of the Hydroxyl Radical with Organic Compounds in Pulse Radiolyisis</u>. New York, Academic Press.

Andersson, T., G. Forsgren, et al. (2005). "The effects of selected aldehydes, ketones and carboxylic acids on off-flavours in water." <u>International Journal of Food Science and Technology</u> **40**(9): 993-1004.

Anselme, C., I. H. Suffet, et al. (1988). "Effects of Ozonation on Tastes and Odors." <u>Journal American Water Works Association</u> **80**(10): 45-51.

AWWA (1991). Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water.

AWWA (1999). <u>Water Quality and Treatment</u>. New York, McGRAW-HILL, Inc.

AWWA, APHA, et al. (2005). <u>Standard Method for the Examination of Water and Wastewater</u>. Washington, DC, American Public Health Association.

AWWARF (1995). Advances in Taste-and-Odor Treatment and Control. I. H. Suffet, J. Mallevialle and E. Kawczynski, AWWARF.

Bader, H. and J. Hoign (1981). "Determination of ozone in water by the indigo method." <u>Water Research</u> **15**(4): 449-456.

Bao, M. L., F. Pantani, et al. (1998). "Determination of carbonyl compounds in water by derivatization - solid-phase microextraction and gas chromatographic analysis." <u>Journal of Chromatography A</u> **809**(1-2): 75-87.

Batterman, S., L. Zhang, et al. (2000). "Quenching of chlorination disinfection by-product formation in drinking water by hydrogen peroxide." <u>Water Research</u> **34**(5): 1652-1658.

Beltran, F. J., G. Ovejero, et al. (1993). "Oxidation of Atrazine in Water by Ultraviolet-Radiation Combined with Hydrogen-Peroxide." <u>Water Research</u> **27**(6): 1013-1021.

Bennett, J. E. and J. A. Howard (1973). "Bimolecular self-reaction of peroxy radicals. Oxygen-18 isotope study." <u>J. Am. Chem. Soc.</u> **95**(12): 4008-4010.

Bolton, J. R. and M. I. Stefan (2002). "Fundamental photochemical approach to the concepts of fluence (UV dose) and electrical energy efficiency in photochemical degradation reactions." <u>Research on Chemical Intermediates</u> **28**(7-9): 857-870.

Bruchet, A. and J. P. Duguet (2004). "Role of oxidants and disinfectants on the removal, masking and generation of tastes and odours." Water Science and Technology **49**(9): 297-306.

Buchanan, W., F. Roddick, et al. (2006). "Formation of hazardous by-products resulting from the irradiation of natural organic matter: Comparison between UV and VUV irradiation." Chemosphere **63**(7): 1130-1141.

Burlingame, G. A. and E. D. Mackey (2007). "Philadelphia obtains useful information from its customers about taste and odour quality." Water Science and Technology **55**(5): 257-263.

Burlingame, G. A., J. J. Muldowney, et al. (1992). "Cucumber Flavor in Philadelphia's Drinking Water." J. American Water Works Association.

Butkovskaya, N. I., A. Kukui, et al. (2004). "Rate Constant and Mechanism of the Reaction of OH Radicals with Acetic Acid in the Temperature Range of 229-300 K." J. Phys. Chem. A **108**(34): 7021-7026.

Carlson, D. A. e. a. (1982). Project Summary: Ultraviolet Disinfection of Water for Small Water Supplies, Environmental Protection Agency.

Cassan, D., B. Mercier, et al. (2006). "Effects of medium-pressure UV lamps radiation on water quality in a chlorinated indoor swimming pool." Chemosphere **62**(9): 1507-1513.

Cater, S. R., M. I. Stefan, et al. (2000). "UV/H2O2 treatment of methyl tert-butyl ether in contaminated waters." Environmental Science & Technology **34**(4): 659-662.

Chang, P. B. L. and T. M. Young (2000). "Kinetics of methyl tert-butyl ether degradation and by-product formation during UV/hydrogen peroxide water treatment." Water Research **34**(8): 2233-2240.

Chin, A. and P. R. Berube (2005). "Removal of disinfection by-product precursors with ozone-UV advanced oxidation process." Water Research **39**(10): 2136-2144.

Cole, S. K., W. J. Cooper, et al. (2007). "Free radical chemistry of disinfection byproducts. 2. Rate constants and degradation mechanisms of trichloronitromethane (chloropicrin)." Environmental Science & Technology **41**(3): 863-869.

Collivignarelli, C. and S. Sorlini (2004). "AOPs with ozone and UV radiation in drinking water: contaminants removal and effects on disinfection byproducts formation." Water Science and Technology **49**(4): 51-56.

Collivignarelli, C., Sorlini S. (2004). "AOPs with ozone and UV radiation in drinking water: contaminants removal and effects on disinfection byproducts formation." Water Science and Technology **49**(4): 51-56.

Cotton, C. A. and J. R. Collins (2006). Dual purpose UV light : Using UV light for Disinfection and for Taste and Odor Oxidation. 2006 WQTC, Denver, CO, USA, AWWA.

Cowman, G. A. and P. C. Singer (1996). "Effect of bromide ion on haloacetic acid speciation

resulting from chlorination and chloramination of aquatic humic substances." Environmental Science & Technology **30**(1): 16-24.

Crittenden, J. C., S. M. Hu, et al. (1999). "A kinetic model for H2O2/UV process in a completely mixed batch reactor." Water Research **33**(10): 2315-2328.

Crittenden, J. C., R. R. Trussell, et al. (2005). Water Treatment: Principles and Design. New Jersey, John Wiley and Sons.

Devesa, R., C. Fabrellas, et al. (2004). "The panel of Aigues de Barcelona: 15 years of history." Water Science and Technology **49**(9): 145-151.

Dietrich, A. M., R. C. Hoen, et al. (1995). "Oxidation of Odorous and Nonodorous Algal Metabolites by Permanganate, Chlorine, and Chlrorine dioxide." Water Science and Technology **31**(11): 223-228.

Echigo, S., S. Itoh, et al. (2004). "Contribution of brominated organic disinfection by-products to the mutagenicity of drinking water." Water Science and Technology **50**(5): 321-328.

EPA (1999). EPA Guidance manual : Alternative Disinfectants and Oxidants.

Fabrellas, C., L. Matia, et al. (2004). "Determination of odour threshold concentrations and dose-response relations in water of several minor disinfection by-products: aldehydes and alkyl nitriles." Water Science and Technology **49**(9): 267-272.

Farkas, E., I. Szilagyi, et al. (2003). "Kinetic isotope effect in the reaction of OH radical with acetone-d(6)." Reaction Kinetics and Catalysis Letters **80**(2): 351-358.

Fliount, R., O. Makogon, et al. (1997). "Radical-mediated degradation mechanisms of tribromo- and other trihalogenated acetic acids in oxygen-free solutions as studied by radiation chemistry methods." Journal of the Chemical Society-Perkin Transactions 2(8): 1535-1545.

Glaze W. H., S. R., Chauncey W., Ruth E. C., Zarnoch J. J., Aieta E. M., Tate C. H., and McGuire M.J. (1990). "Evaluating Oxidants for the Removal of Model Taste and Odor Compounds from a Municipal Water Supply." JAWWA **82**(5): 79-84.

Glaze, W. H., R. Schep, et al. (1990). "Evaluating Oxidants for the Romval of Model Taste and Odor Compound from a Municipal Water-Supply." Journal American Water Works Association **82**(5): 79-84.

Ho, L., J. P. Croue, et al. (2004). "The effect of water quality and NOM character on the ozonation of MIB and geosmin." Water Science and Technology **49**(9): 249-255.

Ho, L., G. Newcombe, et al. (2002). "Influence of the character of NOM on the ozonation of MIB and geosmin." Water Research **36**: 511-518.

Hyun, K. S., Y. J. Kim, et al. (2005). "Profiles of THM and HAAs in the process of Water

Treatment Plants." Journal of Korean Society of Water Science and Technology **13**(1): 55-66.

Jo, C. H., A. M. Dietrich, et al. (2008). Simultaneous Removal of DBPs and Odorants by UV/H2O2 Advanced Oxidation Process

Jüttner, F. and S. B. Watson (2007). "Biochemical and Ecological Control of Geosmin and 2-Methylisoborneol in Source Waters." Applied and Environmental Microbiology **73**(14): 4395-4406.

Khiari, D. (2004). "AWWA's Taste and Odor Committee seeks to understand and solve taste and odor problems in drinking water." Journal American Water Works Association **96**(2): 32-+.

Klassen, N. V., D. Marchington, et al. (1994). "H2O2 Determination by the I-3(-) Method and by KMNO4 Titration." Analytical Chemistry **66**(18): 2921-2925.

KMOE (2006). Tasty water guideline report, Korean Ministry of Environment

KNIER (2000). Comparison of global drinking water quality standards, Korea National Institute of Environmental Research.

Kochany, J. and J. R. Bolton (1992). "Mechanism of Photodegradation of Aqueous Organic Pollutants .2. Measurement of the Primary Rate Constants for Reaction of OH Radicals with Benzene and Some Halobenzenes using an EPR Spin-Trapping Method following the Photolysis of H2O2." Environmental Science & Technology **26**(2): 262-265.

Krasner, S. W., M. J. McGuire, et al. (1985). "Tastes and Odors - The Flavor Profile Method." Journal American Water Works Association **77**(3): 34-39.

Krasner, S. W., M. J. McGuire, et al. (1989). "The Occurrence of Disinfection By-products in US Drinking Water." Journal American Water Works Association **81**(8): 41-53.

Krasner, S. W., H. S. Weinberg, et al. (2006). "Occurrence of a new generation of disinfection byproducts." Environmental Science & Technology **40**(23): 7175-7185.

Kusakabe, K., S. Aso, et al. (1990). "Decomposition of Humic-Acid and Reductin of Trihalomethane Formation Potential in Water by Ozone with UV Irradiation." Water Research **24**(6): 781-785.

Lagoa, A. L. C., H. P. Diogo, et al. (2001). "Energetics of C-Cl, C-Br, and C-I bonds in haloacetic acids: Enthalpies of formation of XCH2COOH (X = Cl, Br, I) compounds and the carboxymethyl radical." Chemistry-a European Journal **7**(2): 483-489.

Lawless, H. T. and H. Heymann (1999). Sensory Evaluation of Food. New York, Chapman & Hall.

Lay, Y. S. (1989). Oxidation of 1,2-dibromo-3-chloropropane in ground water using advanced oxidation processes. Los Angeles, University of California. **Ph.D**.

Legrini, O., E. Oliveros, et al. (1993). "Photochemical Processes for Water-Treatment." Chemical Reviews **93**(2): 671-698.

Li, K., M. I. Stefan, et al. (2004). "UV Photolysis of Trichloroethylene: Product Study and Kinetic Modeling." Environ. Sci. Technol. **38**(24): 6685-6693.

Li, Y., Y. Xie, et al. (2006). "Photocatalytic hydrogen generation in the presence of chloroacetic acids over Pt/TiO2." Chemosphere **63**(8): 1312-1318.

Li, Y. L., W. M. Kwok, et al. (2004). "Water-catalyzed dehalogenation reactions of isobromoform and its reaction products." Abstracts of Papers of the American Chemical Society **227**: U316-U316.

Liang, C. Z., D. S. Wang, et al. (2007). "Kinetics analysis on the ozonation of MIB and geosmin." Ozone-Science & Engineering **29**(3): 185-189.

Liao, C.-H. and M. D. Gurol (1995). "Chemical Oxidation by Photolytic Decomposition of Hydrogen Peroxide." Environmental Science & Technology **29**(12): 3007-3014.

Lifongo, L. L., D. J. Bowden, et al. (2004). "Photodegradation of haloacetic acids in water." Chemosphere **55**(3): 467-476.

Liu, W., S. A. Andrews, et al. (2003). "Optimal methods for quenching H2O2 residuals prior to UFC testing." Water Research **37**: 3697-3703.

Louis, F., C. A. Gonzalez, et al. (2000). "An ab initio study of the kinetics of the reactions of halomethanes with the hydroxyl radical. 1. CH2Br2." Journal of Physical Chemistry A **104**(13): 2931-2938.

Louis, F., C. A. Gonzalez, et al. (2000). "An ab initio study of the kinetics of the reactions of halomethanes with the hydroxyl radical. 2. A comparison between theoretical and experimental values of the kinetic parameters for 12 partially halogenated methanes." Journal of Physical Chemistry A **104**(38): 8773-8778.

Louis, F., C. A. Gonzalez, et al. (2001). "An ab initio study of the kinetics of the reactions of halomethanes with the hydroxyl radical. 3. Kinetic parameters predictions for the potential halon replacements CH2FBr, CHFBr2, CHFClBr, CHCl2Br, and CHClBr2." Journal of Physical Chemistry A **105**(9): 1599-1604.

Louis, F., C. A. Gonzalez, et al. (2004). "Direct combined ab initio/transition state theory study of the kinetics of the abstraction reactions of halogenated methanes with hydrogen atoms." Journal of Physical Chemistry A **108**(47): 10586-10593.

Makogon, O., R. Fliount, et al. (1998). "Formation and Degradation of Halogenated Organic Acids. Radiation versus Photocatalytically Induced Processes." Journal of Advanced Oxidation Technology **3**(1): 11-21.

Mao, Y., C. Schoeneich, et al. (1991). "Identification of organic acids and other intermediates

in oxidative degradation of chlorinated ethanes on titania surfaces en route to mineralization: a combined photocatalytic and radiation chemical study." J. Phys. Chem. **95**(24): 10080-10089.

Martijn, B. J., J. C. Kruithof, et al. (2006). UV/H2O2 treatment : The ultimate solution for organic contaminant control and primary disinfection. Water Quality Technology Conference, Denver, American Water Works Association.

Maruthamuthu, P., S. Padmaja, et al. (1995). "Rate Constants for Some Reactions of Free-radicas with Haloacetates in Aqueous-solution." International Journal of Chemical Kinetics **27**(6): 605-612.

McGivern, W. S., A. Derecskei-Kovacs, et al. (2000). "Computationally efficient methodology to calculate C-H and C-X (X = F, Cl, and Br) bond dissociation energies in haloalkanes." Journal of Physical Chemistry A **104**(2): 436-442.

McGivern, W. S., A. Derecskei-Kovacs, et al. (2000). "Computationally efficient methodology to calculate C-H and C-X (X = F, Cl, and Br) bond dissociation energies in haloalkanes (vol 104A, pg 436, 2000)." Journal of Physical Chemistry A **104**(33): 7916-7916.

McGivern, W. S., J. S. Francisco, et al. (2002). "Investigation of the atmospheric oxidation pathways of bromoform: Initiation via OH/Cl reactions." Journal of Physical Chemistry A **106**(26): 6395-6400.

McGivern, W. S., H. J. Kim, et al. (2004). "Investigation of the atmospheric oxidation pathways of bromoform and dibromomethane: Initiation via UV photolysis and hydrogen abstraction." Journal of Physical Chemistry A **108**(35): 7247-7252.

Meilgaard, M., G. V. Civille, et al. (1999). Sensory Evaluation Techniques. New York, CRC press.

Mezyk, S. P., T. Helgeson, et al. (2006). "Free radical chemistry of disinfection-byproducts. 1. Kinetics of hydrated electron and hydroxyl radical reactions with halonitromethanes in water." Journal of Physical Chemistry A **110**(6): 2176-2180.

Michael, S. E. and U. Von Gunten (1999). "Hydroxyl Radical/Ozone Ratios During Ozonation Processes. The R_{ct} Concept." Ozone-Science & Engineering **21**: 239-260.

Milano, J. C., C. Bernatescallon, et al. (1990). "Photolysis of 1,2-dibromo-3-chloropropane in Water." Water Research **24**(5): 557-564.

Muller, J. P., C. Gottschalk, et al. (2001). "Comparison of advanced oxidation processes in flow-through pilot plants (Part II)." Water Science and Technology **44**(5): 311-315.

Muller, L. P. and M. Jekel (2001). "Comparison of advanced oxidation processes in flow-through pilot plants (Part I)." Water Science and Technology **44**(5): 303-309.

Murray, C. A. and S. A. Parsons (2004). "Comparison of AOPs for the removal of natural organic matter: performance and economic assessment." Water Science and Technology

49(4): 267-272.

Nakatani, N., N. Hashimoto, et al. (2007). "Determination of photoformation rates and scavenging rate constants of hydroxyl radicals in natural waters using an automatic light irradiation and injection system." Analytica Chimica Acta **581**(2): 260-267.

National Water Research Institute, N. (2000). Treatment Technologies for Removal of Methyl Tertiary Butyl Ether (MTBE) from drinking water. G. Melin.

Nicole, I., J. De Laat, et al. (1991). "Degradation of Trihalomethanes in dilute aqueous solution by UV irradiation - Determination of the quantum yield of photolysis at 253.7 nm." Environmental Technology **12**: 21-31.

Nikolaou, A. D., S. K. Golfinopoulos, et al. (2002). "Determination of haloacetic acids in water by acidic methanol esterification-GC-ECD method." Water Research **36**(4): 1089-1094.

Oestman, E., L. Schweitzer, et al. (2004). "Effects of chlorine and chloramines on earthy and musty odors in drinking water." Water Science and Technology **49**(9): 153-159.

Oppenlander, T. (2003). Photochemical Purification of Water and Air, Wiley-VHC.

Paradis, N. and A. Hoffman (2006). Mitigation of Taste and Odour Compounds by UV/H2O2 Advanced Oxidation. 2006 WQTC, Denver, CO, USA, AWWA.

Parsons, A. F. (2000). An introduction to free radical chemistry. Malden, MA, USA, Blackwell Science Ltd.

Paul, H., R. D. Small, et al. (1978). "Hydrogen Abstraction bY Tert-Butoxy radicals - Laser photolysis and Electron-Spin Resonance Study." Journal of the American Chemical Society **100**(14): 4520-4527.

Pereira, V. J., H. S. Weinberg, et al. (2007). "UV Degradation Kinetics and Modeling of Pharmaceutical Compounds in Laboratory Grade and Surface Water via Direct and Indirect Photolysis at 254 nm." Environ. Sci. Technol. **41**(5): 1682-1688.

Peter, A. and U. Von Gunten (2007). "Oxidation kinetics of selected taste and odor compounds during ozonation of drinking water." Environmental Science & Technology **41**(2): 626-631.

Qiao, R. P., N. Li, et al. (2005). "Degradation of microcystin-RR by UV radiation in the presence of hydrogen peroxide." Toxicon **45**(6): 745-752.

Rahn, R. O. (2004). "Spatial distribution of upper-room germicidal UV radiation as measured with tubular actinometry as compared with spherical actinometry." Photochemistry and Photobiology **80**(2): 346-350.

Rahn, R. O., J. Bolton, et al. (2006). "The iodide/iodate actinometer in UV disinfection: Determination of the fluence rate distribution in UV reactors." Photochemistry and Photobiology **82**(2): 611-615.

Rashash, D. M. C., A. M. Dietrich, et al. (1997). "FPA of selected odorous compounds." Journal American Water Works Association **89**(4): 131-141.

Rashash, D. M. C., A. M. Dietrich, et al. (1995). "The Influence of Growth-conditions on Odor-compound Production by 2 Chrysophytes and 2 Cyanobacteria." Water Science and Technology **31**(11): 165-172.

Richardson, S. D., M. J. Plewa, et al. (2007). "Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research." Mutation Research-Reviews in Mutation Research **636**: 178-242.

Richardson, S. D., A. D. Thruston, et al. (2003). "Tribromopyrrole, Brominated Acids, and Other Disinfection Byproducts Produced by Disinfection of Drinking Water Rich in Bromide." Environ. Sci. Technol. **37**(17): 3782-3793.

Rosenfeldt, E. J. and K. G. Linden (2007). "The R-OH,R-UV concept to characterize and the model UV/H2O2 process in natural waters." Environmental Science & Technology **41**(7): 2548-2553.

Rosenfeldt, E. J., B. Melcher, et al. (2005). "UV and UV/H2O2 treatment of methylisoborneol (MIB) and geosmin in water." Journal of Water Supply Research and Technology-Aqua **54**(7): 423-434.

Rosenfeldt, E. J., Melcher Barbara, and Linden, Karl G. (2005). "UV and UV/H2O2 treatment of methylisoborneol(MIB) and geosmin in water." Journal of Water Supply Research and Technology-Aqua **54**(7): 423-434.

Royce, A. and M. I. Stefan (2005). Application of UV in Drinking Water Treatment for Simultaneous Disinfection and Removal of Taste and Odor Compounds. 2005 WQCT, AWWA.

Royce, A. and M. I. Stefan (2005). Application of UV in drinking water treatment for simultaneous disinfection and removal of taste and odor compounds.

Rudra, A., N. P. Thacker, et al. (2005). "Hydrogen peroxide and ultraviolet irradiations in water treatment." Environmental Monitoring and Assessment **109**(1-3): 189-197.

Russell, G. A. (1957). "Deuterium-isotope Effects in the Autoxidation of Aralkyl Hydrocarbons. Mechanism of the Interaction of PEroxy Radicals." J. Am. Chem. Soc. **79**(14): 3871-3877.

Rychlik, M., P. Schieberle, et al. (1998). Compilation of Odor Threshold, Odor Qualities and Retention Indices of Key Food Odorants.

Sarathy, S., Mohseni, M. (2006). "An Overview of UV-based Advanced Oxidation Processes from Drinking Water Treatment." IUVA News **8**(2): 16-27.

Satchwill, T., S. B. Watson, et al. (2007). "Odourous algal-derived alkenes: differences in

stability and treatment responses in drinking water." Water Science and Technology **55**(5): 95-102.

Sharpless, C. M. and K. G. Linden (2003). "Experimental and model comparisons of low- and medium-pressure Hg lamps for the direct and H2O2 assisted UV photodegradation of N-nitrosodimethylamine in simulated drinking water." Environmental Science & Technology **37**(9): 1933-1940.

Shemer, H. and K. G. Linden (2006). "Degradation and by-product formation of diazinon in water during UV and UV/H2O2 treatment (vol 136, pg 553, 2003)." Journal of Hazardous Materials **138**(3): 638-638.

Singer, P. C. (2002). "Occurrence of haloacetic acids in chlorinated drinking water." 3rd World Water Congress: Drinking Water Treatment **2**(5-6): 487-492.

Song, W. and K. E. O'Shea (2007). "Ultrasonically induced degradation of 2-methylisoborneol and geosmin." Water Research **41**: 2672-2678.

Spangenberg, D., U. M?ler, et al. (1996). "Photooxidation of exhaust pollutants IV. Photocatalytic and thermal decomposition of trichloroacetic acid: degradation efficiencies and products." Chemosphere **33**(1): 43-49.

Stefan, M. I. and J. R. Bolton (1998). "Mechanism of the degradation of 1,4-dioxane in dilute aqueous solution using the UV hydrogen peroxide process." Environmental Science & Technology **32**(11): 1588-1595.

Stefan, M. I., A. R. Hoy, et al. (1996). "Kinetics and mechanism of the degradation and mineralization of acetone in dilute aqueous solution sensitized by the UV photolysis of hydrogen peroxide." Environmental Science & Technology **30**(7): 2382-2390.

Stefan, M. I., J. Mack, et al. (2000). "Degradation pathways during the treatment of methyl tert-butyl ether by the UV/H2O2 process." Environmental Science & Technology **34**(4): 650-658.

Suffet, I. H., D. Khiari, et al. (1999). "The drinking water taste and odor wheel for the millennium: Beyond geosmin and 2-methylisoborneol." Water Science and Technology **40**(6): 1-13.

TrojanUV (2003). Design considerations**:** 35-43.

TrojanUV (2003). Understanging EEO : Water Quality Impacts**:** 35-43.

U.S. EPA (1995). EPA method 552.22. Cincinnati, U.S. Environmental Protection Agency.

Vimal, D. and P. S. Stevens (2006). "Experimental and theoretical studies of the kinetics of the reactions of OH radicals with acetic acid, acetic acid-d(3) and acetic acid-d(4) at low pressure." Journal of Physical Chemistry A **110**(40): 11509-11516.

Vohringer-Martinez, E., B. Hansmann, et al. (2007). "Water Catalysis of a Radical-Molecule

Gas-Phase Reaction." Science **315**(5811): 497-501.

von Gunten, U. and J. Hoigne (1994). "Bromate Formation During Ozonation of Bromide-Containing Waters - Interaction of Ozone and Hydroxyl Radical Reactions." Environmental Science & Technology **28**(7): 1234-1242.

Wang, G. S., S. T. Hsieh, et al. (2000). "Destruction of humic acid in water by UV light - Catalyzed oxidation with hydrogen peroxide." Water Research **34**(15): 3882-3887.

Watson, S. B., B. Brownlee, et al. (2000). "Quantitative analysis of trace levels of geosmin and MIB in source and drinking water using headspace SPME." Water Research **34**(10): 2818-2828.

Watson, S. B., B. Brownlee, et al. (1999). "The use of solid phase microextraction (SPME) to monitor for major organoleptic compounds produced by chrysophytes in surface waters." Water Science and Technology **40**(6): 251-256.

Watson, S. B., T. Satchwill, et al. (2001). "Under-ice blooms and source-water odour in a nutrient-poor reservoir: biological, ecological and applied perspectives." Freshwater Biology **46**(11): 1553-1567.

Weinberg, H. S. and W. H. Glaze (1997). "A unified approach to the analysis of polar organic by-products of oxidation in aqueous matrices." Water Research **31**(7): 1555-1572.

Westerhoff, P., B. Nalinakumari, et al. (2006). "Kinetics of MIB and geosmin oxidation during ozonation." Ozone-Science & Engineering **28**(5): 277-286.

White, G. C. (1992). Handbook of Chlorination and Alternative Disinfectants. New York, Van Nostrand Reinhold.

Wu, C., D. Wei, et al. (2001). "Photosonochemical degradation of trichloroacetic acid in aqueous solution." Chemosphere **44**(5): 1293-1297.

Xu, B., N. Y. Gao, et al. (2007). "Photochemical degradation of diethyl phthalate with UV/H2O2." Journal of Hazardous Materials **139**(1): 132-139.

Yokohata, A., T. Ohmura, et al. (1969). "A Dechlorination Reaction in the Radiolysis of Aqueous Monochloroacetic acid Solutions in the presence of Nitrous Oxide." Journal of Physical Chemistry **73**(11): 4013-4014.

Young, W. F., H. Horth, et al. (1996). "Taste and odour threshold concentrations of potential potable water contaminants." Water Research **30**: 331-340.

Zalazar, C. S., M. D. Labas, et al. (2007). "Dichloroacetic acid degradation employing hydrogen peroxide and UV radiation." Chemosphere **66**(5): 808-815.

Zhang, L., W. A. Arnold, et al. (2004). "Kinetics of haloacetic acid reactions with Fe(0)." Environmental Science & Technology **38**(24): 6881-6889.

Zhao, C. Y., X. F. Lin, et al. (2005). "Water-catalyzed dehalogenation reactions of the isomer of CBr4 and its reaction products and a comparison to analogous reactions of the isomers of di- and trihalomethanes." <u>Chemistry-a European Journal</u> **11**(4): 1093-1108.