TREATMENT OF TASTE AND ODOR COMPOUNDS

IN OKLAHOMA SURFACE WATER

By

QIAN ZHAO

Bachelor of Science in Civil and Environmental

Engineering

Shenyang Architecture University

Shenyang, Liaoning, China

2009

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
December, 2012

TREATMENT OF TASTE AND ODOR COMPOUNDS

IN OKLAHOMA SURFACE WATER

Thesis Approved:

Dr. Gregory G. Wilber
_____
Thesis Adviser

Dr. Dee Ann Sanders
_____

Dr. William F. McTernan
_____

ACKNOWLEDGEMENTS

I would like to express my gratitude to many people who have contributed to the information presented in my thesis. First of all, I thank Dr. Gregory G. Wilber, my thesis advisor and committee chair, who offered me an opportunity to pursue the master's research under his guidance. He has been extremely helpful and supportive of my work and provided valuable advice throughout my thesis. His endless guidance, patience, knowledge, time, and faith made this study possible. I appreciate his time on reviewing my study and making revisions. This study work would not have been possible without his help.

I also thank my committee members, Dr. Dee Ann Sanders and Dr. William F. McTernan, for serving on my committee. I appreciate their time on reviewing my thesis drafts and helping me improve, refine, and expand this study. During my graduate education, both of them inspire me in my graduate course works and provide me their best guidance, valuable feedbacks, and extensive knowledge.

In addition, I specially thank Hanbai Park, my fellow researcher and dear friend. He provided me his best support and co-operation for my thesis. Without his guidance, help, and co-operation, this study could not been done. Many thanks for his valuable suggestion, endless inspiration, and best support.

Last, but not the least, I would like to thank all my family members, especially my father Haicheng Zhao and mother Yue Hong for their unconditional love and support all the time. They make all these come true. I also wish to express my gratitude to my

girlfriend Daijiazi Tang, my cousins Mingming Feng, Hongbin Cui, Hong Liu, Zhenhua Sang, Yun Hong, Meizi Jin, and Liang Wang for their understanding, endless love, and emotional support over the past three years.

I owe my deepest gratitude towards Oklahoma State University for offering students like me a chance to work with so much great facilities. Without the support of OSU, this and many other projects like this would just be a distant reality for aspiring engineers.

Name: QIAN ZHAO

Date of Degree: DECEMBER, 2012

Title of Study: TREATMENT OF TASTE AND ODOR COMPOUNDS IN
                OKLAHOMA SURFACE WATER

Major Field: CIVIL ENGINEERING

Abstract: Taste and odor problems in drinking water have been addressed more and more by water utilities around the world. Consumer complaints must be considered by most drinking water treatment plants. A number of studies investigated that geosmin and 2-MIB are major compounds that cause these taste and odor problems in drinking water. The sources of geosmin and 2-MIB are cyanobacteria and actinomycetes. These two bacteria cause earthy and musty odor in drinking water. Although this unpleasant odor can be detected by consumers, currently, there are no regulations on geosmin and 2-MIB since these compounds are not threats to public health. The most successful treatment technologies used by most water treatment plants to remove geosmin and 2-MIB in drinking water are granular/powdered activated carbon (GAC/PAC), advanced oxidation processes (AOP), biofiltration, and other integrated systems. However, these methods are very expensive to install, maintain, and operate. For current and further studies, more efficient and economic taste and odor control technologies need to be addressed and investigated. Algaecides are used to stop the growth of algae; however, recent studies reported that the application of EarthTec®, an example of algaecides, resulted in effective removal of geosmin and 2-MIB in drinking water. Also, Tulsa water treatment plant found that EarthTec® has shown excellent abilities to remove these compounds in lakes. Therefore, this study investigated on algaecide removal of geosmin and 2-MIB in drinking water. Three experiments were conducted and compared. The results found that sorption and biodegradation in the study lake does not result in significant removal of geosmin and 2-MIB. The recommended EarthTec® dosage and twice that dosage water samples without agitation found no significant contribution on the removal of geosmin and 2-MIB. However, the unfiltered lake water with EarthTec® and agitation removed 76.58% geosmin and 78.64% 2-MIB, respectively, over 48 hours.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure   Page

CHAPTER I

INTRODUCTION

1.1 Overview

Taste and odor problems in drinking water have been addressed more and more by water utilities around the world. Consumer complaints must be addressed by most drinking water treatment plants since these problems may threaten the quality and safety of drinking water. Many researchers found that numerous taste and odor compounds, including geosmin and 2-methylisoborneol (2-MIB), make major contributions to this problem (Pirbazari *et al.*, 1993). These compounds are metabolites of actinomycetes and cyanobacteria, low molecular weight volatile tertiary alcohols mostly from blue-green algae and fungus.

Currently, there are no regulations for geosmin and 2-MIB, which are not harmful; however, their presence in drinking water results in aesthetically unpleasant odors. This unpleasant odor in drinking water may deteriorate the reliability of and consumers` trust on water quality. Eventually, it may cause people to switch to alternate drinking water sources, such as bottled water (Watson, 2004).

Many studies have focused on the removal of geosmin and 2-MIB from drinking

water sources; however, these taste and odor-causing compounds are challenging to remove due to their extremely low odor threshold concentrations (OTC), about 1–10 ng/L for geosmin and 4–12 ng/L for 2-MIB (McGuire *et al.*, 1981; Young *et al.*, 1996). Taste and odor-causing compounds show relatively strong resistance to chemical and biological degradation and can persist in dissolved form in water sources (Juttener and Watson, 2007). Therefore, conventional water treatment processes, such as coagulation, sedimentation, and filtration are not effective for the removal of geosmin and 2-MIB.

However, granular/powdered activated carbon (GAC/PAC), advanced oxidation processes (AOP), biofiltration, and other integrated systems have been found to present effective removal of geosmin and 2-MIB and are applied on many water utilities (Srinivasan and Sorial, 2011). The analytical technique used to determine concentrations of geosmin and 2-MIB is solid-phase microextraction (SPME) with gas chromatography/mass spectrometry (GC/MS). A manual assembly SPME with an extraction fiber coated on the outside is an advanced extraction method due to its promptness, potable, and solvent-free (Saito *et al.*, 2008).

Recently, some studies have been investigating the removal of taste and odor-causing compounds, geosmin and 2-MIB, by algaecides. Schweitzer and Ekstrom (2006) found that EarthTec® application resulted in effective removal of these compounds, especially with geosmin. In Tulsa, Oklahoma at one water treatment plant, EarthTec® has shown excellent abilities to remove geosmin and 2-MIB in lakes. Therefore, the assumption that EarthTec® and other similar copper-based algaecides have abilities to remove taste and odor-causing compounds can be made based on these results. Further studies need to be explored to provide accurate evidence about this assumption.

1.2 Objectives

The major objectives for this study are to investigate the parameters that affect the removal of geosmin and 2-MIB and to find the reaction between algaecides, especially EarthTec®, and geosmin and 2-MIB.

➢ To investigate geosmin and 2-MIB reactions under various conditions and to identify the optimum parameters, such as pH, algaecide, sunlight, and temperature.

➢ To investigate geosmin and 2-MIB loss mechanisms including volatilization, photolysis, sorption, and/or biodegradation and examine.

CHAPTER II

REVIEW OF LITERATURE

2.1 Taste and odor compounds

Taste and odor (T&O) problems cause common concerns of water quality for water utilities (Lalezary *et al.*, 1984, 1986). It associates with the reliability and safety of drinking water. Presence of this problem may result in decreased consumer trust and eventually cause decreased water consumption since the public switch to use alternate drinking water sources, such as bottled water and in-home treatment systems (Srinivasan and Sorial, 2011). A large number of volatile organic compounds (VOCs) causing T&O problems can be identified from algal cultures or water samples and are listed in Table 2-1. However, the most prevalent T&O customer complaints are earthy-musty odors, which are primarily the result of two T&O-causing compounds, geosmin (trans-1,10-dimethyl-trans-9 decalol, $C_{12}H_{22}O$) and 2-MIB (2-methyl isoborneol, $C_{11}H_{20}O$), in drinking water obtained from surface water sources (Pirbazari *et al.*, 1993). These two compounds are secondary metabolites of actinomycetes (soil bacteria) and *Cyanobacteria* (blue green algae) (Mamba *et. al.*, 2007). The identification, quantification, and control of these compounds from water are essential since these compounds impact the aesthetic quality and consumer acceptability of drinking water (Sung *et al.*, 2005).

Table 2-1 Survey of major odor compounds identified from algal cultures or field samples

α-Campholene	Isopropyl thiol	Methyl *n*-valerate
γ-Cadinene	Isopropyl trisulfide	Octan-3-ol
Camphor	Isopropyl methyl disulfide	*n*-Heptanal
Chlorophene	Methyl 2-methyl propanethiolate	Octa-1,5-dien-3-ol
Cieneol	Methyl 3-disulfide	Oct-1-ene
Trimethyl	Methyl mercaptan	*n*-Heptanal
Cyclohex-1-ene	Methylbutane	Octene
β-Cyclocitral	Methylethane thiolate	Octane
Hydroxy- β -cylocitral	2,4-Heptadienal	Oct-1-en-3-one
Cyclohexanone	2,4-Decadienal	Ectocarpene
Dihydrotrimethylnapthalene	2,4 –Nonadienal	Dictyopterene A'
Dihydroactinidiolide	2,6 –Nonadienal	Dictyopterene C'
α -Ionone	2-Octene	*n*-Nonadecane
β -Ionone	Oct-1-en-3-ol	*n*-Heptadecane
Geosmin	1,3,5-Octatriene	Heptadec-5-ene
Geranyl acetone	2,4 –Octadienal	2-Pentenal
Geraniol	2-Furfural	Octan-1-ol
Germacrene-D	Propenal	Oct-2-en-1-ol
Limonene	Hexan-1-ol	Isobutyrate
Linalool	*n*-Hexanal	Methyl acetate
Menthone	3-Hexen-1-ol	Methyl butanoate
Methyl gerianate	Pent-1-en-3-one	2-Methyl propan-1-ol
Myrcene	1-Pentanol	3-Methyl butanal
2-Methylisoborneol	*n*-Heptane	2-Methyl but-2-en-1-ol
6-Methyl-5-hepten-2-one	2,4,7-Decatrienal	2-Pentylfuran
6-Methyl-5-hepten-2-ol	Undecan-2-one	2-Methylpent-2-enal
3-Methylbut-2en-1-ol	Heptan-1-ol	3-Methyl -1-butanol
4-Methylpent-3-en-2-one	Pent-1-en-3-ol	3-Methylbut-2-enal
Nerol	Octene	3-Methylbutan-2-one
Phytol	Actetaldehyde	Butanone
Squalene	Heptadec-5-ene	Isobutyl alcohol
Skatol	Heptan-2-ol	Ethyl propionate
Styrene	*n*-Hexanol	Isobutyl acetate
Trimethylcyclohex-2-en-1-one	Octan-3-ol	Isopropyl alcohol
γ -Terpinene	Octan-3-one	Methyl 2-methyl formate
Isopropyl disulfide	Octadecene	Methylbutanoate
Dimethyl sulfide	*n*-Octadecane	2,4,6-Trichloroanisole
Dimethyl trisulfide	*n*-Hexanol	
Dimethyl tetrasulfide	2-Octenal	
	1,3-Octadiene	

(Watson, 1999, 2003)

Geosmin is an organic compound isolated by Gerber and Lechevalier (1965) with molecular formula of $C_{12}H_{22}O$ and molecular weight of 182.3 g/mol. The molecular structure of this compound shows a bicyclic tertiary alcohol in Figure 2-1. Geosmin was first identified in actinomycetes by Gerber and Lechevalier (1965) and in cyanobacteria (blue-green algae) by Safferman *et al.* (1967). It is produced both intracellularly and extracellularly and released to the water when those microbes die.
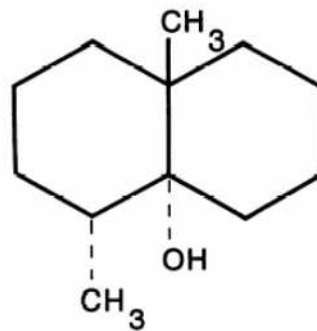
(Gerber and Lechevalier, 1965)

Figure 2-1 Molecular structure of geosmin

Under acidic conditions, geosmin decomposes into odorless substances, such as argosmin (Gerber and LeChevalier, 1965). The term geosmin means "earth odor" (from the Greek "ge" means earth and "osme" means odor). This compound is responsible for an earthy T&O problems in drinking water supplies. These problems are reported by customers at starting concentrations around 7 ng/L (Simpson and MacLeod, 1991a). The odor threshold concentration (OTC) for geosmin is 1 to 10 ng/L at 45°C (McGuire *et al.*, 1981; Rashash *et al.*, 1997). OTCs for other odor compounds are shown in Table 2-2. Other physical and chemical properties of geosmin are listed in Table 2-3.

Table 2-2 Odor threshold concentrations of selected odorous algal metabolites

Compound	OTC µg/L	Odor
Sulfurous		
Dimethyl trisulfide	0.01	Septic, garlic, putrid, swampy
Dimethyl disulfide	<4.0	Septic, garlic, putrid
Methanethiol	2.1	
Ethanethiol	1	
Propanethiol	0.74	
t-Butythiol	0.09	
Dimethyl sulfide	1	
Hydrogen sulfide	7.2	
PUFA derivatives		
n-Heptanal	3	Fishy, oily
n-Hexanal	4.5	Grassy, fatty
3-Methylbutyrate	20	Rotten, rancid
n-Pentanal	60	Fishy
trans-2-Nonenal	0.8	Cucumber
1-Penten-3-one	1.25	Pungent; rancid; fishy
trans-2-Hexenal	17	
cis-3-Hexen-1-ol	70	Grassy
2-Methylpent-2-enal	290	Rum, marzipan
trans-2,*cis*-6-Nonadienal	0.08	Grassy; cucumber
1,3-Octadiene	5600	Earthy/mushroom
trans,cis-2,4-Heptadienal	5	Fishy, oily
trans,cis,cis-2,4,7-Decatrienal	1.5	Fishy, oily
Amines		
Ethanolamine	6.5	Mild ammonia –fishy
Isopropylamine	210	Ammonical, amine
Butylamine	80	Sour, ammonical, amine
Propylamine	90,000	Ammonia
Methylamine	21	Ammonia
Trimethylamine	0.21	Pungent, fishy, ammonia
Dimethylamine	47	
Terpenoids		
α-Ionone	0.007	Violets
β-Ionone	0.007	Violets
Epoxy-α-ionone	0.007	
Geosmin	0.004	Earthy/musty
3-Methylbut-2-enal	0.15	Rancid, putrid
3-Methyl butanal	0.15	Rancid, putrid
2-Methylisoborneol	0.015	Earthy, musty
Limonene	4	Citrus
Linalool	6	Grassy, floral
Cieneole (1,8)	12	Camphor, spicy, cool
6-Methyl-5-hepten-2-one	50	Fruity, esterlike
β-Cyclocitral	19.3	Tobacco, smoky, moldy
Styrene	65	Sweet, balsamic
Pyrazines		
2,6-Dimethyl pyrazine	6	Cocoa, roasted nuts, coffee
3-Methoxy-2-isopropyl pyrazine	0.0002	Earthy/potato bin
2-Isobutyl-3-methoxy pyrazine	0.001	Earthy/potato bin

(Mallevialle & Suffet, 1987; Young *et al.*, 1996; Watson & Ridal, 2002)

Table 2-3 Physical and chemical properties of geosmin and 2-MIB

	Geosmin	2-MIB
Full Name	tran-1, 10-dimethyl-trans-9-decalol	1,2,7,7-Tetramethyl-exo-bicyclo-heptan-2-ol
Chemical Formula	$C_{12}H_{22}O$	$C_{11}H_{20}O$
Molecular Weight (g/mol)	182.31	168.28
Log Kow	3.57	3.31
Water Solubility (mg/L)	156.7	305.1
Vapor Pressure (Pa)	3.57	3.31
Henry`s Law Constant ($atm \cdot m^3/mol$)	1.18E-05	8.90E-06
Boiling Point (°C)	270	196.7

(Pirbazari *et al.*, 1992)

The unpleasant odor produced by geosmin is not only found in drinking water supplies, but also observed in pungent-smelling food. For instance, geosmin has been determined to cause an earthy off-flavor in channel catfish (Lovell and Sackey, 1973); Darriet *et al.* (2000) identified that this compound was also present in the fresh grape juices; further studies have shown that red beets are able to synthesize geosmin endogenously (Lu *et al.*, 2003a; Lu *et al.*, 2003b). The earthy-smelling compound is also observed in cured meat, dry beans, canned mushrooms, and other root crops. (Lloyd and Grimm, 1999; Maga, 1987).

2-MIB is a bridged cycloalkanol with molecular formula of $C_{11}H_{20}O$ and molecular weight of 168.28 g/mol. The molecular structure of 2-MIB shown in Figure

2-2 illustrates that the distinguished characteristic of 2-MIB is aliphatic structure and one hydroxyl group. Pendleton *et al.* (1997) identified that 2-MIB can be considered to be roughly spherical in shape with diameter 0.6 nm. It was first found as a natural metabolite of actinomycetes by Medsker *et al.* (1969) and Gerber (1969). Gerber (1969) first named it as 2-methylisoborneol. In addition, Rosen *et al.* (1970) determined 2-MIB to be produced by an actinomycete in natural waters. Subsequently, many researchers found that 2-MIB is produced as a secondary metabolite by different species of cyanobacteria, actinomycete, and several other blue-green algae (Tabachek and Yurkowski, 1976; Izaguirre *et al.*, 1982). Other physical and chemical properties of 2-MIB are also listed in Table 2-3.
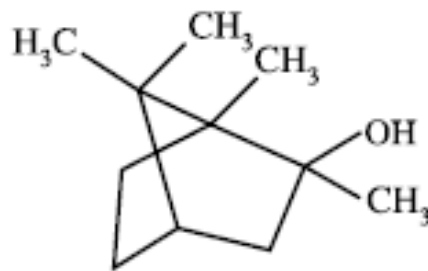
(Gerber, 1969)

Figure 2-2 Molecular structure of 2-MIB

2-MIB is characterized by an earthy-musty odor, which can be detected by people at very low concentration. Different odor threshold concentrations (OTC) of 2-MIB have been investigated. McGuire *et al.* (1981) reported that the OTC of 2-MIB was 4 ng/L. Simpson and MacLeod (1991b) found that no more than 12 ng/L of 2-MIB concentrations could cause customer complaints. Later, Young *et al.* (1996) also documented that OTC of 2-MIB was 6.3 ng/L. Consequently, the range of 2-MIB OTC is 4 to 12 ng/L.

2.2 Sources of geosmin and 2-MIB

In summer, T&O complaints from consumers are frequent problems for water utilities. Relatively high concentrations of geosmin and 2-MIB that exceed the odor thresholds are frequently detected in drinking water sources (Klausen *et al.*, 2004). Geosmin and 2-MIB were first identified in actinomycetes (Gerber, 1968, 1969, 1979, 1983; Blevins, 1980; Yagi *et al.*, 1981, 1983; Bentley and Meganathan, 1981; Schrader and Blevins, 1993), then later in cyanobacteria (Izaguirre *et al.*, 1982; Wu and Jüttner, 1988; Martin *et al.*, 1991; Matsumuto and Tsuchiya, 1988; Tsuchiya *et al.*, 1981; Tsuchiya and Matsumoto, 1988; Schrader and Blevins, 1993; Tabachek and Yurkowski, 1976) and fungi (Kikuchi *et al.*, 1981) that inhabit aquatic and soil environments. Geosmin and 2-MIB-producing species are listed in Table 2-4, Table 2-5, and Table 2-6. However, previous research by Watson (2004) indicated that the primary source of geosmin and 2-MIB in water are cyanobacteria (commonly referred to as blue-green algae). Zaitlin and Watson (2006) demonstrated that the source of these two compounds in water reservoirs can also be attributed to the presence of actinomycetes.

As the major source of the T&O compounds, cyanobacteria have been present on earth for around 2.5 billion years and keep evolving and adapting to our environmental conditions, especially in water sources, such as ocean, lakes, and reservoirs (Paerl *et al.*, 2001). More than 200,000 known species of cyanobacteria have been identified as odor sources, including *Anabaena, Aphanizomenon, Lyngbya, Oscillatoria, Phormidium, Planktothrix, and Pseudanabaena* (Peterson *et al.*, 1995; Sugiura *et al.*, 1997, 1998; Izaguirre and Taylor, 1998; Schrader *et al.*, 1998, 2005; Zimba *et al.*, 1999; Sugiura and Nakano, 2000; Saadoun *et al.*, 2001; Zimba *et al.*, 2001).

Table 2-4 2-MIB-producing species

Species	Origin	Habitat	References
Oscillatoria			
O. perornata (*Planktothrix MS988*)	Fish pond/USA	Planktonic	van der Ploeg *et al.* 1995; Tellez *et al.* 2001a, b; Taylor *et al.* 2006
O. limosa	Lake/USA	Benthic	Izaguirre and Taylor 1995
Oscillatoria sp.	Fish pond/USA	Planktonic	Martin *et al.* 1991
O. tenuis	Japan	Planktonic	Negoro *et al.* 1988
O. geminata	Fish pond/Japan	Fish Pond	Matsumoto and Tsuchiya 1988
O. limnetica	Fish pond/Japan	Fish Pond	Matsumoto and Tsuchiya 1988
Oscillatoria cf. *curviceps*	Lake/USA	Benthic	Izaguirre *et al.* 1982, 1983
O. tenuis	Water supply/USA	Benthic	Izaguirre *et al.* 1983
O. variabilis	Fish farming lake/ Japan	Benthic	Tabachek and Yurakowski 1976
O. chalybea	Reservoir/Israel	Benthic	Leventer and Eren 1970
Phormidium			
Phormidium LP684	Lake/USA	Benthic	Taylor *et al.* 2006
Phormidium aff. formosum	Water supply/ Australia	Benthic	Baker *et al.* 2001
P. favosum	Lake/Japan	Benthic	Sugiura *et al.* 1997
Phormidium	USA	Benthic	Izaguirre 1992
P. tenue	Lake/Japan	Benthic	Sugiura *et al.* 1986
P. tenue	Water supply/ Japan	Planktonic	Yagi *et al.* 1983
Pseudanabaena			
Pseudanabaena	Reservoirs/USA	Planktonic	Izaguirre *et al.* 1999; Taylor *et al.* 2006
Pseudanabaena	Lake/USA	Planktonic	Izaguirre and Taylor 1998
Other species			
Synechococcus sp.	Water reservoirs/USA	Planktonic	Taylor *et al.* 2006
Leptolyngbya sp.	Periphyton, lake/USA		Taylor *et al.* 2006
Lyngbya LO198	Reservoir/USA	Benthic	Taylor *et al.* 2006
Hyella	Aqueduct water/USA	Epiphytic	Izaguirre and Taylor 1995
Lyngbya Cal.Aq.892	Aqueduct lake/USA	Epiphytic	Izaguirre and Taylor 1995
Planktothrix MS988	Catfish pond/ USA	Planktonic	Martin *et al.* 1991
Planktothrix cryptovaginata	Fish, water/Finland	Benthic	Persson 1988
Jaaginema geminatum	River/Japan	Benthic	Tsuchiya and Matsumoto 1988
Synechococcus sp.	Plankton, lake/USA	Planktonic	Izaguirre *et al.* 1984
Lyngbya cf. aestuarii	Fish farming lake / Japan	Benthic	Yurkowski and Tabachek 1980 Tabachek and Yurkowski 1976

Table 2-5 Geosmin-producing species

Species	Origin	Habitat	References
Anabaena			
Anabaena sp.	Lake/USA	Planktonic	Saadoun *et al.* 2001
A. laxa CA 783	Lake plankton/USA	Planktonic	Rashash *et al.* 1996
A. crassa LS698	Lake/USA/Australia	Planktonic	Baker *et al.* 1994; Komarkova-Legnerova and Cronberg 1992
A. circinalis	River/Australia	Planktonic	Bowner *et al.* 1992
A. circinalis	Reservoir/USA	Planktonic	Rosen *et al.* 1992
A. solitaria	Taiwan	Planktonic	Wu *et al.* 1991
A. viguieri	Taiwan	Planktonic	Wu *et al.* 1991
A. macrospora	River/Japan	Planktonic	Tsuchiya and Matsumoto 1998
A. scheremetievi Elenkin	Water supply/USA	Planktonic	Izaguirre *et al.* 1982
Oscillatoria			
O. limosa	River/Spain	Benthic	Vilalta *et al.* 2003, 2004
O. limosa	River/Reservoir/ Netherlands		Van Breeman *et al.* 1992
Oscillatoria sp. (Philadelphia)	Periphyton, river/ USA	Benthic	Burlingame *et al.* 1986
O. brevis	Inland water/Norway	Benthic	Berglind *et al.* 1983b
O. simplicissima	Water supply/USA	Pipeline	Izaguirre *et al.* 1982
O. tenuis	Fish pond/Israel		Aschner *et al.* 1967
Phormidium			
Phormidium LS1283	Algae, lake/USA	Benthic	Taylor *et al.* 2006
Phormidium cf. Inundatum LO584	Reservoir/USA	Sediment	Taylor *et al.* 2006
Phormidium sp. (SDC202a,b,c)	Canal/USA		Taylor *et al.* 2006
Phormidium sp. DCR301	Reservoir/USA	Sediment	Taylor *et al.* 2006
Phormidium sp. ER0100	Reservoir/USA	Sediment	Taylor *et al.* 2006
Phormidium DC 699	Algae/lake/USA	Benthic	Taylor *et al.* 2006
Phormidium sp. LD499	Algae/lake	Benthic	Taylor *et al.* 2006
Phormidium sp. LM494	Lake/USA	Sediment	Taylor *et al.* 2006
Phormidium sp. LS587	Lake/USA	Sediment	Taylor *et al.* 2006
Phormidium sp. R12	Canal/USA		Taylor *et al.* 2006
P. allorgei	Lake/Japan	Benthic	Sugiura *et al.* 1997
Phormidium sp.	Lake/USA	Benthic	Izaguirre and Taylor 1995
P. amoenum	Japan	Benthic	Tsuchiya and Matsumoto 1988
P. simplissimum	Fish, water/Finland	Benthic	Persson 1988
P. formosum	Fish, water/Finland	Benthic	Persson 1988
P. cortianum	Fish farming lake/ Japan	Benthic	Tabachek and Yurakowski 1976

Table 2-5 (continued)

Species	Origin	Habitat	References
Other geosmin-producing species			
Nostoc sp.	Creek/USA	Periphytic	Taylor *et al.* 2006
Microcoleus-like cyano	Aqueduct/USA	Epiphytic	Izaguirre and Taylor 1995
Lyngbya cf. *subtilis*	Aquaculture pond/ USA	Benthic	Schrader and Blevins 1993
Planktothrix prolifica	Norway	Benthic	Naes *et al.* 1988
Aphanizomenon gracile	Lake/Germany	Planktonic	Juttner 1984
Tychonema bornetii	Lake/Norway	Benthic	Berglind *et al.* 1983a
Schizothrix muellerii	Japan	Benthic	Kikuchi *et al.* 1973
Symploca muscorum	Fish farming lake/ Japan	Soil	Tabachek and Yurakowski 1976 (first reported by Medsker *et al.* 1968)
Actinomycetes			
Streptomyces halstedii	Aquaculture pond/ USA	Sediments	Schrader and Blevins 2001
Streptomyces griseus	USA		Gerber and Lechevalier 1965

Table 2-6 Geosmin- and 2-MIB-producing species

Species	Origin	Habitat	References
Phormidium			
Phormidium sp. Cal Aq.0100	Aqueduct/USA	Periphyton	Taylor *et al.* 2006
*Phormidium sp.*HD798	Algae/lake	Periphytic	Taylor *et al.* 2006
Phormidium sp.	Lake/USA	Benthic	Izaguirre 1992
Phormidium sp.	River/Japan	Benthic	Matsumuto and Tsuchiya 1988
Phormidium sp.	Inland water/ Norway	Benthic	Berglind *et al.* 1983b
Other species			
Synechococcus sp. CL792	Lake/USA	Planktonic	Taylor *et al.* 2006
Nostoc sp.	Water treatment Plant/Taiwan		Hu and Chiang 1996
T. granulatum	Japan	Benthic	Tsuchiya and Matsumoto 1988
Planktothrix agardhii	Lake/Norway	Planktonic	Persson 1988 Berglind *et al.* 1983a
O. brevis			Berglind *et al.* 1983b
Actinomycetes			
Streptomyces	Denmark	Streams/ponds	Klausen *et al.* 2005
Streptomyces violaceusniger	Water supply/ Jordon	Sediment	Saadoun *et al.* 1997
Streptomyces sp.	USA		Gerber 1977

Table 2-7 represents cyanobacteria species and classification.

Table 2-7 Cyanobacteria species and classification

Kingdom/Phylum	Genus
Prokaryota	
Cyanobacteria	*Anabaena*
(N_2-fixing)	*Aphanizomenon*
	Cylindrospermopsis
	Gloeotrichia
	Lyngbya
	Nodularia
	Pseudanabaena
(Non-N_2-fixing)	*Gomphosphaeria*
	Microcystis
	Oscillatoria
	Phormidium
	Planktothrix

(Paerl *et al.*, 2001)

Cyanobacteria are prokaryotic. Three basic characteristics of cyanobacteria have been documented by earlier studies. First, both N_2-fixing and non- N_2-fixing cyanobacteria species are filamentous in morphology. Second, they are unicellular in structure. Third, they are found in the plankton and/or parasitize other aquatic plants (Watson, 2003; Humpage *et al.*, 2000).

Cyanobacteria synthesize geosmin and 2-MIB throughout growth, which relates to photosynthesis and pigment synthesis. These algal cells store or release these T&O compounds depending on growth phase and environmental factors that affect these processes (Naes *et al.*, 1988; Rashash *et al.*, 1995, 1996; Srinivasan and Sorial, 2011). Cell damage due to death, senescence, and biodegradation releases geosmin and 2-MIB into water (Srinivasan and Sorial, 2011). Figure 2-3 expresses the formation process of geosmin and 2-MIB.

Cyanobacteria $\xrightarrow[\text{Warmer Temperatures}]{\text{Nutrients}}$ Cyanobacteria bloom $\xrightarrow{\text{Biodegradation}}$ Release of geosmin and 2-MIB in water

(Srinivasan and Sorial, 2011)
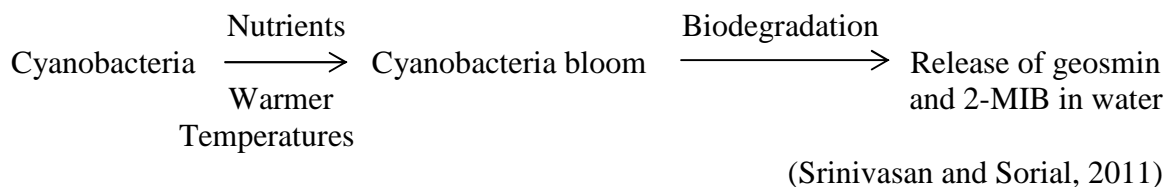
Figure 2-3 Pathway of geosmin and 2-MIB formation

Most of the earthy-musty T&O problems in water sources reported by water supply utilities have also been attributed to actinomycetes (Henley *et al.*, 1969; Rosen *et al.*, 1970; Silvey and Roach, 1953). Actinomyectes, defined as plant pathogenic bacteria, gram-positive, filamentous (most species), and spore-forming bacteria, present in a wide variety of environments including sediments, water, and aquatic plant life (Klausen *et al.*, 2004).

Actinomycetes have been associated with earthy-musty odors in water and fish since the early 1900s (Adams, 1929; Thaysen, 1936) but their actual contribution to odor in freshwater was unknown. In the late 1960s, the T&O compounds, geosmin and 2-MIB, were identified from actinomycete cultures (Gerber and Lechevalier, 1965; Gerber, 1979, 1983). Since then, actinomycetes have attracted considerable attention in the water industry as a major T&O source of drinking water.

The most common actinomycetes explored from freshwater environments include *Actinoplanes, Micromonospora, Rhodococcus, Streptomyces,* and *Thermoactinomyces* (Goodfellow and Williams, 1983). In addition, *Actinomyces, Kitasatosporia*, and *Nocardia* are found in aquatic environments less frequently (Cross, 1981; Jiang and Xu, 1996; Wohl and McArthur, 1998, 2001).

Actinomycetes are common soil inhabitants, where their production of the earthy-odor compounds, geosmin and 2-MIB, contributes significantly to the characteristic odor of soil (Gerber and Lechevalier, 1965; Buttery and Garibaldi, 1976). Stronger smells of those T&O compounds have been associated with periods of increased runoff (Raschke *et al.*, 1975; Hrudey *et al.*, 1992; Jensen *et al.*, 1994), and increased actinomycete concentrations are associated with increased flow rate or turbidity (Jensen *et al.*, 1994; Uhna´kova´ *et al.*, 2002; Lanciotti *et al.*, 2003).

Actinomycetes have also been isolated from sediment near or in water and nearly all aquatic environments, from freshwater to saltwater. Species from these environments do not necessarily mean they are actively growing there, since spores may wash into terrestrial environments and reside in the aquatic environment for extended periods of time (Niemi *et al.*, 1982; Wood *et al.*, 1983; Takizawa, 1993; Zaitlin *et al.*, 2003).

Moreover, in freshwater systems, odor producing actinomycetes have been found in association with cyanobacteria (Sugiura *et al.*, 1994), with aquatic plants (Raschke *et al.*, 1975; Zaitlin *et al.*, 2003), and with zebra mussels (Lange and Wittmeyer, 1997; Zaitlin *et al.*, 2003). Actinomycetes have also been found in association with terrestrial plant litter that had fallen into streams (Raschke *et al.*, 1975; Makkar and Cross, 1982), and with chitin exoskeletons in streams (Aumen, 1980). In artificial environments, actinomycetes were found in association with cat-tail and bulrush roots in a constructed wetland (Hatano *et al.*, 1994), in drinking water pipeline deposits (Zacheus *et al.*, 2001), and in sewage treatment scum (Lemmer, 1986; Jenkins *et al.*, 1993). Many actinomycetes are capable of forming spores, which can survive adverse conditions (e.g. salinity) and

play an important role in their widespread distribution in wind and water-borne sediment (Lloyd, 1969; Goodfellow and Williams, 1983).

2.3 Health effects and regulation

T&O problems in drinking water result in aesthetic concerns and consumer complaints; however, numerous studies indicated that those problems have not been associated with any health effects. Therefore, currently, there are no regulations on the two T&O-causing compounds geosmin and 2-MIB (Dionigi *et al.*, 1993). Although these compounds are not regulated by primary drinking water standards as a direct threat to public health, they are great concern for many water utilities because consumers generally rely on the taste of their water as the primary indicator of its safety. These two compounds can be detected by consumers as a musty-earthy odor at levels as low as 10 ng/L (Cook *et al.*, 2000).

Some consumers express concern about purchasing other products that are contaminated by algae, such as fish, DHA, and other nutrient supplies that associate with contaminated water. However, some researchers have detected that geosmin/2-MIB in various species of fish do not result in any health effects to human (Schulz *et al.*, 2004; Robedson *et al.*, 2006).

Earthy and musty odors, which are the most frequent types of T&O in drinking water, always reduce consumers` trust on water quality safety, even though there is no toxicity to human health (McGuire, 1995). Watson (2004) found that consumers tried to find alternative supplies of drinking water, such as bottled water. Water utilities address

concerns and avoid their consumer complaints by treating those compounds down to concentrations below their OTCs during seasonal outbreaks.

Recently, a study found that these odor-causing compounds, geosmin and 2-MIB, can be influenced by some factors, such as water temperature, pH, light, *et al.* (Whelton and Dietrich, 2004). There are a number of treatment processes for these compounds removals, including GAC/PAC adsorption, advanced oxidation processes, biological treatment, and some other treatment methods.

2.4 Treatment technologies

T&O-causing compounds, geosmin and 2-MIB, present relatively strong stability to their chemical and biological degradation and can persist in dissolved forms in water sources (Juttener and Watson, 2007). Conventional water treatment processes, such as coagulation, sedimentation, and filtration, have been tried for T&O problems control. However, studies have shown that these processes are unable to achieve any significant removal of geosmin and 2-MIB (Kutschera, *et al.*, 2009). Oxidation has been used as another common T&O treatment method. The common oxidants, such as Cl_2, ClO_2, and $KMnO_4$, are not very effective in removing geosmin and 2-MIB (Lalezary *et al.*, 1986; Glaze *et al.*, 1990). Studies have shown that only O_3 has significant removal of these compounds (85% for 3.8 mg/L dosage rate at a contact time (CT) of 6.4 min) (Jung *et al.*, 2004).

Currently, the most successful technologies used by most water treatment plants in removing T&O-causing compounds are granular/powdered activated carbon

(GAC/PAC) and advanced oxidation processes (AOP) (Srinivasan and Sorial, 2009). Some other advanced treatment methods, such as ozonation and membrane filtration, can be applied efficiently as well. Ferguson *et al.* (1990) studied and demonstrated that geosmin and 2-MIB can be removed by using oxidants, such as ozone, hydrogen peroxide, and UV. Juttner (1995) reported that a slow sand filtration unit (flow rate of 420 liters m^{-2} day^{-1}) achieved excellent rates of elimination of geosmin and other terpenoid alcohols. These treatment technologies mentioned above and some others are discussed in detail in the following section.

Although many of these treatment processes are quite effective at geosmin and 2-MIB removal, they are extremely expensive to install, maintain, and operate. For current and future studies, more efficient and economic T&O control technologies need to be addressed and explored by researchers.

2.4.1 GAC/PAC adsorption

Activated carbons can be classified into two categories based on particle size: granular activated carbon (GAC) and powdered activated carbon (PAC). Either one of these activated carbons is being widely used as the most efficient method to adsorb T&O-causing compounds, geosmin and 2-MIB (Ridal *et al.*, 2001).

GAC is used in the form of a filtration bed and is installed as a granular media above the sand/gravel media filter for the removal of geosmin and 2-MIB as the water passes through the filter. The removal efficiency of GAC depends on many factors listed below.

1)   Surface area of GAC

2)   Concentration of dissolved organic carbon(DOC)

3)   Contact time

4)   Types of activated carbon used

5)   Filter age

The surface area of GAC is directly proportional to the removal efficiency of geosmin and 2-MIB. The large surface area can adsorb a large amount of these compounds from water; however, there is a competition between geosmin/2-MIB and other organic compounds to reserve a seat in the activated carbon pores. Ridal *et al.* (2001) concluded that competitive adsorption was a bigger factor for the reduced performance of geosmin and 2-MIB removal than some reasons pointed out above. Simultaneous adsorption between DOC and 2-MIB on GAC was primarily influenced by pore size/volume distribution (Newcombe *et al.*, 2002a). Smaller DOC molecules compete by direct and strong adsorption for the available adsorption sites, larger DOC compounds reduce equilibrium adsorption capacity by adsorbing closer to external surfaces and blocking access to pores (Newcombe *et al.*, 2002b). Another factor which affects GAC performance is contact time. The contact time is the period over which water flows through the GAC filter. The removal efficiency increases as the contact time is increased. Different types of GAC have different absorption rates. Ho *et al.* (2010) studied and compared two different types of GAC: a wood-based carbon and a coal-based carbon. They observed that wood-based carbons are suitable for 2-MIB removal, both at equilibrium and short contact times. The GAC performance also depends on filter age. Newcombe *et al.* (1996) reported that with an empty bed contact time (EBCT) of 20 min, 18 months was the maximum time that their GAC could be expected to reduce 2-MIB

concentrations to below the odor threshold. Ridal *et al.* (2001) found that the removal efficiency of geosmin and 2-MIB substantially decreased after 12 months. They suggested that an economic bed life of GAC filters is less than 2 years.

GAC and other technologies combination treatment method are more effective for geosmin and 2-MIB removal. Srinivasan and Sorial (2009) reported that the complete removal of geosmin and 2-MIB occur in a GAC combined with a biofilter or followed by ozonation. Drikas *et al.* (2009) investigated geosmin and 2-MIB removal for over two years by using GAC followed by either coagulation or microfiltration (MF). Ridal *et al* (2001) removed about 60% of geosmin and 80% of 2-MIB concentrations by using GAC and capped filters after 12 months operation. Although the removal efficiency of GAC is achieved below odor threshold concentrations of those compounds, the complex procedure and high cost of this technology make it difficult to implement in drinking water treatment plant.

PAC is typically added to the water prior to alum treatment and must be added continuously during taste-and-odor outbreak season (Ridal *et al.*, 2001). It is currently the most common technology for geosmin and 2-MIB removal. The primary advantages of PAC are its low capital cost and the ability to apply it only when needed (Najm *et al.*, 1990a). When the taste-and-odor problem becomes long-term, consistent PAC is applied. Gardiner (1973) suggested that PAC can be more economical than GAC to solve taste-and-odor problems if carbon adsorption is required for less than three months per year.

Like GAC, several factors including pore size distribution, surface characteristics, types of PAC, presence of DOC, and PAC dose, influence the PAC effectiveness of

geosmin and 2-MIB removal. Pelekani and Snoeyink (1999, 2000, 2001) reported that the competitive mechanism depends greatly on the pore size distribution of the carbon. They found that a wider pore size distribution in the adsorbent resulted in less pore blockage and consequently less evidence of competition. Bruce *et al.* (2002) described how the effectiveness of PAC for the removal of geosmin and 2-MIB depends on the type of PAC used. They found that bituminous coal-based PAC performed better than lignite or wood-based PAC. Newcomb *et al.* (1997) and Chen *et al.* (1997) also reported that wood-based PAC shows inferior adsorption for 2-MIB compared with coconut- or coal-based PAC. In the case of PAC, optimizing the PAC dosage is an important factor, since overdosing could result in excessive sludge production, reduced filter performance, larger operating costs, and consumer complaints regarding the quality of the water (Cook *et al.*, 2001).

2.4.2 Advanced oxidation process (AOP)

Advanced oxidation processes (AOP), such as ozone, UV, and hydrogen peroxide (H_2O_2), are also effective methods to remove geosmin and 2-MIB. Similar to activated carbons adsorption, the characterization of natural organic matter (NOM) in water can affect ozonation of geosmin and 2-MIB as well (Ho *et al.*, 2002). This study concluded that NOM with higher specific UV absorbance (SUVA) characteristics had lower contact times and faster reaction with ozone; thus, the highest geosmin and 2-MIB removal (98%) is observed for the lowest contact time. In addition, some NOM competed with geosmin and 2-MIB for generating hydroxyl radicals during ozonation (Ho *et al.*, 2002). Although UV/H_2O_2 successfully destroyed geosmin and 2-MIB and removed them, ozone oxidation parameters, such as pH, ozone and H_2O_2 dosage, water temperature, and initial concentrations of geosmin and 2-MIB, can affect the removal efficiencies of both

geosmin and 2-MIB (Rosenfeldt *et al.*, 2005). Nerenberg *et al.* (2000) found that removal efficiencies of these compounds increased with increase in temperature, ozone dosage, pH, and H_2O_2 concentration. Westerhoff *et al.* (2006) investigated that geosmin showed better removal than 2-MIB because of better second order reaction kinetics. AOPs can effectively eliminate geosmin and 2-MIB in water; however, high cost and fouling problems should to be considered before their installation.

2.4.3 Biological treatment

Geosmin and 2-MIB can be biodegraded by gram-positive bacteria because their structure is similar to biodegradable alicyclic alcohols and ketones (Rittmann *et al.* 1995). However, biological processes require electron-donor and electron-acceptor substrates. The substrates transfer electrons from the donor to the acceptor and provide the energy to grow and maintain the bacteria used for geosmin and 2-MIB biodegradation (Odencrantz, 1990). Since the odor threshold concentrations of geosmin and 2-MIB are very low (< 10 ng/L), the presence of these compounds in raw drinking water does not support the growth of microorganisms in biofilters. Hence, geosmin and 2-MIB behave as secondary substrates while biofilm microorganisms are maintained by the primary substrates (Rittmann *et al.* 1995). Assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC) are always considered as primary substrates.

According to previous studies, the most common biological treatment method for taste-and-odor causing compounds removal is biofiltration. Huck *et al.* (1995) performed one of the first studies to investigate biological removal of geosmin and 2-MIB in drinking water. They concluded that these compounds removals were very low and

biodegradation was not the most effective technology to remove these compounds. Conversely, Ho *et al.* (2007) illustrated geosmin and 2-MIB can be removed by a biological sand filtration. Their results showed that rapid biodegradation of these compounds were observed in biological sand filters and four different bacteria were identified to be responsible for this biodegradation. Elhadi *et al.* (2006) found that different factors such as temperature, media type, biodegradable organic matter (BOM) concentration, and influent concentrations, can affect the removal efficiency of geosmin and 2-MIB. The study showed that higher removals were observed at higher temperature, at higher influent concentrations, and at higher BOM concentrations.

2.4.4 Other innovative treatment methods

A number of studies that investigated some of the integrated technologies like GAC + biofiltration and ozonation + biofiltration have shown effective removal of geosmin and 2-MIB and have potential to do further research to apply these technologies. Some other innovative treatment methods have been investigated in recent years. Lawton *et al.* (2003) reported geosmin and 2-MIB can be removed by using titanium dioxide photocatalysis. The results showed rapid degradation of both geosmin and 2-MIB (>99%) removal within 60 minutes. Song and O'Shea (2007) found geosmin and 2-MIB removal in water by ultrasonic irradiation and concluded that the removal process could be achieved in terms of minutes.

2.5 Algaecides

The substances producing taste-and-odor compounds are associated with algae. Algaecides can kill or inhibit the growth of algae either by direct toxicity or by metabolic interference (Wagner, 2004). They are applied in drinking water reservoirs to control taste and odor problems at least once per year, and even more often when algal blooms occur. Algaecides are classified into four categories, including natural, copper-based, synthetic organic, and oxidizers.

2.5.1 Natural algaecides

Natural algaecides are allelopathic chemicals, which inhibit the growth of a plant when they are naturally released by a different plant. This type of algaecide is typically more effective than other types of algaecides, since it provides appropriate amount of increased oxygen demand caused by algal mortality during this algaecide application (Deas *et al.*, 2009).

Barley straw is a kind of natural algaecide. It is typically applied in small water sources, such as farm ponds, small lakes, or small reservoirs. The study reported by Wagner (2004) illustrated that barley straw is a relatively economical treatment due to inexpensive initial and operating cost; however, it is difficult to control precisely due to uncontrollable water chemistry factors. Barley straw has not been applied in large scale fields because it is not a comprehensive, advanced, and desirable algae control technology that contains potentially uncontrollable factors (Deas *et al.*, 2009).

2.5.2 Copper-based algaecides

Copper is an essential micronutrient for growth of algae and *Cyanobacteria*. It has been using in various metabolic and enzyme processes (Cid *et al.*, 1995). However, higher concentration of copper may serve as a cellular toxicant. The mechanism of copper toxicity was found by Kenefick *et al.* (1993) in a study where membrane damage was seen within 24 hours in cultured cells of the cyanobacterium *Microcystis aeruginosa* following treatment with copper (0.64 mg L^{-1} Cu as $CuSO_4$). At lower concentration, copper ions need to be transported into cells by a process of facilitated diffusion through the membrane (Florence and Stauber, 1986). Figure 2-4 shows the transport of copper complexes into the cell membrane by diffusion.
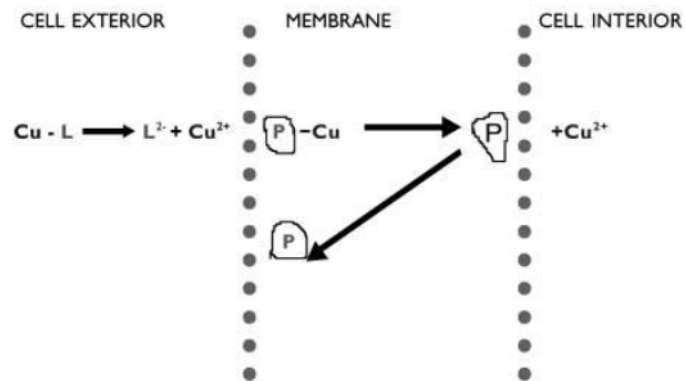
(Florence and Stauber, 1986)

Figure 2-4 The transport of copper complexes into a cell by facilitated diffusion

Copper-based algaecides, including chelated copper and copper sulfate in two forms, have been used for an effective removal and growth inhabitation of algae (Wagner, 2004). Copper-based algaecides treatments tend to inhibit rapid repopulation of algae, particularly chelated forms, since chelated copper form contains less copper than

copper sulfate. Moreover, copper-based algaecides can be less effective in alkaline waters or at lower temperatures, although chelated forms perform better (Wagner, 2004; García-Villada *et al.*, 2004). The application of these algaecides can kill certain algae species if they are applied properly.

2.5.3 Synthetic organic algaecides

Synthetic organic algaecides are absorbed by algae and remove algae by containing "membrane active" chemicals that disrupt algae metabolism (Deas *et al.*, 2009). These quick and useful treatment methods are typically used as a backup plan when copper based algaecides are ineffective. Limitations of synthetic organic algaecides include extended periods of restricted water use after application; non-selective characteristic that they provide; and possibly toxicity to other desirable aquatic fauna (Wagner, 2004). Therefore, synthetic organic algaecides could not be applied in some situations. Toxicity to zooplankton or other grazers affects ecological balance while removing algae in aquatic systems.

2.5.4 Oxidizer algaecides

Oxidizer algaecides have the ability to disrupt cellular functions, such as breaking cellular membranes. That is how these algaecides remove algae in water resources. Sodium carbonate peroxyhydrate is a typical form of oxidizer algaecides. It only effects blue-green algae while leaving other forms of algae in the system to produce oxygen via photosynthesis (Deas *et al.*, 2009). Oxidizer algaecides can work with copper-based algaecides as integrated treatment methods. Oxidizer algaecides also work quickly and are non-persistent in the water body (Solvay Chemicals, 2005). However, oxidizer

algaecides are a relatively new and simple type of algaecide comparing to copper-based algaecides.

The mode of action, example products, general advantages, and general disadvantages of four major types of algaecides discussed above are summarized in Table 2-8. Six commercially available algaecides categorized into different types are listed in Table 2-9. EarthTec® will be investigated in this study as an example and also due to its most efficacy removal of taste-and-odor compounds comparing with other algaecides.

Table 2-8 Types of algaecides and the associated advantages and disadvantages

Algaecide Type		Natural	Copper-Based	Synthetic Organic	Oxidizer
Mode of Action		Allelopathic	Inhibits photosynthesis, nitrogen metabolism and membrane transport	Disrupts algae metabolism	Ruptures the cell membranes and disrupts most cell functions
Example Products		Barley Straw	Algimycin PWF; Captain; Copper Sulfate Crystals; Cutrine Plus; Cutrine Ultra	Hydrothol 191	GreenClean PRO; PAK-27; Phycomycin
General Advantages	Low Cost	×	-	-	-
	Gradual effect	×	-	-	-
	Effective when Copper is not effective	-	-	×	-
	Fast acting	-	×	×	×
	Controls wide range of algae	-	×	-	-
	Approved for differing water bodies	-	×	-	×
	Can be used with copper based algaecide	-	-	-	×
	Non persistent	-	-	-	×
	Selective	-	-	-	×
General Disadvantages	Inconsistent results	×	-	-	×
	Limited to small bodies of water	×	-	-	×
	Restricts water body use after application	-	-	×	-
	Non-selective	-	-	×	-
	Not affective on all algae types	-	-	×	-
	Can be toxic to aquatic fauna	-	×	×	-
	Can be ineffective at cold temperatures	-	×	-	-
	Long-term use results in accumulation	-	×	-	-
	Some algae show resistance	-	×	-	-
	Limited testing/history	-	-	-	×

(Deas *et al.*, 2009)

Table 2-9 Commercially available algaecides

Algaecide	Components	Type	Manufacturer
EarthTec®	Copper Sulfate Pentahydrate: 20.0% Inert Ingredients: 80%	Acidified Copper	Earth Science Laboratories Bentonville, AR
Bluestone	Copper Sulfate Pentahydrate: 99.0% Other ingredients: 1%	Neutral Copper	General Chemical Parsippany, NJ
Aqua-Ox™ 446	Copper Sulfate Pentahydrate: 19 - 21% Soluble Cupric Iron : 4.8 - 5.3% Sodium Permanganate: 4%	Copper/ Permanganate	General Chemical Parsippany, NJ
Cutrine®-Plus	Copper as elemental: 9.0% Inert Ingredients: 91.0%	Chelated Copper	Applied Biochemists Germantown, WI
PAK™ 27	Sodium carbonate peroxyhydrate: 85 % Sodium carbonate: 13% Sodium silicate: 1.5-2%	Hydrogen peroxide	Solvay Chemicals Houston, TX
Sulfuric Acid	H_2SO_4	Acid	Fisher Scientific Pittsburgh, PA

(Wilber *et al.*, 2010)
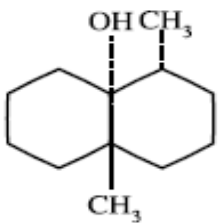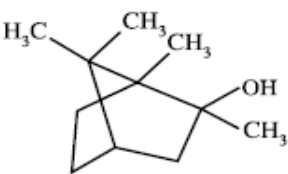
CHAPTER III

MOTHODOLOGY

3.1 Experimental materials

The reagent standards of geosmin (CAS # 23333-91-7) and 2-methylisoborneol (2-MIB) (CAS # 2371-42-8) was purchased from Supelco (Sigma-Aldrich, St. Louis, MO, USA) as a 100 μg/mL solution in methanol. Basic information about these compounds is shown in Table 3-1. The solutions were stored at 4 °C and used after dilution with deionized water or reagent water.

Table 3-1 Compound name, compound structure, molecular formula, molecular weight, and CAS registry number of the compounds used

Compound Name	Compound Structure	Molecular Formula	Molecular Weight	CAS registry number
Geosmin		$C_{12}H_{22}O$	182.3	CAS # 23333-91-7
2-methylisoborneol (2-MIB)		$C_{11}H_{20}O$	168.3	CAS # 2371-42-8

Water was obtained from the Mohawk Drinking Water Treatment Plant (Tulsa, OK). This water plant receives water via a closed-pipe system from Lake Eucha, a water supply reservoir located in Delaware County in northeastern Oklahoma. Water samples were collected from the storage tank before lake water enters into the water plant. At that collection site, during the testing period no geosmin and 2-MIB were found in water samples used as water in experiments.

EarthTec® was obtained from Earth Science Laboratories, Inc. (Bentonville, AR, USA) as an example of algaecides used in this study. It is a copper solution containing 99.99% cupric ions (Cu++), which are toxic to microscopic organisms at low doses. EarthTec® is used in lakes, ponds, municipal drinking reservoirs, or other water systems. It has the ability to remain in suspension over long periods with mathematically predictable copper levels which allow precise control of algae and bacteria without over-treatment (Earth Science Laboratories, Inc. 2009).

A solid phase micro-extraction (SPME) extraction technique was used to analyze the concentrations of geosmin and 2-MIB. Manual assemblies of SPME including a 2cm-50/30μm DVB/Carboxen™/PDMS StableFlex™ SPME coated fiber (Supelco part number 57348–U) and SPME fiber holder (Supelco part number 57330–U) (Figure 3-1) were purchased from Supelco (Bellefonte, PA).

Figure 3-1 SPME fiber holder

Other apparatus and instrumentation used for this study are listed below. They include a GCMS-QP5050A gas chromatograph-mass spectrometer (GC-MS) device (SHIMADZU corporation), GC/MS software (CLASS-5000 Version 2.2), GC carrier gas (helium, 99.999 percent), sodium chloride, electronic balance, laboratory oven, amber sample vials (40mL), heating block (a temperature of 60 to 65 °C), laboratory heater (with magnetic stirrer), magnetic bars, volumetric glassware (50, 250, 500 mL), pipettes (0.2 and 25 mL), laboratory stopwatch.

3.2 Headspace solid-phase microextraction

The SPME method was used to extract target compounds, geosmin and 2-MIB, present in the water samples. The device has a polymer-coated fiber that is fused within a syringe. The type of polymer coating is chosen in order to match the characteristics of the target analytes (Nakamura and Daishima, 2005). For this study, a fiber coated with DVB/Carboxen™/PDMS StableFlex™ with film thickness of 50/30μm was used. To ensure that the fiber was clean before analyzing water samples, it was conditioned at the first time using it. The conditioning was carried out with exposing the fiber in the inlet of the gas chromatograph overnight at 270 °C.

The manual SPME procedure (Figure 3-2) is depicted below. A 25 mL volume of water sample was transferred into a 40 mL screw-cap sample vial with a PTFE septum. 3.37 g of sodium chloride and a PTFE-coated magnetic stir bar were added in the sample vial. The vial with solution was placed in a heating block at 65 °C and was stirred with the magnetic bar. The SPME needle pierced the septum of sample vial and the SPME

fiber was exposed in the sample for 35 minutes for complete adsorption. After extraction, the fiber was retracted into the needle. The SPME assembly was removed from the sample vial and directly injected into the GC-injection port of the GC–MS system. The fiber was exposed in the GC column immediately and the analysis software was started. After 20 minutes analysis, SPME assembly was removed from the GC-injection port and used for the next sample.
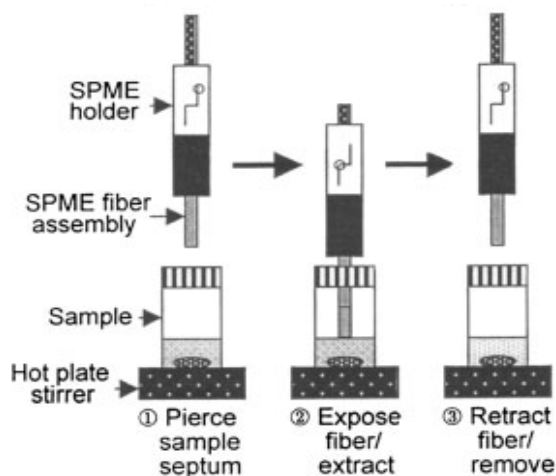
Figure 3-2 The manual SPME procedure

3.3 Gas chromatography–mass spectrometry (GC-MS)

Analysis of water samples using gas chromatography-mass spectrometry (GC-MS) was carried out with a Shimadzu Model QP5050A GC-MS device in conjunction with a CLASS-5000 (Version 2.2) GC-MS workstation. The instrument conditions used for this study are indicated in Table 3-2. This technique is a very useful analyzing tool due to its ability to separate and uniquely identify organic compounds from water

samples (Mallevialle and Suffet, 1987). A number of compounds at parts per trillion to parts per billion levels can be detected.

Table 3-2 GC-MS Conditions

Parameter	Condition
Model	Shimadzu GC/MS-QP5050A
Column type	Equity^{TM}-5 (30m×0.25mm×0.25μm)
Injector	Split-less, 10 min sample exposure
Injector temperature	250°C
Oven temperature	60 °C (hold for 2-4 min) to 250°C at 10°C/min
Carrier gas	Helium, 99.999 percent (at 70 kPa)
Flow rate	7 mL/min
Mass spectrometry	Ion-source temperature, 200 °C.
Mode	SIM (m/z = 112 for geosmin, m/z = 95 for 2-MIB)

The chromatogram peaks from the GC-MS results are proportioned to the concentration of the injected standards compounds. The retention times of different compounds are based on the types of the organic compounds. The type, length, and diameter of column, temperature of GC oven, detector type, and carrier gas flow rate are key factors for consistent separation and were kept constant for every sample. The MS part ionizes the compounds with an electron beam, and then the different fragments are separated according to their mass to charge ratio. The target compound can be identified by the resulting fragmentation pattern.

In this research, geosmin and 2-MIB were desorbed from SPME fiber at the inlet of gas chromatograph and eluted from GC column to the MS for identification. Selected ion monitoring (SIM) mode detections for geosmin and 2-MIB were selected with mass to charge ratios, $m/z = 112$ (geosmin) and $m/z = 95$ (2-MIB). The peak areas were measured to determine concentrations of geosmin and 2-MIB in water samples. The method detection limits (MDLs) for these compounds are 0.5 ng/L.

3.4 Sample preparation

A series of control standards were prepared for a calibration curve at concentrations ranging from 0 to 200 ng/L (0, 25, 50, 100, 150 and 200 ng/L). First, the standard of geosmin and 2-MIB solution in methanol (100 µg/mL) was added to 500 mL deionized water to make a 200 ng/L control standard and then aliquots of the 200 ng/L standard were transferred to different flasks to dilute to 150, 100, 50, and 25 ng/L control standards with deionized water. A blank standard (0 ng/L) was prepared using unspiked deionized water. SPME was used to extract the geosmin and 2-MIB from the control standards and the GC-MS was employed for the analyses of these compounds. Peak areas of geosmin and 2-MIB were found by GC-MS at each standard concentration and then a calibration curve was generated to determine their concentrations of other water samples.

Five water samples were prepared for different removal analyses of geosmin and 2-MIB. The first one is named contaminated water, which was made by unfiltered reagent water, Lake Eucha water, spiked with 200 ng/L geosmin and 2-MIB. The second water sample is filtered reagent water spiked with 200 ng/L geosmin and 2-MIB. Reagent

36

water was filtered through a glass-fiber filter (0.7 μm nominal pore diameter) using a duo-seal vacuum pump to remove bacteria, dissolved solid, and other suspended particulate matters. Another water sample was made by deionized water spiked with 200 ng/L geosmin and 2-MIB to identify the fate of these taste and odor-causing compounds. The other two water samples are treatment samples, which were treated with a commercial algaecide, EarthTec®, at recommended dosage (1.188×10^{-9} mg/L; 1 gal/1,000,000 gal raw water) and twice dosage (2.376×10^{-9} mg/L; 2 gal/1,000,000 gal raw water). Both algaecide dosages were added to contaminated water samples, which is unfiltered reagent water and 200 ng/L geosmin and 2-MIB. All these water samples were tested through SPME extraction method and analyzed by GC-MS at five time points (0, 12, 24, 36, and 48 hours) under room temperature (25°C).

3.5 Experimental design

For this study, three experiments were conducted to analyze the removal and effect of various reaction conditions for earthy and musty odorants, geosmin and 2-MIB, in water samples. This includes the fate of geosmin and 2-MIB experiment, algaecide treatment experiment, and mixing effect experiment.

3.5.1 Experiment one

The first experiment is developed by the analysis of mechanisms of geosmin and 2-MIB in lakes to determine any natural removal mechanisms. The production of geosmin and 2-MIB are from algae added in the experimental lab. Four loss mechanisms including volatilization, photolysis, sorption, and/or biodegradation contributed to the

decreased concentration. Volatilization of geosmin and 2-MIB require long times to make observable change in lakes. Photolysis of these compounds can only be found near the surface of reservoirs; therefore, volatilization and photolysis losses are probably negligible. However, sorption and biodegradation of geosmin and 2-MIB could contribute significant removals of these compounds. Sorption could occur when particulate matter is present in lakes. Biodegradation as the major mechanism could affect the removal of geosmin and 2-MIB by native bacteria. Therefore, the purpose of this experiment is to identify the sorption and biodegradation of analytes that affect the removal of these compounds. Unfiltered lake water with dissolved solid and bacteria and filtered lake water without them spiked separately with 200 ng/L geosmin and 2-MIB were tested simultaneously for 48 hours. A control water sample of deionized water with 200 ng/L geosmin/2-MIB was compared to determine the removal efficiency of analytes in other two water samples, unfiltered lake water and filtered lake water with 200 ng/L geosmin/2-MIB, respectively.

3.5.2 Experiment two

Algaecides have the ability to stop the growth of algae in lakes, ponds, reservoirs, or other water bodies. Recent studies conducted at a Tulsa water treatment plant found that algaecides can also contribute to the removal of taste and odor-causing compounds, geosmin and 2-MIB. Schweitzer and Ekstrom (2006) indicated that algaecide is effective in reducing taste and odor causing-compounds concentrations, especially with geosmin. Therefore, the purpose of algaecide treatment experiment in this study is to identify the removal of analytes by EarthTec®, which is used as an example of algaecide due to its most effective removal. Manufactured recommended dosage (1.188×10^{-9} mg/L;

1gal/1,000,000gal raw water) and twice dosage (2.376×10^{-9} mg/L; 2gal/1,000,000gal raw water) of EarthTec® treatment water samples with unfiltered lake water were conducted simultaneously in this experiment and compared the removal efficiency of geosmin and 2-MIB. A control sample without algaecide was run as a control simultaneously as well to verify the stability of these compounds in solution.

3.5.3 Experiment three

In water treatment plants, water sources are obtained from surface water bodies, such as lakes, rivers, or reservoirs. The common way to transport raw water from water sources to water treatment plants is using pipelines. For certain study cases, the removal of geosmin and 2-MIB by algaecides was found in pipelines while raw water was traveling through them. The algaecide was injected at the intake point of surface water body and raw water was traveling for about two days to water treatment plant. The water is unstable while traveling through pipelines; therefore, the purpose of the mixing effect experiment is to simulate the reality of the situation of water inside the pipelines and to identify the removal of geosmin and 2-MIB under this environment. Two water samples treated by twice recommended dosage (2gal/1,000,000gal raw water) of EarthTec® with and without agitation were conducted simultaneously in mixing effect experiment to compare and identify the removal of geosmin and 2-MIB. A control sample with 200 ng/L geosmin/2-MIB and unfiltered lake water (without agitation) was tested as a standard to determine the removal efficiency of analytes. In addition, a water sample with 200 ng/L geosmin/2-MIB and unfiltered lake water (with agitation) was conducted as well as a reference.

CHAPTER IV

FINDINGS

4.1 Calibration curve

The analysis of the removal of earthy and musty odorants, geosmin and 2-MIB, in water samples were conducted with the SPME extraction technique and GC-MS analysis method. Results and discussions of each of three experiments are described below. Duplicate samples under the equivalent condition were conducted at each data point. In order to minimize experimental errors, the averages of duplicate samples` results were used as final results of these experiments. The relative percentage difference within 20 percent for final geosmin/2-MIB concentration of each extraction set is the goal of these experiments.

$$RPD = \left| \frac{X_1 - X_2}{\bar{X}} \right| \times 100,$$

where RPD = relative percentage difference;

$|X_1 - X_2|$ = absolute value of the difference between the two values; and

$\bar{X}$ = average of the two values.

The GC-MS chromatogram of 200 ng/L geosmin and 2-MIB standards is obtained from another source (Mamba *et. al.*, 2007) and shown as an example in Figure 4-1. It illustrates geosmin and 2-MIB peaks at retention times of 10.3 and 11.7 min, respectively. This chromatogram is used as the reference chromatogram in the determination of geosmin and 2-MIB in the water samples. The target compounds are also detected by comparing their spectra with those in standard NIST reference libraries, which are in the software.
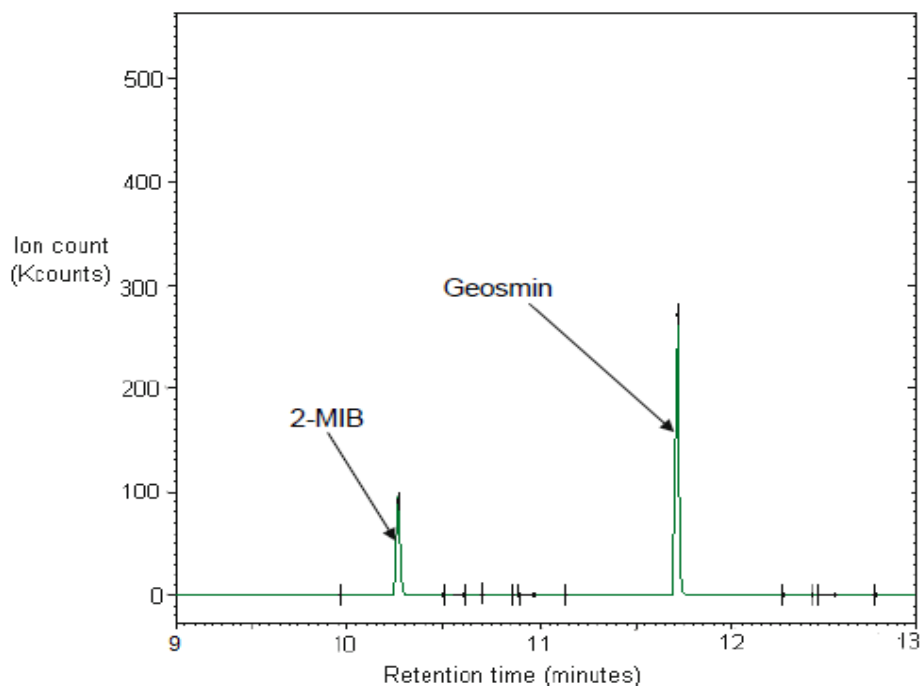
Figure 4-1 The GC-MS chromatogram of 200 ng/L geosmin and 2-MIB standards

Two calibration curves of geosmin and 2-MIB at concentrations ranging from 0 to 200 ng/L (0, 25, 50, 100, 150 and 200 ng/L) were generated from each of three experiments to determine their concentrations in other water samples. A number of calibration curves were obtained and the slopes of them are relatively similar. Thus, Figure 4-2 and Figure 4-3 are representative calibration curves of geosmin and 2-MIB.

Excellent linearity is obtained for both geosmin and 2-MIB with R^2 values of 0.9933 and 0.9957, respectively. Peak areas of analytes are found in Table 4-1 and Table 4-2 by GC-MS at each standard concentration.
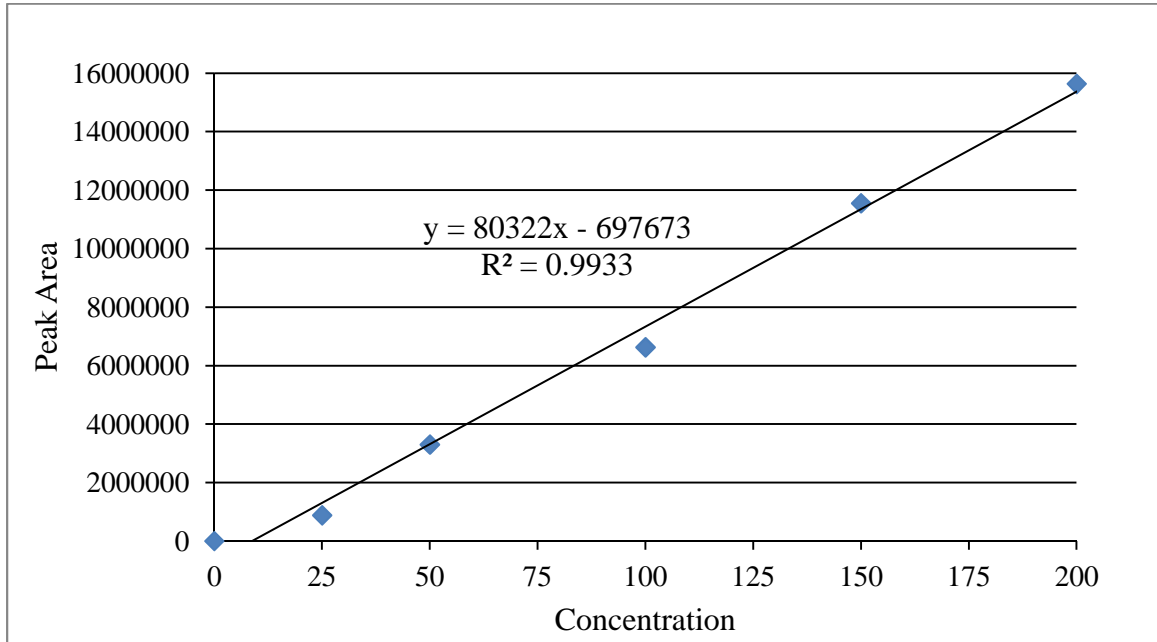
Figure 4-2 Calibration curve of geosmin at concentration ranging from 0 to 200 ng/L

Table 4-1 Peak areas of geosmin at each standard concentration

Calibration Curve	Set 1	Set 2	Average Area
0	0	0	0
25	1112796	649096	880946
50	3286277	3307871	3297074
100	6667865	6580972	6624418.5
150	13278533	9815629	11547081
200	16428125	14838617	15633371
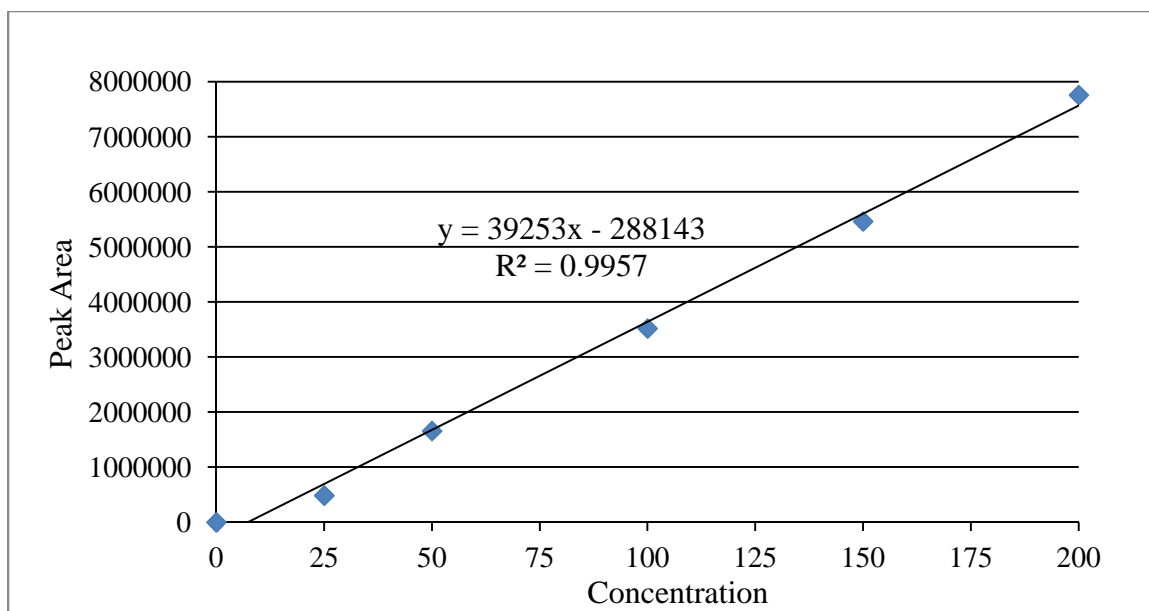
Figure 4-3 Calibration curve of 2-MIB at concentration ranging from 0 to 200 ng/L

Table 4-2 Peak areas of 2-MIB at each standard concentration

Calibration Curve	Set 1	Set 2	Average Area
0	0	0	0
25	462905	509134	486019.5
50	1631465	1683905	1657685
100	3891530	3144448	3517989
150	5988644	4933410	5461027
200	8248732	7263620	7756176

4.2 Result and discussion

4.2.1 Experiment one

The first experiment is designed by the analysis of mechanisms of geosmin and 2-MIB in lakes to determine any natural removal mechanisms. The results of geosmin fate

experiment are listed in Table 4-3 and Figure 4-4. These results indicate that 200 ng/L geosmin is removed by 14.78% in unfiltered lake water sample and 9.62% in filtered lake water sample. However, comparing with the control water sample, which is deionized water, slight differences of final concentrations can be found in these two water samples. The conclusion from the results is that two major mechanisms, sorption and biodegradation, could not make effective contribution on the removal of geosmin in lakes since the concentrations of geosmin in unfiltered lake water, filtered lake water, and deionized water are relatively similar over 48 hours.

The results of 2-MIB for this experiment are shown in Table 4-4 and Figure 4-5. Similar conclusions are found here. Since the slightly different concentrations 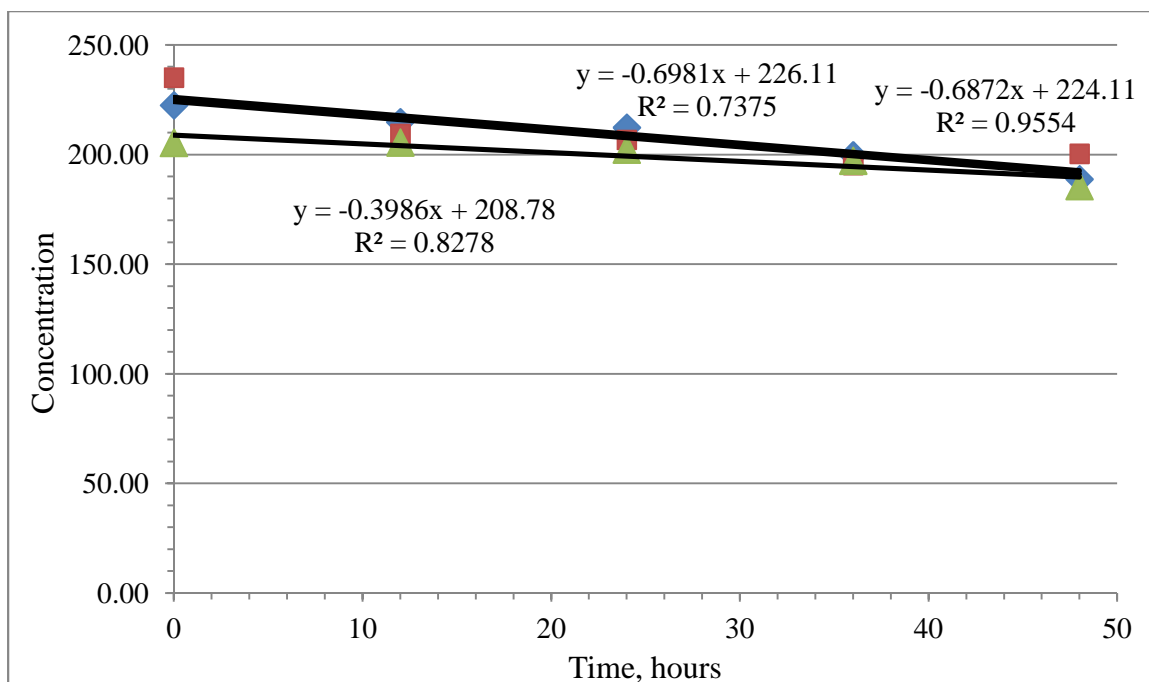of three water samples in this experiment, little removal of 2-MIB was caused by mechanisms in the lake, such as sorption and biodegradation.

Table 4-3 The concentrations of geosmin for the compound fate experiment

Experiment 1		Concentration				
Water Sample	Time, hrs	0	12	24	36	48
200ng/L Geosmin + Deionized Water	Set 1	228.86	223.28	213.01	207.67	197.38
	Set 2	216.08	206.31	211.67	191.73	180.18
	Average	222.47	214.79	212.34	199.70	188.78
200ng/L Geosmin + Unfiltered Lake Water	Set 1	239.86	219.98	207.64	203.04	204.91
	Set 2	230.33	198.95	205.77	187.31	195.79
	Average	235.09	209.47	206.71	195.17	200.35
200ng/L Geosmin + Filtered Lake Water	Set 1	205.96	215.29	213.69	202.76	198.60
	Set 2	204.77	195.87	190.83	191.73	172.63
	Average	205.37	205.58	202.26	197.25	185.62

$y = -0.6981x + 226.11$
$R^2 = 0.7375$

$y = -0.6872x + 224.11$
$R^2 = 0.9554$

$y = -0.3986x + 208.78$
$R^2 = 0.8278$

(◆ is 200ng/L Geosmin + Deionized Water; ■ is 200ng/L Geosmin + Unfiltered Lake Water; ▲ is 200ng/L Geosmin + Filtered Lake Water)

Figure 4-4 The plots of geosmin concentrations for the compound fate experiment

Table 4-4 The concentrations of 2-MIB for the compound fate experiment

Experiment 1		Concentration				
Water Sample	Time, hrs	0	12	24	36	48
200ng/L 2-MIB + Deionized Water	Set 1	200.61	160.76	171.99	176.02	173.45
	Set 2	205.72	216.57	186.41	207.10	151.28
	Average	203.16	188.66	179.20	191.56	162.36
200ng/L 2-MIB + Unfiltered Lake Water	Set 1	202.47	165.70	166.04	186.87	176.87
	Set 2	255.01	227.97	242.72	218.35	233.84
	Average	228.74	196.83	204.38	202.61	205.35
200ng/L 2-MIB + Filtered Lake Water	Set 1	167.04	178.22	165.79	170.58	158.73
	Set 2	183.64	173.67	158.35	172.78	159.65
	Average	175.34	175.95	162.07	171.68	159.19

$$y = -0.3416x + 215.78$$
$$R^2 = 0.2786$$

$$y = -0.3047x + 176.16$$
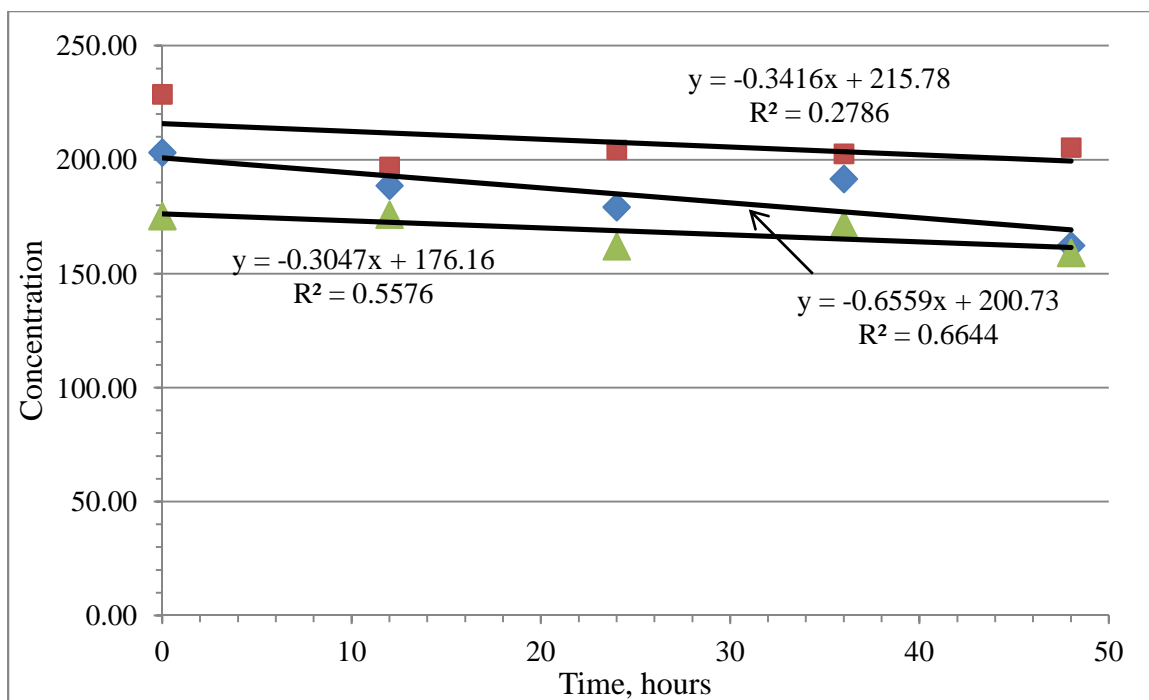$$R^2 = 0.5576$$

$$y = -0.6559x + 200.73$$
$$R^2 = 0.6644$$

(◆ is 200ng/L 2-MIB + Deionized Water; ■ is 200ng/L 2-MIB + Unfiltered Lake Water; ▲ is 200ng/L 2-MIB + Filtered Lake Water)

Figure 4-5 The plots of 2-MIB concentrations for the compound fate experiment

The mass balance of geosmin/2-MIB in actual lakes includes production and loss of these compounds. Four major loss mechanisms, volatilization, photolysis, sorption, and biodegradation, may affect the concentrations of geosmin and 2-MIB in reservoirs. Volatilization of geosmin and 2-MIB depends on their Henry`s constants (H_c), depth and surface area of lakes or reservoirs, and average wind speed. The degradation processes of these compounds by volatilization are too slow to be considered significant. Photolysis of geosmin and 2-MIB has been found near the surface of water bodies; however, Wetzel (1983) documented that UV light is too hard to penetrate deep enough into large lakes or reservoirs. A small percentage of photolysis near the surface of lakes could not contribute significantly to removal of geosmin and 2-MIB.

The experiment comparing unfiltered lake water with filtered lake water in this study investigated the potential effects of sorption and biodegradation of geosmin and 2-MIB. Although the conclusion of the experiment is that no analytes can be removed by sorption and biodegradation due to low suspended solids in the study lake, a number of studies investigated this and reported these two mechanisms could effectively remove the analytes instead. Sorption may remove geosmin and 2-MIB onto particulate matter in lakes. It may be important in lakes with high suspended particulate concentrations. Biodegradation in lakes is the dominant mechanism since other potential mechanisms are minimized. Although the above experiment with bacteria and organisms in water samples does not show any impressive removals, much evidence for geosmin 2-MIB biodegradation is available from literatures. Hoehn (1965) reported that *Bacillus cereus* has been suggested as the major *Bacillus* species responsible for degradation of earthy-musty odors in lakes and sand filters. He observed increased population of gram positive heterotrophic bacilli when concentrations of earthy-musty odors were highest. The disappearance of the earthy-musty odors was obtained in his study by decreases in bacillus populations. Therefore, native bacteria could be responsible for geosmin and 2-MIB degradation in the lakes.

4.2.2 Experiment two

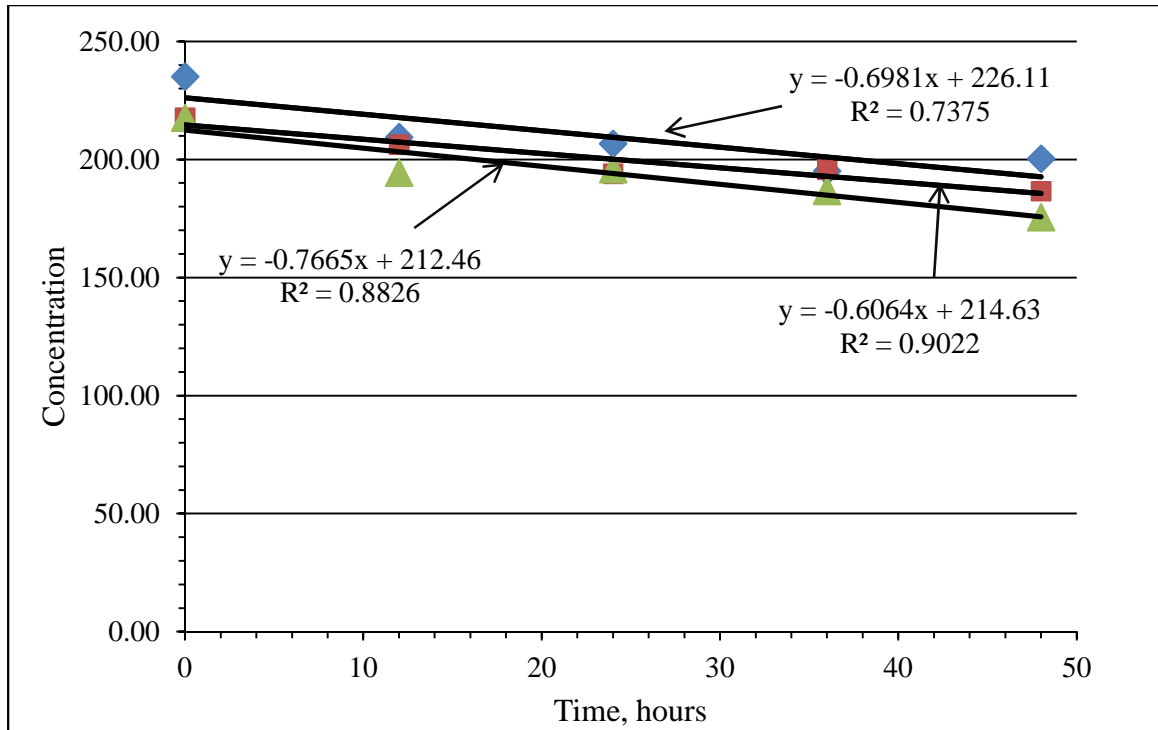The purpose of the second experiment in this study is to identify the removal of analytes by EarthTec®. The results of the algaecide treatment experiment for both geosmin and 2-MIB are shown in Table 4-5 and Table 4-6 and plots are displayed in Figure 4-6 and Figure 4-7. According to the results of geosmin, they show the removals are 14.27% and 19.36% for recommended dosage (1.188×10^{-9} mg/L; 1 gal/1,000,000 gal

raw water) and twice dosage (2.376×10^{-9} mg/L; 2gal/1,000,000gal raw water) of EarthTec®, respectively. The differences of final analytes concentrations between control sample and both dosage samples are 6.85% and 12.37%, respectively. The results of 2-MIB conclude that the removals of both recommended dosage and twice dosage of EarthTec® are 9.5% and 17.31%, respectively. The differences between control sample and both dosage samples are 12.36% and 19.93%, respectively.

Therefore, the conclusion of the algaecide treatment experiment is that the algaecide does not show significant contribution to the removal of both geosmin and 2-MIB and the algaecide dosage could not significantly affect the removal efficiency of analytes since the removal efficiencies and differences between control samples and algaecide treated samples with two dosages are relatively low, within 20%. This low percentage removals could be caused by EarthTec®, instrument deviations, or operation errors.

Table 4-5 The concentrations of geosmin for algaecide treatment experiment

Experiment 2		Concentration				
Water Sample	Time, hrs	0	12	24	36	48
200ng/L Geosmin + Unfiltered Lake Water	Set 1	239.86	219.98	207.64	203.04	204.91
	Set 2	230.33	198.95	205.77	187.31	195.79
	Average	235.09	209.47	206.71	195.17	200.35
200ng/L Geosmin + Unfiltered Lake Water + EarthTec (1gal/1,000,000gal raw water)	Set 1	237.43	221.04	209.85	202.05	203.53
	Set 2	197.97	191.67	178.11	189.40	169.73
	Average	217.70	206.35	193.98	195.73	186.63
200ng/L Geosmin + Unfiltered Lake Water + EarthTec (2gal/1,000,000gal raw water)	Set 1	237.43	197.18	206.44	195.33	182.05
	Set 2	197.97	191.67	185.41	178.13	169.07
	Average	217.70	194.43	195.93	186.73	175.56

$y = -0.6981x + 226.11$
$R^2 = 0.7375$

$y = -0.7665x + 212.46$
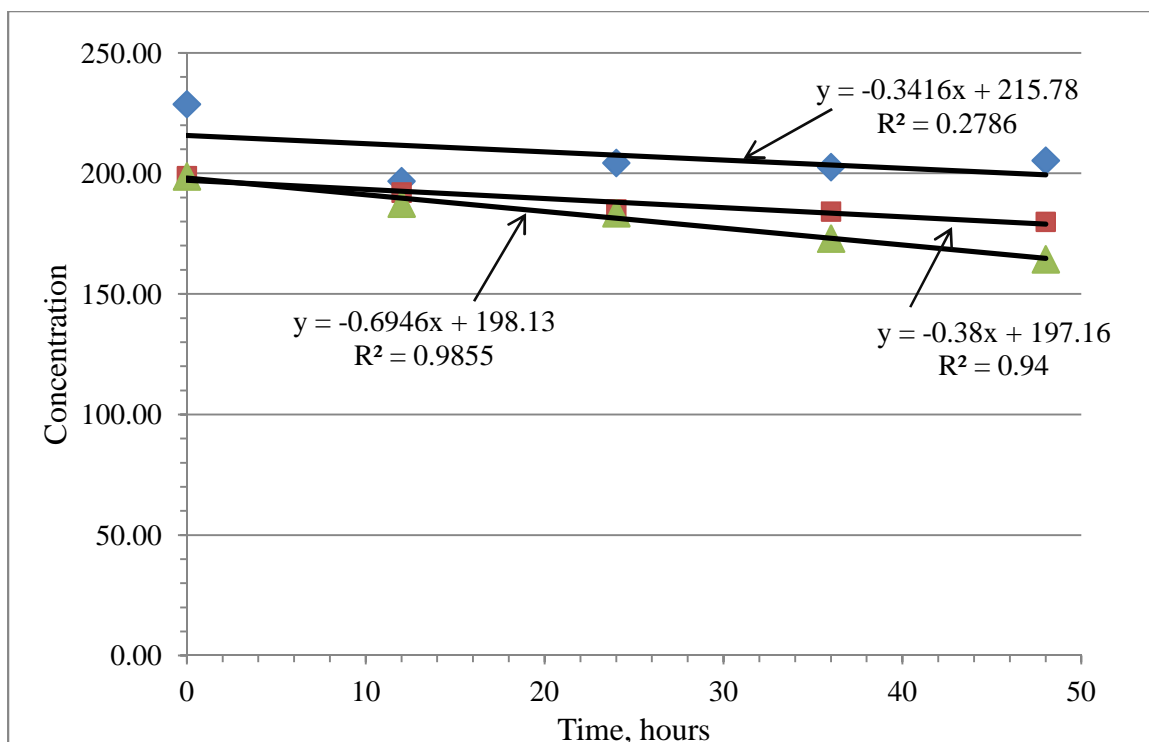$R^2 = 0.8826$

$y = -0.6064x + 214.63$
$R^2 = 0.9022$

(◆ is 200ng/L Geosmin + Unfiltered Lake Water; ■ is 200ng/L Geosmin + Unfiltered Lake Water + EarthTec (1gal/1,000,000gal raw water); ▲ is 200ng/L Geosmin + Unfiltered Lake Water + EarthTec (2gal/1,000,000gal raw water))

Figure 4-6 The plots of geosmin concentrations for algaecide treatment experiment

Table 4-6 The concentrations of 2-MIB for algaecide treatment experiment

Experiment 2		Concentration				
Water Sample	Time, hrs	0	12	24	36	48
200ng/L 2-MIB + Unfiltered Lake Water	Set 1	202.47	165.70	166.04	186.87	176.87
	Set 2	255.01	227.97	242.72	218.35	233.84
	Average	228.74	196.83	204.38	202.61	205.35
200ng/L 2-MIB + Unfiltered Lake Water + EarthTec (1gal/1,000,000gal raw water)	Set 1	213.45	206.38	197.68	199.69	189.18
	Set 2	184.22	177.75	172.55	168.75	170.73
	Average	198.84	192.06	185.12	184.22	179.96
200ng/L 2-MIB + Unfiltered Lake Water + EarthTec (2gal/1,000,000gal raw water)	Set 1	213.45	201.70	192.64	184.53	171.65
	Set 2	184.22	173.30	174.44	161.43	157.18
	Average	198.84	187.50	183.54	172.98	164.42

$$y = -0.3416x + 215.78$$
$$R^2 = 0.2786$$

$$y = -0.6946x + 198.13$$
$$R^2 = 0.9855$$

$$y = -0.38x + 197.16$$
$$R^2 = 0.94$$

(◆ is 200ng/L 2-MIB + Unfiltered Lake Water; ■ is 200ng/L 2-MIB + Unfiltered Lake Water + EarthTec (1gal/1,000,000gal raw water); ▲ is 200ng/L 2-MIB + Unfiltered Lake Water + EarthTec (2gal/1,000,000gal raw water))

Figure 4-7 The plots of 2-MIB concentrations for algaecide treatment experiment

Although the algaecide treatment experiment in this study does not show significant removal of geosmin and 2-MIB, earlies studies (Park, 2012) with 100 times the algaecide dosage indicates significant removal of geosmin and 2-MIB in water samples. It demonstrated that these taste and odor-causing compounds can be readily removed under acidic conditions. EarthTec®, a biologically active form of cupric ion (Cu++), is applied as an example of algaecide in this study not only to stop the growth of algae and the production of geosmin and 2-MIB, but also to reduce the concentrations of these compounds in water solutions. The acidity of EarthTec® removes the odor of geosmin by converting geosmin to argosmin or other odorless products (Schweitzer, 2006). Schweitzer (2006) proposed that EarthTec® decreases the concentrations of

geosmin and 2-MIB in two ways, by dehydration reactions under acidic conditions and by killing the biomass that produces geosmin and 2-MIB. She reported that the pH was reduced in the water solution at the point EarthTec® was injected. Subsequently, geosmin converted into argosmin by acid dehydration; meanwhile, the copper of EarthTec® entered the organic cells and stopped the production and release of geosmin.

Although no experiments with pH as a variable were conducted in this study and the pH of all water samples in this study were in the neighborhood of neutral, a series of investigations for the effect of pH on the removals of geosmin and 2-MIB were documented in literature reviews. The results from previous studies indicate that the solution pH has an important impact on the determination of geosmin and 2-MIB. Hsich *et al.* (2012) detected that the concentrations of geosmin and 2-MIB were significantly reduced in acidic water samples and the effect was more pronounced at low pH condition. For geosmin, the concentration was decreased significantly at pH less than approximately 5.0 in water samples. Similarly, much more 2-MIB was removed at acidic conditions, especially at pH less than 4.6. They also concluded that the results of experiments show similar pH-dependent behaviors in both natural water and deionized water.

Dehydration reactions of geosmin and 2-MIB under acidic conditions have also been reported in experiments testing pH-dependent behaviors of these analytes. Odorless products were converted due to dehydration of these compounds (Gerber and Lechevalier 1965; Gerber 1967). Dehydration reactions of tertiary alcohols, such as geosmin and 2-MIB, are more rapid under acidic conditions. The dehydration products of 2-MIB are 2-methyl-2-bornene, 2-methylenebornane, and 1-methylcamphene; argosmin is produced
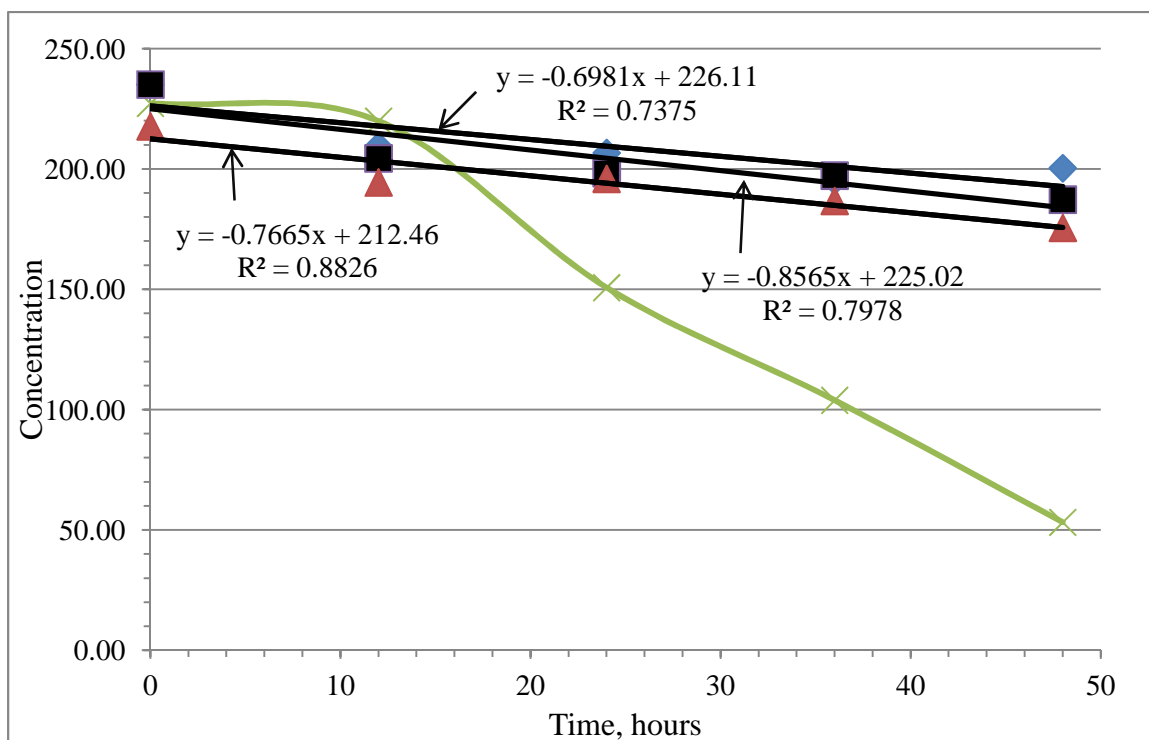
from geosmin as a dehydration product. Current studies (Park, 2012) have also observed these products under acidic conditions.

4.2.3 Experiment three

The purpose of the last experiment is to simulate the reality situation of water in the closed pipeline system and to identify the removal of geosmin and 2-MIB under this condition. The results of mixing effect experiment (Table 4-7 and Figure 4-8) show that geosmin in treated water sample without agitation is removed by 19.36%; however, the significant removal of geosmin in treated water sample with agitation is obtained, which is 76.58%. There is obvious difference between treated water sample and control sample. In addition, the water sample with 200 ng/L geosmin/2-MIB and unfiltered lake water (with agitation) shows slightly removal. Therefore, the conclusion from these results is that most geosmin can be removed by twice EarthTec® dosage with agitation in water samples.

Table 4-7 The concentrations of geosmin for mixing effect experiment

Experiment 3		Concentration				
Water Sample	Time, hrs	0	12	24	36	48
200ng/L Geosmin + Unfiltered Lake Water (w/o agitation)	Set 1	239.86	219.98	207.64	203.04	204.91
	Set 2	230.33	198.95	205.77	187.31	195.79
	Average	235.09	209.47	206.71	195.17	200.35
200ng/L Geosmin + Unfiltered Lake Water (w/ agitation)	Set 1	239.86	214.80	207.32	206.15	193.66
	Set 2	230.33	193.99	189.23	188.38	180.87
	Average	235.09	204.39	198.27	197.27	187.27
200ng/L Geosmin + Unfiltered Lake Water + EarthTec (2gal/1,000,000gal raw water) (w/o agitation)	Set 1	237.43	197.18	206.44	195.33	182.05
	Set 2	197.97	191.67	185.41	178.13	169.07
	Average	217.70	194.43	195.93	186.73	175.56
200ng/L Geosmin + Unfiltered Lake Water + EarthTec (2gal/1,000,000gal raw water) (w/ agitation)	Set 1	234.10	221.84	207.30	109.20	51.06
	Set 2	220.33	217.90	94.12	98.61	55.36
	Average	227.21	219.87	150.71	103.91	53.21

$$y = -0.6981x + 226.11$$
$$R^2 = 0.7375$$

$$y = -0.7665x + 212.46$$
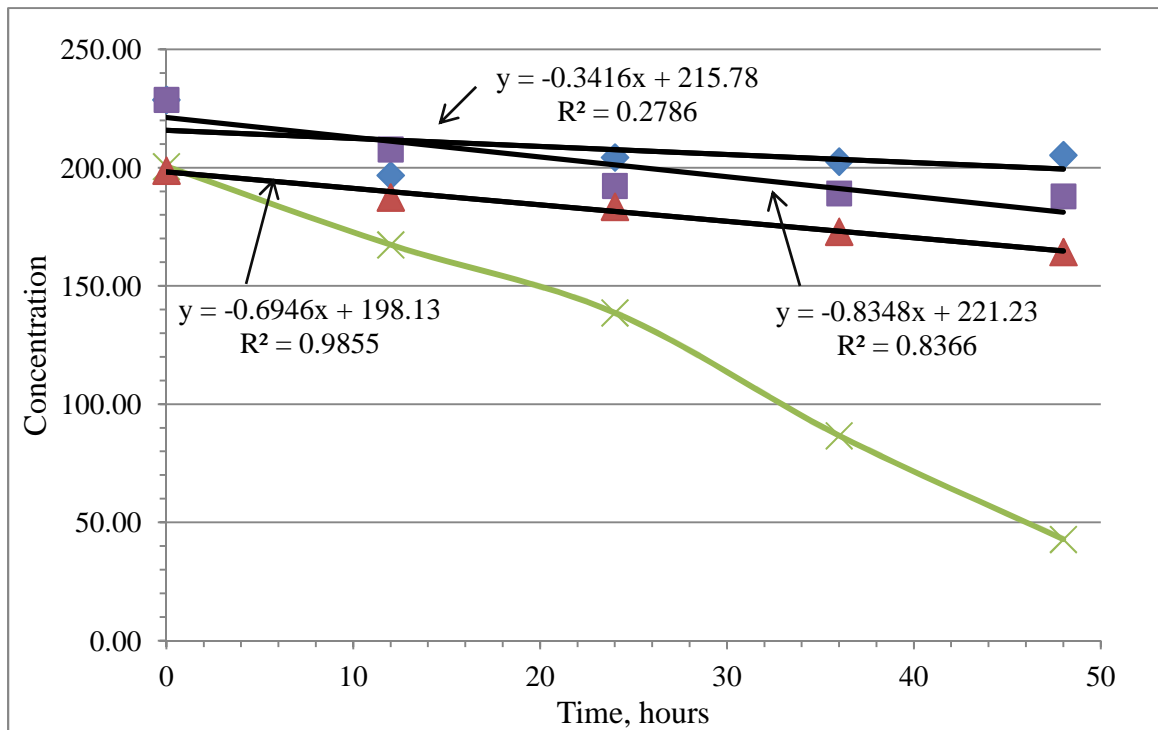$$R^2 = 0.8826$$

$$y = -0.8565x + 225.02$$
$$R^2 = 0.7978$$

(◆ is 200ng/L Geosmin + Unfiltered Lake Water (w/o agitation); ■ is 200ng/L Geosmin + Unfiltered Lake Water (w/ agitation); ▲ is 200ng/L Geosmin + Unfiltered Lake Water + EarthTec (2gal/1,000,000gal raw water) (w/o agitation); × is 200ng/L Geosmin + Unfiltered Lake Water + EarthTec (2gal/1,000,000gal raw water) (w/ agitation))

Figure 4-8 The plots of geosmin concentrations for mixing effect experiment

The experiments of 2-MIB show similar results (Table 4-8 and Figure 4-9). The removal of 2-MIB in treated water sample without agitation is 17.31%; however, 2-MIB in treated water sample with agitation was removed 78.64%. Although the final concentrations of geosmin and 2-MIB do not drop to odor threshold concentrations (10ng/L), the significant removals of both compounds with twice recommended EarthTec® dosage and sample mixing are concluded from the results of this experiment.

Table 4-8 The concentrations of 2-MIB for mixing effect experiment

Experiment 3		Concentration				
Water Sample	Time, hrs	0	12	24	36	48
200ng/L 2-MIB + Unfiltered Lake Water (w/o agitation)	Set 1	202.47	165.70	166.04	186.87	176.87
	Set 2	255.01	227.97	242.72	218.35	233.84
	Average	228.74	196.83	204.38	202.61	205.35
200ng/L 2-MIB + Unfiltered Lake Water (w/ agitation)	Set 1	202.47	217.92	201.26	196.80	195.42
	Set 2	255.01	197.60	183.45	181.63	180.42
	Average	228.74	207.76	192.36	189.22	187.92
200ng/L 2-MIB + Unfiltered Lake Water + EarthTec (2gal/1,000,000gal raw water) (w/o agitation)	Set 1	213.45	201.70	192.64	184.53	171.65
	Set 2	184.22	173.30	174.44	161.43	157.18
	Average	198.84	187.50	183.54	172.98	164.42
200ng/L 2-MIB + Unfiltered Lake Water + EarthTec (2gal/1,000,000gal raw water) (w/ agitation)	Set 1	207.60	174.31	176.21	120.57	40.23
	Set 2	193.45	160.56	101.08	52.84	45.46
	Average	200.53	167.44	138.64	86.70	42.84

y = -0.3416x + 215.78
R² = 0.2786

y = -0.6946x + 198.13
R² = 0.9855

y = -0.8348x + 221.23
R² = 0.8366

(◆ is 200ng/L 2-MIB + Unfiltered Lake Water (w/o agitation); ■ is 200ng/L 2-MIB + Unfiltered Lake Water (w/ agitation); ▲ is 200ng/L 2-MIB + Unfiltered Lake Water + EarthTec (2gal/1,000,000gal raw water) (w/o agitation); × is 200ng/L 2-MIB + Unfiltered Lake Water + EarthTec (2gal/1,000,000gal raw water) (w/ agitation))

Figure 4-9 The plots of 2-MIB concentrations for mixing effect experiment

Sample agitation may promote organisms' activities and enhance reactions in lake water. A Tulsa water treatment plant observed significant removal of geosmin and 2-MIB with lake water which is obtained from surface water source through pipelines. Since water travel through pipelines with complete mixing, this experiment was conducted to simulate the same condition on mixing. Much reaction was observed between EarthTec® and geosmin/2-MIB present in unfiltered lake water with agitation. Therefore, the results of mixing effect experiment show significant removal of geosmin and 2-MIB in EarthTec® and unfiltered lake water sample with agitation. Further studies can be investigated to confirm the conclusion.

4.3 Other variables

The seasonal change of geosmin and 2-MIB concentrations is documented in literature. Temperature is a factor in the growth of algal and production of geosmin and 2-MIB. Organisms in lakes, such as actinomycetes and cyanobacteria are responsible for producing these compounds; their development in water environment is dependent on temperature. Several studies investigated the performance of different temperatures (a range of 10 to 35°C) on the removals of geosmin and 2-MIB in water samples. Zhang *et al.* (2009) indicated that higher temperatures may promote the releases of geosmin and 2-MIB into water columns. Therefore, taste and odor problems caused by algae are more serious from late spring to early autumn.

Some studies found that light can affect the concentrations of geosmin and 2-MIB in lakes or reservoirs. Light intensity (10, 20, and 75 µmol m^{-2} s^{-1}) experiments were

conducted by Zhang *et al.* (2009) to determine the effect of geosmin and 2-MIB concentrations. They reported that the maximum concentrations of these compounds were found at 20 μmol m^{-2} s^{-1} since this optimum light intensity condition promotes cells growth and enhances geosmin and 2-MIB productions. Therefore, low light intensity (<20 μmol m^{-2} s^{-1}) can contribute the T&O problems control.

CHAPTER V

CONCLUSION

Geosmin and 2-MIB have been identified as common taste and odor-causing compounds in drinking water. Although these compounds have been not been associated with any serious health effects, water utilities aim to remove these odor-causing compounds due to consumers` complaints. Granular/powdered activated carbon (GAC/PAC), advanced oxidation processes (AOP), ozonation, and biofitration are the most effective techniques to remove geosmin and 2-MIB in most water treatment plants. However, these removal methods are extremely expensive to install, maintain, and operate. More efficient and economic taste and odor control technologies would be welcome.

In this study, the analysis of effecting removal factors of geosmin and 2-MIB in water samples were determined. It was determined that when biomass concentration is low (less than 10 ng/L), sorption and biodegradation did not effectively contribute to the significant removal of these odor-causing compounds. The algaecide treatment experiment finds that the recommended dosage (1.188×10^{-9} mg/L; 1gal/1,000,000gal raw water) and twice dosage (2.376×10^{-9} mg/L; 2gal/1,000,000gal raw water) of EarthTec® do not significantly reduce the concentrations geosmin and 2-MIB in treated water

samples. However, the experiment with greater mixing identifies that 76.58% geosmin and 78.64% 2-MIB can be removed at the doubled EarthTec® dosage with agitation over 48 hours in water samples.

Further studies can be investigated to confirm the results from this study in several ways. First, biodegradation may yet prove significant on reducing the concentrations of geosmin and 2-MIB in lakes. Alterative experiment designs using varying concentrations of biomass should be employed to determine the difference more accurately. In addition, further data sets on the effects of mixing should be done in subsequent experiments. The other recommendation is that the design of agitation removal experiment could be done better. The principle of this experiment is to simulate the water traveling through pipelines at water treatment plant; therefore, more similar design to real water condition needs to be conducted in further study.

REFERENCES

Adams, B. A. (1929). Odours in the water of the Nile River. *Water and Water Eng., 31,* 309–314.

Aumen, N. G. (1980). Microbial succession on a chitinous substrate in a woodland stream. *Microbial Ecol., 6*(4), 317–327.

Bentley, R., & Meganathan, R. (1981). Geosmin and methylisoborneol biosynthesis in streptomycetes: evidence for an isoprenoid pathway and its absence in nondifferentiating isolates. *FEBS Lett, 125*(2), 220–222.

Blevins, W. (1980). Geosmin and other odourous metabolites of microbial origin. In: Introduction to Environmental Toxicology. Elsevier, New York, 350–357.

Bruce, D., westerhoff, P., & Brawley-Chesworth, A. (2002). Removal of 2-methylisoborneol and geosmin in surface water treatment plants in Arizona. *Journal of Water Supply, 51*, 183-197.

Buttery, R. G., & Garibaldi, J. A. (1976). Geosmin and methylisoborneol in garden soil. *J. Agr. Food Chem., 24*(6), 1246–1247.

Chen, G., Dussert, B. W., & Suffet, I. H. (1997). Evaluation of granular activated carbons for removal of methylisoborneol to below odor threshold concentration in drinking water. *Water Research, 31*(5), 1155-1163..

Cid, A., Herrero, C., Torres, E., & Abalde, J. (1995). Copper toxicity on the marine microalga Phaeodactylum tricomutum: effects on photosynthesis and related parameters. *Aquat. Toxicol., 31*, 165-174.

Cook, D., Newcombe, G., & Sztajnbok, P. (2000). The application of powdered activated carbon for MIB and Geosmin removal: Predicting PAC doses in four raw waters. *Water Research, 35*, 1325-1333.

Cook, D., Newcombe, G., & Sztajnbok, P. (2001). The application of powdered activated carbon for MIB and geosmin removal: predicting PAC doses in four raw waters. *Water Research, 35*, 1325–1333.

Cross, T. (1981). Aquatic actinomycetes: a critical survey of the occurrence, growth and role of actinomycetes in aquatic habitats. *J. Appl. Bacteriol., 50*(3), 397–423.

Darriet, P., Pons, M., Lamy, S., & Dubourdieu, D. (2000). Identification and quantification of geosmin, an earthy odorant contaminating wines. *Journal Agricultural Food Chemistry, 48*(10), 4835-4838.

Dionigi, C. P., Lawlor, T. E., McFarland, J. E., & Johnsen, P. B. (1993). Evaluation of geosmin and 2-methylisoborneol on the histidine dependence of TA98 and TA100 *Salmonella typhimurium* tester strains. *Water Research, 27*, 1615–1618.

Drikas, M., Dixon, M., & Morran, J. (2009). Removal of MIB and geosmin using granular activated carbon with and without MIEX pre-treatment. *Water Resource, 43*(20), 5151-5159.

Earth Science Laboratories, Inc. (2009). Product summary. *Earth Science Laboratories, Inc.* Bentonville, AR, USA.

Elhadi, S. L. N., Huck, P. M., & Slawson, R. M. (2006). Factors affecting the removal of geosmin and MIB in drinking water biofilters. *Journal of the American Water Works Association, 98,* 108–120.

Ferguson, D. W., McGuire, M. J., Koch, B., Wolfe, R. L., & Aieta, E. (1990). Comparing peroxone and ozone for controlling taste and odor compound, disinfection by-products, and microorganisms. *Journal of the American Water Works Association, 82*, 181-191.

Florence, T. M., & Stauber, J. L. (1986). Toxicity of copper complexes to the marine diatom Nitzschia closterium. *Aquat. Tox., 8*, 11-26.

García-Villada, L., Rico, M., Altamirano, M. M., Sánchez-Martín, L., López-Rodas, V., & Costas, E. (2004). Occurrence of copper resistant mutants in the toxic cyanobacteria *Microcystis aeruginosa*: characterisation and future implications in the use of copper sulphate as algaecide. *Water Resources, 38(8),* 2207-2213.

Gardiner, E. R. (1973). Experience with powered activated carbon for taste and odor control. *Proc. Water Research Assoc. Conf.* (pp. 241-262). England: Reading.

Gerber, N. N. (1968). Geosmin from micro-organisms is *trans*-1,10-dimethyl-*trans*-9-decalol. *Tetrahedron Lett, 25*, 2971–2974.

Gerber, N. N. (1969). A volatile metabolite of actinomycetes, 2-methylisoborneol. *J. Antibiot. 22*, 508-509.

Gerber, N. N. (1979). Volatile substances from actinomycetes: their role in the odor pollution of water. *Crit Rev Microbiol, 7*, 191–214.

Gerber, N. N. (1983). Volatile substances from actinomycetes: their role in the odour pollution of water. *Water Sci Technol, 15*, 115–125.

Gerber, N. N., & Lechavalier, H. A. (1965). Geosmin, an earthy-smelling substance isolated from actinomycetes. *Applied Microbiology, 13*, 395.

Glaze, W. H., Zarnoch, J. J., Ruth, E. C., Chauncey, W., & Schep, R. (1990). Evaluating oxidants for the removal of model taste and odor compounds from a municipal water supply. *Journal of the American Water Works Association, 82*, 79-84.

Goodfellow, M., & Williams, S.T. (1983). Ecology of actinomycetes. *Ann. Rev. Microbiol., 37*, 189–216.

Hatano, K., Frederick, D. J., & Moore, J. A. (1994). Microbial ecology of constructed wetlands used for treating pulp mill wastewater. *Water Sci. Technol., 29*(4), 233–239.

Henley, D. E., Glaze, W. H., & Silvey, J. K. G. (1969). Isolation and identification of odor compound produced by selected aquatic actinomycete. *Environ. Sci. Technol., 3*, 268-271.

Ho, L., & Newcombe, G. (2010). Granular activated carbon adsorption of 2-methylisoborneol (MIB): pilot- and laboratory-scale evaluations. *Journal of Environmental Engineering, 136*(9), 965-974.

Ho, L., Hoefel, D., Bock, F., Saint, C. P., & Newcombe, G. (2007). Biodegradation rates of 2-methylisoborneol (MIB) and geosmin through sand filters and in bioreactors. *Chemosphere, 66,* 2210–2218.

Ho, L., Newcombe, G., & Croue, J. (2002). Influence of the character of NOM on the ozonation of MIB and geosmin. *Water Research, 36,* 511–518.

Hoehn, R. (1965). Biological methods for the control of tastes and odors. *Southwest Water Works J. 47*(3), 26–30.

Hrudey, S. E., Rector, D., & Motkosky, N. (1992). Characterization of drinking water odour arising from spring thaw for an icecovered upland river source. *Water Sci. Technol., 25*(2), 65–72.

Hsieh, W. H., Hung, W. N., Wang, G. S., Hsieh, S. T., & Lin, T. F. (2012). Effect of pH on the analysis of 2-MIB and geosmin in water. *Water Air Soil Pollut, 223,* 715–721.

Huck, P. M., Kenefick, S. L., Hrudey, S. E., & Zhang, S. (1995). Bench scale determination of the removal of odour compounds with biological treatment. *Water Science and Technology, 31,* 203–209.

Humpage, A. R., Hardy, S. J., Moore, E. J., Froscio, S. M., & Falconer, I. R. (2000). Microcystins (cyanobacterial toxins) in drinking water enhance the growth of aberrant crypt foci in the mouse colon. *J. Toxicol. Environ. Health, A 61*, 155–165.

Izaguirre, G. (1982). Geosmin and 2-methylisoborneol from cyanobacteria in three water supply systems. *Appl. Envir. Microbiol., 43,* 708-714.

Izaguirre, G., & Taylor, W. D. (1998). A Pseudanabaena species from Castaic Lake, California, that produces 2-methylisoborneol. *Water Res., 32*(5), 1673–1677.

Izaguirre, G., Hwang, C. J., Krasner, S. W., & McGuire, M. J. (1982). Geosmin and 2-methylisoborneol from cyanobacteria in three water supply systems. *Appl Environ Microbiol, 43*, 708–714.

Jenkins, D., Richard, M. G., & Daigger, G. T. (1993). Manual on the Causes and Control of Activated Sludge Bulking and Foaming, second ed. CRC Press, Boca Raton.

Jensen, S. E., Anders, C. L., Goatcher, L. J., Perley, T., Kenefick, S., & Hrudey, S. E. (1994). Actinomycetes as a factor in odour problems affecting drinking water from the North Saskatchewan River. *Water Res., 28*(6), 1393–1401.

Jiang, C. L., & Xu, L. H. (1996). Diversity of aquatic actinomycetes in lakes of the middle plateau, Yunnan, China. *Appl. Environ. Microbiol., 62*(1), 249–253.

Jung, S. W., Baek, K. H., & Yu, M. J. (2004). Treatment of taste and odor material by oxidation and adsorption. *Water Science and Technology, 49*, 289-295.

Juttner, F. (1995). Elimination of terpenoid odorous compounds by slow sand and river bank filtration of the Ruhr River, Germany. *Water Science Technology, 31*, 211-217.

Juttner, F., & Watson, S. B. (2007). Biochemical and ecological control of geosmin and 2-methylisoborneol in source waters. *Applied and Environmental Microbiology, 73*, 4395-4406.

Kennefick, S. L., Hrudey, S. E., Peterson, H. G., & Prepas, E. E. (1993). Toxin release from Microcystis aeruginosa after chemical treatment. *Water Sci. Tech., 27*(3), 433-440.

Kikuchi, T., Kadota, S., Suehara, H., Nishi, A., & Tsubaki, K. (1981). Odorous metabolites of a fungus, *Chaetomium globosum* Kinze ex Fr. Identification of geosmin, musty-smelling compound. *Chem Pharm Bull, 29*, 1781–1784.

Klausen, C., Jorgensen, N. O. G., Burford, M., & O`Donahue, M. (2004). Occurrence of odour-producing actinomycetes and other bacteria in the North Pine River Dam, Brisbane, Australia. In manuscript.

Kutschera, K., Bornick, H., & Worch, E. (2009). Photoinitiated oxidation of geosmin and 2-methylisoborneol by irradiation with 254 nm and 185 nm UV light. *Water Research, 43*, 2224-2232.

Lalezary, S., Pirbazari, M., & McGuire, M. J. (1986). Evaluating activated carbons for removing low concentrations of taste-producing and odor-producing organics. *Journal American Water Works Association, 78*(11), 76-82.

Lalezary, S., Pirbazari, M., McGuire, M. J., & Krasner, S. W. (1984). Air stripping of taste and odor compounds from water. *Journal American Water Works Association, 76*(3), 83-87.

Lanciotti, E., Santini, C., Lupi, E., & Burrini, D. (2003). Actinomycetes, cyanobacteria and algae causing tastes and odours in water of the River Arno used for the water supply of Florence. *J. Water Supply: Res. Technol.—AQUA, 52*(7), 489–499.

Lange, C. L., & Wittmeyer, S. A. (1997). Production of drinking water tastes and odors in zebra mussel colonies. *Dreissena!, 7*(4), 11–12.

Lawton, L. A., Robertson, P. K. J., Robertson, R. F., & Bruce, F. G. (2003). The destruction of 2-methylisoborneol and geosmin using titanium dioxide photocatalysis. *Applied Catalysis B: Environmental, 44,* 9–13.

Lemmer, H. (1986). The ecology of scum causing actinomycetes in sewage-treatment plants. *Water Res., 20*(4), 531–535.

Lloyd, A. B. (1969). Dispersal of streptomycetes in air. *J. Gen. Microbiol. 57*, 35–40.

Lloyd, S. W., & Grimm, C. C. (1999). Analysis of 2-methylisoborneol and geosmin in catfish by microwave distillation-solid-phase microextraction. *Journal Agricultural Food Chemistry, 47*, 164-169.

Lovell, R. T., & Sackey, L. A. (1973). Absorption by channel catfish of earthy-musty flavor compounds synthesized by cultures of blue-green algae. *Trans. Am. Fish. Soc., 102*(1973), 774–777.

Lu, G., Fellman, J. K., Edwards, C. G., Mattinson, D. S., & Navazio, J. (2003a). The quantitative determination of geosmin in red beets (Beta vulgaris L.) using headspace solid-phase microextraction. *Journal Agricultural Food Chemistry, 51*(4), 1021-1025.

Lu, G., Fellman, J. K., Edwards, C. G., Mattinson, D. S., & Navazio, J. (2003b). Biosynthetic origin of geosmin in red beets (Beta vulgaris L.). *Journal Agricultural Food Chemistry, 51*(4), 1026-1029.

Maga, J. A. (1987). Musty/earthy aromas. *Journal International Food Rev., 3*, 269-284.

Makkar, N. S., & Cross, T. (1982). Actinoplanetes in soil and on plant litter from freshwater habitats. *J. Appl. Bacteriol., 52*, 209–218.

Mallevialle, J., & Suffet, I. H. (1987). Identification and treatment of tastes and odors in drinking water. *American Water Works Association Research Foundation/Lyonnaise des Eaux, AWWA, Denver, CO. AWWARF Report,* 118.

Mamba, B. B., Krause, R. W., Malefetse, T. J., Mhlanga, S. D., Sithole, S. P., Salipira, K. L., & Nxumalo, E. N. (2007). Removal of geosmin and 2-methylisorboneol (2-MIB) in water from Zuikerbosch Treatment Plant (Rand Water) using β-cyclodextrin polyurethanes. *Water SA, 33*(2), 223-227.

Martin, J. F., Izaguirre, G., & Waterstrat, P. (1991). A planktonic *Oscillatoria* species from Mississippi catfish ponds that produces the off-flavor compound 2-methylisoborneol. *Water. Res. 25*, 1447–1451.

Matsumoto, A., & Tsuchiya, Y. (1988). Earthy-musty odor-producing cyanophytes isolated from five water areas in Tokyo. *Water Sci Technol, 20*(8/9), 179–183.

McGuire, M. J., Krasner, S. W., Hwang, C. J., & Izaguirre, G. (1981). Closed-loop stripping analysis as a tool for solving taste and odor problems. *Journal American Water Works Association, 73*(10), 530-537.

Medsker, L. L., Jenkins, D., Thomas, J. F., & Koch, C. (1969). Odorous compounds in natural waters: 2-exo-hydroxy-2-methylbornane, the major odorous compound produced by several actinomycetes. *Environ. Sci. Technol. 3*, 476-477.

Michael, D. L., Jennifer, V. C., & Stacy, T. K. (2009). *Algaecide pilot study: Copco reservoir 2008.* California, CA: Watercourse Engineering, Inc.

Naes, H., Utkilen, H., & Post, A. (1988). Factors influencing geosmin production by the cyanobacterium *Oscillatoria brevis*. *Water Sci. Technol., 20*, 125–131.

Najm, I. N., Snoeyink, V. L., Suidan, M. T., Lee, C. H., & Richard, Y. (1990). Effect of particle size and background natural organics on the adsorption efficiency of PAC. *Jour. AWWA, 82*(1), 65-72.

Nakamura, S., & Daishima, S. (2005). Simultaneous detection of 22 volatile organic compounds, methyl-tertbutylether, 1,4-dioxane, 2-methylisorboneol and geosmin in water by headspace solid phase microextraction-gas chromatography-mass spectrometry. *Anal. Chim. Acta., 548*, 79-85.

Nerenberg, R., Rittmann, B. E., & Soucie, W. J. (2000). Ozone/biofiltration for removing MIB and geosmin. *Journal of the American Water Works Association, 92,* 85–97.

Newcombe, G., Collet, A., Drikas, M., & Roberts, B. (1996). Granular activated carbon pilot plant studies. *Water: Journal of Australian Water Association, 23*, 29-31.

Newcombe, G., Drikas, M., & Hayes, R. (1997). Influence of characterised natural organic material on activated carbon adsorption: II. effect of pore volume distribution and adsorption of 2-methylisoborneol. *Water Research, 31*(5), 1065-1073.

Newcombe, G., Morrison, J., & Hepplewhite, C. (2002a). Simultaneous adsorption of MIB and NOM onto activated carbon. I. Characterisation of the system and NOM adsorption. *Carbon, 40*, 2135-2146.

Newcombe, G., Morrison, J., Hepplewhite, C., & Knappe, D. R. (2002b). Simultaneous adsorption of MIB and NOM onto activated carbon-II. Competitive effects. *Carbon, 40*, 2147-2156.

Niemi, R. M., Knuth, S., & Lundstro¨m, K. (1982). Actinomycetes and fungi in surface waters and potable water. *Appl. Environ. Microbiol., 43*(2), 378–388.

Odencrantz, J. E. (1990). Simulation of biologically active zones (BAZ's) in porous media by electron-acceptor injection. *Journal of contaminant hydrology, 6,* 37-45.

Paerl, H. W., Fulton, R. S., Moisander, P. H., & Dyble, J. (2001). Harmful freshwater algal blooms, with an emphasis on cyanobacteria. *The Scientific World, 1*, 76-113.

Park, H. (2012). Unpublished data.

Pelekani, C., & Snoeyink, V. L. (1999). Competitive adsorption in natural water: role of activated carbon pore size. *Water Research, 33*(5), 1209-1219.

Pelekani, C., & Snoeyink, V. L. (2000). Competitive adsorption between atrazine and methylene blue on activated carbon: the importance of pore size distribution. *Carbon, 38*(10), 1423-1436.

Pelekani, C., & Snoeyink, V. L. (2001). A kinetic and equilibrium study of competitive adsorption between atrazine and congo red dye on activated carbon: the importance of pore size distribution. *Carbon, 39*(1), 25-27.

Pendleton, P., Wong, S. H., Schumann, R., Levay, G., Denoyel, R., & Rouquerol, J. (1997). Properties of activated carbon controlling 2-methylisoborneol adsorption.*Carbon*, *35*(8), 1141-1149.

Peterson, H. G., Hrudey, S. E., Cantin, I. A., Perley, T. R., & Kenefick, S. L. (1995). Physiological toxicity, cell membrane damage and the release of dissolved organic carbon and geosmin by Aphanizomenon flosaquae after exposure to water treatment chemicals. *Water Res., 29*(6), 1515–1523.

Pirbazari, M., Borrow, H. S., Craig, S., Ravindran, V., & McGuire, M. J. (1992). Physical chemical characterization of five earthy-musty-smelling compounds. *Water Science and Technology, 25*(2), 81-88.

Pirbazari, M., Ravindran, V., Badriyha, B. N., Craig, S., & McGuire, M. J. (1993). GAC adsorber design protocol for the removal of off-flavors. *Water Research, 27*, 1153–1166.

Raschke, R. L., Carroll, B., & Tebo, L. B. (1975). The relationship between substrate content, water quality, actinomycetes and musty odours in the Broad River basin. *J. Appl. Ecol., 12*(2), 535–560.

Rashash, D., Dietrich, A., & Hoehn, R. (1997). Flavor profile analysis of selected odorous compounds, *Journal American Water Works Association, 89*(2), 131-142.

Rashash, D., Dietrich, A., Hoehn, R., & Parker, B. (1995). The influence of growth conditions on odorcompound production by two chrysophytes and two cyanobacteria. *Water Sci. Technol., 31*, 165–172.

Rashash, D., Hoehn, R., Dietrich, A., & Grizzard, T. (1996). Identification and control of odorous algal metabolites. AWWARF, Denver, CO. AWWARF Research Report 716.

Ridal, J., Brownlee, B., McKenna, G., & Levac, N. (2001). Removal of taste and odor compounds by conventional granular activated carbon filtration. *Water Quality Research Journal of Canada, 36*, 43-54.

Rittmann, B. E., Gantzer, C., & Montiel, A. (1995). Biological treatment to control taste-and-odor compounds in drinking water treatment. *Advances in taste-and-odor treatment and control.* AWWA Research Foundation and Lyonnaise des Eaux., 209-246.

Robedson, R. F., Hammond, A., Jauncey, K., Beveridge, M. C. M., & Lawton, L. A. (2006). An investigation into the occurrence of geosmin responsible for earthy-musty taints in UK farmed rainbow trout *Onchorhynchus mykiss*. *Aquaculture, 259*, 153–163.

Rosen, A. A., Mashni, C. I., & Safferman, R. S. (1970). Recent developments in the chemistry of odour in water: the cause of earthy/musty odour. *Water Treat. Exam., 19*, 106-119.

Rosenfeldt, E. J., Melcher, B., & Linden, K. G. (2005). UV and UV/H_2O_2 treatment of methylisoborneol (MIB) and geosmin in water. *Journal of Water Supply, 54,* 423–434.

Saadoun, I. M. K., Schrader, K. K., & Blevins, W. T. (2001). Environmental and nutritional factors affecting geosmin synthesis by Anabaena sp. *Water Res., 35*(5), 1209–1218.

Safferman, R. S., Rosen, A. A., Mashni, C. I., & Morris, M. E. (1967). Earthy-smelling substance from a blue-green alga. *Environmental Science and Technology, 1*(5), 429-430.

Saito, K., Okamura, K., & Kataoka, H. (2008). Determination of musty odorants, 2-methylisoborneol and geosmin, in environmental water by headspace solid-phase mirroextraction and gas chromatography-mass spectrometry. *Journal of Chromatography A, 1186*, 434-437.

Schrader, K. K., Dayan, F. E., & Nanayakkara, N. P. D. (2005). Generation of reactive oxygen species by a novel anthraquinone derivative in the cyanobacterium Planktothrix perornata (Skuja). *Pestic Biochem Physiol, 81*(3), 198–207.

Schrader, K. K., de-Regt, M. Q., Tidwell, P. D., Tucker, C. S., & Duke, S. O. (1998). Compounds with selective toxicity towards the off-flavor metabolite-producing cyanobacterium Oscillatoria cf. chalybea. *Aquaculture, 163*(1–2), 85–99.

Schrader, K., & Blevins, W. (1993). Geosmin producing species of *Streptomyces* and *Lyngbya* from aquaculture ponds. *Can J Microbiol 39*, 834–840.

Schulz, S., Fuhlendor, J., & Reichenbach, H. (2004). Identification and synthesis of volatiles released by the myxobacterium *Chondromyces crocatus*. *Tetrahedron*, *60*, 3863–3872.

Schweitzer, & Ekstrom. (Nov, 2006). Removal of Natural organic Matter, Disinfection Byproducts, and taste-and-odor compounds from drinking water by application of

Earth Tec Algaecide. *Department of Chemistry, Oakland University, Rochester, MI*.

Silvey, J. K. G., & Roach, A. W. (1953). Actinomycetes in the Oklahoma City water supply. *J. Am. Water Works Assoc., 45*, 409-416.

Simpson, M. R., & MacLeod, B. W. (1991a). Comparison of various powdered activated carbons for the removal of geosmin and 2-methylisoborneol in selected water conditions. *AWWA Annual Conference Proceedings*, Philadelphia, PA.

Simpson, M. R., & MacLeod, B. W. (1991b). Using closed loop stripping and Jar tests to determine powdered activated carbon dose needed for removal of geosmin: Manatee Countys Experience. *In Proceedings of the AWWA Water Quality Technology Conference*, Orlando, FL.

Solvay Chemicals. (2005). *Technical Publication II-958 PAK™ 27.* Houston, TX: Solvay Chemicals, Inc.

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

Srinivasan, R., & Sorial, G. A. (2009). Adsorption of geosmin and MIB on activated carbon - single and binary solute systems. *Water, Air, & Soil Pollution: Focus, 9*, 223-235.

Srinivasan, R., & Sorial, G. A. (2011). Treatment of taste and odor causing compounds 2-methyl isoborneol and geosmin in drinking water: A critical review. *Journal of Environmental Sciences*, 23(1) 1–13.

Sugiura, N., & Nakano, K. (2000). Causative microorganisms for musty odor occurrence in the eutrophic Lake Kasumigaura. *Hydrobiologia, 434*(1–3), 145–150.

Sugiura, N., Inamori, Y., Hosaka, Y., Sudo, R., & Takahashi, G. (1994). Algae enhancing musty odor production by actinomycetes in Lake Kasumigaura. *Hydrobiologia, 288*(1), 57–64.

Sugiura, N., Iwami, N., Inamori, Y., Nishimura, O., & Sudo, R. (1998). Significance of attached cyanobacteria relevant to the occurrence of musty odor in Lake Kasumigaura. *Water Res., 32*(12), 3549–3554.

Sugiura, N., Nishimura, O., Inamori, Y., Ouchiyama, T., & Sudo, R. (1997). Grazing characteristics of musty-odor-compound-producing Phormidium tenue by a microflagellate, Monas guttula. *Water Res., 31*(11), 2792–2796.

Sung, Y., Li, T., & Huang, S. (2005). Analysis of earthy and musty odors in water samples coupled with gas chromatography/ion trap mass spectrometry. *Talanta, 65*(2), 518-524.

Tabachek, J. L., & Yurkowski, M. (1976). Isolation and identification of blue-green algae producing muddy odour metabolites, geosmin and 2-methylisoborneol, in Saline Lakes in Manitobal. *Jour. Fish. Res. Bd. Can., 33,* 25-35.

Takizawa, M., Colwell, R. R., Hill, R. T. (1993). Isolation and diversity of actinomycetes in the Chesapeake Bay. *Appl. Environ. Microbiol., 59*(4), 997–1002.

Thaysen, A.C. (1936). The origin of an earthy or muddy taint in fish. *Ann. Appl. Biol., 23*, 99–104.

Tsuchiya, Y., & Matsumuto, A. (1988). Identification of volatile metabolites produced by blue-green algae. *Water Sci Technol, 20*, 149–155.

Tsuchiya, Y., Matsumoto, A., & Okamoto, T. (1981). Identification of volatile metabolites produced by blue-green algae, *Oscillatoria splendida, O. amoena, O. geminata*, and *Aphanizomenon* sp. *Yakugaku Zasshi, 101*, 852. (in Japanese).

Uhna´kova´, B., Harichova, J., & Augustin, J. (2002). Seasonal dynamics of actinomycetes in the Danube River in 1999. *Ekologia (Bratislava), 21*(2), 148–154.

Wagner, K. J. (2004). "The Practical Guide to Lake Management in Massachusetts: A Companion to the Final Generic Environmental Impact Report on Eutrophication and Aquatic Plant Management in Massachusetts." Commonwealth of Massachusetts Executive Office of Environmental Affairs.

Watson, S. B. (1999). Outbreaks of taste/odour causing algal species: Theoretical, mechanistic and applied approaches. PhD thesis, University of Calgary, Calgary.

Watson, S. B. (2003). Cyanobacterial and eukaryotic algal odour compounds: Signals or side-products? A review of their biological activity. *Phycologia, 42*(4), 332–350.

Watson, S. B. (2004). Aquatic taste and odor: a primary signal of drinking-water integrity. *Journal of Toxicology and Environmental Health, Part A, 67*. 1779–1795.

Watson, S. B., & Ridal, J. (2002). Periphyton: A primary source of widespread and severe taste and odour. *Wat. Sci. Technol. 49*(9), 33-39.

Westerhoff, P., Nalinakumari, B., & Pei, P. (2006). Kinetics of MIB and geosmin oxidation during ozonation. *Ozone Science and Engineering, 28,* 277–286.

Wetzel, R.G. (1983). Limnology. Saunders College Publishing, New York, NY.

Whelton, A. J., & Dietrich, A. M. (2004). Relationship between intensity, concentration, and temperature for drinking water odorants. *Water Research*, *38*, 1604–1614.

Wilber, G. G., Sanders, D. A., & Veenstra, J. N. (2010). *Investigating the use of algaecides for removal of geosmin, methylisoborneol and other trace organic contaminants.* Stillwater, OK: School of Civil and Environmental Engineering, Oklahoma State Univercity.

Wohl, D. L., & McArthur, J. V. (1998). Actinomycete-flora associated with submersed freshwater macrophytes. *FEMS Microbial Ecol., 26*(2), 135–140.

Wohl, D. L., & McArthur, J. V. (2001). Aquatic actinomycete–fungal interactions and their effects on organic matter decomposition: a microcosm study. *Microbial Ecol., 42*(3), 446–457.

Wood, S., Williams, S. T., White, W. R., & Jones, F. (1983). Factors influencing geosmin production by a streptomycetes and their relevance to the occurrence of earthy taints in reservoirs. *Water Sci. Technol., 15,* 191–198.

Wu, J., & Jüttner, F. (1988). Differential partitioning of geosmin and 2-methylisoborneol between cellular constituents in *Oscillatoria tenuis*. *Arch Microbiol, 150*, 580–583.

Yagi, M., Kajino, M., Matsuo, U., Ashitani, K., Kita, T., & Nakamura, T. (1983). Odour problems in Lake Biwa. *Water Sci Technol, 15*(6/7), 311–321.

Yagi, O., Sugiura, N., & Sudo, R. (1981). Odorous compounds produced by *Streptomyces* in Lake Kasumigaura. *Verh. Int. Ver. Limnol. 21*, 641–645.

Young, W. F., Horth, H., Crane, R., Ogden, T., & Arnott, M. (1996). Taste and odour threshold concentrations of potential potable water contaminants. *Water Research*, *30*(2), 331-340.

Zacheus, O. M., Lehtola, M. J., Korhonen, L. K., & Martikainen, P. J. (2001). Soft deposits, the key site for microbial growth in drinking water distribution networks. *Water Res. 35*(7), 1757–1765.

Zaitlin, B., & Watson, S. B. (2006). Actinomycetes in relation to taste and odour in drinking water: Myths, tenets and truths. *Water Research, 40*, 1741–1753.

Zaitlin, B., Watson, S., Ridal, J., Satchwill, T., & Parkinson, D. (2003). Actinomycetes in Lake Ontario: habitats and geosmin and MIB production. *J. Am. Water Works Assoc., 95*(2), 113–118.

Zhang, T., Li, L., Song, L., & Chen, W. (2009). Effects of temperature and light on the growth and geosmin production of Lyngbya kuetzingii (Cyanophyta). *J. Appl. Phycol., 21,* 279–285.

Zimba, P. V., Dionigi, C. P., & Millie, D. F. (1999). Evaluating the relationship between photopigments and secondary metabolite accumulation in cyanobacteria. *J. Phycol, 35*(6), 1422–1429.

Zimba, P. V., Grimm, C. C., & Dionigi, C. P. (2001). Phytoplankton community structure, biomass, and off-flavor: pond-size relationships in Louisiana catfish ponds. *J. World Aquacult Soc. 32*, 96–104.

VITA

Qian Zhao

Candidate for the Degree of

Master of Science

Thesis: TREATMENT OF TASTE AND ODOR COMPOUNDS IN OKLAHOMA SURFACE WATER

Major Field: Civil Engineering

Biographical:

Education:

Completed the requirements for the Master of Science in Civil Engineering at Oklahoma State University, Stillwater, Oklahoma in December, 2012.

Completed the requirements for the Bachelor of Science in Civil and Environmental Engineering at Shenyang Architecture University, Shenyang, Liaoning, China in 2009.

Experience:

Research Assistant at Environmental Engineering Department, Oklahoma State University, Stillwater, Oklahoma in 2012.

Teaching Assistant at Environmental Engineering Department, Oklahoma State University, Stillwater, Oklahoma in 2011.

Engineering Intern at Jinzhou Environmental Protection Agency, Jinzhou, Liaoning, China in 2008.