REMOVAL OF GEOSMIN AND 2-METHYLISOBORNEOL USING ALGAECIDES AND CHEMICALS IN POTABLE WATER

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Common taste and odor compounds in drinking water include 2-methylisoborneol (2-MIB) and trans-1,10-dimethyl-trans-9-decalol (geosmin). These compounds are difficult to remove through conventional water treatment. Thus, additional research is necessary to find cost-effective methods for removal of geosmin and MIB. The effects of algaecides and chemicals in various conditions (dosage, pH, temperature, turbulence, biodegradation) on geosmin and MIB were investigated, and compounds were analyzed through gas chromatograph and mass spectrometric methods (GC/MS) with solid-phase microextraction (SPME). The experiments were performed using both deionized water and lake water samples. At the recommended manufacturer's dosages of six chemicals (Earth Tec® , Cutrine Plus, Algimycin PWF, Sulfuric Acid, Phycomycin SCP, Calcium chloride dehydrate), removals of geosmin and MIB were unsatisfactory. Acidic conditions were shown to remove the compounds through dehydration. In pH experiments, MIB started to be removed as pH was reduced and was completely removed at pH 3.0. Geosmin showed removal at pH 3.5 and complete removal at pH 2.0. When the samples were returned to neutral (pH=7.5) using sodium hydroxide, geosmin was recovered around 50%, while MIB remained dehydrated. For biodegradation experiments, geosmin was volatilized around 10 -30% and MIB was volatilized around 5-10% for 8 days, but there was negligible impact of biodegradation. In temperature and turbulence experiments, geosmin and MIB removals showed negligible impacts of temperature and turbulence. In futher experiments, three chemicals were found to remove geosmin and MIB as follows: sodium sulfate 70-80%, calcium chloride dehydrate 40-50%, copper sulfate 40%-70%, all at high dosages.

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CHAPTER I

Introduction

1.1 Overview

Safe drinking water has been a concern for decades around the world. While conventional water treatment processes can control most water contaminants, such as organic chemical and heavy metals, some water contaminants, such as pharmaceutical residues, cyanotoxins, geosmin and 2-Methylisoborneol (MIB) from blue algae, and some other water pathogens, cannot be completely removed by common water treatment processes. Algal products such as geosmin and MIB, which cause objectionable tastes and odors in drinking water, are common problems in municipal water systems around the world. Westerhoff et al. (2003) conducted a survey of more than 800 water utilities in the United States and Canada and found that 16 percent of utilities experienced serious taste and odor problems. Moreover, these utilities spent approximately 4.5 % of their total budget to control taste and odor problems. Based on these experiences, new treatment technologies are needed by water treatment systems to remove these contaminants. Several technologies, such as activated carbon, biofitration, and oxidation, have been developed for removal of geosmin and MIB. Although some of them are successfully applied and can remove these contaminants, most technologies require high capital or operation costs, even when they do not fully remove geosmin and MIB. A technology which can reduce costs and remove effectively geosmin and MIB would be very useful for for drinking water treatment systems. In the dissertation, a new cost-effective method of removing geosmin and MIB using algaecides and other chemicals will be investigated.

1.2 History of water treatment in the United State

The world's first documented treatment of drinking water to remove taste and odor compounds was recorded approximately 4000 B. C in ancient Sanskrit and Greece. They used charcoal, sunlight, boiling and straining (EPA, 2000). By the early 1800s, water treatment systems using slow sand filtration were first used in Europe. During the 1800s, several scientists published their theories of invisible drinking water contaminants (EPA, 2000). In 1855, Dr. John Snow proved that a London public well was contaminated by sewage and indicated that cholera was spread in this manner. At the same time, people in Philadelphia, Pennsylvania, experienced a cholera epidemic. The first water treatment system using slow sand filters was installed for control of sediment and discoloration at Richmond, Virginia in 1832 (Kranzberg et al., 1967). In 1908, chlorine was used for the first time as a primary disinfectant of drinking water in Jersey City, New Jersey. The use of other disinfectants such as ozone began in Europe approximately this time, but was not employed in the U.S. until several decades later (EPA, 2000). Since Federal regulation of drinking water quality started in 1914, water quality in the U.S has developed further and fatalities were reduced much in drinking water.

However, emerging contaminants such as the pharmaceutical and personal care products, disinfection by products, algae, and some pathogens are still challenging to treat in common water treatment systems. Among these, algal by products, especially geosmin and MIB, are raising serious consumer concerns because of their earthy and musty tastes and odors, even at low concentrations. Suffet *et al*. (1996) reported 377 instances of taste and odor problems in drinking water experienced by 826 water utilities approximately the U.S and Canada. Their research found that 16%, more than 377, utilities had suffered serious taste and odor problems and 43% had experienced the taste and odor problems for at least a week. Although many researchers and scientists are working on removal of taste and odor problems using variety of methods, there remains a challenge to effectively treat the problems due to the low taste and odor thresholds (the average person can detect the presence of these compounds in the 10 to 30 ng/l (ppt) concentration range).

1.3 Taste and Odor problems

Taste and odor problems in drinking water have caused customer complaints for decades. Most taste and odor problems are of no concern to human health, but they raise customer’s suspicions of water safety. There are several taste and odor problems related to drinking water shown in Table 1. Chlorine and chloramines are a common cause of customers’ complaint. However, these problems are easy to remedy through control of dosages or filtration. Sometimes, iron and manganese (mainly in ground water) are detected and can be removed by lime soda treatment. When summer algae bloom occurs, geosmin and MIB can be formed and cause an earthy and musty taste and odor. Geosmin and MIB removal is challenging due to their low odor threshold.

Table 1 Common Drinking Water Problems

Chemical cause	**Taste/odor**	**Origin**
Geosmin	earthy or grassy odors	Produced by actinomycetes, blue-green algae, and green algae.
2-Methylisoborneol (MIB)	musty odor	Produced by actinomycetes and blue-green algae.
2t, 4c, 7c-decatrienal	fishy odor	Produced by blue-green algae.
Chlorine	bleach, chlorinous, or medicinal taste and odor	Addition of chlorine as a disinfectant.
Chloramines	swimming pool, bleach, or geranium odor	Addition of chlorine and ammonia as a disinfectant.
Aldehydes	fruity odor	Ozonation of water for disinfection.
Phenols and Chlorophenols	pharmaceutical or medicinal taste	Phenols usually originate in industrial waste. Chlorophenols are formed when phenols react with disinfecting chlorine.
Iron	rusty or metallic taste	Minerals in the ground.
Manganese	rusty or metallic taste	Minerals in the ground.
Hydrogen sulfide	rotten egg odor	Produced by anaerobic microorganisms in surface water or by sulfates in the ground.
Methane gas	garlic taste	Decomposition of organic matter.
Isobutanal	Sweet/fruity or malty-odor	Byproduct from ozonation, chlorination and chloramination

(Hou and Clancy, 1997)

Although taste-and-odor compounds do not cause health problems, there still remains a negative impression that the water is unsafe. To alleviate consumer concerns, many researchers have been developing new technologies to remove MIB and geosmin (Palmer, 1962). Lalezary et al.(1986) mentioned that conventional water treatment technologies, consisting of breakpoint pre-chlorination, coagulation, sedimentation, and post chlorination, are not effective in removing geosmin and MIB from potable water to below its odor threshold of 10 ng/l. Widely used technologies for removal of these compounds include activated carbon, advanced oxidation processes (AOP), chlorination, biofiltration, and some integrated systems (usually, combination of water treatment technologies). Among these technologies, some have limitations in removing all MIB and geosmin, especially for high concentration during algae blooms. Some systems such as advanced oxidation processes and chlorination generate undesirable compounds called disinfection by products (DBP) which include trihalomethanes, haloacetic acids and others products known to cause birth defects and cancer. Other systems such as activated carbon, biofitration and integrated systems are often cost ineffective for existing drinking water plants especially for high concentrations of MIB and geosmin water. However, activated carbon treatments are widely used for taste and odor events (Srinivasan and Sorial, 2011). The cities of Tulsa and Oklahoma City use activated carbon systems when necessary to remove taste and odor compounds.

Water treatment plants in Tulsa, Oklahoma, use Earth Tec® to remove algae; plant operators discovered that geosmin and MIB were also removed effectively by this treatment. However, there has been no research to determine the effectiveness or mechanisms related to the use of Earth Tec® . The focus on this dissertation will be the evaluation of Earth Tec® and other algaecides for removal of geosmin and MIB. Specific objective of this research are listed at the end of this Introduction.

1.4 Cyanobacteria and actinomycetes

Cyanobacteria and actinomycetes are known to release geosmin and 2-methylisoborneol into fresh water (Gerber and Lechevalier, 1965; Jüttner and Watson, 2007). Cyanobacteria (also called blue green algae) form toxic compounds such as hepatoxins, cytotoxins, neurotoxins, and dermatoxins, which threaten human, domestic and wild animal health. Actinomycetes are common soil inhabitants, where their production of the earthy-smelling geosmin and MIB contributes significantly to the characteristic odor of soil (Gerber and Lechevalier, 1965; Buttery and Garibaldi, 1976). Figure 1 describes how geosmin and MIB are produced by algae.

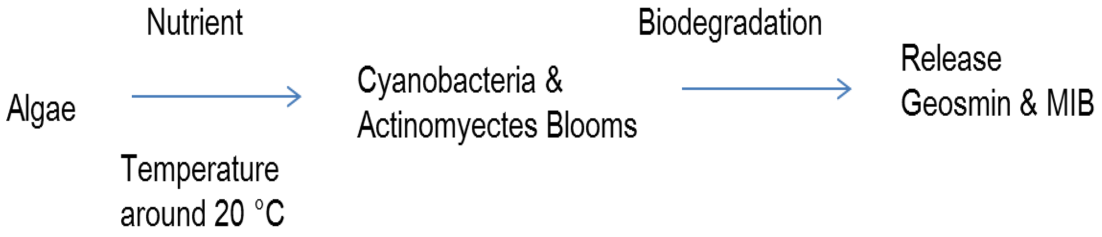


Figure 1 Procedure for Geosmin and MIB release (Srinivasan and Sorial, 2011)

Cyanobacteria

Cyanobacteria consist of a large and morphologically heterogeneous group of phototrophic bacteria. They live in fresh and marine water around the world. Normally, a small amount of cyanobacteria does not cause problems. When cyanobacteria experience rapid growth, these algal cells release odorants (geosmin and MIB), causing taste and odor problems. Izaguirre and Taylor (2004) observed, in drinking water supplies in the U.S., that known geosmin-and MIB-producing cyanobacteria belong to genera such as Anabaena, Oscillatoria, Phormidium, Lyngbya, Leptolyngbya, Microcoleus, Nostoc, Planktothrix, Pseudanabaena, Hyella, and Synechococcus . Many MIB- and geosmin-producing Oscillatoria strains have been isolated from water supplies in California (Izaguirre et al., 1982). In any event, when the algae blooms occur, they can cause serious problems such as depleting oxygen in the water by sun blocking, toxin generations, and taste-odor release in the water. Crucial incidents related to cyanotoxins are shown below.

- Palmland, Australia, in 1979: 140 children and 10 adults contaminated by hepatoxins (Byth, 1980).

- Itaparica Dam and reservoir, Bahia, Brazil in 1988: 88 fatality and more than 2000 cases in 42 days (El Saadi O, 1993).

- Caruaru, Brazil, in 1994: 136 people contaminated by microcystins, with 75 deaths.

- The Ohio River, Ohio, United States in 1931: First reported cyanobacteria blooms in

1931, with 4000 to 7000 cases of abdominal pain, vomiting, and diarrhea (Tisdale, 1931).

Currently cyanotoxins which can harm human health are well treated by the conventional water treatment systems, but taste and odor compounds (geosmin and MIB) are still presenting problems due to their low odor thresholds of about 10 to 30 ng/L. Cyanobacteria blooms are dependent on sunlight, high nutrient concentrations, warm temperatures, and moderate pH, though some exceptional bacteria can grow under ice and frozen water (e.g. Planktothrix) and in extremely high temperature regions (Chorus and Bartram, 1999). The WHO limits cyanotoxins concentrations to 1 μg/L for safe water supplies.

Actinomyectes

Actinomycetes bacteria are major contributors of geosmin and MIB problems in drinking water (Gerber and Lechevalier, 1965). Actinomycetes, rod-shaped and filamentous bacteria from common soil fungi, are often found in terrestrial environments and fresh water. Some varieties of actinomycetes are able to form spores, which are carried by wind or water-borne sediment to settle in water (Lloyd, 1969; Goodfellow and Williams, 1983). Henley (1970) first reported geosmin production by Anabaena circinalis, Anabaena laxa, and Symploca muscorum. The common types of actinomycetes are Actinoplanes, Micromonospora, Rhodococcus, Streptomyces and Thermoactinomyces (Goodfellow and Williams, 1983). Actinomycetes have been implicated in a number of documented taste and odor episodes (Raschke et al., 1975; Jensen et al., 1994; Sugiura and Nakano, 2000). Negri et al. (1995) discovered that Anabaena circinalis, which produces geosmin along with saxitoxin, has been responsible for the deaths of animals.

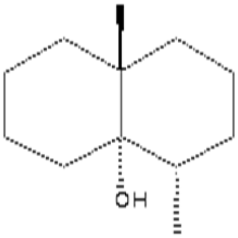
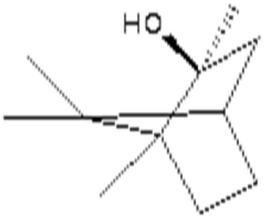
1.5 Geosmin

Geosmin is known as trans-1,10-dimethyl-trans-9-decalol and was first isolated by Gerber et al. (1965). Geosmin is produced by several classes of microbes, including cyanobacteria (blue-green algae) and actinobacteria especially through Streptomyces, which release geosmin when these microbes die. During the summer, algae blooms can occur under nutrient-rich conditions and high water temperatures (above 20℃), resulting in taste and odor problems and deceased over all water quality (Baudin, 2006).

1.6 MIB (2-Methylisoborneol)

2-Methylisoborneol (MIB) is known as 1,6,7,7-tetramethylbicyclo[2.2.1]heptan-6-ol and is an organic chemical with a low odor threshold. MIB was also discovered by Gerber et al. (1969). MIB is as challenging as geosmin to remove by conventional water treatment technologies due to its low odor threshold of about 35 ng/L. MIB often is accompanied by geosmin when cyanobacteria and actinobacteria are abundant in water. Table 2 displays the characteristics of MIB and geosmin. Table 3 provides information of geosmin and MIB species.

Table 2 GSM and MIB Characteristics

Compounds	**Geosmin**	**2-Methylisoborneol**
Molecular Formula	$C_{12}H_{22}O$	$C_{11}H_{20}O$
Molar Mass	182.3025 g/mol	168.2759 g/mol
Boiling Point	270 to 271 ℃ at 101.325 kPa	207.00 to 209.00 ℃ at 101.325 kPa
Flash Point	103.89℃	83.33 ℃
Henry's Law Constant (Pa m^3/mol)	6.75	5.84
Vapor pressure (Pa)	5.56	6.76
Odor threshold	0.015 µg/L	0.035 µg/L
Structure		

(Reference: Juttner and Watson, 2007)

Table 3 Cyanobacteria species to produce geosmin and MIB

Species	Origin	References
Geosmin		
Anabaena circinalis Kutz.	Lake/USA	Henley (1970)
A. crassa Lemmermann	Lake/USA	Watson (2003)
A. laxa	Lake/USA	Rashash et al. (1995)
Lyngbya cryptovaginata	Lake/USA	Schrader and Blevins (1993)
Lyngbya aestuarii	Lake/Japan	Tabachek and Yurkowski (1976)
A.solitaria	Lake/USA	Saadoun et al. (2005)
Oscillatoria limosa	River/Spain	Vilalta et al. (2004)
Oscillatoria amphibia	Lake/USA	Juttner and Watson (2007)
Phormidium LS1283	Reservoir/USA	Taylor et al. (2006)
Phoridium sp.(SDC202a,b,c)	Reservoir/USA	
Phormidium DCR 301	Reservoir/USA	
Phormidium ER 0100	Reservoir/USA	
Phormidium sp. LD499	Reservoir/USA	
Rivularia sp. Ketones	Lake/Switzerland	Hockelmann and Juttner (2005)
Streptomyces halstedii	Pond/USA	Schrader& Belvins (2001)
Streptomyces	Pond/Denmark	Klausen et al. (2005)
MIB		
Oscillatoria Peronata	Pond/USA	Taylor et al. (2006)
Oscillatoria limosa	Aqueduct/USA	Izaguirre &Taylor (1995)
Oscillatoria curiceps	Lake/USA	Izaguirre et al. (1982)
Oscillatoria tenuis	Lake/USA	
Oscillatoria variabilis Rao	Lake/Japan	Tabachec and Yurkowaski (1976)
Phormidiuim LP684	Lake/USA	Taylor et al. (2006)
Peseudanabaena	Lake/USA	Izaguirre & Taylor (1998)
Plankto. perornata f.	Lake/ Netherlands	Van der Ploeg et al. (1995)
Synechococcus sp.	Lake/USA	Lzaguirre et al. (1984)
Leptolyngbya sp.	Reservoir/USA	Taylor et al. (2006)
Lyngbya Lo198	Reservoir/USA	

1.7 Health Effects

Blue-green algae (Anabaena, Microcystis, Oscillatoria, Gloeotrichia, Nodularia, Aphanizomenon, Cylindrospermopsis) produce various substances such as geosmin and MIB. Some products include toxins which can be fatal to human and animals. For example, anabaena produces anatoxin-a, anatoxin-a(s), which can cause nerve system problems such as impairing coordination, muscular fasciculation, convulsions and respiratory paralysis. Microcystis produces microcystins, a type of hepatotoxins causing serious damage to the liver of animals and humans. Lethal dosages of microcystin-RR, microcystin-LR are 600 mg/kg and 50mg/kg. In 1996, over 50 people died from exposure to microcystins (Azevedo et al., 2002). Other products contain various toxins which can endanger human health. However, geosmin and MIB have not been shown to produce any health problems and are not regulated by any law. Though they cause no adverse health effects, consumers are more susceptible to geosmin and MIB exposure because their low taste and odor thresholds in drinking water.

Research Objectives. Specific objectives of this research include:

- To investigate the reactions between commercially available algaecides and MIB and geosmin,
- To develop the reactions in variety of conditions (dosage, pH, temperatue, tubulence, biodegradation)
- To identify important treatment variables using lab scale experiment results.

The project involved Oklahoma State University's School of Civil and Environmental Engineering, and the public water treatment facilities of both Tulsa and Oklahoma City, Oklahoma.

CHAPTER II

REVIEW OF LITERATURE

REMOVAL OF GSM AND MIB FROM DRINKING WATER

When taste and odor problems occur in drinking water, the general water treatment process cannot remove the whole amount of the compounds as a result of extreme low odor threshold of geosmin of 15 ng/L and MIB of 35 ng/L. Lalezary et al.(1986) found that conventional water treatment technologies, consisting of breakpoint pre-chlorination, coagulation, sedimentation, and post chlorination, are not effective in removing geosmin and MIB from potable water to below its odor threshold. For this reason, conventional water treatment process requires advanced treatment processes to remove geosmin and MIB compounds. The advanced technologies include biological treatment, advanced oxidation processes (AOP), chlorination, and some integrated systems.

2.1 Biofiltration

Biofiltration is one of the most commonly used methods to remove geosmin and MIB in drinking water. The main biofiltration systems used for geosmin and MIB removal are activated carbon, slow sand filtration, and ultra/nano filtrations. Removal rates of geosmin and MIB by biofiltration are dependent on biofilter media, biomass, temperature, and contact time. Some soil and aquatic bacteria are capable of biodegrading MIB and geosmin, though there is no evidence of significant removal. Temperature of the water, which is typically between 10-20 ℃, does not have a significant impact on removal of geosmin and MIB. Contact time is a significant factor.

2.1.1 Activated Carbon

Activated carbon is one of the most widely used methods to remove geosmin and MIB in water utilities. Activated carbon can be categorized into two different systems depending upon its particle size: granular-activated carbon (GAC) and powdered activated carbon (PAC). In GAC, the activated carbon is used as a granular media above the sand/gravel media filter for the removal of geosmin and MIB from the water passing through it. PAC is basically used in the rapid mix stage and reacts with contaminants of the water and, finally, removed as sludge after filtration process. Both GAC and PAC are commonly used and are known to be effective for control of geosmin and MIB. Although the removal of geosmin and MIB by activated carbon is achieved below odor threshold concentrations, the complex procedure and high cost of activated carbon make the method challenging to implement in conventional drinking water treatment plants. The removal efficiency of activated carbon depends upon many factors stated below.

- ✓ Surface area of activated carbon
- ✓ Concentration of dissolved organic carbon (DOC)
- ✓ Contact time
- ✓ Types of activated carbon used
- ✓ Filter age for GAC
- ✓ Amount of activated carbon used for GAC

The surface area of activated carbon directly affects efficiencies and is mainly proportional to the removal rates of geosmin and MIB. However, whenever the concentration of other organic compounds in the water are high, it directly affects the removal efficiencies of activated carbon towards the target compounds (Geosmin/MIB). The other main factors which affect the activated carbon performance are types of activated carbon, contact time and filter age. The contact time is the period which water flows through the GAC filter. The removal efficiency normally increases as the contact time is increases. The activated carbon performance is dependent on a filter age; the removal efficiency of geosmin and MIB decreased below an odor threshold level after 12 months (Jeff Ridal et al., 2001).

There have been several studies of the removal of geosmin and MIB using GAC. Drikas et al. (2009) used pilot granular activated carbon (GAC) filters followed by either coagulation or microfiltration (MF) for the removal of the taste and odor compounds (MIB and geosmin) from a surface drinking water source over a two-year period and found that MIB and geosmin were removed completely after 10 months of operation. Ridal et al (2001) removed an average of 60% of geosmin and 80% of MIB in finished water using GAC–capped filters after 12 months of filter operation. Ho et al. (2010) studied pilot- and laboratory-scale with two different granular activated carbons: a wood-based carbon and a coal-based carbon. After a 6-month operation, complete MIB removal was observed with up to 80% attributed to adsorption, and the remaining 20% attributed to biodegradation. More studies of geosmin and MIB removal by GAC are shown in Table 3.

Table 4 GAC studies of Geosmin and MIB

Concentration of Geosmin or MIB	**Sort**	**GAC filter**	**Removal Rate**		**Contact time**	**Reference**
			Geosmin	**MIB**		
70 to 110 ng/L	used bituminous GAC (Picacarb, Pica Carbon)	25 to 30 cm	10%	-	5 min	Ndiongue et al.(2006)
	new bituminous GAC (Filtrasorb 820, Calgon) Carbon)	25 to 30 cm	83%	5%	5min	
	Used bituminous GAC (Filtrasorb 820, Calgon Carbon)	95 cm	78%	43%	7.5 min	
59.9 ng/L	β-CD/TDI and β-CD/HMDI polymer	500 mg/500mL	88%	-	10.3 min	Mamba et al. (2007)
104.16 ng/L			95%	-	13.7 min,	
20-5ng/L	GAC(Filtrasorb 300)	20-50cm	96%	96%	30 min	Persson et al.(2007)
	EC (crushed expanded clay, Filtralite NC 0.8-1.6 mm)		88%	82%		
560 ng/L	Chryseobacterium sp., Sinorhizobium sp., Stenotrophomonas sp.	-	84.8%, 82.3%, 82.5%	-	48 hrs	Zhou et al. (2011)
1000 ng/L	D_{40}	0.5mg/L	90-99% Diameter: 0.4-0.5 μm	90-99% Diameter: 2-2.5 μm	60 min	Matsui et al.(2013)
15.6 ng/L	GAC with post-O_3	1,000 mg/g	70-80%	-	15 min	Kim et al. (1997)
	GAC		60-70%	-		

A powdered activated carbon system is a different way of using activated carbon in water treatment system and is only used during taste and odor episodes. PAC is currently the most common technology for MIB and geosmin removal. PAC dosages are determined by experience and the concentrations of geosmin and MIB. Normally, PAC can be added at the intake or to the flocculation and sedimentation basins. Geosmin and MIB removal by powdered activated carbon (PAC) have been studied by various researchers. Cook et al. (2001) in jar tests determined the effective doses to produce water of the desired quality in three of the four water samples. The poor predictions found in the fourth water sample, which had a considerably higher turbidity, were attributed to the incorporation of PAC in a larger, denser, floc, leading to a reduced effective contact time of the adsorbent. Higher doses of PAC were required for both compounds to produce acceptable quality water when turbidities rose above 26 NTU. Park et al. (2010) investigated removal of geosmin and MIB using PAC adsorption and air stripping processes and determined that removal efficiency of geosmin above 93% and MIB above 73% by simultaneous PAC adsorption and air stripping under the same conditions. Various PAC studies are shown in Table 5.

Table 5 PAC studies of Geosmin and MIB

Concentration of Geosmin or MIB	PAC Sort	PAC dose	Removal Rate		Contact time	Reference
			Geosmin	MIB		
20-300 ng/L	Picactif 1100	22-29 mg/L for geosmin 42-55 mg/L for MIB	188 NTU: 40% 60 NTU: 50% 26 NTU: 55%	40 to 60%	50 min	Cook et al (2001)
10 µg/L	Filtrasorb 400	150-250 mg/500 mL of geosmin water	98%	-	2 hr	Ng et al.(2002)
37.6–70.8 ng/L	Coconut-based PAC with hydraulic baffled-channel	5-30 mg/L	48-98%	-	20 min	Kim et al.(2007)
10-50 ng/L	Hydrodarco-B	5-30 mg/L	50-70%	-	45 min	Koester et al. (2011)
60 ng/L	Wood	20 mg/L	77.60%	-	1 hr	Linde et al.(2000)
	Bituminous Coal		77%	-		
	Coal		74%	-		
	Lignite		53%	-		

In the case of PAC, a higher dosage is necessary for higher concentration of GSM and MIB. This situation causes two problems: higher cost of purchasing PAC and production of large amounts of sludge. Both problems result in higher operating costs (Srinivasan and Sorial, 2011).

In spite of activated carbon effectiveness, it is uneconomical at higher MIB concentrations (Herzing et al., 1977) and treatment of GSM by activated carbon is often hindered by the presence of other far more abundant natural organic matter (NOM) within the source water (Cook et al., 2001).

2.1.2 Other biofiltration technologies for removal of geosmin and MIB

Biofilters for removal of geosmin and MIB other than activated carbon filter include slow sand filters, clay, and ultra/nano filters. Among these, slow sand filters and ultra/nano filters are known to effectively removing geosmin and MIB. Studies are shown in Table 6.

Table 6 Biological Treatment Studies for Geosmin and MIB removal

References	**Treatment technology**	**Findings**
McDowall (2009)	Sand filtration with bacteria	A bacterial consortium shown to be capable of effectively degrading geosmin up to 75% through sand columns.
Ho (2007)	Sand filtration with bacteria	16S rRNA-directed PCR-DGGE identified four bacteria(a Pseudomonas sp., Alphaproteobacterium, Sphingomonas sp. and an Acidobacteriaceae member) can biodegrade geosmin within the sand filters and bioreactors.
Park et al.(2006)	Ultra filtration	The removals of 2,4,6-trichloroanisole (90%) by the tight-UF membranes
Mody (2004)	Nano filtration	Achieving rejections of 91 to 94 % for TOC and 88 to 91 % for THMFP.
Taylor et al. (1999)	Nano filtration	98% removal of both geosmin and MIB using an NF membrane (LFC 1) with a 200 MWCO
Dixon. et al. (2011)	Nano filtration	Above 75 % of MIB and GSM were removed effectively (above 75%) by tight NF.
Persson et al. (2007)	GAC+EC	97 % geosmin and MIB removal with an empty bed contact time of 30 minutes at 15℃
Terrauchi et al. (1995)	Pilot biofilter with porous granular ceramic	60-80% MIB removal with a contact time of 12.7 min.
Hsieh et al.(2005)	Slow sand filtration	With a filtration rate of 5 m/day, the simulated SSF degraded MIB from 48% to 69% and geosmin from 87% to 96%

Slow sand filtration does remove geosmin and MIB, though it does not provide great removal efficiencies itself. Moreover, if high NOM concentration is present in the raw water, it results in poor efficiency of removal of geosmin and MIB. Therefore, effective biofilters are ultra and nano filters. However, these filters require high capital and operational costs.

2.2 Advanced oxidation process (AOP)

Oxidation processes using ozone and other oxidants combined with UV/VUV has been proven effective in the removal of geosmin and MIB (Kristin et al., 2009). Most oxidation processes use ozone as the main oxidant to remove geosmin and MIB. However, the oxidation reaction is known to produce disinfection by-product (DBP), which can cause birth defects and cancer. Currently, the use of ozone combined with other technologies, commonly UV radiation, is known to be effective. Lundgren et al. (1988) removed more than 95% of geosmin and MIB using 7 mg/L ozone in 50 ng/L of MIB and geosmin water. Koch et al. (1992) used the ozone dosages of 1, 2, and 4 mg/L with hydrogen peroxide (0.2 mg/mg O_3) and improved 20% of MIB removal. Haw-Ja Lee et al. (2007) also used ozone (2 mg/L) with hydrogen peroxide (10 mg/L) and found 8.5 times increase in removal of geosmin and MIB. Moreover, recent technology used ozone with UV/VUV. Linden et al. (2002) used hydrogen peroxide with 10,000 J/m^2 UV radiation and reduced MIB and geosmin to non-detectable concentrations. Collivignarelli and Sorlini (2004) proved that 1.5- 3 mg/L of ozone with low-pressure lamp (5000-6000 J/m^2) completely removed geosmin and MIB. Rosenfeldt et al. (2005) experimented using 7.2 mg/L of hydrogen peroxide with low and medium-pressure lamps (1000 J/m^2) and found more than 70% of removal of geosmin and MIB, but found better removal with medium-pressure lamps. More studies in advanced oxidation process are in Table 7.

Table 7 AOP studies for Geosmin and MIB

Reference	Findings
Kutschera et al.(2009)	Vacuum UV irradiation performed better than UV for MIB and geosmin removal
Nalinakumari (2002)	MIB removal of 70 to 90% at an ozone dose of 1.5 mg/L. Geosmin oxidation was on an average 15 % higher than MIB oxidation.
Collivignarelli et al.(2004)	Ozone with UV has increased the removal efficiency up to 90% (ozone 50%)
Qi et al.(2008)	Bauxite catalyzed ozonation (75% removal) has better performance of MIB removal than just ozonation (28% removal)
Peter and Gunten (2007)	Using UV/H_2O_2 has 50-70% of geosmin removal efficiency
Xue (2011)	For the Ti/IrO_2–Pt anode, geosmin concentration decreased from approximately 600 to 8 ng/L after 60 min of electrolysis with 3.0 g/L NaCl as supporting electrolyte at the current density of 40 mA/cm^2
Qi (2013)	2-isopropyl-3-methoxypyrazine was removed by catalytic ozonation by C-AlOOH (HAO) 94.2% and c-Al2O3 (RAO) 90.0%.
Jo (2011)	Tribromomethane and dibromochloromethane were degraded by 99% and 80% at the UV dose of 1200 mJ/cm2 with 6 mg/L H_2O_2, whereas 90% of the geosmin and 60% of the 2-methylisoborneol were removed.
Miao Li (2010)	At a current density of $40mAcm^{-2}$, the geosmin concentration decreased from 600 ng L^{-1} to $6ngL^{-1}$ in 60 min in the presence of 3.0 g L^{-1} NaCl at the Ti/RuO_2–Pt anode

Advanced oxidation processes have advantages for removal of geosmin and MIB: easy access of oxidant and simple operation. However, AOP normally combines high capital and energy costs, and the oxidation can produce byproducts (DBPs).

Oxidation Mechanisms

O_3 and H_2O_2 are used common oxidants for removal of geosmin and MIB. Therefore, understanding the kinetics of removal geosmin and MIB by ozone and hydrogen peroxide is necessary. HO- radicals are the most significant factor for geosmin and MIB oxidation. Increasing HO- radicals results in higher removal of geosmin and MIB. O_3 and H_2O_2 oxidants are also a key factor for HO- radicals. The oxidation processes are shown below:

$$O_3 + OH^- \rightarrow \cdot HO_2 + \cdot O_2{}^-$$

$$\cdot HO_2 \leftrightarrow H^+ + \cdot O_2{}^-$$

$$O_3 + O_2{}^- + HO_2 \rightarrow \cdot OH + OH^- + 2O_2$$

$$O_3 + \cdot OH \rightarrow \cdot HO_2 + O_2$$

During the reaction, R_{CT} is an indirect measurement of the concentration of HO• radicals. R_{CT} increases with increasing HO• concentrations. The ratio R_{CT} of ozone and HO- can be calculated by the below equation. The equation 1 demonstrate the disappearance of an ozone-resistant probe compound (e.g., para-chlorobenzoic acid, pCBA) (Elovitz and von Gunten 1999a, 1999b; von Gunten, 2003)

$$R_{CT} = \frac{\int HO^- dt}{\int O_3 dt} \approx \frac{[HO^-]}{O_3} \text{……………………..Equation 1}$$

The value of R_{CT} can be calculated from the change in ozone residual and the disappearance of the ozone-resistant concentration over time. If the probe is pCBA, the equation1 changes to:

$$R_{CT} = \frac{ln\left(\frac{[pCBA]}{[pCBA]_0}\right)}{K_{HO^- pCBA} \int O_3 dt} \text{…………………………Equation 2}$$

2.3 Integrated technologies

Due to the difficulty of removal of taste and odor compounds, scientists have tried to combine the possible technologies to enhance removal of MIB and geosmin in water. The combination of beneficial methods provides positive aspects to the removal of geosmin and MIB. While there are many researches, few technologies are proposed as possible applications in water treatment system. Since activated carbon filtration and oxidation filtration are effective methods for removal of geosmin and MIB, combination of these two are effective methods to improve the removal performance. Table 8 shows the integrated technology studies.

Table 8 Integrated technologies for Geosmin and MIB removal

References	Treatment technology	Findings
Elhadi et al. (2004)	GAC/sand biofilter	Geosmin removal (86%) and MIB removal (52%)
Matsui et al.(2007)	Super-PAC/Microfiltration	90% of savings on S-PAC dose
Jung et al.(2004)	Oxidation/PAC	70% removal on geosmin and MIB
Nerenberg et al. (2000)	Ozonation / Biofiltration	Byproduct (nonbiodegradable NOM) from Ozonation can be used by the bacteria as substrate. This enhances the ability of the biofilter to remove geosmin and MIB
Huck et al. (1998)	rapid mix/flocculation/ sedimentation/ozonation/ four parallel biological filters	70-90 % geosmin and MIB removal
Young Wan Ham (2012)	O_3/GAC process	Single O_3 showed 89% removal efficiency and combined O_3/GAC process displayed above 95% removal efficiency

In Table 8, GAC plus sand biofiltration and PAC plus microfiltration display impressive removal efficiencies of geosmin and MIB. Further development of combination of these technologies is necessary to provide positive aspects of removal geosmin and MIB.

2.4 Algaecides and chemicals

Algaecides and some other chemicals have been used to kill or suppress algal growth. Some chemicals, such as copper sulfate, chelated-copper compounds, and diuron (3-[3, 4-dichlorophenyl]-1, 1-dimethylurea), USEPA-approved compounds, are used in catfish production ponds as algaecides (Schrader et al., 1998a, b,; Schrader and Harries, 2001; Tucker and Leard 1999). Algaecides can be divided into four major categories: natural, copper-based, synthetic organic, and oxidizers. Natural algaecides include barley straw, which is often used for farm ponds and similar sized reservoirs and lake systems. They are economical and easy to use while a precise control of algae is challenging. Copper-based algaecides, typically chelated forms containing less copper than copper sulfate, have been used for an effective removal and inhibition of rapid repopulation of algae. Copper-based algaecides could be less effective in alkaline waters or at colder temperatures, although chelated forms perform better. A typical oxidizer algaecide is a sodium carbonate peroxyhydrate. It is a trihalomethane (THM) precursor as well as haloacetic acids (HAA). One researcher found that the acidity of EarthTec® reduces the odor of geosmin by converting geosmin to argosmin and other transformation products (Schweitzer et al., 2006a, 2006b, not yet published).

In this project, six commercially available algaecides based on different chemicals as shown in Table 9 were investigated to develop the optimal product and quantity of algaecide for removal of geosmin and 2-MIB. As Earth Tec® is currently used by Tulsa water treatment utilities, Earth Tec® was the standard algaecide to compare removal efficiency of taste-and-odor compounds with other algaecides.

Table 9 Tested Algaecides and chemicals

Algaecide	Components	Type	Manufacturer
EarthTec®	Copper Sulfate Pentahydrate: 20.0% Inert Ingredients: 80%	Acidified Copper	Earth Science Laboratories, INC. Bentonville, AR
AB Algimycin PWF	Citric acid, Copper sulfate pentahydrate, Sodium Gluconate	Acidified Copper	Applied Biochemists Germantown, WI
Phycomycin SCP	Sodium Carbonate Sodium carbonate peroxyhydrate Sodium metasilicate	Sodium carbonate peroxyhydrate	Applied Biochemists Germantown, WI
CUTRINE® - PLUS	Copper as elemental: 9.0% Inert Ingredients: 91.0%	Chelated Copper	Applied Biochemists Germantown, WI
Copper sulfate	$CuSO_4 \cdot 5H_2O$ 99%	Chelated Copper	Fisher Scientific Pittsburgh, PA
Phosphorus pentoxide	99% of Phosphorus pentoxide	Phosphorus pentoxide	Acros Organics, NJ
Variety of acids	Phosphoric Acid, Ascorbic Acid, Sulfuric Acid	Acid	Fisher Scientific Pittsburgh, PA
Magnesium sulfate	$MgSO_4 \cdot 7H_2O$ 99%	Crystal magnesium sulfate	Fisher Scientific Pittsburgh, PA
Sodium Sulfate Decahydrate	Sodium Sulfate Decahydrate: ≥99.0%	Sodium Sulfate	Fisher Scientific Pittsburgh, PA
Calcium Chloride Dihydrate	$CaCl_2 \cdot 2H_2O$	Calcium Chloride	Fisher Scientific Pittsburgh, PA

Other strategies used to manage taste and odor problems include treating different areas of a reservoir or lake at different times, location specific treatments that target blooms, implementing a seasonal program that is aimed at managing bloom conditions throughout the growth season, using different algaecides depending on conditions (e.g., targeting specific species), and using algaecides in combination with different reservoir prescriptions to attain desired results.

CHAPTER III

Methodology

3.1 Objectives

The main goals for the project are to investigate the removal of taste and odor compounds by various algaecides and to optimize the results for use in public water treatment facilities in Tulsa and Oklahoma City. For the effective control and treatment of geosmin and MIB, engineering decisions based on analytical data should be made at the following steps:

1. To study MIB, geosmin, six algaecides will be investigated. Reactions between taste-odor compounds and algaecides will be determined for efficient removal. Experiments will be done at the bench scale .

   The lab scale experiment using six different algaecides including EarthTec® will be applied to each 100 ng/L MIB and geosmin contaminated sample to identify the reactions and removal rates between MIB/geosmin and algaecides. In the process, the effective algaecides will be determined and an optimal dosage of algaecides for efficient removal rates will be developed.
2. To investigate the optimum parameters that could affect the removal reactions of MIB and geosmin. Identify MIB and geosmin mechanisms on various reaction conditions such as pH, sunlight, temperature and nutrient using several algaecides. Optimum pH is expected to be approximately 7.2-7.8, according to the manufacture recommendation. Temperature will be ranged from 10-20℃, based on water temperatures in Oklahoma.

High MIB and geosmin concentrations are expected in the presence of sunlight. More nutrients in water will have higher MIB and geosmin concentrations.

3. To analyze the results from objective 1 and 2 by using GC/MS/SPME analysis. GC/MS/SPME analysis will be performed to identify the reactions between taste and odor compounds and algaecides. Generated spectra will be analyzed based on existing mass spectrum libraries. The results will be used in objective 4 to develop the optimal results for Tulsa and Oklahoma water utilities.
4. To analyze geosmin and MIB conversion to any other products. Geosmin can be converted to non-odorous argosmin by dehydration (Schweitzer and Ekstrom, 2006) and MIB can be converted to 2-Methyl-2-Bornene (2-M-2-B). The kinetics of trasformation geosmin to argosmin and MIB to 2-M-2-B will be analyzed.
5. To determine a variety of factors such as kinetics, temperature, pH and optimal quantity to design the effective control of geosmin and MIB for utilities in Tulsa and Oklahoma. This step will determine the optimal parameters from step 1 and 2 results and identify the optimal algaecide design for both Tulsa and Oklahoma water utilities.

3.2 ANALYSIS OF 2-METHYLISOBORNEOL AND GEOSMIN

3.2.1 Analytical Method

The compounds geosmin and MIB have extremely low odor thresholds of 10–42 ng L^{-1} concentrations which are very difficult to detect using common analytical procedures. Extraction methods for geosmin and MIB can be divided into closed loop stripping, purge and trap techniques, and solid phase micro-extraction. During the period 1980 to 1990, closed loop stripping (Hassett and Rohwer, 1999; Huck et al., 2000) and conventional purge and trap techniques (George et al., 1997) were used to detect geosmin and MIB. Closed loop stripping analysis (CLSA) is normally used for volatile organic compounds extraction. The procedure is

VOCs in the liquid phase are trapped on a multichannel sorbent trap by pumping the purge gas in a closed circuit via aqueous phase and the trap. The trap retains the VOCs that are then extracted from the trap using small amounts of appropriate solvent. Coupling SPME and CLSA was proposed for the analysis of MIB and geosmin in drinking waters. Further, they concluded that CLSA/SPME provided a faster, solvent-free and less labor-intensive method than CLSA alone. Purge and trap methods (P and T) have been the majority of extraction method for the analysis of VOCs in water before SPME. Figure 3 shows the procedure. Purge gas is introduced into the sample and samples with VOC are extracted with methanol and trapped, then carried to a GC/MS. This method has the advantages of precision and possibility of automation. The drawbacks of P and T are its complexity and the interference of water vapor generated in the purge stage. Campillo et al. (2004) used capillary trap and thermally desorbed P and T for the determination of volatile halogens and trihalomethanes in drinking waters. A purge-gas flow rate of 40 mL/min, desorption time of 4 min and temperature up to 200 ℃ were reported to achieve improved extraction efficiencies with the highest peak areas for all the THMs analyzed.

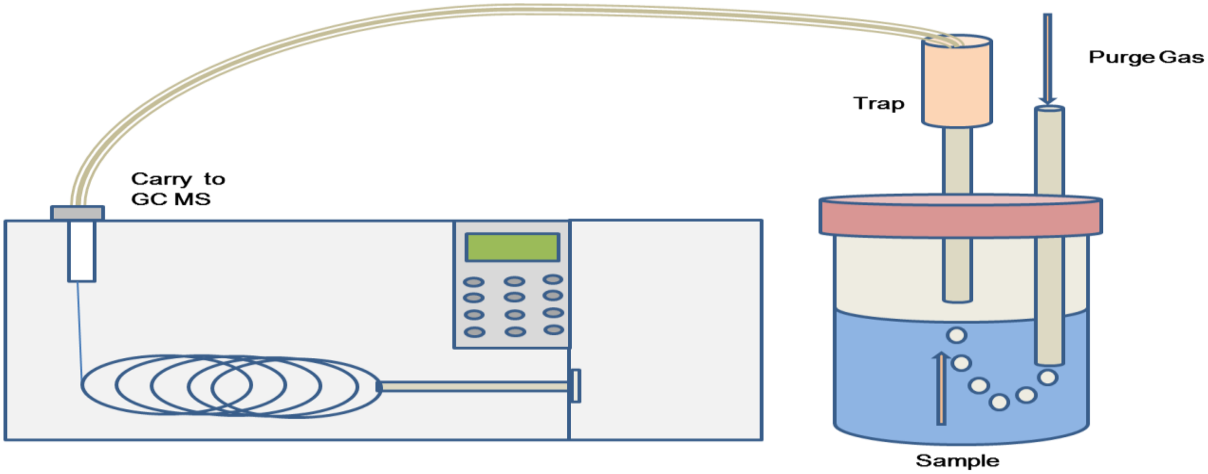


Figure 2 Purge and Trap Methods

However, closed loop stripping requires large sample volumes (100-1000 ml) and a complex apparatus and uses toxic elution solvent. The purge and trap technology also requires large sample volume and low sensitivity without technological challenges (Lloyd et al., 1998).

3.2.2 Solid Phase Microextraction (SPME)

Since late 1990s, Gas Chromatography-Mass Spectrometry-Solid Phase Microextration (GC/MS/SPME) analysis has been used for the analysis of geosmin and MIB (Lin et al., 2003; Sung et al., 2005; Lauderdale, 2004; Tung et al., 2008). The SPME method does not require a large volume of sample (only 25 mL), expensive equipment, or time consuming efforts (only 30 min to 1 hour). SPME relies on the partitioning of organic compounds from a matrix directly into a solid phase. SPME integrates sampling, extraction, concentration and sample introduction in a simple process, and most importantly, it uses no solvent during extraction. The extensive applications of SPME were almost based exclusively on separation and analysis by gas chromatography (Sung et al., 2005). This technique was first used by the Des Moines Water Works for taste and odor analysis and employed by the City of Tampa for the analysis of MIB and geosmin (Brand, 1995). The SPME-GC/MS method has been accepted as Standard Method 6040D (APHA, 2001). The SPME method utilizes a SPME fiber that is exposed to the headspace of the sample being evaluated.

As shown in Figure 3, equipment for a manual SPME are heater and stirrer, heating block, 40 mL amber or clear vial and SPME.

Experimental Steps

1. Prepare a 100 ng/L Geosmin and MIB standard in a bottle with proper seals due to the volatility of geosmin.

2. Prepare a 10 ng/L Geosmin and MIB standard using the 100ng/L standard. (Take 100 mL of 100 ng/L of Geosmin and fill up to 1000 mL)

3. Transfer 25mL of 100 ng/L geosmin into SPME 40 mL vials for each batch reactor experiment.

4. Dilute 1 mL or 1 mg of each algaecide into 1 L of distilled water to make proper input amounts (Input amounts of each algaecide are shown in Table 9).
5. Inject a proper amount into each 40 mL vial.
6. Prepare a spike of surrogate standard (Spike 25 μL of surrogate standard (0.06 ng/μL IPMP in methanol) and inject into each vial (USGS, Open-File Report 02-337).
7. Condition each sample: Add 3.375g sodium chloride (30% NaCl (W/V) (Vesna et al., 2004), 3g/20mL (James Chang et al., Application note: 10213), 13.5g NaCl/66mL (USGS, Open-File Report 02-337), 0.75g /4mL (Saito et al., 2008), 0.3g/2mL (Kevin, 2010)) to each 40mL vial sample and mix properly.
8. Assemble a SPME holder and a fiber.
9. Rapidly stir each sample and heat to 65 ℃ in the heating block.
10. Place the fiber in the sample for 35 minutes for complete adsorption. (This step requires fibers only in the sample not needles)
11. Remove the fiber from the sample and directly inject into the port of a GC/MS system.
12. Analytes will be desorbed by a GC/MS for analysis for 10-15 min.

The minimum detectable concentration of MIB analyzed by these methods is < 5 ng/l and the recovery of the laboratory control standard of 20 ng/l is 95±10%.

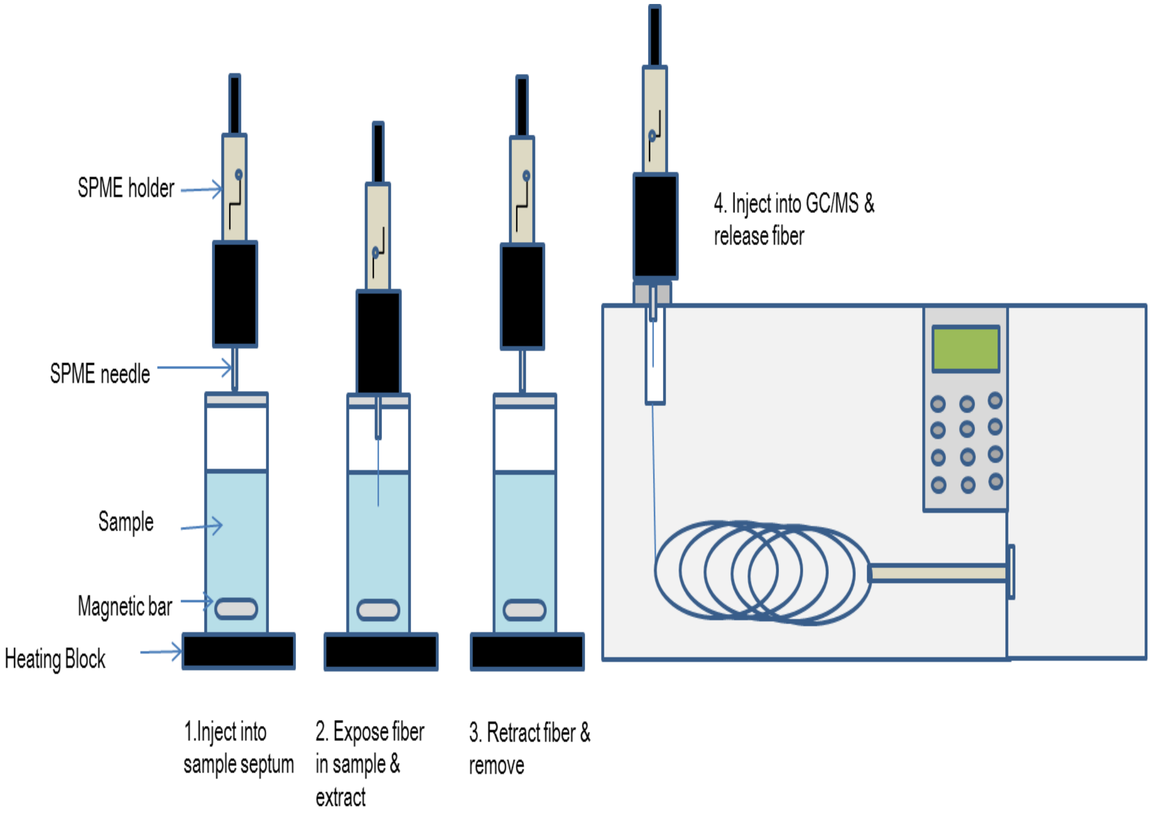


Figure 3 Analytical Procedure

3.2.3 GC/MS Conditioning

GC/MS conditioning is based on the Shimadzu Environmental Geosmin and MIB Analysis Guide Book, as outlined in Table 10.

Table 10 GC/MS Conditions for GSM and MIB analysis

Model	Shimadzu GC/MS-QP5050A	**References**
Carrier gas	Helium 99.999%(served at a pressure of 100 kPa)	Shimadzu Environmental Analysis Guide Book
Method	SIM monitor mass : CH M/Z (Geosmin:112, 125, 182), (MIB: 95, 107) Sampling Rate: 0.2 sec Target compound Rate : geosmin (10-14 min:12.87) Split (ratio : 1), Detector voltage: 1.5 uv GC Program Time: 20 min Micro Scan: 1amu	
Inlet Temperature	Oven Temp: 40℃, 3 min raise 15℃ up to injector Temp: 230℃ Interface Temp: 250℃	
Capillary Column	Equity$^{\text{TM}}$-5 (30m*0.25mm*0.25μm film thickness) Column pressure: 14.5 psi Column Flow : 1.8 ml/min Linear velocity: 48.3 Total Flow: 6.6 mL/min	

3.3 Experimental Setup

Three or more main lab experiments (based on algaecides and various chemicals) will be performed as stated in the objectives. For the batch experimental set up, each 22 mL vial (Sigma-Aldrich, St. Louis) will be analyzed 10 times. The initial GSM and MIB concentrations will range from 100 ng/L to 200 ng/L. First, six algaecides including Earth Tec® will be used to investigate removal abilities and relations between algaecides and geosmin/MIB contaminated water. Next, the algaecide with the best removal rates from the first experiment will be evaluated using different conditions such as sample water geosmin/MIB concentrations, pH, presence or absence of sunlight, algaecide dosages, and temperature. All of the results from the first and second experiments will be analyzed by Gas Chromatography-Mass Spectrometry-Solid Phase Microextration (GC/MS/SPME). Finally, based on the experimental results, a variety of factors such as kinetics, temperature, pH and optimal quantity of algaecide for effective control of geosmin and MIB for each concentration will be determined and provided for water treatment plants in Tulsa, Oklahoma. Samples for this phase of the study will use water from Lake Eucha, the water supply reservoir for Tulsa. All experiments will be performed in duplicate.

3.4 Geosmin and MIB Chromatograms

Geosmin

Mass fragments of geosmin are listed as M/Z (112, 125, 182) in the Shimadzu Environmental Analysis Guide Book. A mass spectrum of 112 was determined to be applicable to this project, based on the spectrum shown in Figure 4.

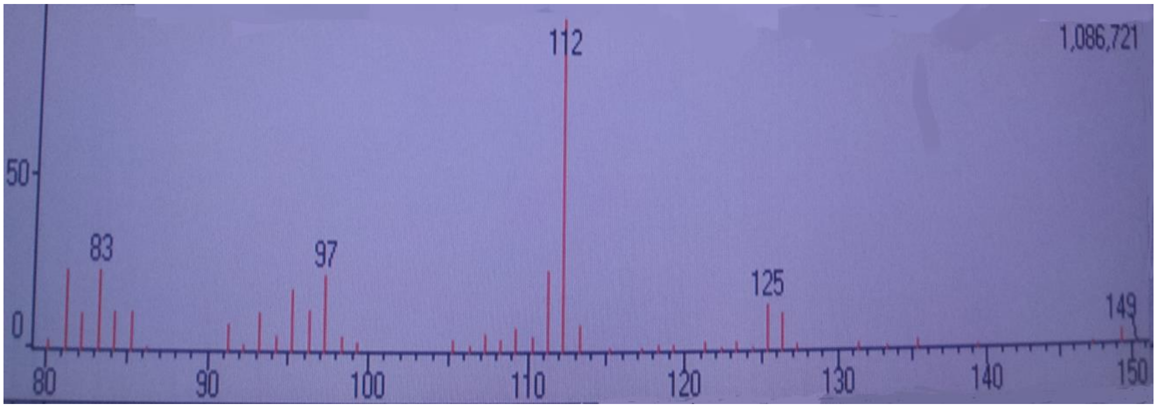


Figure 4 Geosmin spectrum

By using a 112 mass spectrum, concentrations of geosmin were determined by the area under each peak. The detection time of the 112 mass spectrum was determined to be 12.51 minutes as shown in the chromatogram in Figure 5.

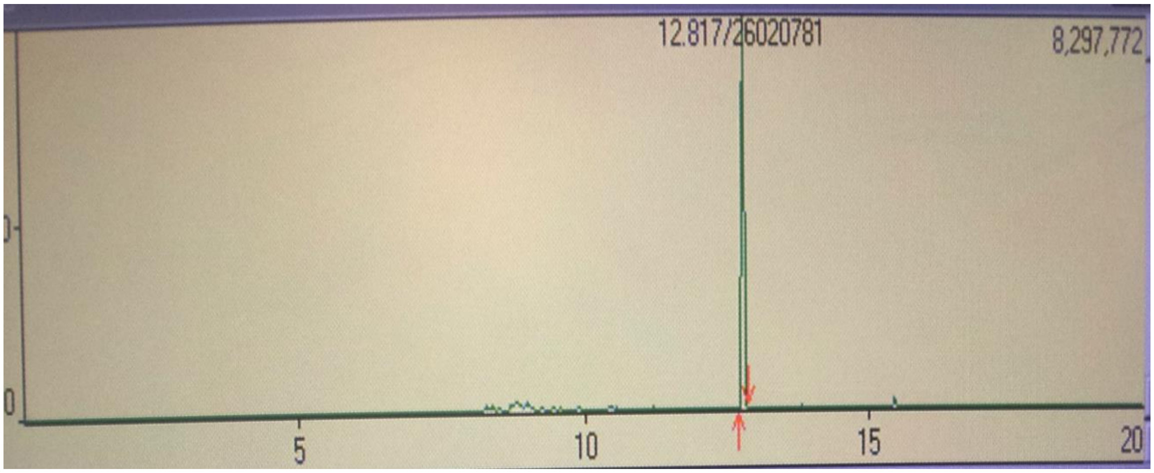


Figure 5 Geosmin chromatogram at 100 ng/L

MIB

MIB mass fragments were identified as M/Z (95,108) from the Shimadzu Environmental Analysis Guide Book. A spectrum corresponding to a mass of 95 was determined to be best for this project, as shown in Figure 6.

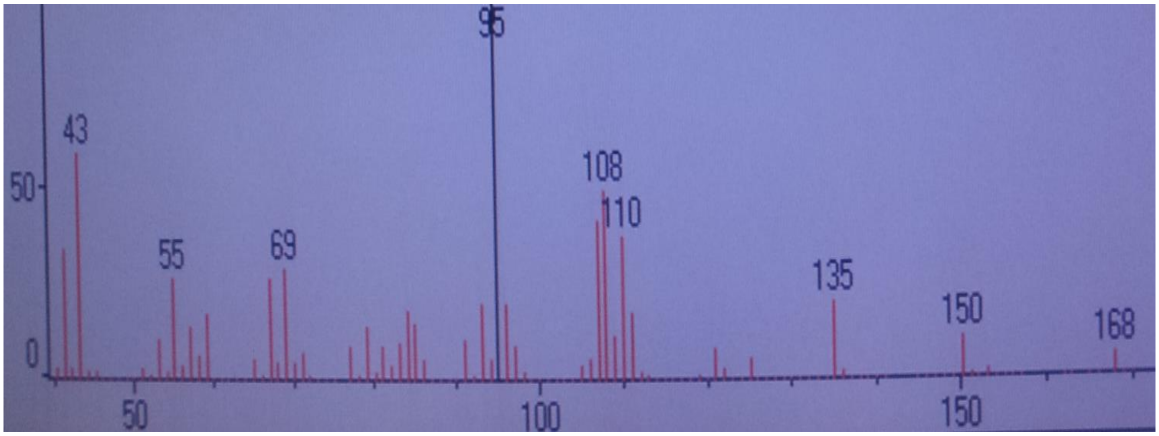


Figure 6 MIB spectrum

The detection time of MIB was measured as 10 min 23 seconds as shown in Figure 7, and the area under the MIB peak was 1338441 units with a concentration of 100 ng/L.

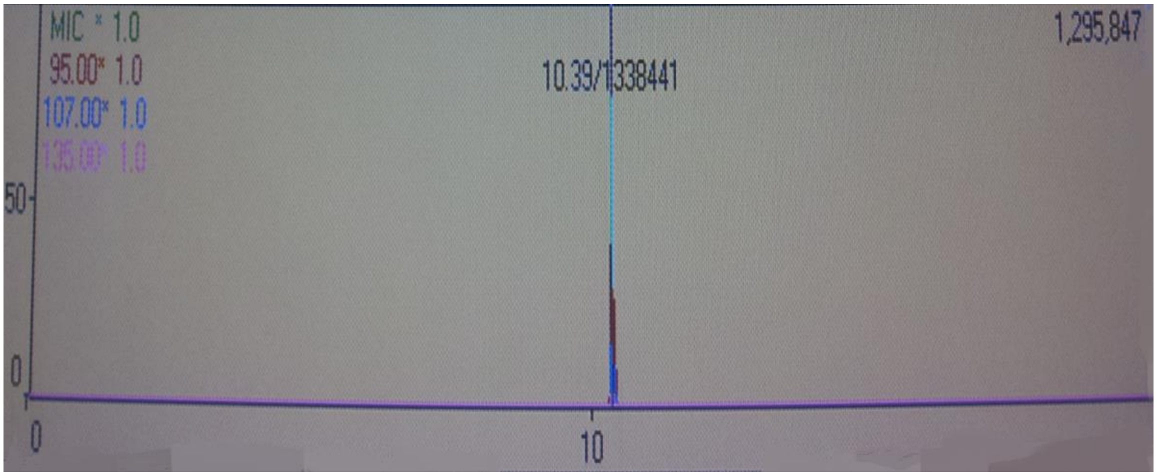


Figure 7 MIB chromatogram at 100 ng/L

3. 5 Calibration

A calibration curve was developed to determine the unknown sample concentration by comparing the unknown to a set of standard samples of known concentration. From the calibration curve, unknown analyte concentration could be determined using a plot of instrumental response changes. This experiment is focused on determination of geosmin and MIB concentration.

Geosmin Calibration

Two modes for calibration are available through GC/MS. One is called a splitless mode, which does not split samples usually used for a small quantity of sample. The other is a split mode, which is normally used for a medium or large quantity of sample. In this experiment, the split mode was used because detector saturation problems might exist when applying a high quantity of samples during the process. Splitless mode often resulted in detector saturation problems; thus, split mode is used for calibration and further experiments.

The optimum calibration curve was made based on the three calibration data. The R^2 square value was high, 0.9935, which indicated high linearity.

Table 11 Optimized Calibration Curve Data from 3 split method experiments

Concentration(ng/L)	Area
1	208080
2	348380
10	1115102
25	1508913
50	2652503
75	4081733
100	5308607

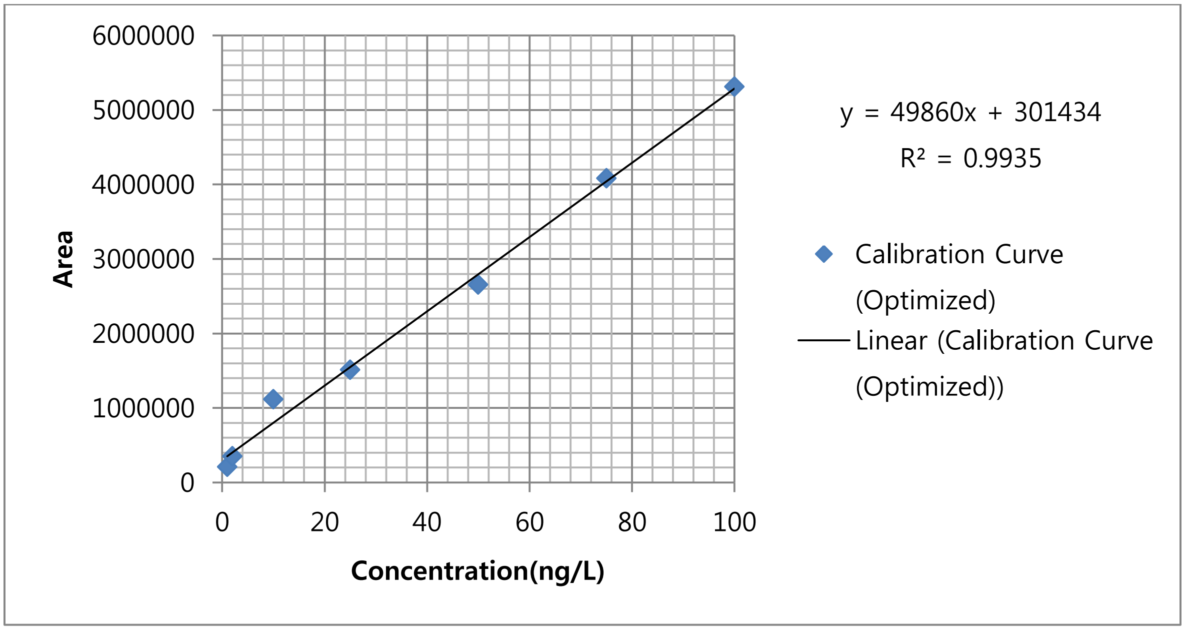


Figure 8 Area vs Concentration of geosmin

MIB Calibration

The split mode was also used to develop the MIB calibration curve. Two times of the calibration data was achieved through SIM mode. The optimized calibration cure was found from the first and the second calibration data. The R-square value is better than 0.99. This number will be used to estimate concentration of MIB in GC/MS.

Table 12 Optimized Calibration Curve Data from 3 split method experiments

Concentration (ng/L)	Area
100	1528562
75	1275871
50	937032
25	655432
10	452998
2	364678

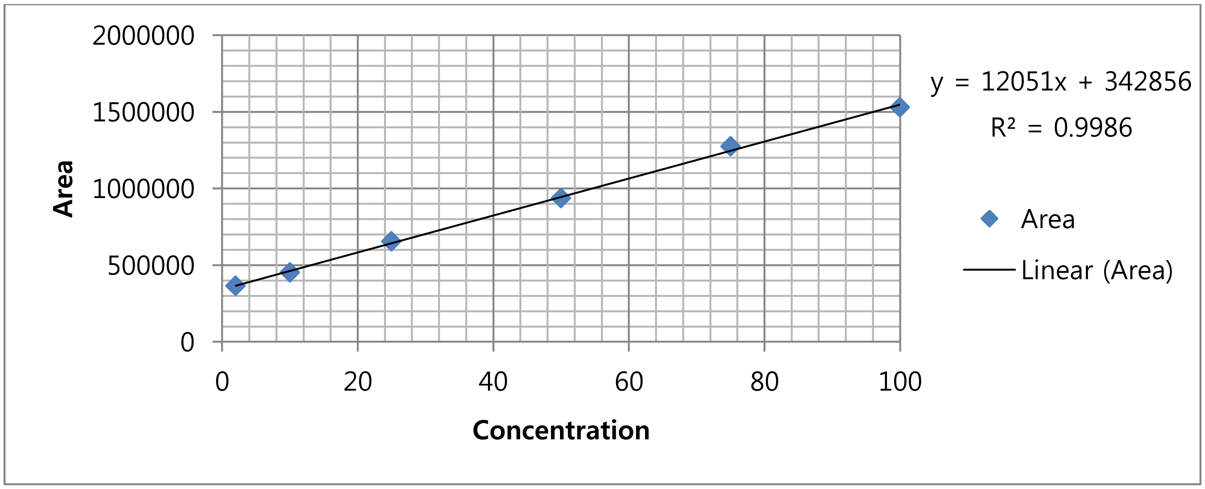


Figure 9 Area VS Concentration of MIB

CHAPTER IV

FINDINGS

Geosmin and MIB removal using algaecides and other chemicals has not been extensively studied. In a water treatment plant of the City of Tulsa, operators found that Earth Tec® , used for removal of algae, also removed geosmin down to non-detectable levels. It was decided to investigate the hypothesis that some compounds used to remove algae would also remove taste and odor compounds. Several experiments were designed to prove or disprove this hypothesis. The key variables investigated were chemical, dosages, solution pH, temperature, the presence and absence of sunlight (biodegradation), and turbulence of samples. These factors were varied based upon general practices and recommendations as shown in Table 13. The other important variables such as initial alkalinity, hardness, total dissolved solids (TOS), natural organic matter (NOM) were held constant for simplicity of analysis. Based on the information, following five main parts of research were provided.

1. Different algaecides with dosage changes

Earth Tec® was found to remove geosmin and MIB in lake water, though it has not been experimentally proven. It is possible that other algaecides and different dosages might provide better results. A set of experiments was designed to evaluate removal of geosmin and MIB in water by different algaecides with changing dosages.

2. pH effects on geosmin and MIB

A research study (Schweitzer and Ekstrom, 2006) reported that pH is the most important factor in removing geosmin from water. Wen-Hsing Hsieh (2011) proved that MIB and geosmin are tertiary alcohols and determined that geosmin concentrations dropped 31% at pH of 2.8 compared to pH 6, and MIB concentration also reduced 87% at pH 2.8 compared to pH 6.8. Several experiments were conducted to investigate the impact of pH on removal of geosmin and MIB.

3. Biodegradation experiments

Biodegradation of geosmin and MIB in lake water has not been extensively investigated. Geosmin and MIB are semi-volatile compounds, and volatilization and/or bacterial biodegradation could be responsible for some removal seen in lake water. A series of experiments was designed to investigate bacterial degradation and volatility of geosmin and MIB.

4. Temperature and Turbulence effects

The pipe line from the supply reservoir to the Tulsa water treatment plant provides for turbulent flow and temperature changes in the supply water. A series of experiments was conducted to determine the effects of turbulence in the pipe line and temperature of water.

5. Other chemicals

Other algaecides and other chemicals were evaluated to remove geosmin and MIB. In the experiments, three possibilities were evaluated. The first one is that different dosages of algaecide might have different effects on geosmin and MIB concentrations. The second possibility is that bacterial degradation is a function only of bacteria in the water or may be accelerated by the addition of Earth Tec® . The third possibility is Earth Tec® itself causes some removal under specific environmental conditions.

4.1 Different algaecides with dosage changes

4.1.1 Experimental Set-up

The purpose of these experiments was to determine the removal efficiencies of geosmin and MIB by using different dosages of each algaecide in lake water. Six different compounds were evaluated for geosmin removal. Earth Tec® was the first algaecide investigated, due to the experiences of the Tulsa water treatment plant. Cutrine plus, a copper-based algaecide and Phycomycin SCP will be used as alternative algaecides. Lake water (Eucha Lake, the supply lake for the City of Tulsa) was spiked with 100 ng/L of geosmin. Phycomycin SCP is an 85% active concentrated form of sodium carbonate peroxyhydrate and is used for algaecide in lakes, ponds, drinking water reservoirs and aquaculture. These and the other algaecides investigated are shown in Table 13.

Table 13 Six Algaecides Investigated

Algaecide	Pros	Cons	Typical Dosage
EarthTec®	* Reduce TOCs and THM, HAA levels without creating disinfection by-products (DBPs) * Well proven non-toxin algaecide * Dissolved completely in water	* Oxygen depletion	1gal/1,000,000 gal raw water (0.06 ppm copper)
Calcium chloride dihydrate	Effectively drying water molecules	* No proven for fish and plant in water	Not known
AB Algimycin PWF	EPA proven algaecide for swimming, domestic uses and livestock watering	Copper toxin at high dosage	1.5 gallons/325851 gallons

CUTRINE ® - PLUS	Effective in controlling a broad range of algae: Chara, Spirogyra, Cladophora, Vaucheria, Ulothrix, Microcystis, Oscillatoria	*Corrosive and overdose toxic to some types of fish	0.2-0.1 copper ppm
Phycomycin SCP	*Broad range application * Safe algaecide	Algae decaying might cause oxygen depletion	9.0 to 307 lbs/million gals (0.3 to 10.2 ppm H_2O_2)
Sulfuric acid	Cheap comparing to other algaecides	No proven for safe use	- Not known

The key variables considered will be initial algaecide concentrations and different algaecide dosages. Table 14 shows factors for consideration.

Table 14 Different dosage of EarthTec for GSM and MIB removal experiments

Variables	**GSM/MIB Concentration**	**Algaecide Concentration**
Factors	100 to 200 ng/L samples	Manufacturer's recommended dose to 100 times high dose

All reactors of 40 mL bottles will be prepared in duplicate. The experiments will be performed with geosmin in Lake Eucha water using different dosages of five algaecides and one chemical including Earth Tec® in 100ng/L to 200 ng/L of geosmin concentration samples.

The samples of geosmin are made by using Supelco 100 µg geosmin /mL in methanol (47522_U); dosages for each algaecide are calculated based on the recommended dosage from manufacturers. A GC/MS/SPME analysis method will be performed to estimate geosmin and MIB in the reactors. For a solid phase extraction method, 40mL SPME vials are used for batch reactors. Temperature will be maintained at 15℃. The observation time will be 1 to 7days.

4.1.2 Removal of Geosmin

Earth Tec®

Operators at a water treatment facility in Tulsa, Oklahoma, found that Earth Tec® removes geosmin. The Earth Tec® is added in the pipeline that transports water from a distant lake to the water treatment facility; travel time is two days. The mechanism of the reaction has not been investigated. Therefore, one objective of this study is to identify a possible removal mechanism of geosmin using the EarthTec® . In these experiments, different dosages of EarthTec ® (from the recommended dosage to a dosage 100 times higher) were applied to determine removal rates under different environments.

Conditions of Sample: Geosmin Concentration: 100 ng/L geosmin; Earth Tec® dosage: recommended (0.001 ml/L) to 100 times the recommended dosage (0.1 ml/L); pH of sample: 7.82 to 2.6, Lake Water pH: 8.77 (used replicate bottles in all experiments).

Results and Discussion

Results of the first experiment are listed in Table 15 and plotted in Figure 10.

Table 15 Geosmin Concentrations at various dosages of Earth Tec®

Time (days)	Geosmin Concentration (ng/L)						
	Dosage	0.001mL/L	0.002mL/L	0.005mL/L	0.01mL/L	0.05 mL/L	0.1mL/L
0.0		100 ng/L	100 ng/L	100 ng/L	100 ng/L	97 ng/L	100 ng/L
0.2		93 ng/L	-	-	-	-	-
0.4		87 ng/L	93 ng/L	78 ng/L	99 ng/L	-	-
0.8		71 ng/L	91 ng/L	78 ng/L	100 ng/L	-	-
1.0		-	-	-	-	85 ng/L	99 ng/L
1.3		92 ng/L	89 ng/L	-	95 ng/L	-	-
1.7		-	83 ng/L	-	90 ng/L	-	-
1.9		88 ng/L	-	77 ng/L	87ng/L	-	-
2.0		85 ng/L	83 ng/L	75ng/L	79ng/L	75 ng/L	76 ng/L
3.0		83ng/L	82 ng/L	74ng/L	73ng/L	35 ng/L	54 ng/L
4.0		84ng/L	80 ng/L	75ng/L	72ng/L	26 ng/L	16 ng/L

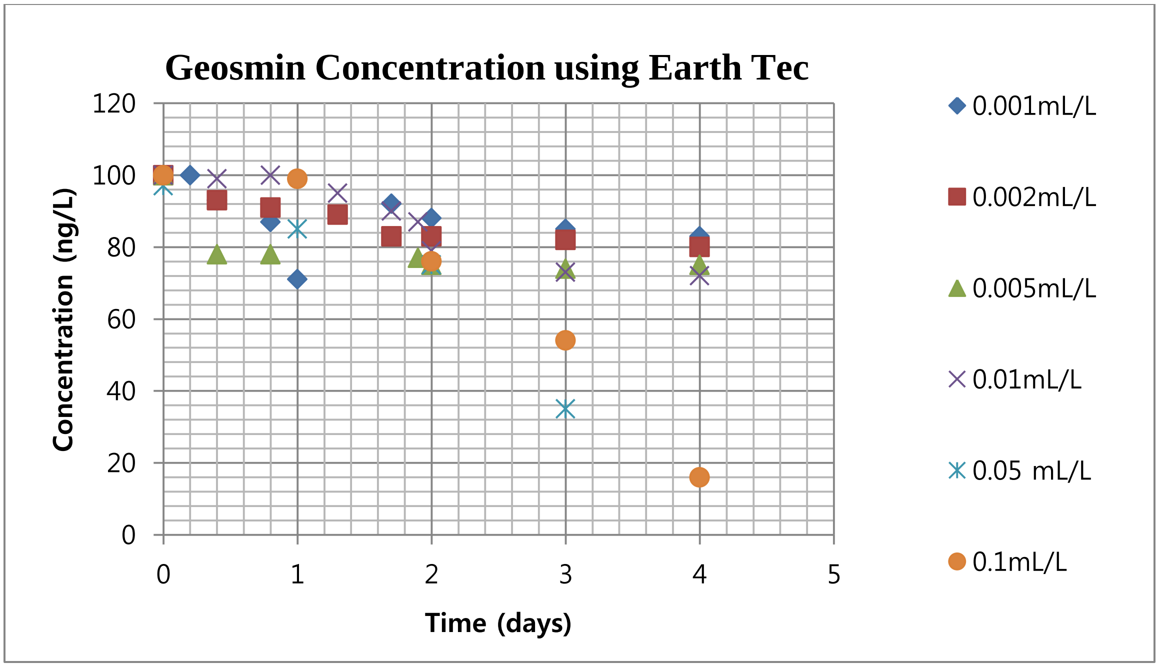


Figure 10 Geosmin Concentrations at different dosages of Earth Tec

Geosmin was reduced from 100 ng/L to 84 ng/L at 0.001 ml/L, 80 ng/L at 0.002 ml/L, 75 ng/L at 0.005 ml/L, 72 ng/L at 0.01 ml/L, 26 ng/L at 0.05 ml/L, and 16 ng/L at 0.1 ml/L after 4days. Geosmin was removed 15 to 28 percent at doses ranging from 0.001 ml/L to 0.01 ml/L, 74% at 0.05 ml/L, and 84% removal at the 0.1 ml/L dose. Therefore, effective geosmin removal with Earth Tec® requires higher than 50 times the recommended Earth Tec® dosage. These results raised the question of why the higher dosages removed geosmin more effectively. One possibility is the pH effects of the higher dosages. The pH in samples with 0.01 ml/L and 0.05 ml/L of Earth Tec® were measured as 3.8 and 2.6. Thus, removals could be due to the low pH. These results will be investigated by evaluating the impact of pH on geosmin concentration.

Cutrine Plus

Cutrine Plus is a copper-based algaecide and is commonly used for removal of algae in lakes or swimming pools. The main difference between EarthTec® and Cutrine Plus is pH. While Earth Tec® is a strong acid (pH 1.8-2.0), Cutrine plus is a base (pH 10.3-10.5). The purpose is this series of experiments was to evaluate removal of geosmin using a base algaecide. As was used in the Earth Tec® experiments, different dosages of Cutrine Plus (recommended dosage to 100 times the recommended dosage) was applied to evaluate geosmin removal by a base algaecide using Lake Eucha water.

Conditions of Sample: Geosmin Concentration: 100 ng/L geosmin, Cutrine plus dosage: recommended (005 ml/L) to 100 times the recommended dosage (5 ml/L), pH of sample: 7.8 to 10.5, lake water pH: 8.77 (All samples were duplicated).

Results and Discussion

Results of the Cutrine Plus experiment are listed in Table 16 and plotted in Figure 11.

Table 16 Geosmin Concentrations at various dosages of Cutrine Plus

Time (days)	Geosmin Concentration (ng/L)				
	Dosage	0.05mL/L	0.1mL/L	0.5mL/L	5mL/L
0		102 ng/L	96 ng/L	98 ng/L	95 ng/L
0.2		89 ng/L	-	-	-
0.4		85 ng/L	90 ng/L	-	-
0.8		75 ng/L	86 ng/L	-	-
1		91 ng/L	-	89 ng/L	85 ng/L
1.3		93 ng/L	89 ng/L	-	-
1.7		84 ng/L	82 ng/L	-	-
1.9		71 ng/L	-	-	-
2		73 ng/L-	82 ng/L	78 ng/L	83 ng/L
3		72 ng/L	80 ng/L	75 ng/L	70 ng/L
4		70 ng/L	74 ng/L	73 ng/L	70 ng/L

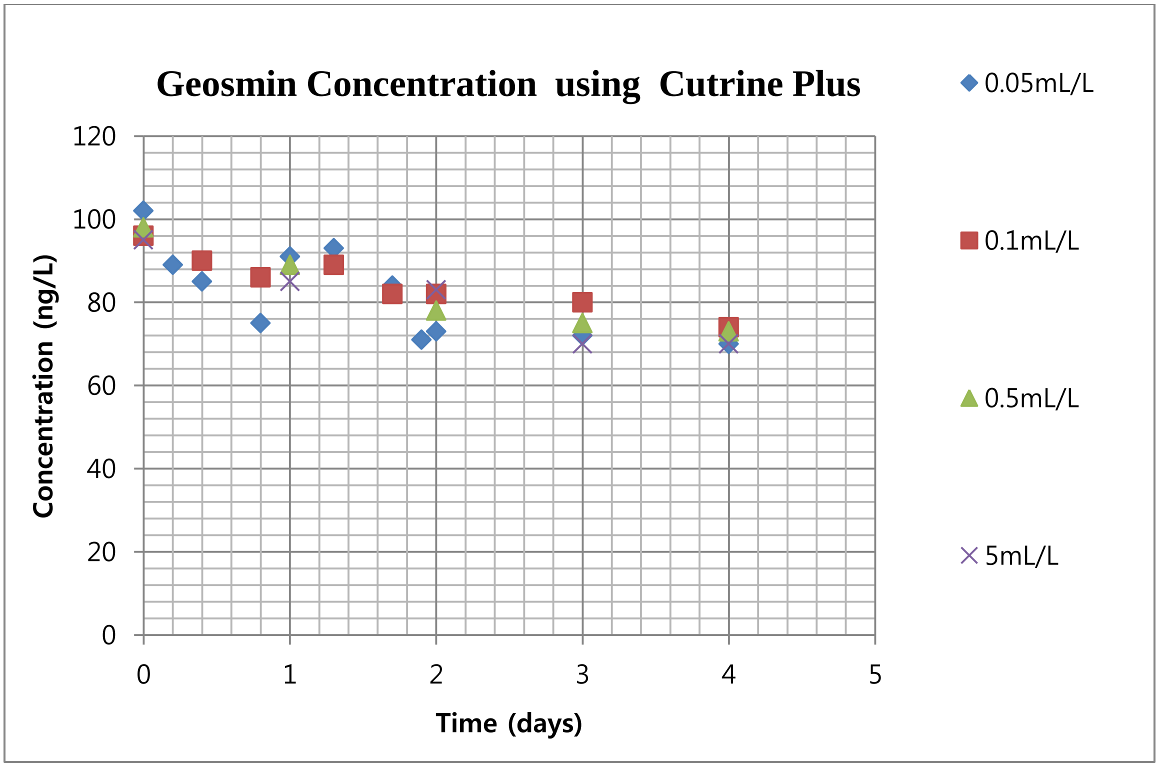


Figure 11 Geosmin Concentrations at different dosages of Cutrine Plus

Geosmin reductions varied from 26 percent for the 0.05 ml/L dose to 30 percent for the 0.5 ml/L dose. A reduction of 26 to 30 percent is not sufficient for use as a treatment chemical; therefore, Cutrine Plus is not a suitable chemical for removal of geosmin. Other copper/base algaecides likely have the same characteristics as Cutrine Plus.

Algimycin PWF

Algimycin PWF is an EPA-registered algaecide for use in drinking water reservoirs, ponds, lakes, and irrigation water conveyance systems such as canals, laterals and ditches. It is a copper based algaecide and has an acid characteristic. It has similar characteristics to Earth Tec® .

Conditions of Sample: Geosmin Concentration: 100 ng/L geosmin**,** Algimycin PWF dosage: recommended (0.2 ml/L) to 100 times higher (2.0 ml/L), pH of sample: 7.82-3.2, Lake Eucha water pH: 8.77 (All samples were duplicated).

Results and Discussion

Results of this experiment are listed in Table 17 and plotted in Figure 12.

Table 17 Geosmin Concentrations at various dosages of Algimycin PWF

Time (days)	**Geosmin Concentration (ng/L)**				
	Dosage	**0.02mL/L**	**0.04mL/L**	**1mL/L**	**2mL/L**
0	92 ng/L		97 ng/L	95 ng/L	91 ng/L
0.2	95 ng/L		-	-	-
0.4	94 ng/L		94 ng/L	-	-
0.8	92 ng/L		91 ng/L	-	-
1	85 ng/L		-	67 ng/L	54 ng/L
1.2	88 ng/L		90 ng/L	-	-
1.7	-		86 ng/L	-	-
1.9	85 ng/L		-	-	-
2	86 ng/L		83 ng/L	53 ng/L	44 ng/L
3	83 ng/L		82 ng/L	50 ng/L	40 ng/L
4	84 ng/L		82 ng/L	48 ng/L	35 ng/L

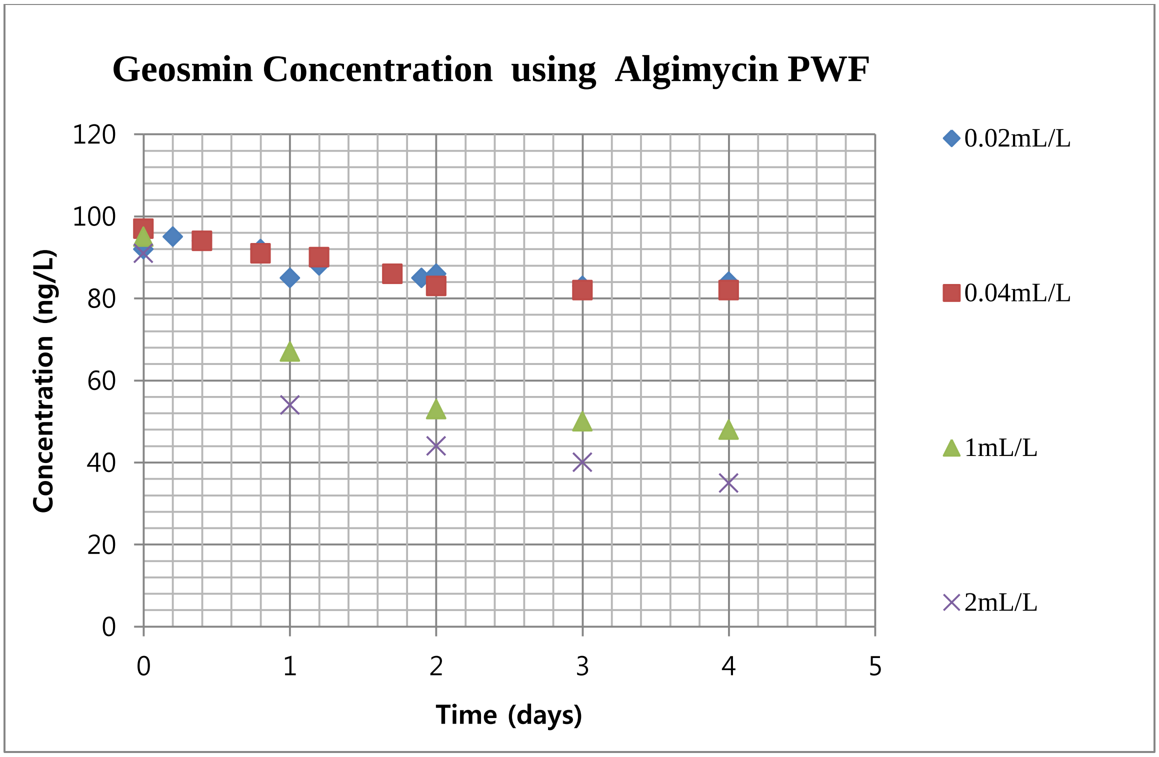


Figure 12 Geosmin Concentrations at different dosages of Algimycin PWF

Geosmin concentration was reduced from 95 ng/L to 84 ng/L with the 0.02 ml/L dosage of Algimycin PWF, to 82 ng/L with an Algimycin PWF dosage of 0.04 ml/L, to 48 ng/L with the 0.1 ml/L dosage, and to 35 ng/L with the 2 ml/L dosage. The pH of samples with the Algimycin PWF dosages of 1 ml/L and 2 ml/L were 4.3 and 3.2, respectively. The highest removal rate of geosmin was 65% in the 2 ml/L dosage. This result is similar to that seen with Earth Tec® .

Sulfuric Acid

Since Earth Tec® is strongly acidic (pH=0.5), it was decided to investigate if geosmin removal was due to the low pH of the treated water. In this experiment, sulfuric acid is used for geosmin removal (acid dehydration process). Different dosages of sulfuric acids were used for verification of acid dehydration of geosmin in Lake Eucha water.

Conditions of Sample: Geosmin Concentration: 100 ng/L geosmin; Sulfuric Acid dosage: 0.25 mL/L (0.0092 eq/L) to 25 mL/L (0.092 eq/L); pH of sample: 7.82 to 2.1, Eucha Lake water pH:

8.77 (All samples were duplicated).

Results and Discussion

Results using sulfuric acid are listed in Table 18 and plotted in Figure 13.

Table 18 Geosmin Concentrations at various dosages of Sulfuric Acid

<table>
<tr><th rowspan="2">Time (days)</th><th colspan="5">Sulfuric Acid/Concentration (ng/L)</th></tr>
<tr><th>Dosage</th><th>0.0092Eq/L</th><th>0.0184Eq/L</th><th>0.046 Eq/L</th><th>0.92 Eq/L</th></tr>
<tr><td>0</td><td colspan="2">95 ng/L</td><td>98 ng/L</td><td>97 ng/L</td><td>97 ng/L</td></tr>
<tr><td>0.2</td><td colspan="2">93 ng/L</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>0.4</td><td colspan="2">90 ng/L</td><td>87 ng/L</td><td>-</td><td>-</td></tr>
<tr><td>0.8</td><td colspan="2">89 ng/L</td><td>79 ng/L</td><td>-</td><td>-</td></tr>
<tr><td>1</td><td colspan="2">74 ng/L</td><td>-</td><td>70 ng/L</td><td>24 ng/L</td></tr>
<tr><td>1.2</td><td colspan="2">82 ng/L</td><td>75 ng/L</td><td>-</td><td>-</td></tr>
<tr><td>1.7</td><td colspan="2">-</td><td>73 ng/L</td><td>-</td><td>-</td></tr>
<tr><td>1.9</td><td colspan="2">83 ng/L</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>2</td><td colspan="2">82 ng/L</td><td>70 ng/L</td><td>69 ng/L</td><td>5 ng/L</td></tr>
<tr><td>3</td><td colspan="2">80 ng/L</td><td>68 ng/L</td><td>67 ng/L</td><td>2 ng/L</td></tr>
<tr><td>4</td><td colspan="2">79 ng/L</td><td>68 ng/L</td><td>65 ng/L</td><td>0 ng/L</td></tr>
</table>

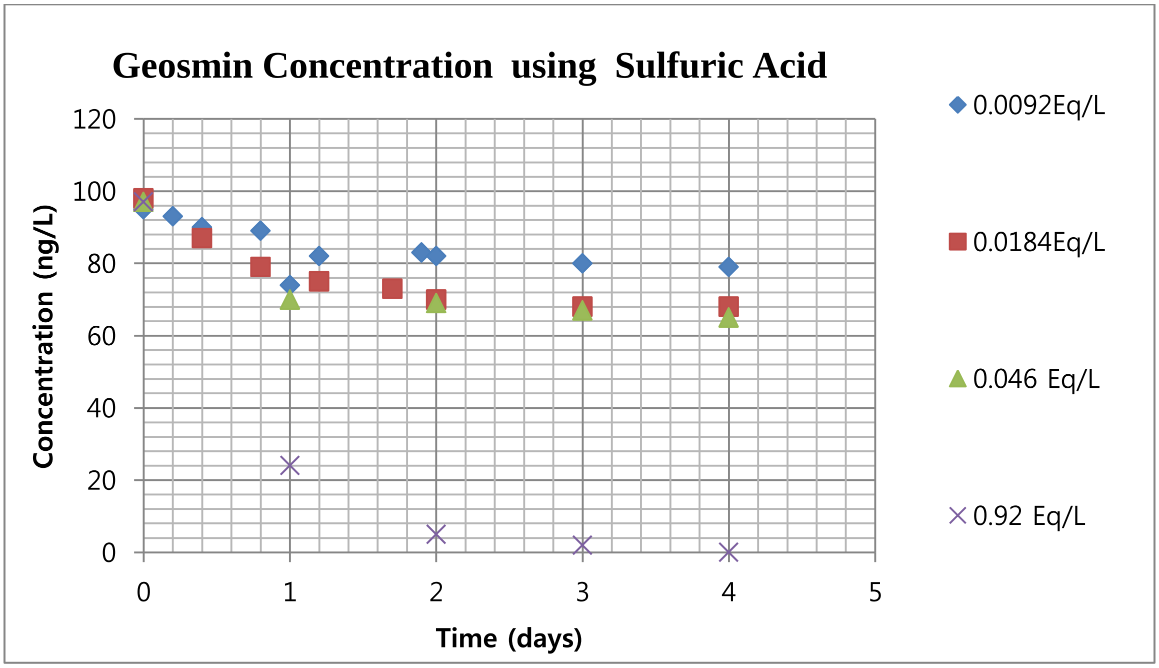


Figure 13 Geosmin Concentrations at different dosages of Sulfuric Acid

Geosmin concentrations with added sulfuric acid were reduced from 98 ng/L to 79 ng/L in 0.0092 eq/L of sulfuric acid, to 68 ng/L in 0.0184 eq/L of sulfuric acid, to 65 ng/L in 0.046 eq/L of sulfuric acid, and to below detection in 0.92 eq/L of sulfuric acid. Samples receiving from 0.0092 eq/L to 0.046 eq/L sulfuric acid had geosmin reduced by 35percent with a pH reduction from 7.82 to 5.0. Addition of 0.92 eq/L sulfuric acid exhibited complete removal from 97 ng/L to below detection. This result indicates that a dehydration process destroys all geosmin as the pH approaches 2.0.

Phycomycin SCP

Phycomycin SCP, a peroxyhydrate based algaecide, is frequently used to kill various types of algae in swimming pools, lakes and ponds. The pH of Phycomycin SCP ranges from 10.4 to 11.8. Hydrogen peroxide (H_2O_2) is considered a mild oxidizer, forming water molecules and releasing dissolved O_2 into the water column. Phycomycin SCP was chosen because it was not a copper-based algaecide, as is Earth Tec® . Four different dosages of Phycomycin SCP were investigated in this set of experiments.

Conditions of Sample: Geosmin Concentration: 100 ng/L geosmin; Phycomycin SCP dosage: manufacturer’s recommended dose to a dose 100 times higher, pH of sample: 7.82-11.3, Filtered Eucha Lake water pH: 8.77.

Results and Discussion

Results using Phycomycin SCP are listed in Table 19 and plotted in Figure 14.

Table 19 Geosmin Concentrations at various dosages of Phycomycin SCP

Time (days)	**Geosmin Concentration (ng/L)**				
	Dosage	**1mg/0.94L**	**2mg/0.94L**	**50mg/0.94L**	**100mg/0.94L**
0		96 ng/L	97 ng/L	91 ng/L	89 ng/L
0.2		92 ng/L	-	-	-
0.4		90 ng/L	84 ng/L	-	-
0.8		85 ng/L	63 ng/L	-	-
1		89 ng/L	-	85 ng/L	82 ng/L
1.2		91 ng/L	68 ng/L	-	-
1.7		-	72 ng/L	-	-
1.9		83 ng/L	-	-	-
2		84 ng/L	75 ng/L	84 ng/L	79 ng/L
3		83 ng/L	73 ng/L	82 ng/L	75 ng/L
4		85 ng/L	72 ng/L	77 ng/L	72 ng/L

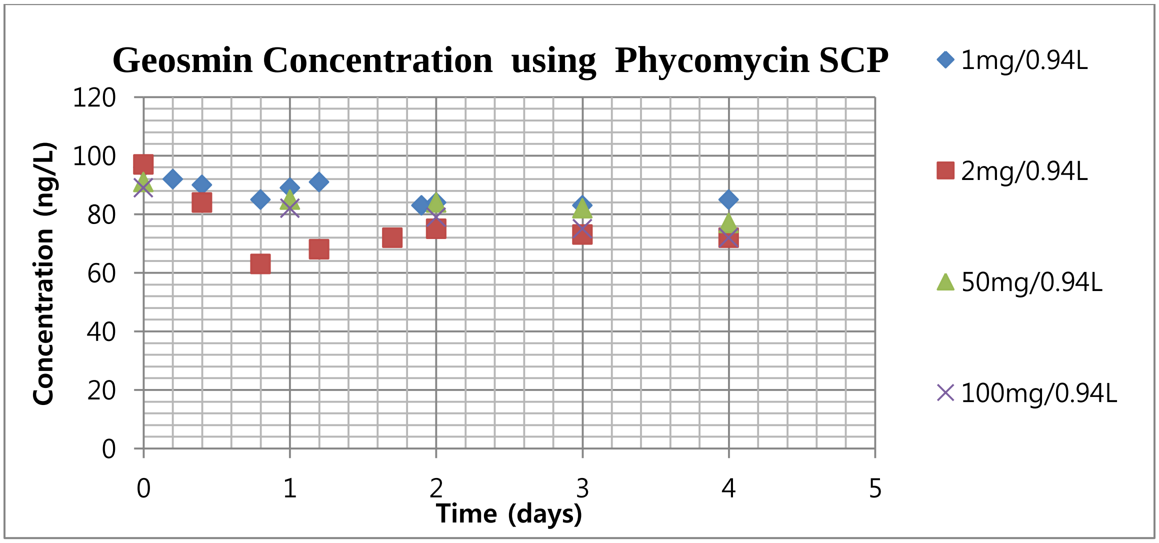


Figure 14 Geosmin Concentrations at different dosages of Phycomycin SCP

Geosmin reductions were only 30 percent, even at dosages of 50 to 100 mg/L (100 times the recommended dose), and there was no consistent effect with dose. It appears that Phycomycin SCP does not have any effect on geosmin removal.

Calcium chloride dihydrate

Dehydration processes form water molecules from solvents by removing hydrogen. It was thought that dehydration might be effective as a treatment mechanism for geosmin. Calcium chloride dihydrate was chosen for investigation as a treatment chemical due to its characteristics as a good dying agent for various solvents. In addition, calcium chloride dihydrate does not have a significant impact on pH. In the experiment, as the similar to Earth Tec® experiment, four different dosages of calcium chloride dihydrate were evaluated for removal efficiency of geosmin.

Conditions of Sample: Geosmin Concentration: approximately 200 ng/L geosmin; Calcium chloride dihydrate dosage: 0.1 g/100 mL to 2.5 g/100 mL, pH of sample:6.8-6.0, Eucha Lake water pH: 7.8.

Results and Discussion

Results of this experiment are listed in Table 20 and plotted in Figure 15.

Table 20 Geosmin Concentrations at various dosages of Calcium Chloride

Time (days)	Calcium chloride Dose/Concentration (ng/L)				
	Dosage	0.1 g/100 mL	0.5 g/100 mL	1 g/ 100 mL	2.5 g/100 mL
0		177	180	180	180
1		162	173	111	166
2		154	173	157	159
3		147	181	100	103
4		141	188	110	68

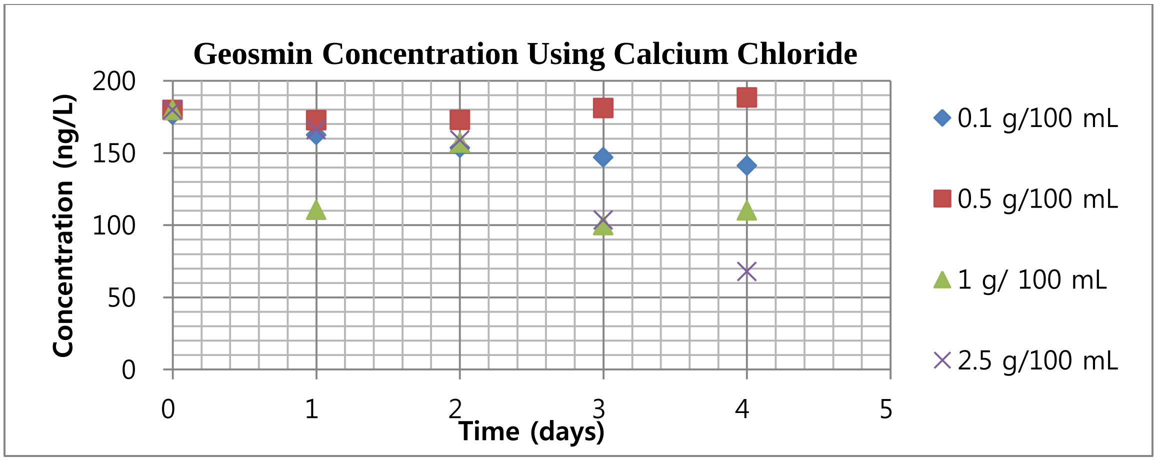


Figure 15 Geosmin Concentrations at different dosages of Calcium Chloride

Results and Discussion

Geosmin was only slightly removed at the dosages of 0.1 g/100 mL and 0.5 g/100 mL, but was significantly reduced, from 180 ng/L to110 ng/L and 68 ng/L at the dosages of 1g/100 mL and 2.5 g/100 mL. These reductions indicate that a high dosage of calcium chloride could remove about 50% of geosmin in Lake Eucha water. The pH values of samples were acceptable, approximately pH 6.0 to 6.8. Calcium chloride is an effective drying agent, with a similar reaction to dehydration. More evaluation of calcium chloride and other drying agents would be warranted for removal of geosmin in Lake Eucha water.

4.1.3 Removal of MIB

Earth Tec®

As mentioned in the literature review, MIB is also a taste and odor causing compounds. MIB analysis in Lake Eucha water will be performed as with the geosmin studies to evaluate MIB removal by using Earth Tec® and five other compounds. Six different dosages of Earth Tec® will be applied in order to clarify removal rates of MIB.

Conditions of Sample: MIB Concentration: 100 to 200 ng/L MIB as indicated in the tables below; Earth Tec dose: recommended to 100 times high dose; pH of sample: 7.82-2.5, Eucha

Lake water pH: 8.77.

Results and Discussion

Results of this experiment are listed in Table 21 and plotted in Figure 16.

Table 21 MIB Concentrations at various dosages of Earth Tec

<table>
<tr><th rowspan="2">Time (days)</th><th colspan="7">Concentration (ng/L)</th></tr>
<tr><th>Dosage</th><th>0.001mL/L</th><th>0.002mL/L</th><th>0.005mL/L</th><th>0.01mL/L</th><th>0.05mL/L</th><th>0.1mL/L</th></tr>
<tr><td>0.0</td><td colspan="2">98 ng/L</td><td>187 ng/L</td><td>192 ng/L</td><td>185 ng/L</td><td>183 ng/L</td><td>196 ng/L</td></tr>
<tr><td>0.2</td><td colspan="2">96 ng/L</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>0.4</td><td colspan="2">89 ng/L</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>0.8</td><td colspan="2">95 ng/L</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>1.0</td><td colspan="2">-</td><td>183 ng/L</td><td>185 ng/L</td><td>167 ng/L</td><td>153 ng/L</td><td>75 ng/L</td></tr>
<tr><td>1.3</td><td colspan="2">87 ng/L</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>1.7</td><td colspan="2">-</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>1.9</td><td colspan="2">92 ng/L</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>2.0</td><td colspan="2">88 ng/L</td><td>179 ng/L</td><td>169 ng/L</td><td>172 ng/L</td><td>112 ng/L</td><td>52 ng/L</td></tr>
<tr><td>3.0</td><td colspan="2">87 ng/L</td><td>181 ng/L</td><td>172 ng/L</td><td>158 ng/L</td><td>85 ng/L</td><td>15 ng/L</td></tr>
<tr><td>4.0</td><td colspan="2">90 ng/L</td><td>164 ng/L</td><td>165 ng/L</td><td>155 ng/L</td><td>10 ng/L</td><td>0 ng/L</td></tr>
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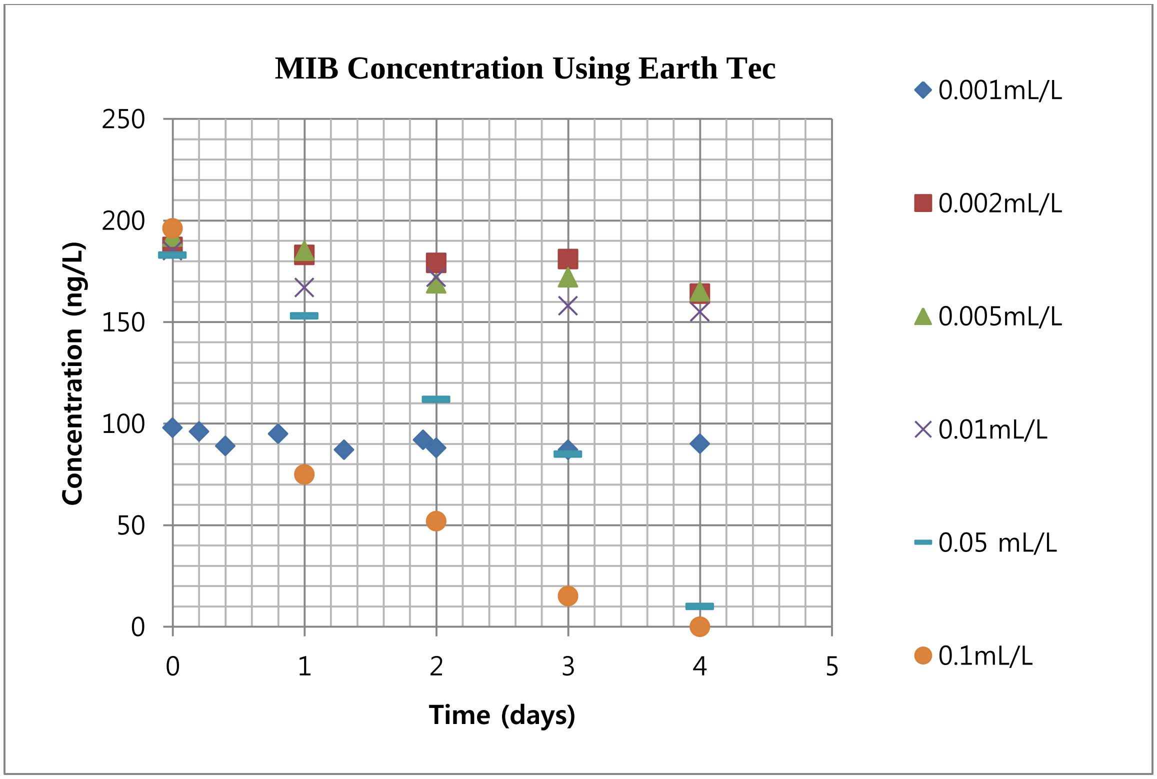


Figure 16 MIB Concentrations at different dosages of Earth Tec

Results and Discussion

MIB reductions were achieved at the dosage of 50 times the manufacturer's recommended dose, from 183 ng/L to 10 ng/L with 4 days reaction time at pH 3.7. Complete MIB removal was detected at a dose of 100 times the recommended dose of EarthTec® , from 196 ng/L to 0 ng/L at pH 2.6. This result shows that MIB can be removed or transformed to other products with these doses, and a resulting pH of 3.7 to 2.6.

Algimycin PWF

Five different dosages of Algimycin PWF were applied in MIB-containing water in the same manner of geosmin experiments.

Conditions of Sample: MIB Concentration: approximately 200 ng/L, Algimycin PWF dosage: recommended (0.02 ml/L) to 100 times the recommended dosage (2.0 ml/L); pH of sample: 7.82-3.0, Eucha Lake water pH: 8.77**.**

Results and Discussion

Results of this experiment are listed in Table 22 and plotted in Figure 17.

Table 22 MIB Concentrations at various dosages of Algimycin PWF

Time (days)	Concentration (ng/L)					
	Dosage	0.02mL/L	0.1mL/L	0.2mL/L	1mL/L	2mL/L
0		185 ng/L	192 ng/L	182 ng/L	190 ng/L	182 ng/L
1		182 ng/L	188 ng/L	167 ng/L	132 ng/L	84 ng/L
2		174 ng/L	181 ng/L	155 ng/L	124 ng/L	48 ng/L
3		180 ng/L	174 ng/L	152 ng/L	96 ng/L	32ng/L
4		178 ng/L	169 ng/L	153ng/L	53 ng/L	12 ng/L

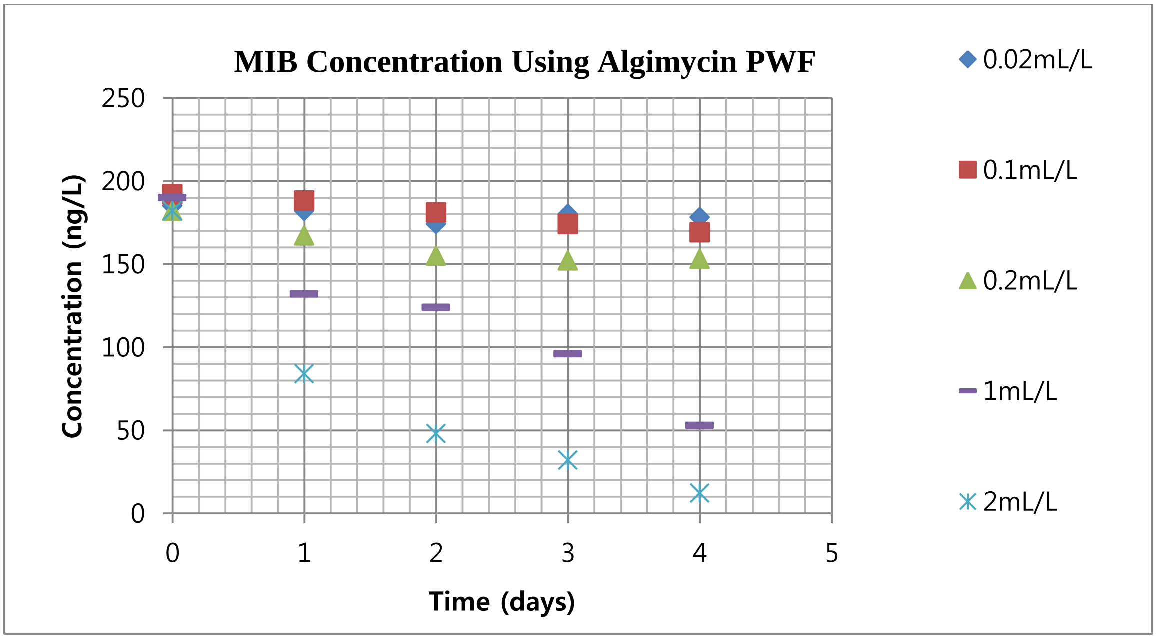


Figure 17 MIB Concentrations at different dosages of Algimycin PWF

At the recommended and 5 times higher dosages of Algimycin PWF, geosmin concentrations were reduced only from 185ng/L and 192ng/L to 178 ng/L and 169 ng/L, respectively. This is less than a 20% reduction. At dosages of 10 to 100 times higher of Algimycin PWF, MIB in Lake water samples was reduced by 75 to 95 percent with a minimum pH of 3.0. Algimycin PWF could be causing dehydration reactions by its characteristics of acidity.

Calcium chloride dehydrate

Calcium chloride dehydration was investigated for MIB removal. Four different dosages were provided to evaluate calcium chloride dehydration efficiency.

Conditions of Sample: MIB Concentration: approximately 200 ng/L, Calcium chloride dosage: 0.1 g/100 mL to 2.5 g/100; pH of sample:6.8; Eucha Lake water pH: 7.8.

Results and Discussion

Results of this experiment are listed in Table 23 and plotted in Figure 18.

Table 23 Table 21 MIB Concentrations at various dosages of Calcium chloride

Time (days)	Concentration (ng/L)			
	1 g/L	5 g/L	10 g/L	25 g/L
0	197	200	200	200
1	174	155	164	113
2	150	147	172	144
3	150	149	124	146
4	145	161	168	109

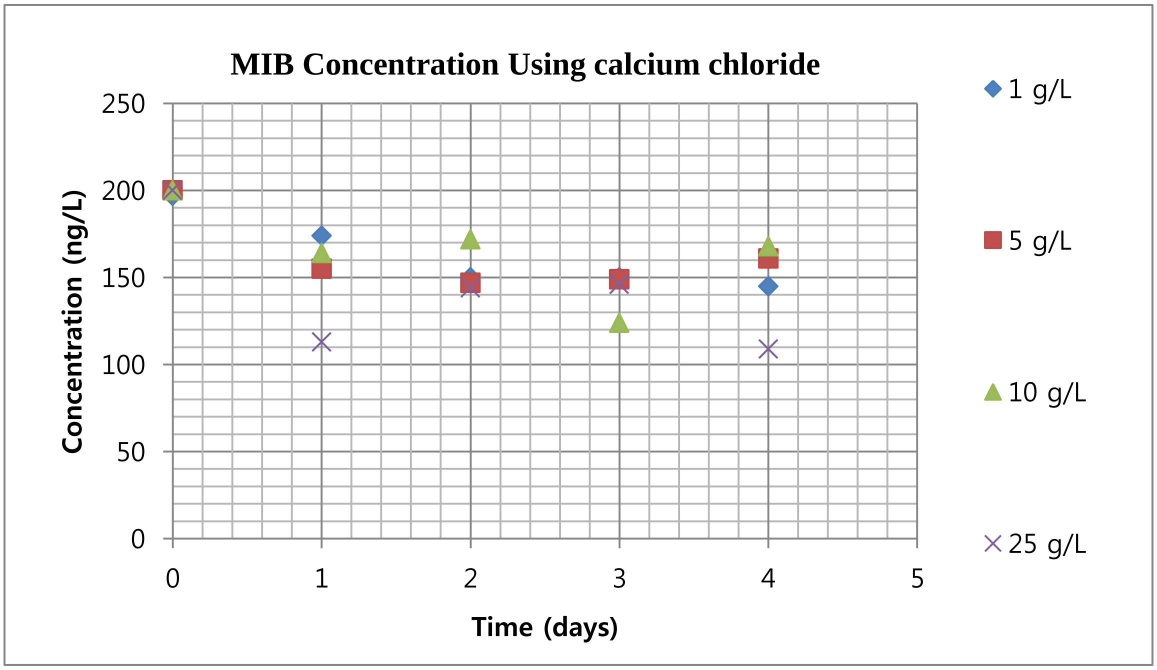


Figure 18 MIB Concentrations at different dosages of Calcium chloride

Calcium chloride dosages of 1 g/L, 5 g/L and 10 g/L achieved only 30% reduction in MIB concentration. At the dosage of 25g/L, MIB was reduced from 200 ng/L to 109 ng/L. This corresponds to approximately 45% removal of MIB.

4.1.4 Conclusion

Six different compounds, including four algaecides, were investigated for removal of geosmin and MIB. Results of the work are shown in Table 24 below.

Table 24 Summary of different algaecides with different dosages

Product	Dosage	Sample conditions	Result
Earth Tec®	Recommended (0.001mL/L)- 100 time high (0.1mL/L)	Geosmin concentration: 100 ng/L, pH:7.82 to 2.6, MIB concentration: 100-200 ng/L, Lake Water Reaction time: 4 days	Geosmin:0.001mL/L (5% removal) 0.002mL/L (20% removal) 0.01mL/L (30% removal) 0.05 mL/L (74% removal) 0.1mL/L (84% removal)
			MIB: 0.001mL/L (10% removal) 0.002mL/L (18% removal) 0.01mL/L (25% removal) 0.05 mL/L (97% removal) 0.1mL/L (99% removal)
Cutrine Plus	Recommended (0.05mL/L)- 100 time high (5mL/L)	Geosmin concentration: 100 ng/L, pH:7.8 to 10.5, Lake water, Reation time: 4 days	Geosmin: 0.05mL/L (30% removal) 0.1mL/L (26% removal) 0.5mL/L (37% removal) 5mL/L (30% removal)
Algimycin PWF	Recommended (0.02mL/L) to 100 times high dosage (2mL/L).	Geosmin Concentration: 100 ng/L, pH of sample: 7.82-3.2, Lake water, Reaction time: 4 days	Geosmin: 0.02mL/L (16% removal), 0.04mL/L (18% removal) 1mL/L (52% removal) 2mL/L (65% removal)
		MIB Concentration: 200 ng/L, pH of sample: 7.82-3.0, Lake water, Reaction time: 4 days	MIB: 0.02mL/L (11% removal) 0.04mL/L (16% removal) 0.2mL/L (24 % removal) 1mL/L (74% removal) 2mL/L (94% removal)
Sulfuric Acid	0.25 mL/L to 25 mL/L	Geosmin Concentration: 100 ng/L, pH of sample: 7.82 to 2.1, Reaction time: 4 days Lake water	Geosmin: 0.25 mL/L (21 % removal) 0.5mL/L (32 % removal) 1.25 mL/L (35 % removal) 25 mL/L (100 % removal)
Phycomycin SCP	Recommended (1mg/0.94L)to 100 time high (100mg/0.94L)	Geosmin Concentration: 100 ng/L, pH of sample: 7.82-11.3,	Geosmin: 1mg/0.94L (15% removal) 2mg/0.94L (28% removal) 50mg/0.94L (23% removal)

		Filtered Lake water Reaction time: 4 days	100mg/0.94L (28% removal)
Calcium chloride dihydrate	1 g/L to 25 g/ L geosmin water and MIB water	Geosmin Concentration: 200 ng/L, pH of sample: :6.8-6.0, Lake water, Reaction time: 4 days	Geosmin: 1 g/L (30% removal) 5 g/L (10% removal) 10 g/ L (45% removal) 25 g/L (66% removal)
		MIB Concentration: 200 ng/L, Lake water, pH of sample: :6.8-6.0, reaction time: 4 days	MIB: 1 g/L (28% removal) 5 g/L (20% removal) 10 g/ L (16% removal) 25 g/L (46% removal)

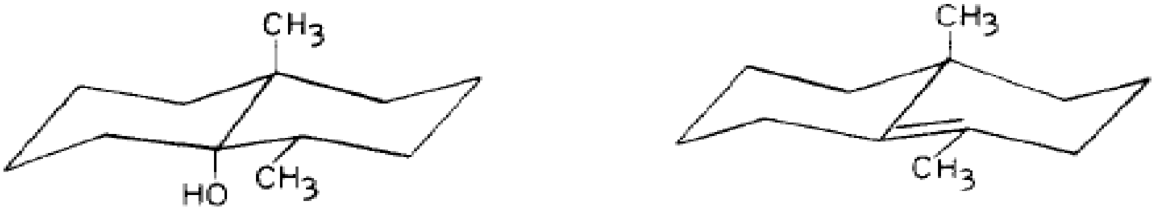
Six different chemicals (Earth Tec® , Cutrine plus, Algimycin PWF, Phycomycin SCP, sulfuric acid, Calcium chloride dehydrate) were evaluated to remove geosmin using dosages from the manufacturer's recommended to 100 times higher. Earth Tec® , Algimycin PWF and sulfuric acid were strong acids and, at dosages approximately 50-100 times higher than recommended, removed geosmin, probably due to the low pH produced in the samples. Cutrine plus and Phycomycin SCP, high pH (basic) algaecides did not remove significant amounts of geosmin even at high dosages. In fact, geosmin was not effectively removed using recommended dosages of any algaecide. Calcium chloride dehydrate was the one effective option to remove geosmin despite its high dosage.

Based on the geosmin experimental results, only three chemicals (Earth Tec® , Algimycin PWF, and calcium chloride dehydrate) were chosen to evaluate MIB reduction in Lake Eucha water. Earth Tec® and Algimycin PWF have similar characteristics, as they are strongly acidic copper-based algaecides. Both Earth Tec® and Algimycin PWF provided a similar result in MIB removal. A difference between them is acidity (Acidity of Earth Tec® is stronger than Algimycin PWF). As expected, Earth Tec® removed more MIB than Algimycin PWF and resulted in a lower pH value in the sample. For calcium chloride dehydration, MIB reduction was similar to geosmin reduction, at approximately 40-50 percent.

Overall, acidity experiments should be provided in order to determine geosmin and MIB removal due to reduction in pH. Drying agents like calcium chloride should be considered as a second option for geosmin and MIB removal.

4.2 The effect of pH on Geosmin and MIB

The effect of pH on geosmin and MIB has not been extensively investigated, although it is known that tertiary alcohols are susceptible to acid dehydration (Solomons, 1984). The work by Schweitzer and Ekstrom (2006) reported that pH has a significant impact on concentration of geosmin in water. Hsieh (2011) proved that MIB and geosmin are tertiary alcohols and found that geosmin concentration dropped 31% at pH of 2.8 compared to pH 6, and MIB concentrations were reduced 87% at pH 2.8 compared to pH 6.8. When MIB is dehydrated under acidic condtions, it can generate 2-methyl-2-bornene, 2-methylenebornane, and 1-methylcamphene analyzed by ^{1}H and ^{13}C NMR (Sumitomo et al. 1987; Martin et al. 1988). These studies concluded that geosmin and MIB are pH-dependent compounds. Dehydration of geosmin results in the formation of argosmin (Schweitzer and Ekstrom, 2006). Geosmin ($C_{12}H_{22}O$) and argosmin ($C_{12}H_{20}$) molacular formulas are shown in Figure 19.



geosmin argosmin

Figure 19 Geosmin and Argosmin molecular formulas (Thomas P. Hemarling and Susan K. Waaget, 1990)

As shown in Figure 19, HO has been removed from geosmin by dehydration, forming argosmin (an odorless compound).

The MIB dehydration process is shown in Figure 20.

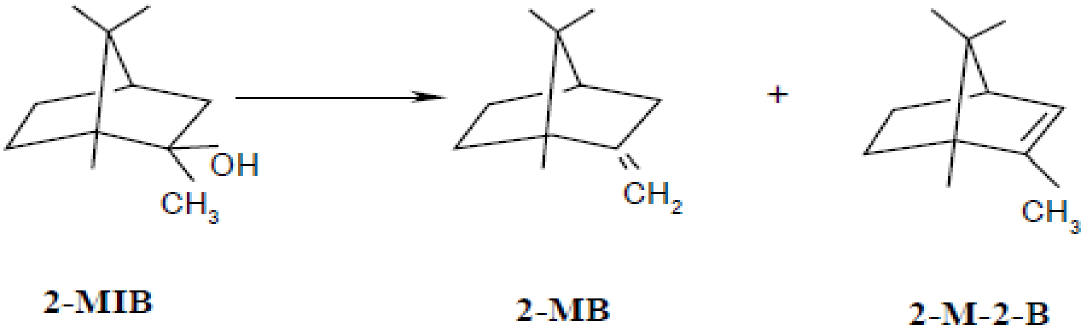


Figure 20 2-MIB and 2-M-2-B molecular formulas (Thavrin and Wilson, 2012)

The tranformation of geosmin and MIB by acid dehydration has been proposed as a removal mechanism, and it was decided to investigate this transformation as part of this study.

Dehydration

Dehydration is one mechanism of forming water molecules using acidic agents. The dehydration process is shown in Figure 21.

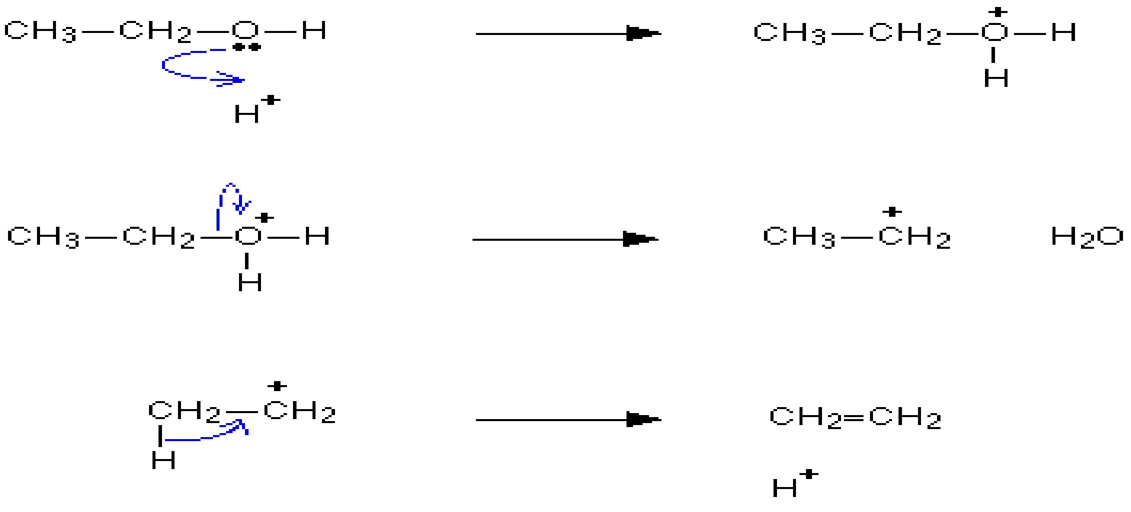


Figure 21 Dehydration process of alcohol

In dehydration, one of the lone pairs of electrons on the oxygen picks up a hydrogen ion from the acidic agent and produces a water molecule. The protonated alcohol without a hydrogen ion provides carbocation. In the final stage, a hydrogen ion from the acidic agent pulls off another hydrogen ion from the carbocation. This carbocation is not very stable and can be reversed by returning pH to neutral.

Argosmin

It is known that geosmin breaks down to a non-odorous product called argosmin by dehydration (Gerber and Lechevalier 1965; Gerber 1967). Argosmin is one of the dehydration products and the concentration of argosmin is related to amount of geosmin removed. Dehydration is likely to occur when pH is reduced using acidic agents. Figures 22 and 23 show the argosmin mass spectrum and chromatogram using the Shimadzu GC/MS-QP5050A. The most dominant mass spectrum of argosmin was found at MW 149; argosmin retention time is 11.11 minutes.

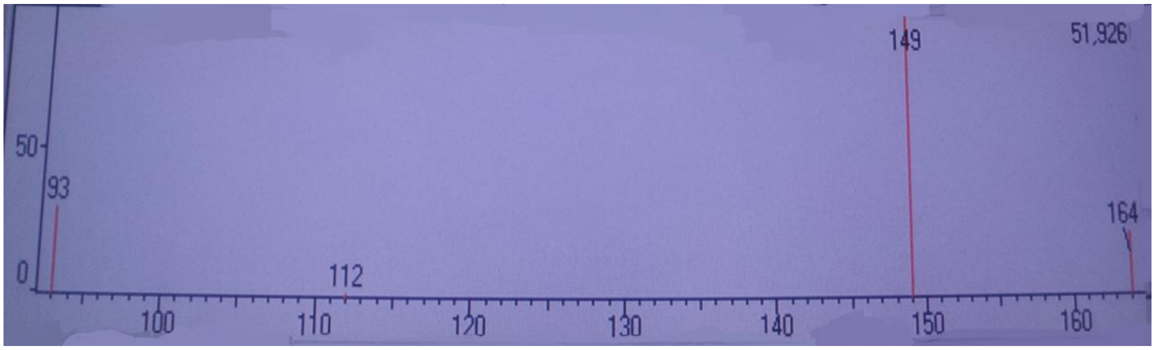


Figure 22 Argosmin spectrum by adding Earth Tec (pH approximately 2)

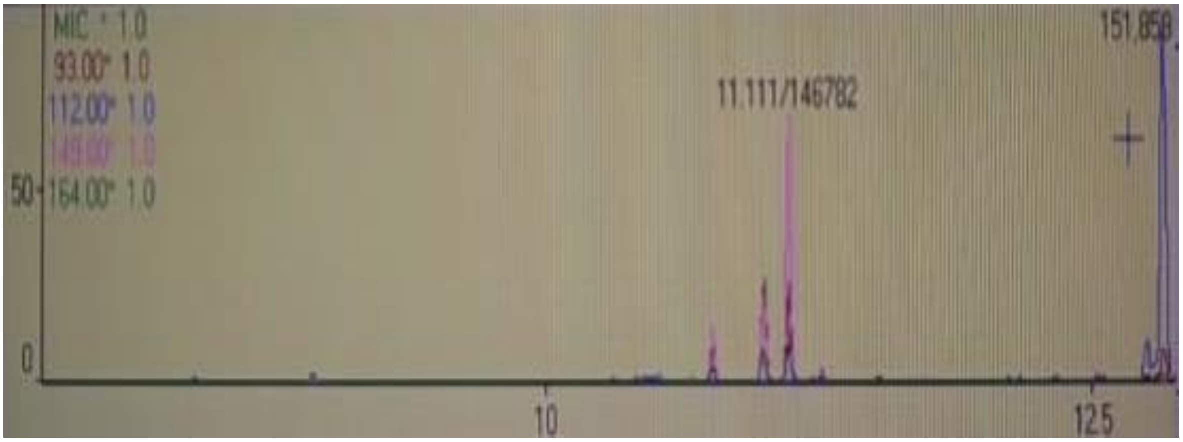


Figure 23 Argosmin chromatogram formation from geosmin by adding Earth Tec (pH approximately 2)

2-Methyl-2-Bornene (2-M-2-B)

2-Methyl-2-Bornene (2-M-2-B) is a non-odorous product from 2-MIB dehydration. The amount of 2-M-2-B is related to MIB removal. The dominated 2-M-2-B spectrum is 107 and the retention time is 7.8-8.3 using the Shimadzu GC/MS-QP5050A. Figures 24 and 25 show the 2-M-2-B mass spectrum and chromatogram..

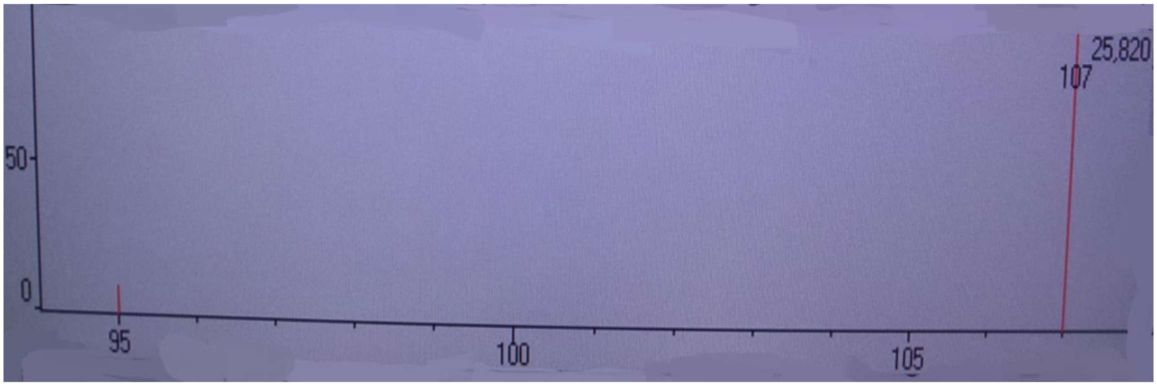


Figure 24 2-M-2-B spectrum by adding Earth Tec (pH 2.5)

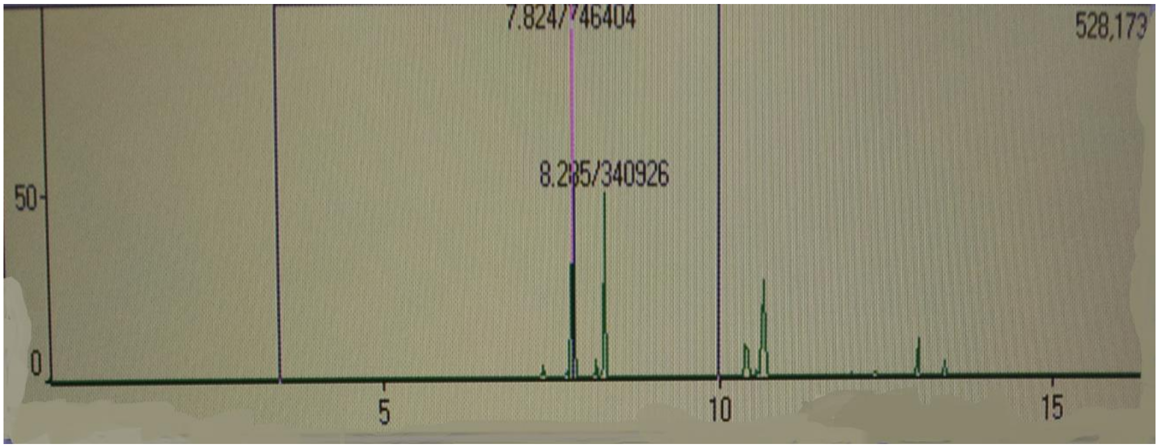


Figure 25 2-M-2-B chromatogram formation from MIB by adding Earth Tec (pH 2.5)

4.2.1 pH Reduction using Earth Tec® .

Several researchers have shown that geomsin and MIB are somewhat pH dependent; pH is known to have an impact on dehydration reactions between tertiary alcohols and acids (Solomons 1984; Schweitzer and Ekstrom, 2006; Hsieh, 2011). In this study, samples containing 100 ng/L MIB and geosmin at an initial pH of 7.8 (baseline pH of the Eucha samples), were treated with Earth Tec to drop the pH to 2, where the dehydration reaction is considered complete. Two different reaction time were used to evaluate different geosmin and MIB final concentrationss.

Geosmin removal

Conditions of Sample: Geosmin Concentration: 100 ng/L geosmin, Earth Tec® dose until pH 2.0, deionized water: pH 6.5.

Results and discussion. Results of this experiment are shown in Table 25 and Figures 26 and 27 below.

Table 25 Geosmin Concentration using Earth Tec for pH Reduction

pH	Sample 1 (18 hours)		Sample 2 (4 days)	
	Geosmin (ng/L)	Argosmin (Area)	Geosmin (ng/L)	Argosmin (Area)
5.4	77.8	0	90.5	0
4	76.3	1286	79	2541
3.5	66.4	19654	77.8	96345
2.3	81.8	156873	10.8	289653
2	137	275670	0	356789

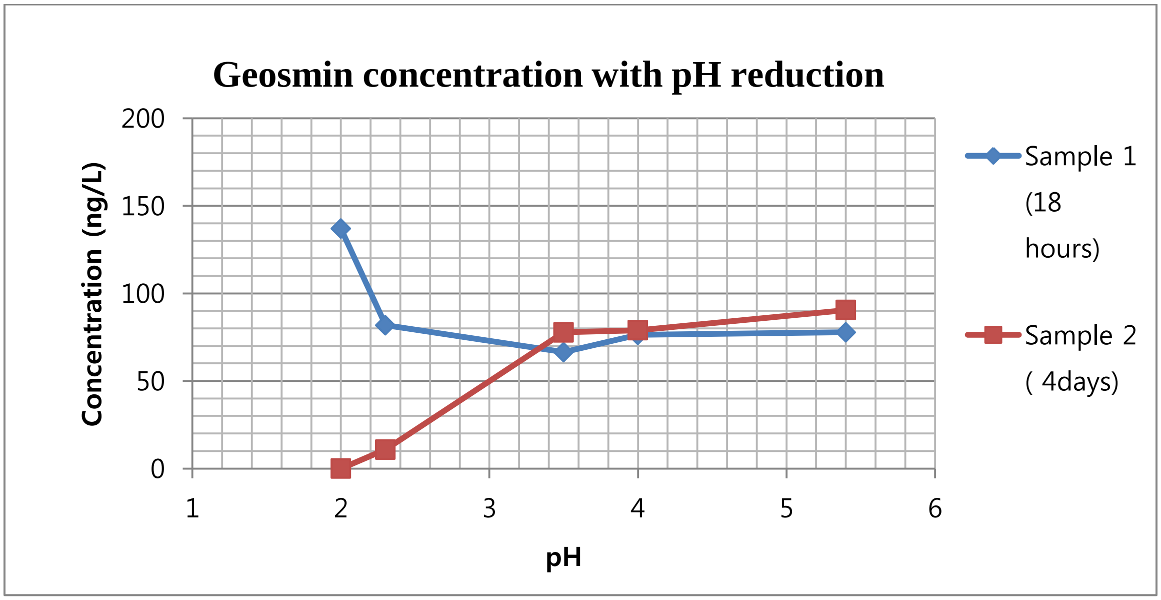


Figure 26 Geosmin Concentration with pH Reduction using Earth Tec

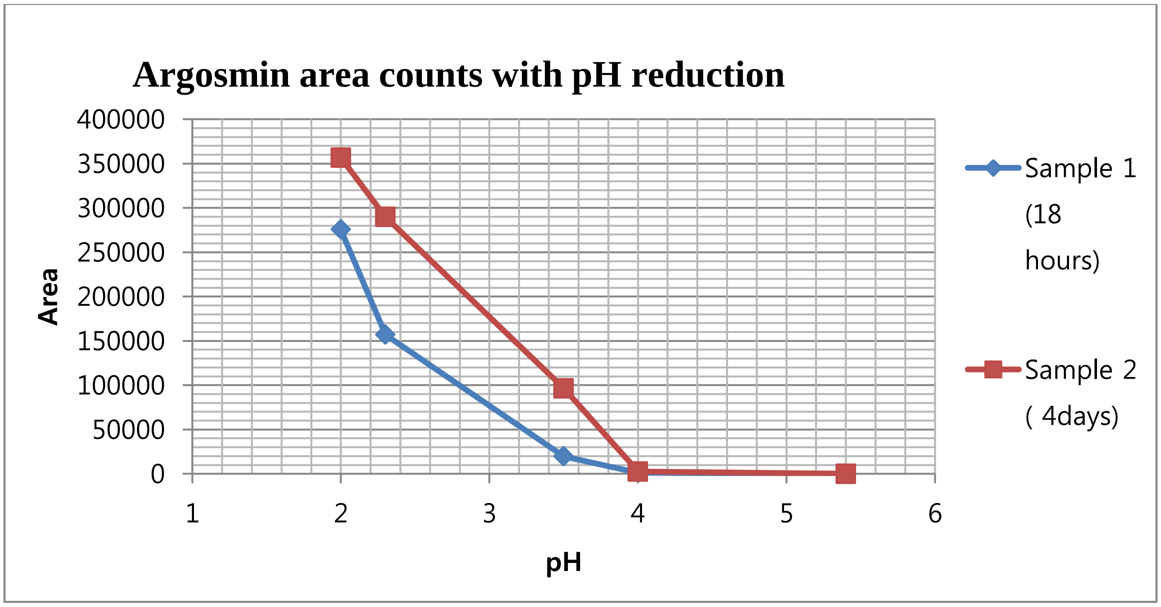


Figure 27 Argosmin Area Counts with pH Reduction using Earth Tec

Approximately 90 to 80 ng/L geosmin samples were performed to evaluate removal of geosmin with acidic algaecide (Earth Tec). Geosmin concentrations displayed the complete removal at pH 2 with 4 day retention time. In sample 1, the amounts of geosmin increase with 18 hour retention time due to the production of hydroxyl ions on the cathode. After the all reactions, the amounts of geosmin are dehydrated and are converted to other products called argosmin. In Figure 27, argosmin conversion firstly exhibited at pH 4 and was completely processed at pH 2. The gaps between the sample 1 and the sample 2 are due to the different retention time. It indicates that more than 1 day retention time is necessary for complete removal of geosmin. All consumption of hydroxyl anions and production of hydrogen cations in the dissociation reactions of HOCl and OCl^- require more than 1 day retention time. Moreover, geosmin reacts slowly than MIB by comparing Figure 28 and Figure 29. Overall, geosmin removal is dependent on pH.

MIB removal

Conditions of Sample: MIB Concentration: 100 ng/L geosmin, Earth Tec® dose sufficient to reduce pH to 2.0, deionized water: pH 6.5.

Results and discussion. Results of these experiments are shown in Table 26 and Figures 28 and 29.

Table 26 MIB Concentration and 2-M-2-B area using Earth Tec

pH	Sample 1 (18 hours)		pH	Sample 2 (4 days)	
	MIB (ng/L)	2-M-2-B (Area)		MIB (ng/L)	2-M-2-B (Area)
6.6	88.5	1123	6.6	89.3	985
5.4	66.5	3429	4.7	71.7	50876
3.8	67.2	78960	3.9	65.7	156899
3.1	65.6	159878	2.9	12.0	401766
2	0	378535	2.1	0	412987

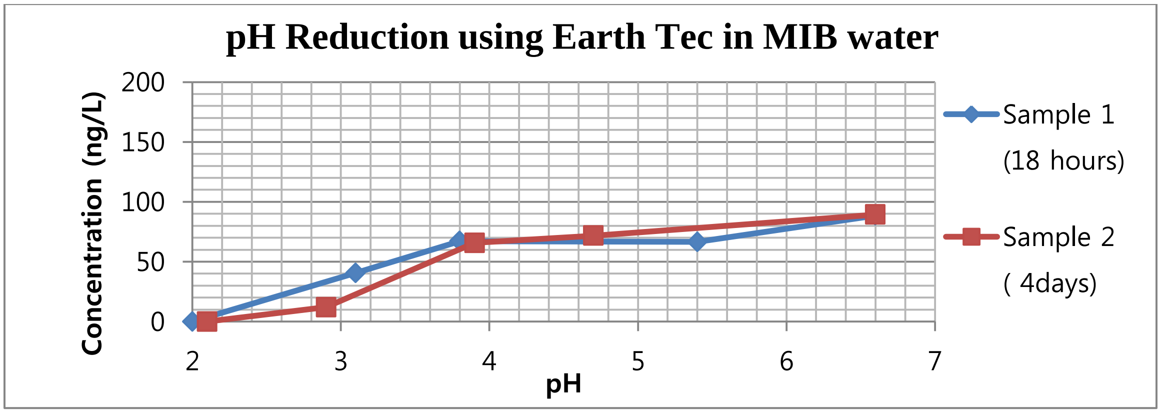


Figure 28 MIB Concentration by lowering pH using Earth Tec

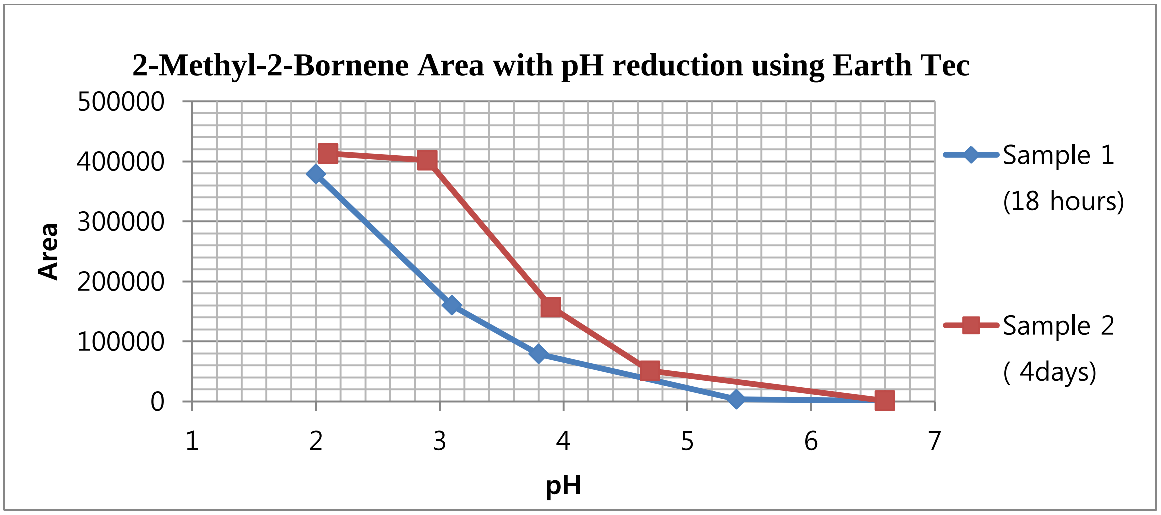


Figure 29 2-M-2-B area by lowering pH using Earth Tec

Samples containing 100 ng/L MIB in deionized water were treated with Earth Tec until the pH reached 2.0. MIB concentration was reduced at pH 4.5 and was non-detectable at pH 2.0. Concentration of 2-M-2-B (as measured by area counts) shows an increase proportionally from 100,000 to approximately 400,000. The change in final pH value suggests that the production of H^+ did not match the production of OH^- ions. The drop in pH was caused by gradual consumption of hydroxyl anions as well as production of hydrogen cations in the dissociation reactions of HOCl and OCl^-, along with the reaction of HOCl in the treated MIB solution. In this experiment, sample 2 displayed better removal than the sample 1. In sample 1, the concentration of 2-M-2-B was significantly reduced in 18 hours retention time.

4.2.2 pH effects on geosmin and MIB using various acids

The previous experiment indicated that both geosmin and MIB are pH dependent for removal through dehydration. Because Earth Tec® is a strong acids, other acids (phosphoric acid, ascorbic acid, sulfuric acid, boric acid, ferrous sulfate, potassium thiosulphate and an acidic algaecide) will be evaluated to determine if different acids affect the removal of geosmin and MIB in both Lake

Eucha and deionized water. Samples containing 200 ng/L geosmin and MIB will be prepared and held for sufficient reaction times. Since dehydration is known to be a reversible reaction, pH will be returned to neutral by adding sodium hydroxide after dropping the pH.

Geosmin

Conditions of Sample: Approximately 200 ng/L of geosmin in Lake Eucha water, Acidic agent dose: until pH reaches at 2, Sodium hydroxide dose: until pH reaches at 7.6, Eucha water pH (7.6), Reaction time: 2 days.

Results and Discussion. Results of this series of experiments are presented in Table 27 and Figures 30 and 31.

Table 27 Geosmin concentrations by using various Acids at approximately pH 2 and at pH 7.6

Time (days)	**0**		**1 at pH 2**		**2 at pH 7.6**	
	Geosmin (ng/L)	**Argosmin (Area)**	**Geosmin (ng/L)**	**Argosmin (Area)**	**Geosmin (ng/L)**	**Argosmin (Area)**
Earth Tec (ng/L)	207	0	26	988776	83	587766
Phosphoric Acid (ng/L)	198	0	9	1003808	70	654433
Ascorbic Acid (ng/L)	189	0	1	1218876	94	538779
Sulfuric Acid (ng/L)	203	0	24	965447	86	557879

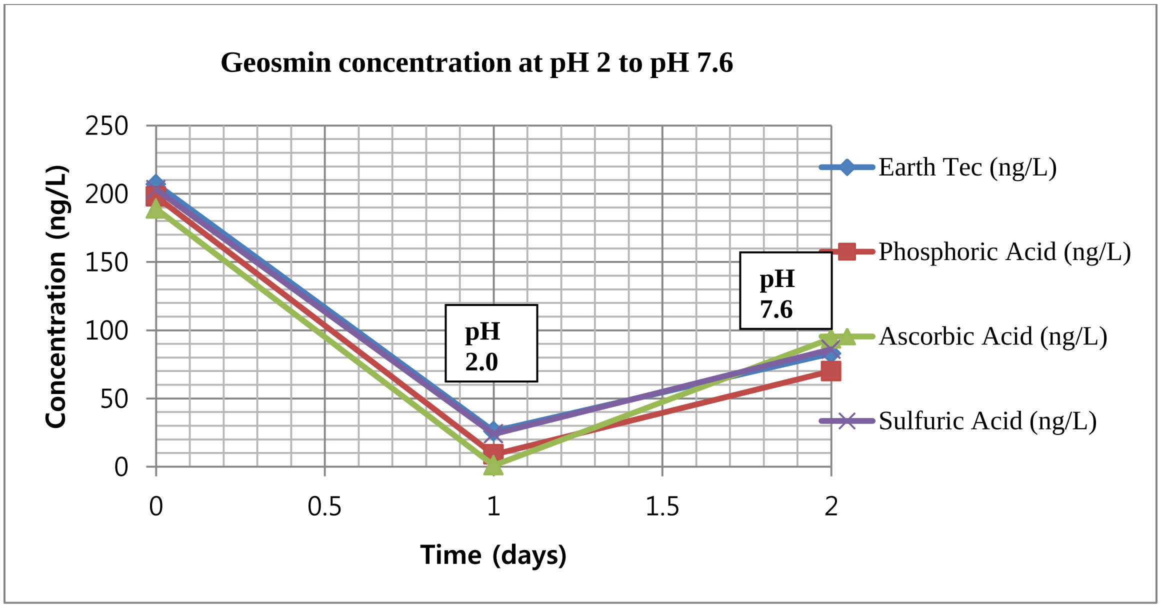


Figure 30 Geosmin concentrations by using various Acids at approximately pH 2 and at pH 7.6

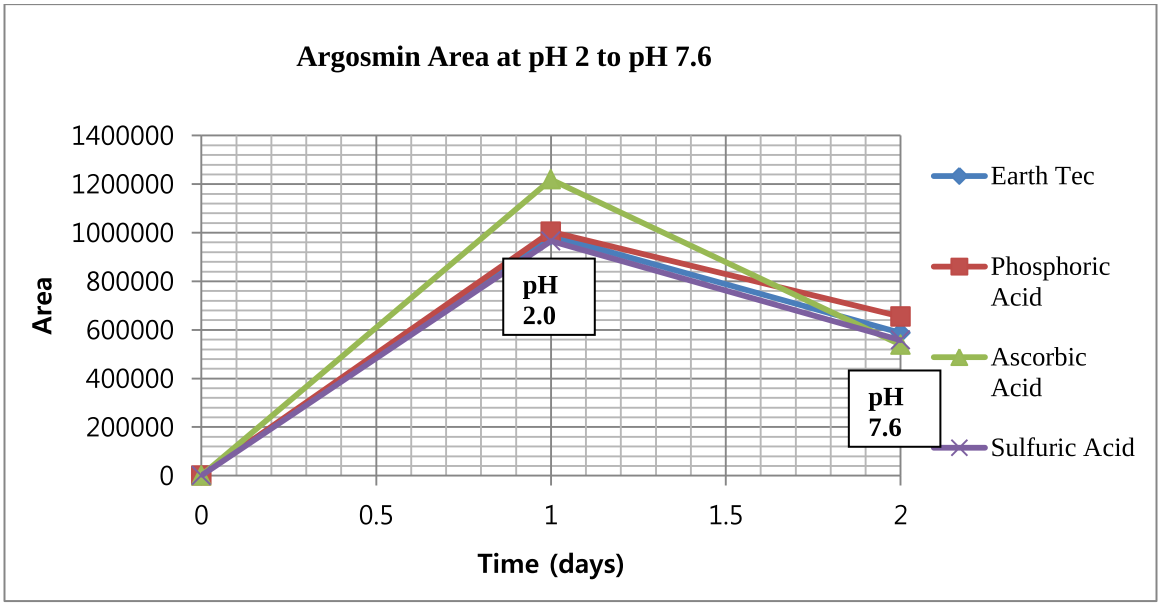


Figure 31 Argosmin area by using various acids at approximately pH 2 and at pH 7.6

Results of these experiments were consistent with the earlier ones. The concentrations of geosmin in four different acids are reduced more than 95% for 1 day. The removal efficiency did not depend on the acid. In all cases, geosmin dehydration was reversed approximately 50% upon the return to neutral pH using NaOH. Geosmin is recovered through increasing hydroxyl anions as well as consumption of cations. Geosmin removal through reduction of pH to low values is impracticable for application at water treatment plants.

MIB

Conditions of Sample: 186 ng/L MIB in Lake Eucha water, Acidic agent dosage: until pH reaches 2; Sodium hydroxide dosage: until pH reaches 7.6; Eucha water pH (7.6), Retention time: 2 days.

Results and Discussion. Results of this set of experiments are shown in Table 28 and Figures 32 and 33.

Table 28 MIB concentrations by using various Acids at approximately pH 2 and at pH 7.6

Time (days)	0		1 at pH 2		2 at pH 7.6	
	MIB (ng/L)	2-M-2-B (Area)	MIB (ng/L)	2-M-2-B (Area)	MIB (ng/L)	2-M-2-B (Area)
Earth Tec	186	2134	8.2	498535	0	323456
Phosphoric Acid	186	2134	6.4	521940	0	498767
Ascorbic Acid	186	2134	0	589859	0	467889
Sulfuric Acid	186	2134	12.4	438572	0	488009

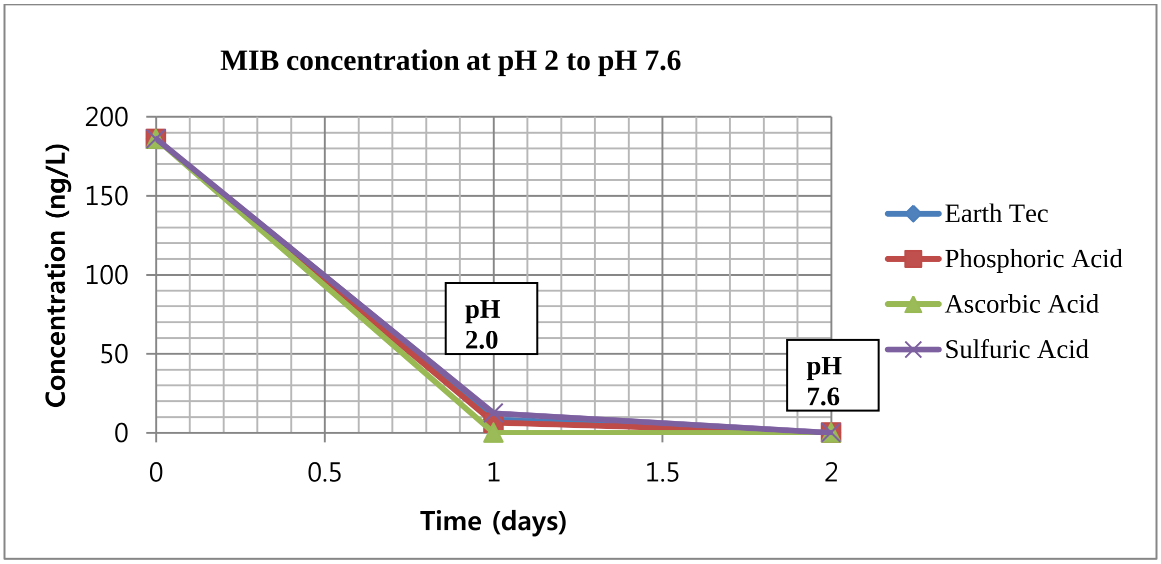


Figure 32 MIB concentrations by using various Acids at approximately pH 2 and at pH 7.6

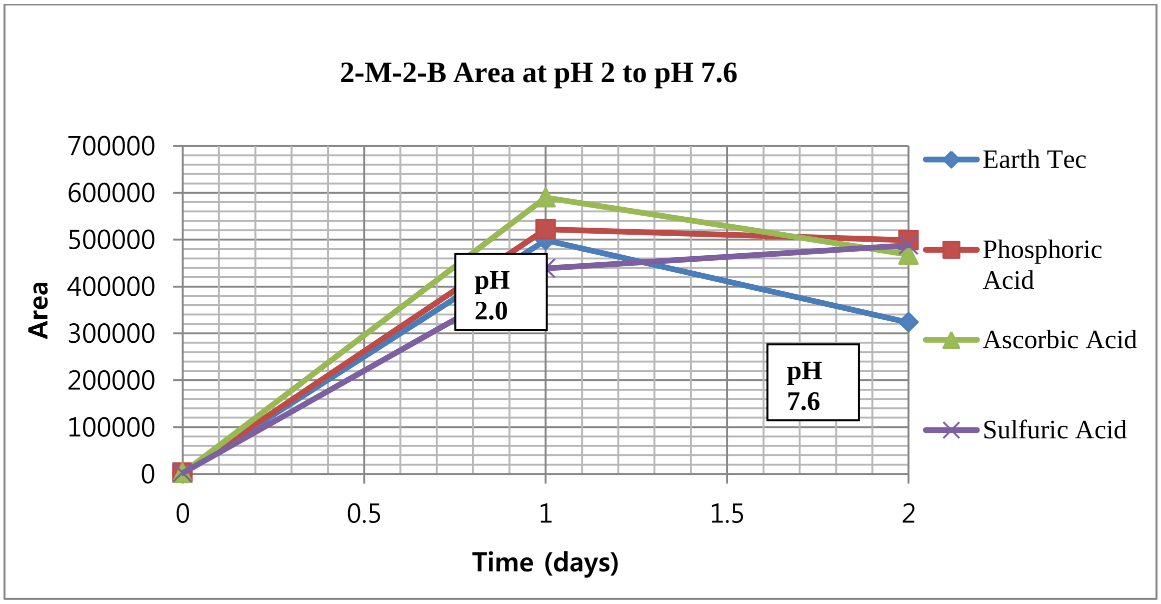


Figure 33 2-M-2-B Area by using various acids at approximately pH 2 and at pH 7.6

Most of the MIB in the samples was removed at pH 2. When samples were returned to their original pH (approximately 7.6), MIB concentrations in Lake water did not display any dramatic change. This result is different from the geosmin experiment. It appears that the MIB acid dehydration is resistant to a reversal using sodium hydroxide.

4.2.3 Geosmin and MIB concentration in Lake and deionized water

Previous experimental results showed the relationships between various acids and geosmin and MIB when the sample pH is reduced to 2.0. An additional series of experiments using both deionized and Lake Eucha water was run where pH was reduced only to 2.5.

Geosmin in Lake Water

Conditions of Sample: Approximately 200 ng/L of geosmin in Lake Eucha water, Acidic agent dosage: until pH reaches at 2.5, Sodium hydroxide dosage: until pH reaches at 7.6, Eucha water pH (7.6), Retention time: 2 days.

Results and Discussion. Results of this set of experiments are shown in Table 29 and Figures 34 and 35.

Table 29 Geosmin concentrations and Argosmin areas by different acids at approximately pH 2.5 and at pH 7.6 in Lake Eucha Water

Time (days)	0		1 at pH 2.5		2 at pH 7.6	
	Geosmin (ng/L)	Argosmin (Area)	Geosmin (ng/L)	Argosmin (Area)	Geosmin (ng/L)	Argosmin (Area)
Earth Tec (ng/L)	163	0	26	1033786	83	284984
Phosphoric Acid (ng/L)	172	0	9	1260399	70	115539
Ascorbic Acid (ng/L)	165	0	1	1009987	94	117229
Sulfuric Acid (ng/L)	175	0	24	1344306	86	23526

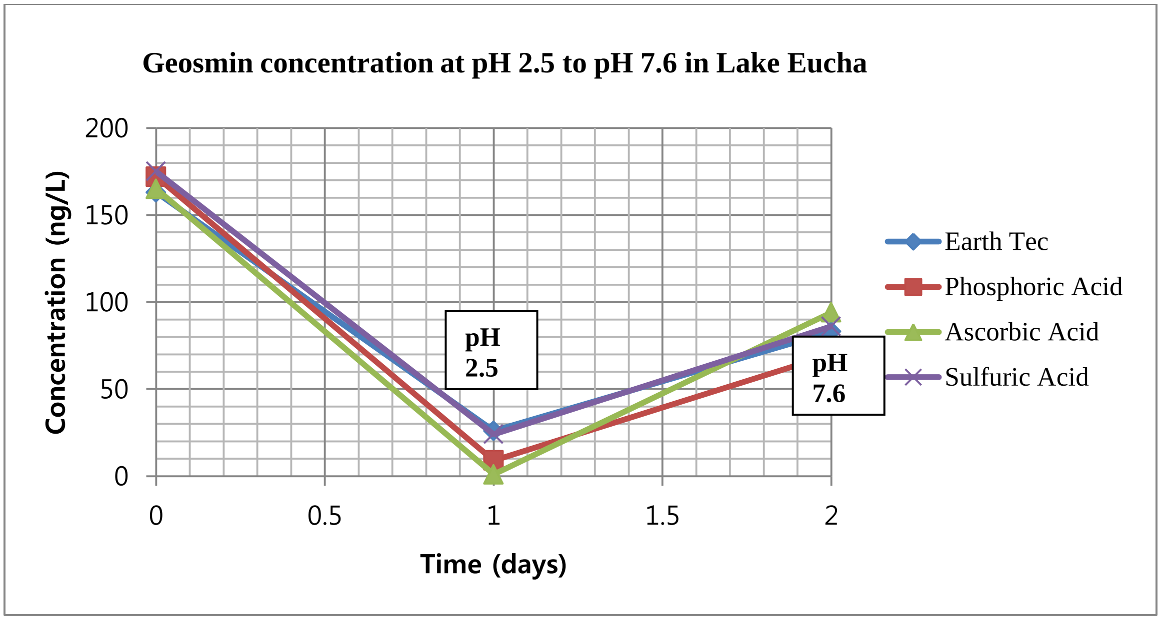


Figure 34 Geosmin concentrations by different acids at approximately pH 2.5 and at pH 7.6 in Lake Eucha Water

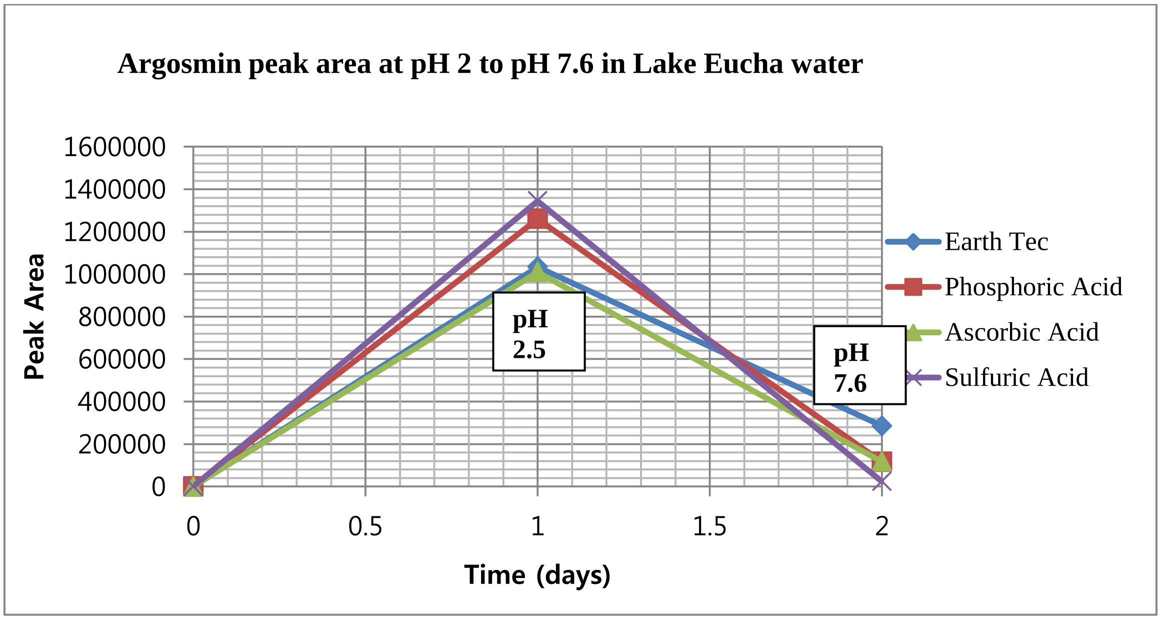


Figure 35 Argosmin Area by different acids at approximately pH 2.5 and at pH 7.6 in Lake Eucha Water

Geosmin concentrations using four different acids including EarthTec® were reduced from 163 ng/L, 172 ng/L, 165 ng/L, 175 ng/L, respectively, to 26 ng/L (EarthTec®), 9 ng/L (Phosphoric acid), 1 ng/L (Ascorbic acid), and 24 ng/L (Sulfuric acid) at pH 2.5. Argosmin area increased from 0 to approximately 1,300,000. The results indicate that dehydration reactions have occurred and that argosmin, a break down product of geosmin, had been produced. At pH 2.5, the geosmin concentration plot, Figure 34, is inversely proportional to the argosmin plot, Figure 35. Upon returning the pH to 7.5 with sodium hydroxide, geosmin concentrations increased from 26 ng/L (Earth Tec), 9 ng/L (Phosphoric acid), 1 ng/L (Ascorbic acid), 24 ng/L (Sulfuric acid) to 83 ng/L, 70 ng/L, 94ng/L, 86 ng/L. Argosmin areas with four different acids were then reduced approximately 10 to 50 times. The results indicate the geosmin dehydration at pH = 2.5 can be reversed by returning the pH to neutral, and that and argosmin formation and loss are inversely proportional to the geosmin loss and reformation.

MIB in Lake Eucha water

Conditions of Sample: Approximately 200 ng/L of MIB in Lake Eucha water, Acidic agent dosage: until pH reaches at 2.5, Sodium hydroxide dosage: until pH reaches at 7.6, Eucha water pH (7.6), Retention time: 2 days.

Results and Discussion. Results of this set of experiments are shown in Table 30 and Figures 38 and 39.

Table 30 MIB concentrations and 2-M-2-B areas by different acids at approximately pH 2.5 and at pH 7.6 in Lake Eucha Water

Time (days)	**0**		**1 at pH 2.5**		**2 at pH 7.6**	
	MIB (ng/L)	**2-M-2-B (Area)**	**MIB (ng/L)**	**2-M-2-B (Area)**	**MIB (ng/L)**	**2-M-2-B (Area)**
Earth Tec	185	30345	0	698789	0	578798
Phosphoric Acid	180	23452	0	723455	9	476897
Ascorbic Acid	176	34567	0	656792	17	438792
Sulfuric Acid	192	29887	0	659878	20	459830

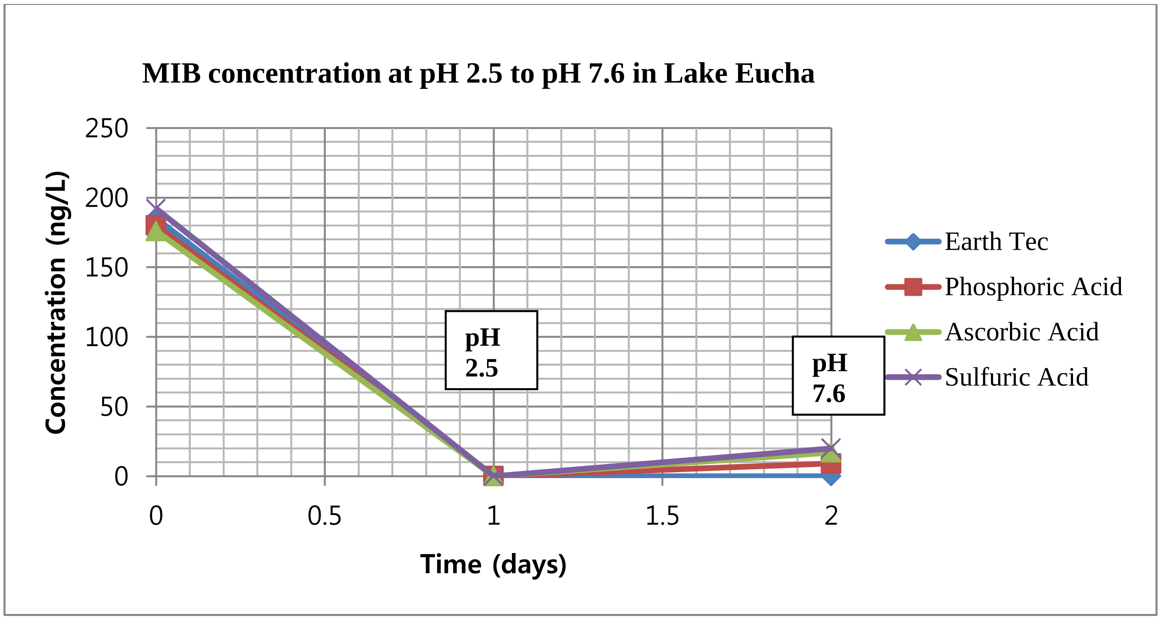


Figure 36 MIB concentrations by different acids at approximately pH 2.5 and at pH 7.6 in Lake Eucha Water

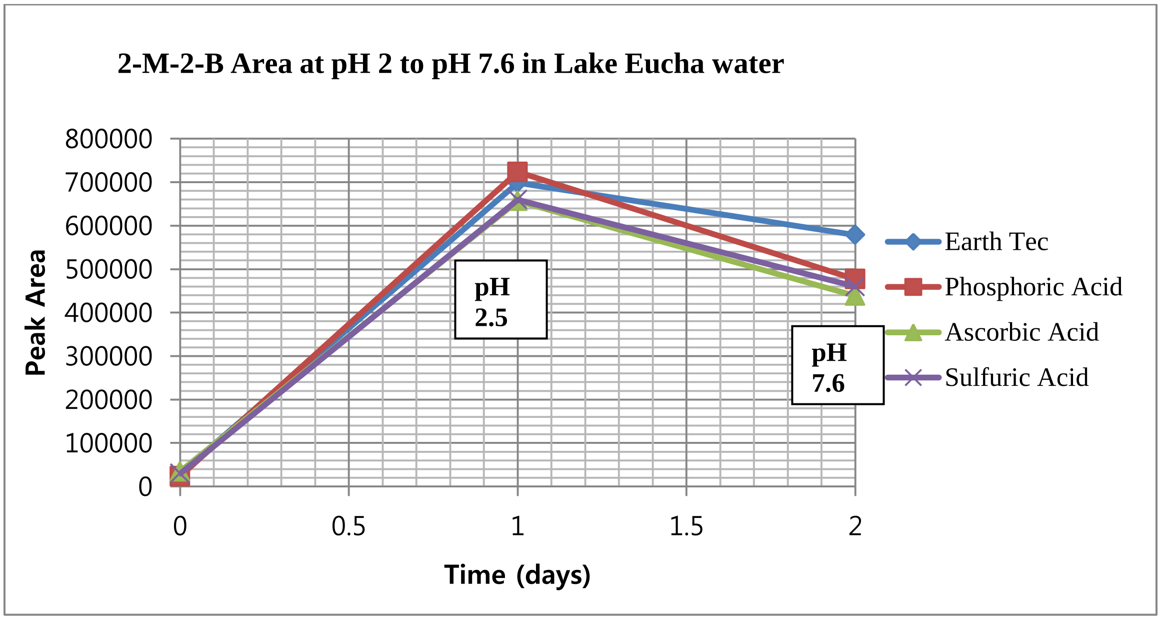


Figure 37 2-M-2-B Area by different acids at approximately pH 2.5 and at pH 7.6 in Lake Eucha Water

Four different acids completely removed MIB at pH 2.5, and the peak area of 2-M-2-B increased to a high point at pH 2.5. The results indicate that MIB can be removed at a pH above 2.0, and that 2-M-2-B is a dehydration product of MIB. Upon returning the pH to 7.6, MIB concentrations treated with four different acids increased only slightly. 2-M-2-B (dehydration by products) area counts showed a slight decrease.

Geosmin in deionized water

Conditions of Sample: Approximately 200 ng/L of geosmin in deionized water, Acidic agent dosage: until pH reaches at 2.5, Sodium hydroxide dosage: until pH reaches at 7.6, Eucha water pH (7.6), Retention time: 2 days.

Results and Discussion. Results of this set of experiments are shown in Table 31 and Figures 38 and 39.

Table 31 Geosmin concentrations and Argosmin areas in Deionized Water samples treated with different acids at approximately pH 2.5 and returned to pH 7.6

Time (days)	**0**		**1 at pH 2.5**		**2 at pH 7.6**	
	Geosmin (ng/L)	**Argosmin (Area)**	**Geosmin (ng/L)**	**Argosmin (Area)**	**Geosmin (ng/L)**	**Argosmin (Area)**
Earth Tec (ng/L)	206	0	32.8	708084	167	344573
Phosphoric Acid (ng/L)	203	0	0.5	2208835	138	518426
Ascorbic Acid (ng/L)	205	0	70	1564332	169	54742
Sulfuric Acid (ng/L)	201	0	1.5	1773087	68	437699

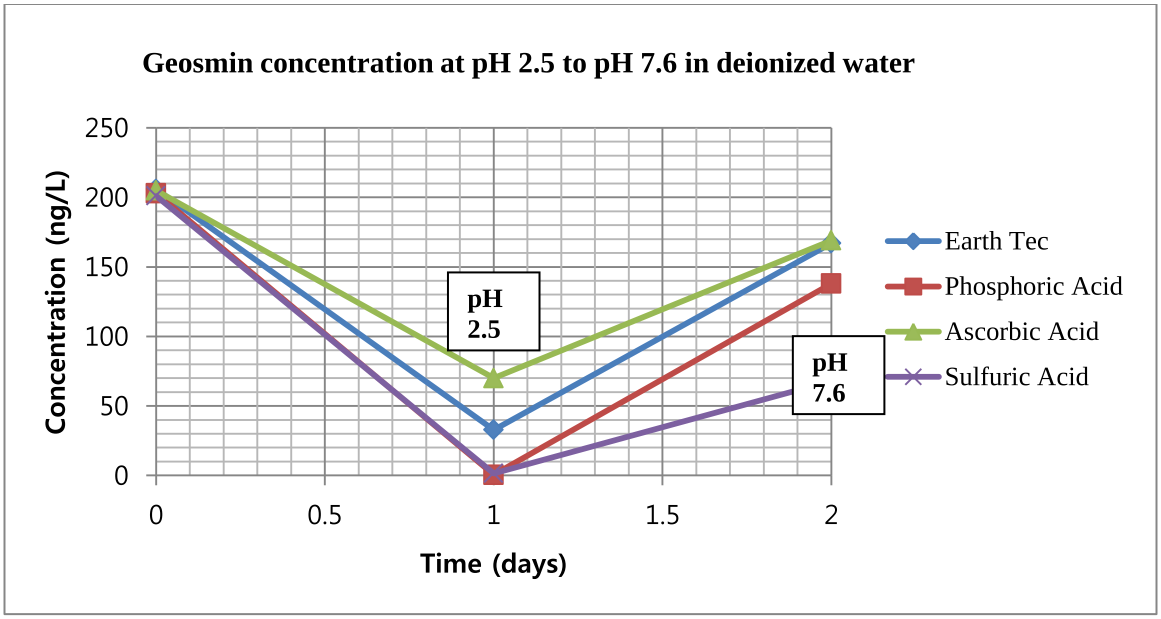


Figure 38 Geosmin concentrations by different acids at approximately pH 2.5 and at pH 7.6 in deionized Water

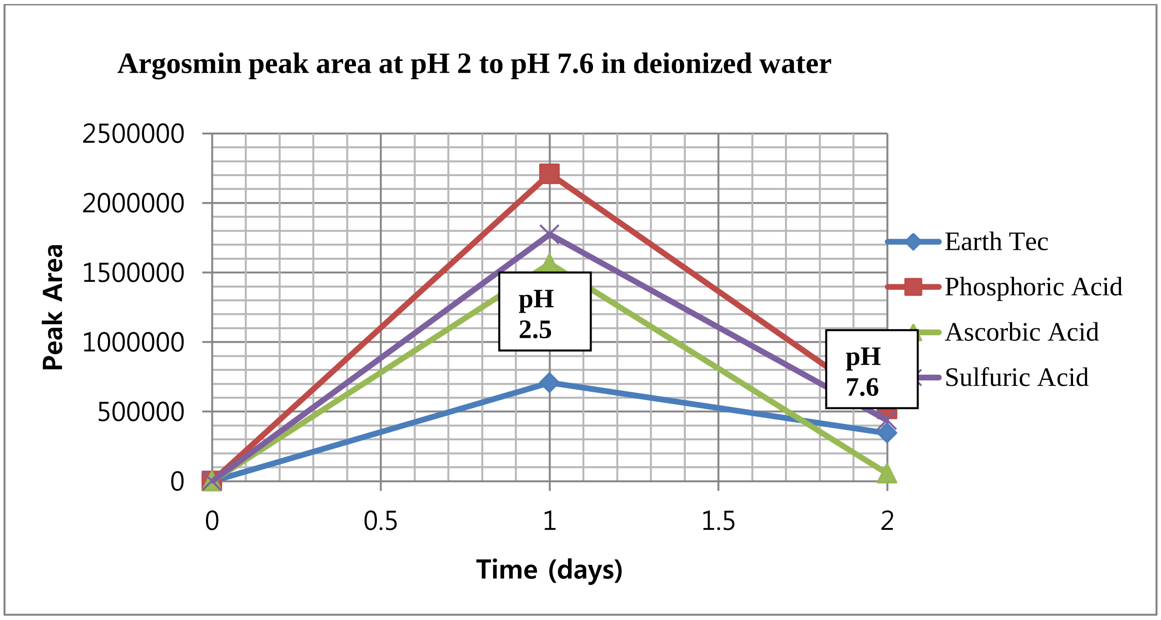


Figure 39 Argosmin Area by different acids at approximately pH 2.5 and at pH 7.6 in deionized Water

Geosmin concentrations in deionized water samples treated with four different acids were reduced from 206 ng/L, 203 ng/L, 205 ng/L, 201 ng/L, respectively to 32 ng/L (Earth Tec), 0.5 ng/L (Phosphoric acid), 70 ng/L (Ascorbic acid), and 1.5 ng/L (Sulfuric acid) at pH 2.5. Geosmin was not completely removed at pH 2.5, in contrast to the complete removal at pH 2.0, thus, complete removal of geosmin requires a reduction of pH to approximately pH 2.0. The argosmin areas increased from 0 to approximately 710000-2200000. The increase in peak areas of argosmin demonstrates a dehydration reaction. Upon returning to pH 7.6, geosmin concentrations increased from 32 ng/L (Earth Tec), 0.5 ng/L (Phosphoric acid), 70 ng/L (Ascorbic acid), 1.5 ng/L (Sulfuric acid) to 167 ng/L, 138 ng/L, 169 ng/L, 68 ng/L, and argosmin areas were reduced to the range 50000-500000. Both results indicate that the geosmin dehydration reaction is reversible and argosmin can turn into geosmin again.

MIB in deionized water

Conditions of Sample: approximately 200 ng/L of MIB in deionized water, Acidic agent dosage: until pH reaches at 2.5, Sodium hydroxide dosage: until pH reaches at 7.6, Eucha water pH (7.6), Reaction time: 2 days.

Results and Discussion. Results of this set of experiments are shown in Table 32 and Figures 40 and 41.

Table 32 MIB concentrations and 2-M-2-B areas in deionized water treated with different acids at approximately pH 2.5 and returned to pH 7.6

Time (days)	0		1 at pH 2.5		2 at pH 7.6	
	MIB (ng/L)	2-M-2-B (Area)	MIB (ng/L)	2-M-2-B (Area)	MIB (ng/L)	2-M-2-B (Area)
Earth Tec	201	12838	0	756568	0	678798
Phosphoric Acid	197	27678	0	890897	19	437689
Ascorbic Acid	194	42576	0	766564	28	388676
Sulfuric Acid	203	28765	0	817565	21	465879

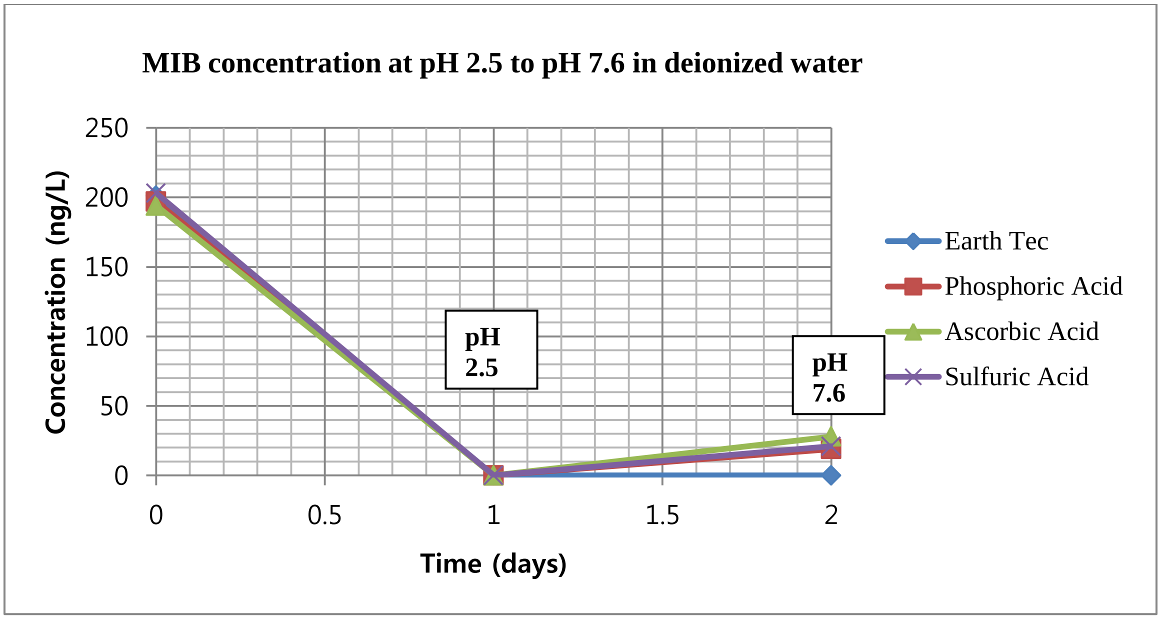


Figure 40 MIB concentrations by different acids at approximately pH 2.5 and at pH 7.6 in deionized Water

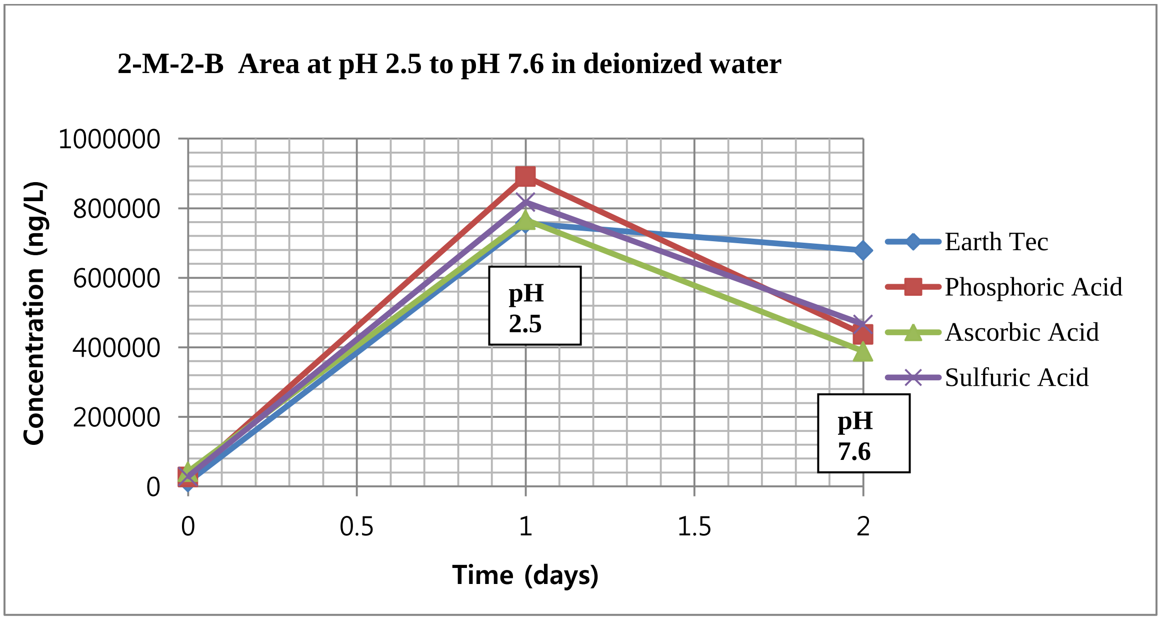


Figure 41 2-M-2-B Area by different acids at approximately pH 2.5 and at pH 7.6 in deionized Water

At pH 2.5, MIB concentrations of four different acids were reduced to non-detectable, and the areas of 2-M-2-B were approximately 750,000 to 890,000. The results indicate that a dehydration reaction occurs and that MIB can be removed at above pH 2.0. Upon returning to pH 7.6, MIB concentrations of four acids increased from non-detectable in all samples, to 0 ng/L (Earth Tec), 19 ng/L Phosphoric acid), 28 ng/L (Ascorbic acid), and 21 ng/L(Sulfuric acid). Area counts of 2-M-2-B decreased from approximately 670000 to 380000. The results indicate that the dehydration reaction for MIB is partially reversible, though not as reversible as for geosmin.

4.2.4 Conclusions

Several series of experiments were conducted to determine the impact of sample pH on the fate of geosmin and MIB in lake water and deionized water. Results are summarized in Table 33.

Table 33 Summary of pH experiments

Product	pH	Sample conditions	Result
Earth Tec®	5.4 -2	Geosmin Concentration: 100 ng/L, Deionized water: pH 6.5, 4 days reaction time	Geosmin: pH 5.4 (10% removal) pH 4 (21% removal) pH 3.5 (23% removal) pH 2.3 (89 % removal) pH 2 (100 % removal)
	6.6-2	MIB Concentration: 100 ng/L, Deionized water: pH 6.5, 4 days reaction time	MIB: pH 6.6 (11% removal) pH 4.7 (29% removal) pH 3.8 (35% removal) pH 3.1 (88 % removal) pH 2 (100 % removal)
Earth Tec®	2	Geosmin Concentration: 200 ng/L, Eucha water pH (7.6), Reaction time: 2 days	Geosmin 87% removal
Phosphoric Acid			96% removal
Ascorbic Acid			99% removal
Sulfuric Acid			88% removal
Earth Tec®	2	MIB Concentration: 200 ng/L, Eucha water pH (7.6), Reaction time: 2 days	MIB 96% removal
Phosphoric Acid			97% removal
Ascorbic Acid			100% removal
Sulfuric Acid			94% removal
Earth Tec	2.5	Geosmin Concentration: 200 ng/L, Deionized water: pH 6.5, reaction time: 2days	Geosmin 84% removal
Phosphoric Acid			99% removal
Ascorbic Acid			65% removal
Sulfuric Acid			99% removal
Earth Tec	2.5	MIB Concentration: 200 ng/L, Deionized water pH (6.5), Reaction time: 2 days	MIB 100% removal
Phosphoric Acid			100% removal
Ascorbic Acid			100% removal
Sulfuric Acid			100% removal

This study investigated the effects of pH on geosmin and MIB under various conditions of pH. From this study the following conclusions can be drawn:

- Geosmin removal began at pH 3.5 and was completely converted to argosmin at pH 2.0.
- MIB removal began at pH 4.5 and was complete at pH 3.0.
- The break-down product of geosmin, argosmin, increased as pH approached pH 2.0 and decreased ≅40% when the samples were returned to neutral pH. Recovery rates of geosmin as pH returned to neutral was ≅50%.
- 2-M-2-B (MIB break-down product) concentrations started to increase at pH 5.5 and were the highest at pH 3.0. After returning pH to neutral, 2-M-2-B experienced an ≅20% decrease. MIB concentrations as pH was returned to neutral recovered less than 5% .
- Using different acids did not impact geosmin and MIB concentration significantly (less than 10% difference).
- For different types of aqueous samples (lake, deionized, filtered, unfiltered), deionized water experienced 10-20% better removal efficiency of both geosmin and MIB.

The results provide additional information regarding the nature of geosmin and MIB loss in the presence of low pH. Geosmin and MIB are pH dependent in dehydration processes. Results also demonstrated that the dehydration of geosmin is reversible at neutral pH, where the dehydration of MIB is largely irreversible.

4.3 Biodegradation

MIB and geosmin in aqueous systems can be biodegraded by a variety of microorganisms, though the efficiencies have not been demonstrated. The known microorganisms for removal of MIB are Pseudomonas spp , Enterobacter spp (Tanaka et al., 1996), Pseudomonas putida (Oikawa et al., 1995), Bacillus spp. (Ishida and Miyaji, 1992), Candida spp.(Sumitomo, 1988), and Flavobacterium spp. (Egashira et al., 1992). The microorganisms for geosmin removal are Bacillus cereus (Silvey et al. , 1970), Arthrobacter atrocyaneus, Arthrobacter globiformis, Rhodococcus moris, and Arthrobacter atrocyaneus Saadoun, Chlorophenolicus strain N-1053 (Saadoun and El-Migdadi, 1998) . The biodegradation processes of geosmin and MIB are not proposed definitively. Trudgill (1984) suggested that MIB and geosmin biodegradation processes are attributed to their structural similarity to biodegradable alicyclic alcohols and ketones. Experiments were conducted in this study to estimate possible biodegradation microorganisms in Lake Eucha water.

4.3.1 Geosmin in Filtered and Unfiltered Lake water

Conditions of Sample: approximately 200 ng/L of geosmin in filtered and unfiltered Lake Eucha water, Eucha water pH (7.6), indirect sunlight for better biodegradation, Reaction time: 4 days.

Results and discussion. The results of this set of experiments are shown in Table 34 and Figure 42.

Table 34 Geosmin concentrations in Indirect Sunlight, Filtered and Unfiltered Lake water

Time (days)	Filtered Lake water (ng/L)		Unfiltered Lake water (ng/L)	
	With headspace	Without headspace	With headspace	Without headspace
0	211	150	197	150
1	139	148	169	150
2	126	162	110	150
3	74	134	57	145
4	71	137	29	136

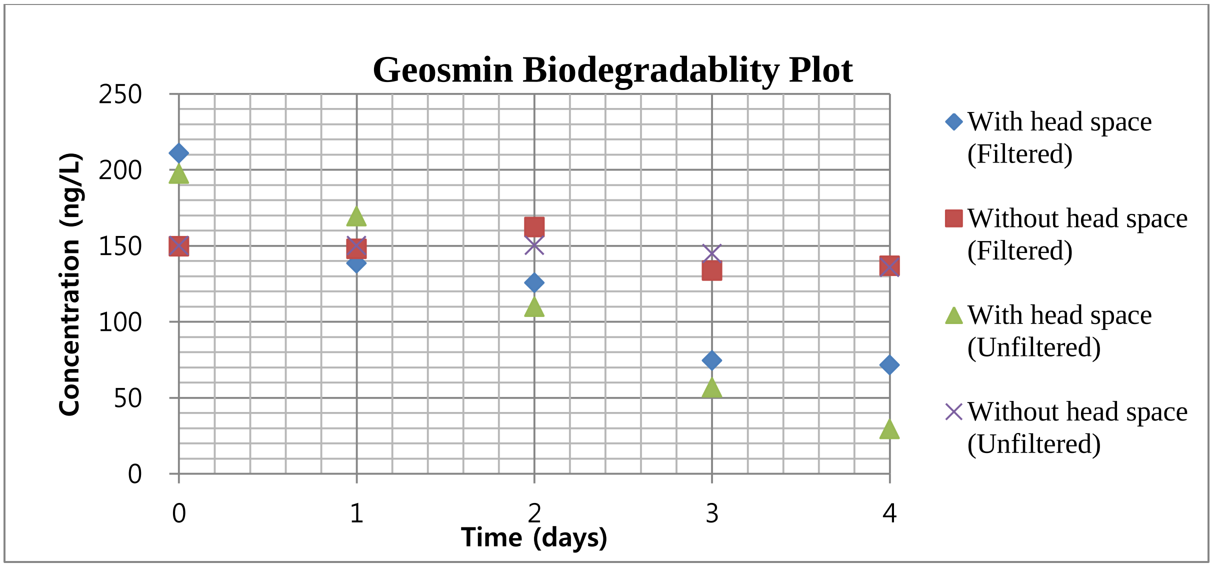


Figure 42 Geosmin concentrations in Filtered and Unfiltered Lake water

Geosmin concentrations in unfiltered Lake Eucha water were degraded from 197 ng/L and 150 ng/L to 29 ng/L and 136 ng/L, respectively, in indirect sunlight. Although the results appear to show a reduction, this difference is more likely due to the volatility of geosmin. Samples with headspace in unfiltered Lake Eucha offered more than 80% reduction in geosmin concentration while samples without headspace only showed 10% reduction. In filtered water, samples with headspace also showed greater removals of geosmin, approximately 77%, while samples without headspace only offered 10% removal of geosmin. These removal efficiencies show that geosmin is volatilized in indirect sunlight.

MIB in Filtered and Unfiltered Lake water

Conditions of Sample: approximately 200 ng/L of MIB in filtered and unfiltered Lake Eucha water, Eucha water pH (7.6), indirect sunlight for better biodegradation, Retention time: 4 days.

Results and discussion. Results of this series of experiments are shown in Table 35 and Figure 43.

Table 35 MIB concentrations in Filtered and Unfiltered Lake water

Time (days)	Filtered Lake water(ng/L)		Unfiltered Lake water (ng/L)	
	With headspace	Without headspace	With headspace	Without headspace
0	190	183	184	171
1	189	169	177	173
2	181	179	176	178
3	144	177	139	189
4	158	181	143	169

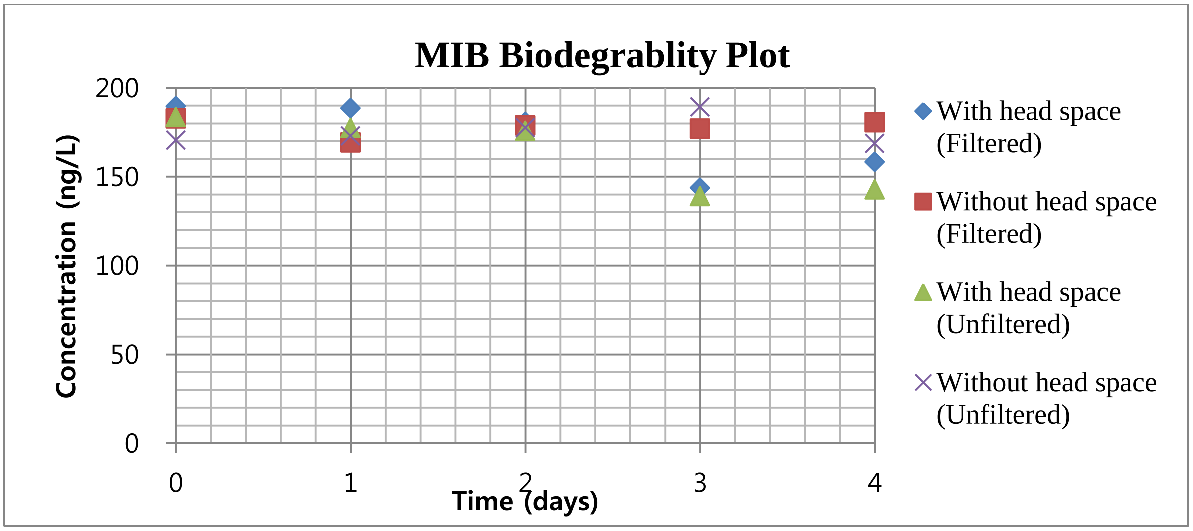


Figure 43 MIB concentrations in Filtered and Unfiltered Lake water

Concentrations of MIB in unfiltered Lake Eucha water were reduced from 184 and 171 ng/L with and without headspace, to 143 ng/L and 169 ng/L, respectively. The removal efficiencies were 23% with headspace and 1% without headspace. The results indicate that MIB is volatilized in indirect sunlight, though not as much as is geosmin. In filtered Lake Eucha water, MIB concentrations were reduced from 190 ng/L and 183 ng/L to 158 ng/L with headspace and 181 ng/L without headspace. These results are similar to unfiltered Lake Eucha water samples. Differences in reduction of MIB are within ±5%. Samples in both unfiltered and filtered lake water are probably not biodegraded, but rather volatized.

4.3.2 Comparison by Unfiltered, Filtered Lake water and Deionized water

The previous biodegradation experiments showed only that geosmin and MIB are volatile in water samples. Additional work is necessary to show that biodegradation is not occurring. Thus, three additional conditions were added: no headspace for all samples, deionized water samples, and eight days retention time.

Geosmin

Conditions of Sample: approximately 200 ng/L of geosmin in filtered, unfiltered Lake Eucha water and deionized water, Eucha water pH (7.6), deionized water pH (6.5), Indirect sunlight for better biodegradation, No headspace, Retention time: 8 days.

Results and discussion. Results of the first set of experiments, geosmin removal in deionized water, filtered and unfiltered lake water with eight days' retention time as shown in Table 36 and Figure 44.

Table 36 Geosmin concentrations in Deionized water, Filtered and Unfiltered Lake water

Time (days)	Unfiltered Lake water (ng/L)	Filtered Lake Water (ng/L)	Deionized water (ng/L)
0	201	193	178
1	196	190	166
2	195	188	150
3	179	178	149
4	191	177	140
5	155	172	137
6	149	165	148
7	142	160	144
8	139	155	142

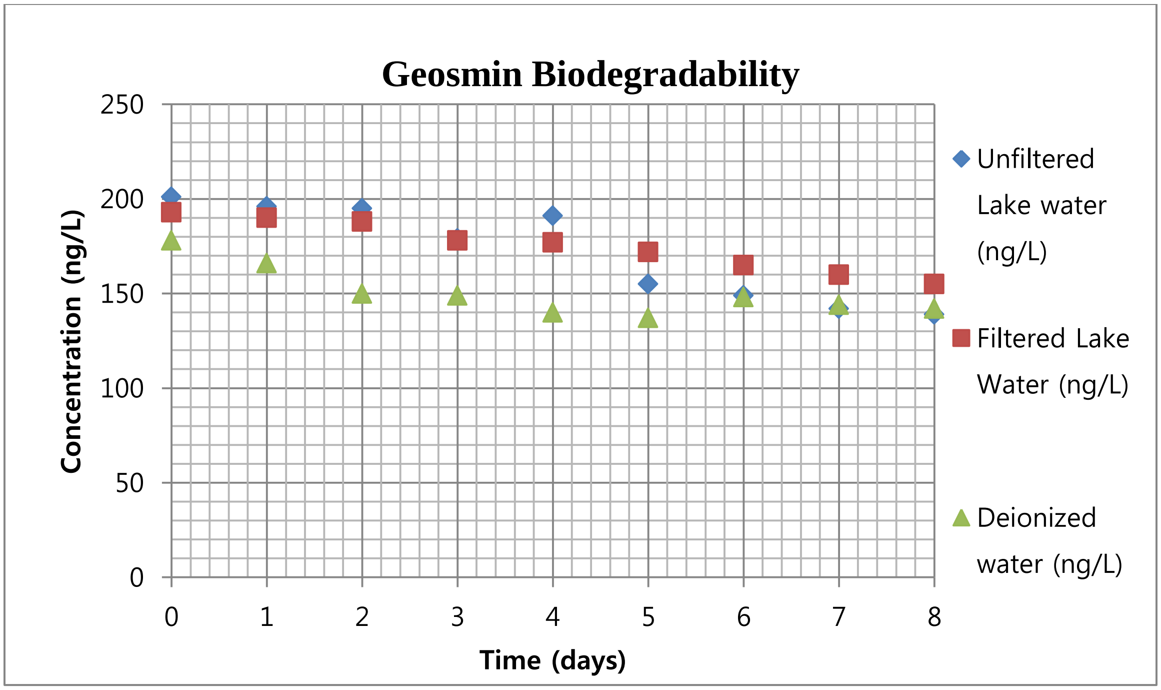


Figure 44 Geosmin Biodegradability plot with Deionized water, Filtered and Unfiltered Lake water

Geosmin concentrations in deionized water, filtered and unfiltered lake water changed from 178 ng/L, 193 ng/L, 201 ng/L, respectively to 139 ng/L, 155 ng/L, and 142 ng/L with eight days retention time. The removal rates of geosmin were 20% for deionized water samples, 20% for filtered Lake water samples, and 30% for unfiltered water samples. Since the removal efficiencies for deionized water and filtered Lake water were the same, this indicates that filtration did have an impact on geosmin removal. Unfiltered water samples showed a 10% higher removal rate of geosmin. While the errors of SPME are ±5% ranges, a 5% high removal rate does not provide definitive proof of biodegradation. Thus, it cannot be concluded that geosmin is being biodegraded in Lake Eucha water.

MIB

Conditions of Sample: Approximately 200 ng/L of MIB in filtered, unfiltered Lake Eucha water and deionized water, Eucha water pH (7.6), deionized water pH (6.5), No headspace, Indirect sunlight for better biodegradation, Retention time: eight days.

Results and discussion. Results of the second set of experiments, MIB removal in deionized water, filtered and unfiltered lake water with eight days' retention time are shown in Table 37 and Figure 45.

Table 37 MIB concentrations in Deionized water, Filtered and Unfiltered Lake water

Time (days)	Unfiltered Lake water (ng/L)	Filtered Lake water (ng/L)	Deionized water (ng/L)
0	201	193	178
1	198	190	180
2	196	191	175
3	179	189	178
4	186	190	175
5	175	185	170
6	193	184	172
7	191	185	164
8	181	183	170

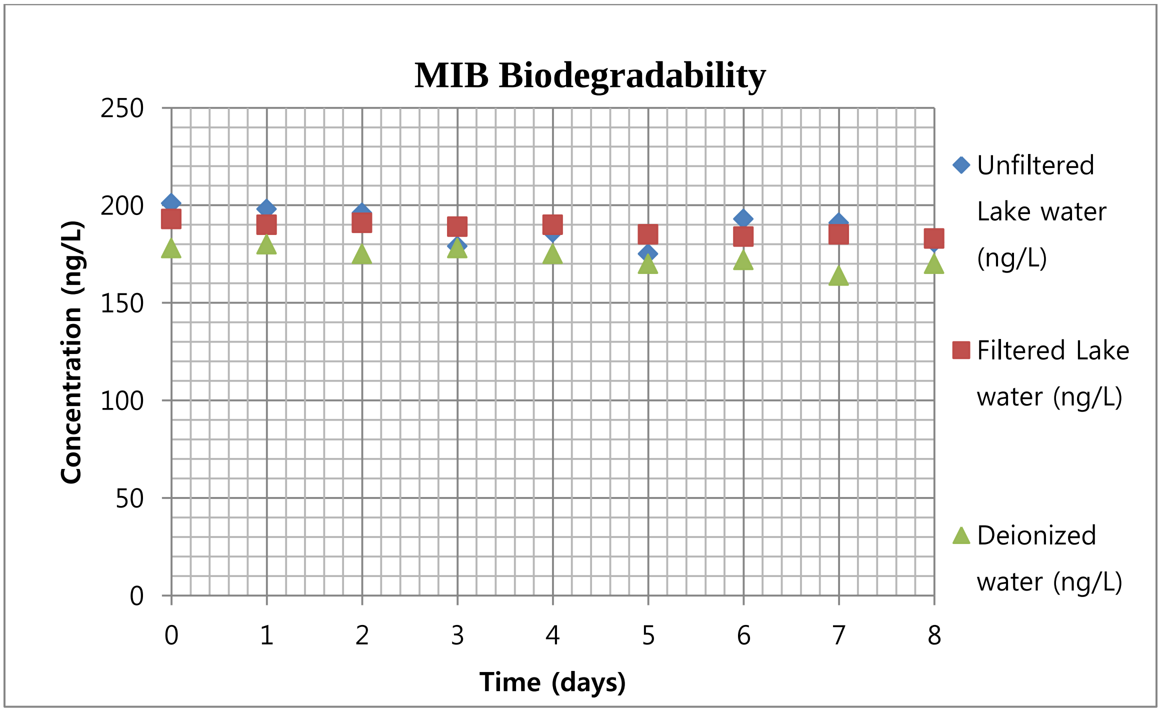


Figure 45 MIB Biodegradability plot with Deionized water, Filtered and Unfiltered Lake water

MIB concentrations in deionized water, filtered and unfiltered lake water changed from 178 ng/L, 193 ng/L, and 201 ng/L, to 170 ng/L, 183ng/L, and 181 ng/L, respectively, after eight days' retention time. The MIB removal efficiencies in deionized water, filtered and unfiltered lake water were 5-10%. The removal efficiency of 5-10% is within ±5% of the error ranges of SPME. Thus, it cannot be concluded that biodegradation occurs under these conditions.

4.3.3 Conclusions

Biodegradation experiments of geosmin and MIB were performed to determine any bacterial reaction. According to Figures 42-45, the results indicate no bacterial effects on removal of geosmin and MIB. However, the volatility of geosmin (20-30%) and MIB (5-10%) was demonstrated.

Table 38 Summary of biodegradation experiments

Water Conditions	**Sample conditions**	**Result**	
Filtered Lake water	150-200 ng/L of geosmin, Indirect sunlight, Lake Eucha water pH (7.6), Reaction time: 4 days	Geosmin	With headspace : 75% removal Without headspace : 9% removal
Unfiltered Lake water			With headspace : 85% removal Without headspace : 9% removal
Filtered Lake water		MIB	With headspace : 17% removal Without headspace : 1% removal
Unfiltered Lake water			With headspace : 20% removal Without headspace : 1% removal
Unfiltered Lake water	201 ng/L geosmin water, Eucha water pH (7.6), Reaction time: 8 days, No headspace, indirect sunlight	Geosmin :30 % removal, MIB: 10% removal	
Filtered Lake Water	196 ng/L geosmin water, Eucha water pH (7.6), Reaction time: 8 days, No headspace, indirect sunlight	Geosmin :31 % removal, MIB: 7% removal	
Deionized water	178 ng/L geosmin water, deionized water pH (6.5), Reaction time: 8 days, No headspace, indirect sunlight	Geosmin :30 % removal, MIB: 5% removal	

4.4 Temperature and pipeline flow turbulence

Temperatures for geosmin and MIB production are between 15-30℃ in the natural environment. It is possible that temperature might affect geosmin and MIB concentrations in water, even with samples containing only geosmin and MIB. Pangborn and Bertolero (1972) found that the taste-intensity scores ranked 22 > 37 > 55 > 0 ℃ and concluded that both heating and chilling decreased intensity. Sarah et al. (2006) experimented with temperature ranges from 20℃ to 8℃ in GAC filters and found that a decrease in temperature resulted in a measurable decrease in removals of geosmin and MIB for biofiltration at both high and low concentrations.

Pipeline turbulence is another factor that could impact removal of geosmin and MIB. Tulsa's main water treatment plant uses the pipeline to transport water from Lake Eucha, and Earth Tec is injected at the start of the pipeline. Flow rates are sufficient to produce turbulent flow, which could affect geosmin and MIB concentrations.

4.4.1 Temperature effects on Geosmin and MIB

Conditions of Sample: Approximately 200 ng/L of geosmin and MIB in Lake Eucha water Eucha water pH (7.6), Water temperature: 4℃, 18℃, 23℃, 0.001 ml/L Earth Tec dosage, Reaction time: 5 days.

Results and discussion. Results of temperature experiments, using temperatures of 4℃, 18℃, and 23℃ are shown in Table 39 and Figures 46 and 47.

Table 39 MIB and geosmin concentrations in 4℃, 18℃, and 23℃ Lake Eucha water

Time (days)	Concentration (ng/L)					
	MIB			Geosmin		
	4℃	18℃	23℃	4℃	18℃	23℃
0	194	194	194	203	203	203
1	183	190	200	190	198	202
2	180	192	202	179	195	200
3	181	188	198	175	190	198
4	182	190	199	178	185	190
5	184	192	192	179	182	192

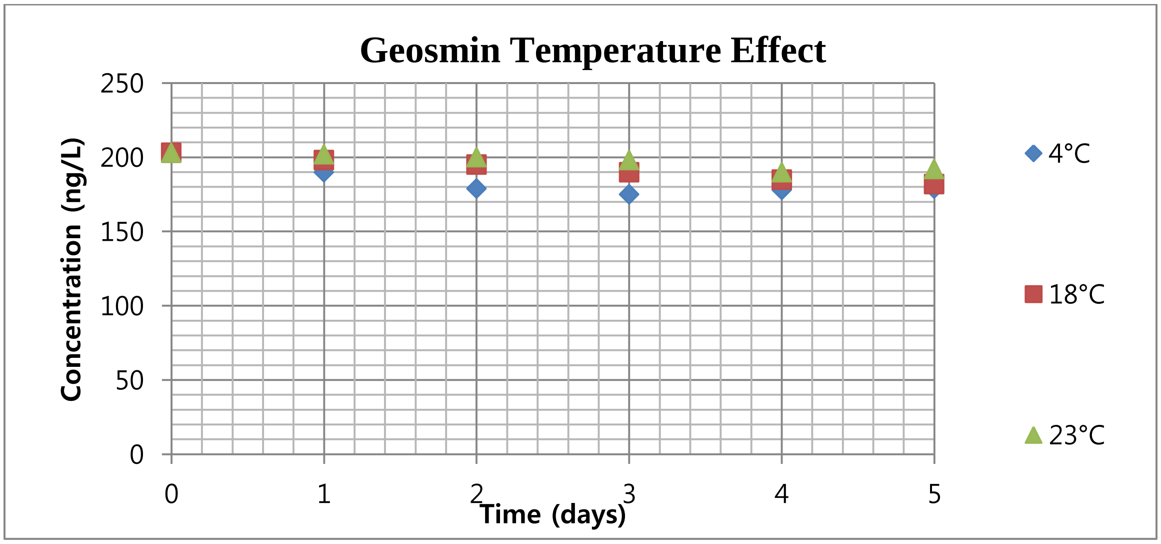


Figure 46 Geosmin temperature effect plot at 4℃, 18℃, and 23℃

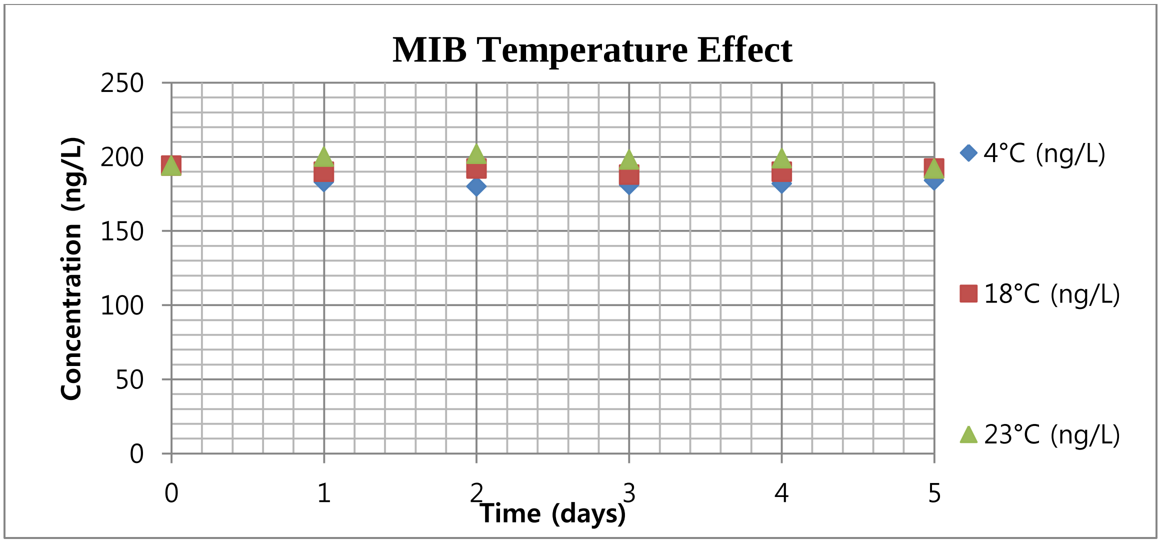


Figure 47 MIB temperature effect plot at 4℃, 18℃, and 23℃

The initial and final concentrations and of MIB at 4℃, 18℃, and 23℃ were similar, 194 ng/L (initial) to 184 ng/L (4℃), 192 ng/L (18℃), and 192 ng/L (23℃) after 5 days. The highest removal of MIB concentration was at 4℃, but the differences between temperatures are too slight to conclude that temperature has an impact. Geosmin concentrations also changed little from 203 ng/L to 179 ng/L (4℃), 182 ng/L (18℃), and 192 ng/L (23℃) after 5days. At 4℃, geosmin was removed approximately 12% while other temperatures showed a 10% removal. The results indicate water temperatures have minimal impact on geosmin and MIB concentration.

4.4.2 Pipeline turbulence effects on Geosmin and MIB

Conditions of Samples: 186-192 ng/L of geosmin and 176-183 ng/L of MIB in Lake Eucha water Eucha water pH (7.6), Unstirred and Stirred by magnetic bars at speed 7 (Fisher stirrer), Recommended EarthTec dosage, Retention time: 5 days.

Results and discussion. Results of turbulence experiments, simulated with stirred and unstirred samples, are shown in Table 40 and Figures 48 and 49.

Table 40 MIB and geosmin concentrations with stirred and unstirred Lake Eucha water samples

Time (days)	Concentration (ng/L)			
	MIB		Geosmin	
	Stirred	Unstirred	Stirred	Unstirred
0	176	183	186	192
1	168	190	173	189
2	160	180	165	178
3	158	182	160	180
4	147	179	155	188
5	148	175	150	176

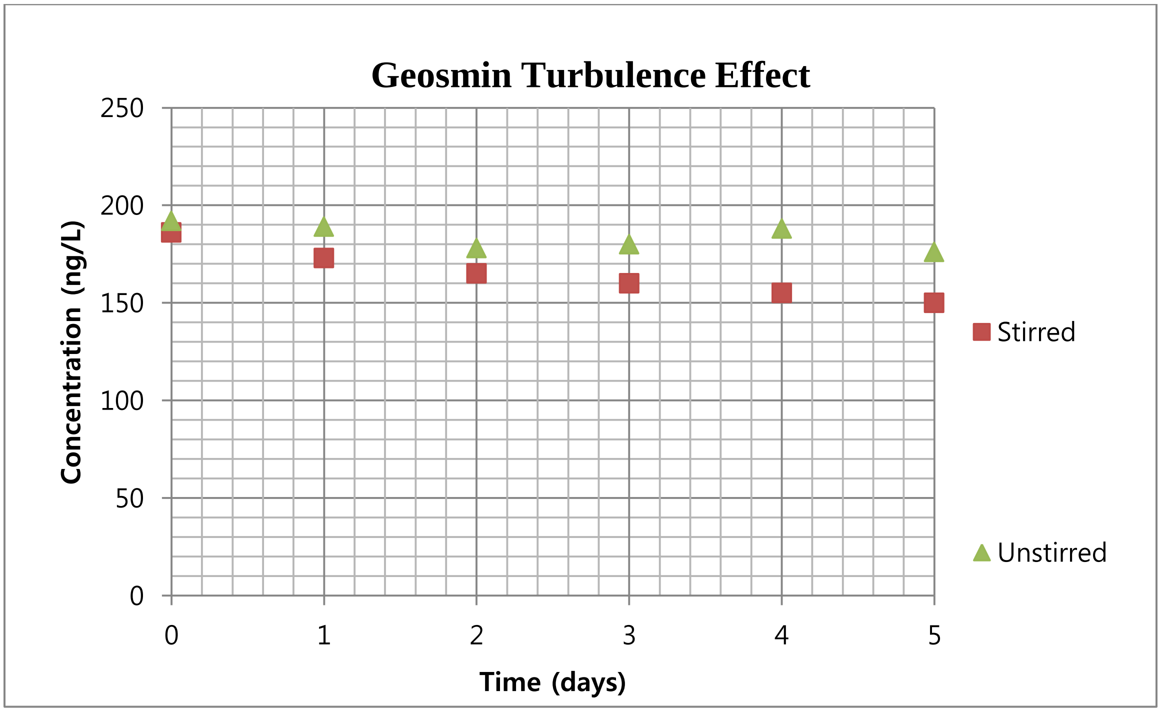


Figure 48 Geosmin Turbulence Effect plot

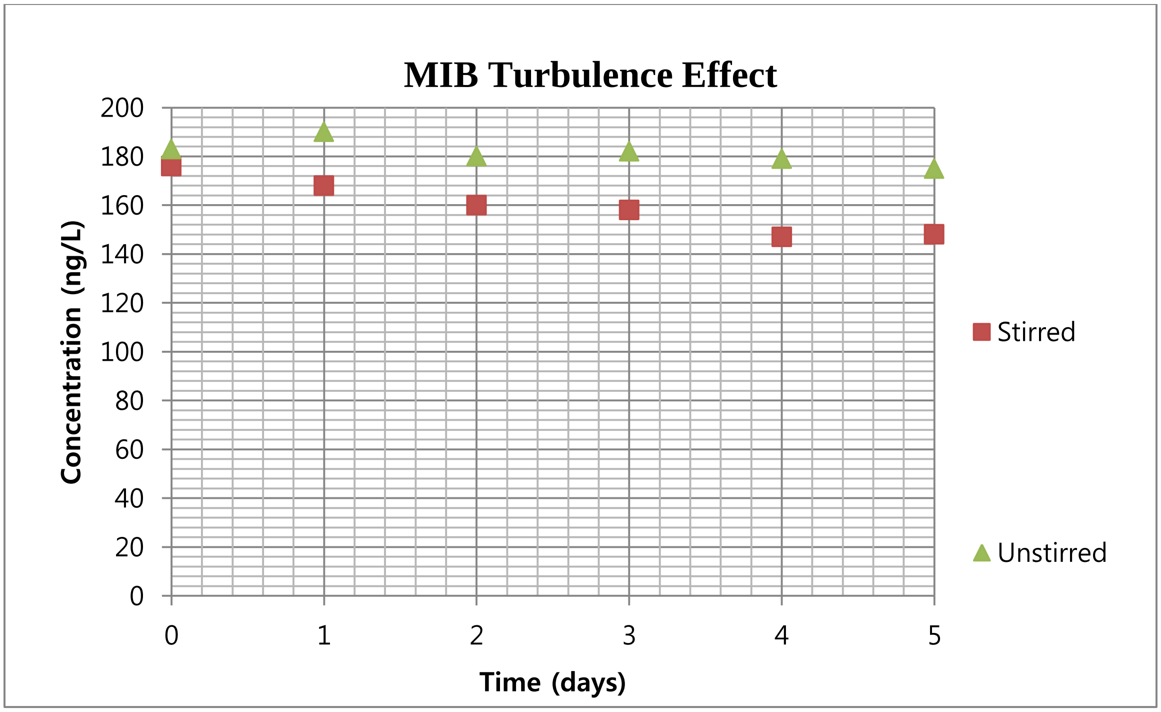


Figure 49 MIB Turbulence Effect plot

Geosmin and MIB concentrations with unstirred Lake Eucha water samples changed slightly from 192 ng/L to 176 ng/L and from 183 ng/L to 175 ng/L for 5 days reaction. For stirred Lake Eucha water samples, geosmin and MIB concentrations were reduced from 186 ng/L to 150 ng/L and from 176 ng/L to 148 ng/L. By comparing both samples, unstirred water samples only removed around 5 % of geomsin and MIB in Lake water while stirred water samples removed approximately 15 % - 18 % of geoosmin and MIB in Lake water. Removal of 5% geomsin and MIB is within the error range of ±5% for the analytical method, indicating that there is no reaction. A reduction of approximately 17% of geosmin and MIB in stirred water samples is greater than that seen in unstirred water. However, the differences are small. Thus, turbulent flow in the Tulsa water plant pipeline affects only slightly the concentrations of MIB seen in the samples.

4.4.3 Conclusion

Table 41 Summary of temperature and turbulence experiments

Variable		Sample conditions	Result
Temperature	4℃	194 ng/L MIB water, 203 ng/L geosmin water, Recommended EarthTec dosage, Sample pH:7.6 Reaction time: 5 days,	Geosmin: 12% removal, MIB: 8% removal
	18℃		Geosmin: 11% removal, MIB: 2% removal
	23℃		Geosmin: 6% removal, MIB: 2% removal
Turbulence	Stirred	186-192 ng/L of geosmin and 176-183 ng/L of MIB, Lake Eucha water pH (7.6), Recommended EarthTec dosage, Reaction time: 5 days	Geosmin: 20% removal, MIB: 16% removal
	Not Stirred		Geosmin: 9% removal, MIB: 5% removal

Temperature effects on geosmin and MIB

At 4℃, geosmin was removed approximately 12% while higher temperatures showed 10% removal. The results show only a slight difference. Overall, temperatures differences have insignificant impact on geosmin and MIB concentrations.

Turbulence effects on geosmin and MIB

The removal of 5% geomsin and MIB in unstirred samples is within the error range of ±5% of the analytical method, indicating that there is no reaction. A removal efficiency of approximately 17 % of geosmin and MIB in stirred water samples is slightly higher, offers better removal than unstirred water though 17 % removal is still low. Thus, turbulent flow in Tulsa water plant pipeline affects only slightly the geosmin and MIB concentration of water in the pipeline from Lake Eucha to the water treatment plant.

4.5 Other Chemicals with the Potential to remove geosmin and MIB

4.5.1 Cupric Sulfate (Copper Sulfate)

Copper (II) sulfate pentahydrate is one of the active compounds in Earth Tec®; the formula is $CuSO_4 \cdot 5H_2O$. It is often used as a fungicide, herbicide, or algaecide. Most algal species can be controlled with low concentrations of copper sulfate. In this series of experiments, the efficiency of copper sulfate to remove geosmin and MIB will be investigated by using different dosages of copper sulfate.

Geosmin

Conditions of Sample: Geosmin Concentration: approximately 100-125 ng/L geosmin, copper sulfate dosage: 0.1 g/100 mL geosmin water to 0.9 g/100 mL geosmin water, pH of sample: for the 0.1 g/100mL dose, pH=6.85); for the 0.3 g/100mL dose, pH=6.44; for the 0.6 g/100mL dose, pH =6.18; for the 0.9g/100mL dose, pH=6.03, and Lake Water pH: 7.8.

Results and discussion. Results of the cupric sulfate experiments are shown in Table 42 and Figure 50. The impacts on formation of argosmin are shown in Table 43 and Figure 51.

Table 42 Geosmin Concentrations at various dosages of Cupric Sulfate

Time (days)	Cupric Sulfate Dose/Concentration (ng/L)			
	0.1 g/100 mL	0.3 g/100 mL	0.6 g/ 100 mL	0.9 g/100 mL
0	125	125	125	125
1	144	130	156	120
2	117	107	102	99
3	119	108	97	108
4	115	107	104	103
5	91	75	82	88

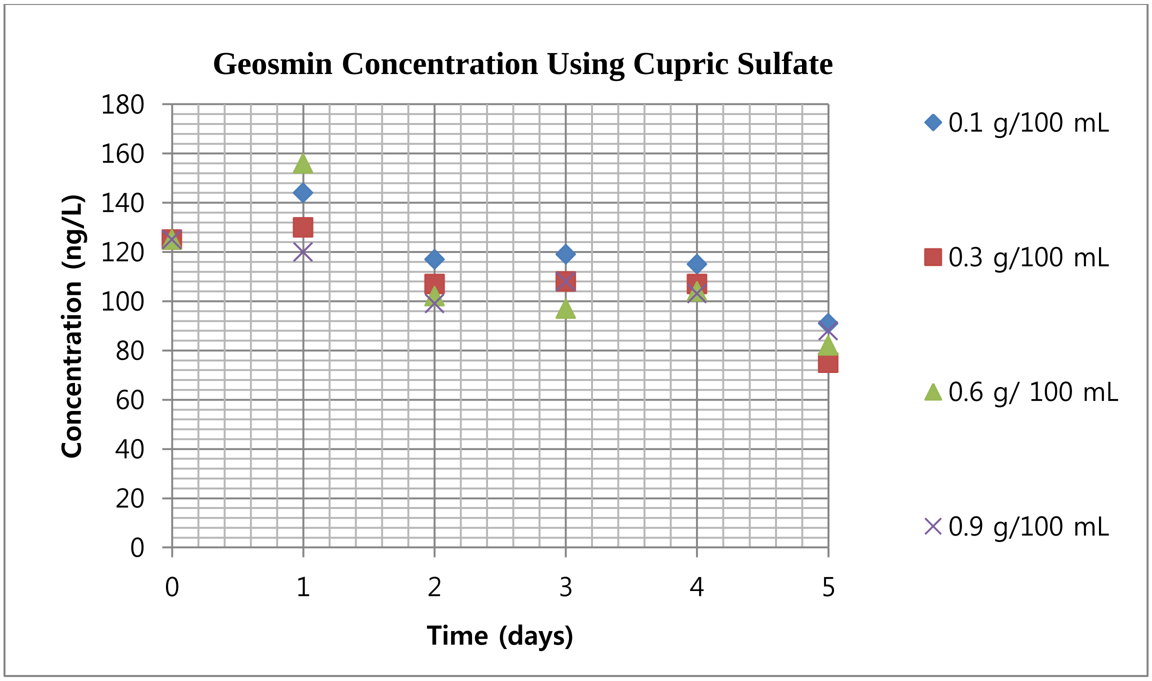


Figure 50 Geosmin Concentrations at different dosages of Cupric Sulfate

Table 43 Argosmin area at various dosages of Cupric Sulfate

Time (days)	**Cupric Sulfate Dose/Concentration (ng/L)**			
	0.1 g/100 mL	**0.3 g/100 mL**	**0.6 g/ 100 mL**	**0.9 g/100 mL**
0	20993	20993	20993	20993
1	34053	78090	106419	109332
2	56787	74865	109883	152189
3	70260	74205	91079	156884
4	82276	91774	108914	123835
5	75367	75585	99016	106557

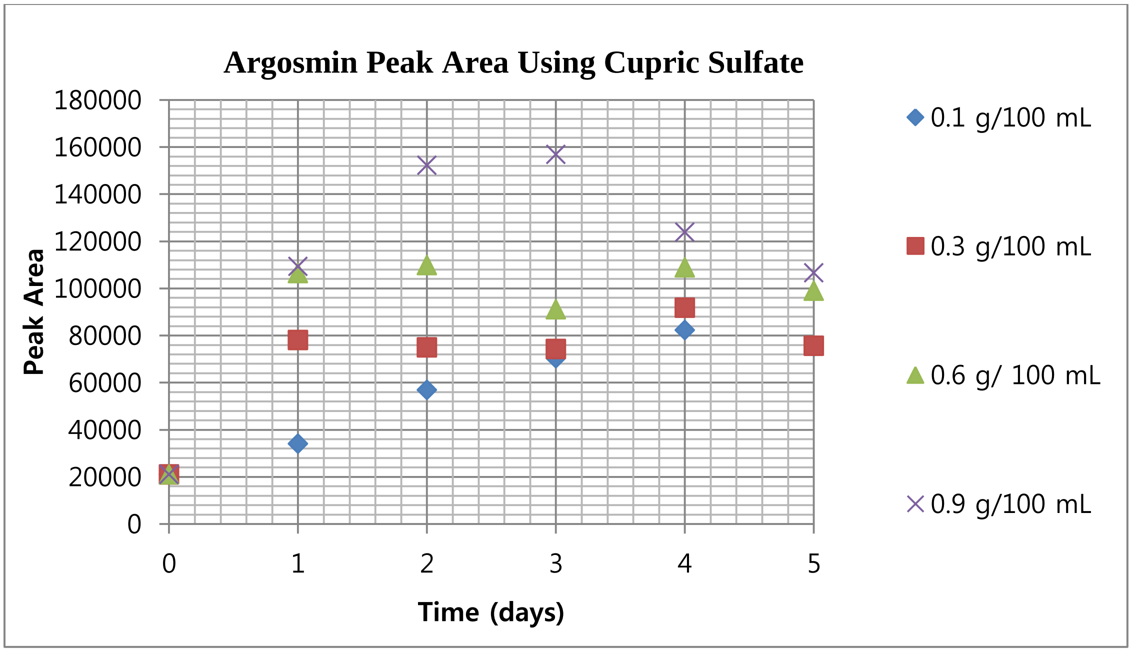


Figure 51 Argosmin Peak Area at different dosages of Cupric Sulfate

Geosmin was reduced from 125 ng/L to 91 ng/L at 0.1 g copper sulfate /100 mL geosmin water, 75 ng/L at 0.3 g copper sulfate /100 mL geosmin water, 82 ng/L at 0.6 g copper sulfate /100 mL geosmin water, and 88 ng/L at 0.9 g copper sulfate /100 mL geosmin water. While geosmin removal of each sample only varied from 22 to 36 percent, dehydration was confirmed as indicated by checking the argosmin peak area shown in Figure 51. Argosmin only increases due to dehydration. The peak area of argosmin increased 3 times at 0.1 g copper sulfate/100 mL geosmin water and 5 times at 0.9 g copper sulfate /100 mL geosmin water. Thus, cupric sulfate presents a dehydration reaction of geosmin. More evaluation of copper sulfate is warranted for removal of geosmin from lake water.

MIB

Conditions of Sample: MIB Concentration: approximately 100-120 ng/L MIB, copper sulfate dosage: 0.1 g/100 mL MIB water to 0.9 g/100 mL MIB water, pH of sample: 0.1 g/100mL (pH 6.85), 0.3 g/100mL (pH 6.44), 0.6 g/100mL (6.18), 0.9g/100mL (6.03), and Lake Water pH: 7.8

Results and discussion. Results of experiments with cupric sulfate on MIB concentrations are shown in Tables 44 and 45 and Figures 52 and 53.

Table 44 MIB Concentrations at various dosages of Cupric Sulfate

Time (days)	**Cupric Sulfate Dose/Concentration (ng/L)**			
	0.1 g/100 mL	**0.3 g/100 mL**	**0.6 g/ 100 mL**	**0.9 g/100 mL**
0	118	118	118	118
1	91	67	34	34
2	78	57	34	31
3	72	48	35	29
4	57	43	28	28
5	55	34	26	27

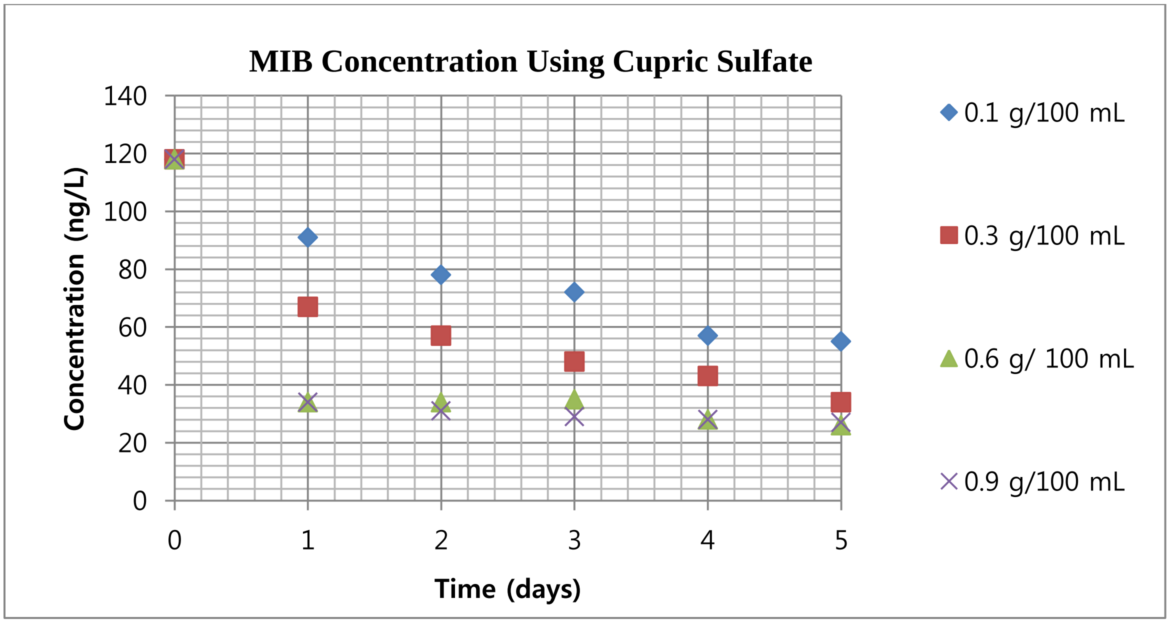


Figure 52 MIB Concentrations at different dosages of Cupric Sulfate

2-Methyl-2-Bornene (2-M-2-B)

Table 45 2-M-2-B Area at various dosages of Cupric Sulfate

Time (days)	Cupric Sulfate Dose/Area			
	0.1 g/100 mL	0.3 g/100 mL	0.6 g/ 100 mL	0.9 g/100 mL
0	156478	156478	156478	156478
1	443231	774757	1269864	1407543
2	502123	834551	1148455	1485867
3	540227	982075	1155293	1524367
4	822874	957588	1118887	1326945
5	667083	746860	1209337	1358545

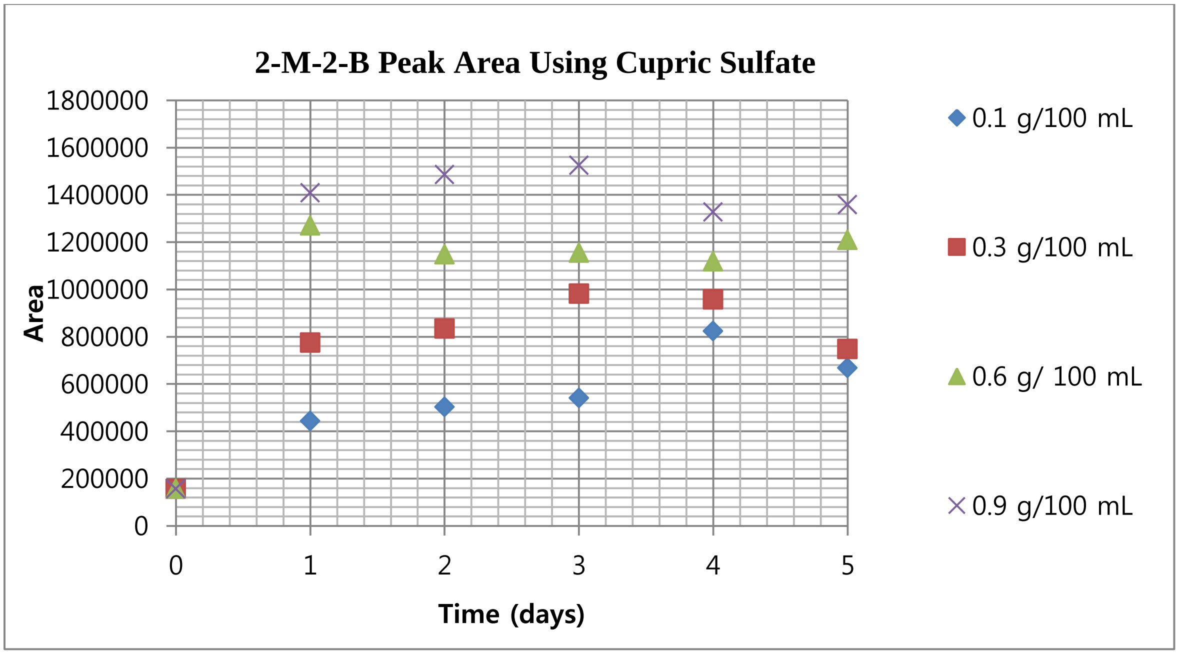


Figure 53 2-M-2-B Area at different dosages of Cupric Sulfate

A initial concentration of 113 ng/L of MIB was treated with four different dosages of cupric sulfate to evaluate possible reduction of MIB in Lake Eucha water. Removal efficiencies of MIB by different dosages of copper sulfate for 5 days' reaction time were 53 percent at the dosage of 0.1 g/100 mL MIB water, 71 percent at 0.3 g/100 mL, 77 percent at 0.6 g/100mL and 78 percent at 0.9 g/100mL. These removal percentages are evidence of MIB removal by cupric sulfate. The lowest removal percentage of 53 at the dosage of 0.1 g/100 mL MIB water is significant; the highest removal percentage of MIB is 78 percent at 0.9 g/100mL.

The generation of the MIB dehydration byproduct 2-Methyl-2-Bornene (2-M-2-B) was checked in order to determine verify the dehydration reaction process. All the dosages of copper sulfate presented an increase in area of 2-M-2-B as high as 5 times to 10 times. At the dosage of 0.1g/100 mL MIB water, the area of 2-M-2-B increased in 5 times, and 10 times at the dosage of 0.3 g/100mL. These numbers present the relationship of dehydration reaction by different dosages and show more generation of 2-M-2-B at the high dosage of copper sulfate. Thus, cooper sulfate is reacting with MIB by removing water molecules and generating MIB byproducts. More experiments with copper sulfate are necessary to determine a concrete result.

4.5.2 Drying process

Drying process shows a similar trend to dehydration process by removing water molecules using chemicals. If the drying process removes water from some compounds, it is worthwhile to apply some drying agents for removal of geosmin and MIB. Commonly used drying agents in organic laboratories are calcium chloride ($CaCl_2$), sodium sulfate (Na_2SO_4) calcium sulfate $CaSO_4$, and magnesium sulfate ($MgSO_4$). All four readily form hydrates at low temperatures according to

$$A + nH_2O \rightleftharpoons A*(H_2O)_n$$

Their efficiencies measured by intensity, capacity and velocity can greatly vary from one solvent to the other. Capacity refers to the maximum numbers of moles of water that the drying agent can bind (n).

4.5.2.1 Sodium Sulfate

Sodium Sulfate is a sodium salt of sulfuric acid and is used as a drying agent. It is very efficient at absorbing water molecules from liquids. In this set of experiments, different dosages of sodium sulfate were evaluated to determine the removals of geosmin and MIB.

Geosmin

Conditions of Sample: Geosmin Concentration: 101 ng/L, Sodium sulfate dosage: 0.05 g/100 mL geosmin water to 0.8 g/100 mL, pH of samples: 0.05 g/100mL (pH 7.6), 0.2 g/100mL (pH 7.4), 0.4 g/100mL (7.3), 0.8g/100mL (7.2), and Lake Water pH: 7.8

Results and discussion. Results of this set of experiments are shown in Tables 46 and 47 and Figures 54 and 55.

Table 46 Geosmin Concentrations at various dosages of Sodium sulfate

Time (days)	Sodium Sulfate Dose/Concentration (ng/L)			
	0.05 g/100 mL	0.2 g/100 mL	0.4 g/ 100 mL	0.8 g/100 mL
0	101	101	101	101
1	74	93	75	102
2	41	86	58	61
3	40	48	46	38
4	39	61	46	39
5	23	21	19	27

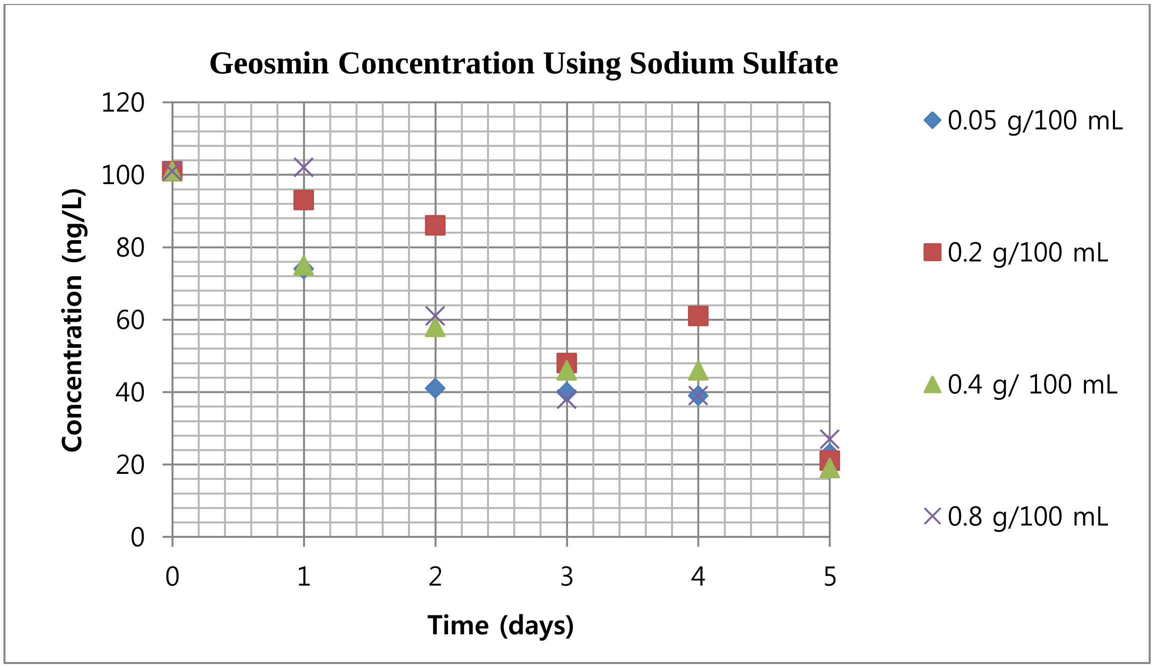


Figure 54 Geosmin Concentrations at different dosages of Sodium sulfate

Table 47 Argosmin area at various dosages of sodium sulfate

Time (days)	**Sodium Sulfate Dose/Area**			
	0.05 g/100 mL	**0.2 g/100 mL**	**0.4 g/ 100 mL**	**0.8 g/100 mL**
0	22320	22320	22320	22320
1	14972	15193	20379	21092
2	12170	7796	4746	4180
3	7098	6904	4879	4567
4	5608	3570	3531	3605
5	6136	2931	2059	3186

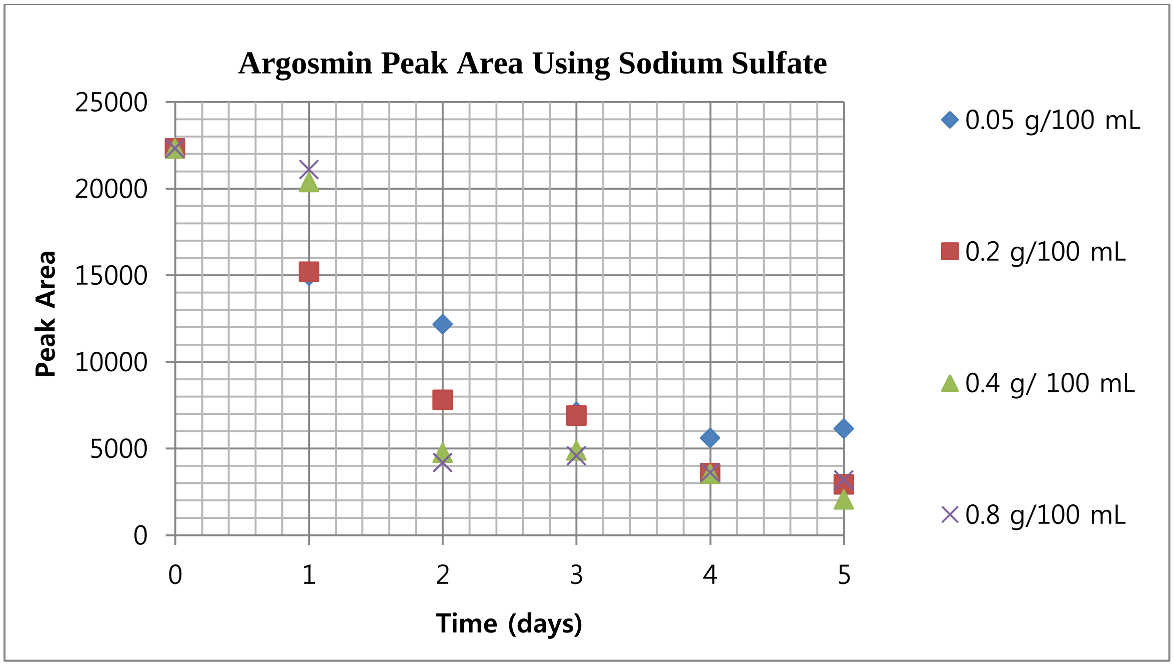


Figure 55 Argosmin Concentrations at different dosages of Sodium sulfate

Geosmin is effectively removed from 101 ng/L to 23 ng/L with 0.05 g sodium sulfate /100mL, 21 ng/L with 0.2 g sodium sulfate/100mL, 19 ng/L with 0.4 g sodium sulfate/100mL, 27 ng/L with 0.8g sodium sulfate/100mL after 5 days' reaction time. The highest removal of 82% was observed at 0.4 g sodium sulfate in 100 mL, while other removals exceeded 73%. These removals demonstrate that sodium sulfate has the ability to remove geosmin.

Argosmin (geosmin byproduct) peaks were low for all doses during 5days' reaction time, as shown in Figure 55. The very low formation of argosmin demonstrates that the sodium sulfate reaction is different from the dehydration reaction seen with acids.

MIB

Conditions of Sample: MIB Concentration: 104 ng/L, Sodium sulfate dosage: 0.05 g/100 mL MIB water to 0.8 g/100 mL, pH of samples: 0.05 g/100mL (pH 7.6), 0.2 g/100mL (pH 7.4), 0.4 g/100mL (7.3), 0.8g/100mL (7.2), and Lake Water pH: 7.8.

Results and discussion. Results of this set of experiments are shown in Tables 48 and 49 and Figures 56 and 57.

Table 48 MIB Concentrations at various dosages of Sodium Sulfate

Time (days)	Sodium Sulfate Dose/Concentration (ng/L)			
	0.05 g/100 mL	0.2 g/100 mL	0.4 g/ 100 mL	0.8 g/100 mL
0	104	104	104	104
1	95	113	100	100
2	78	102	85	81
3	86	91	85	71
4	90	90	39	62
5	52	25	26	31

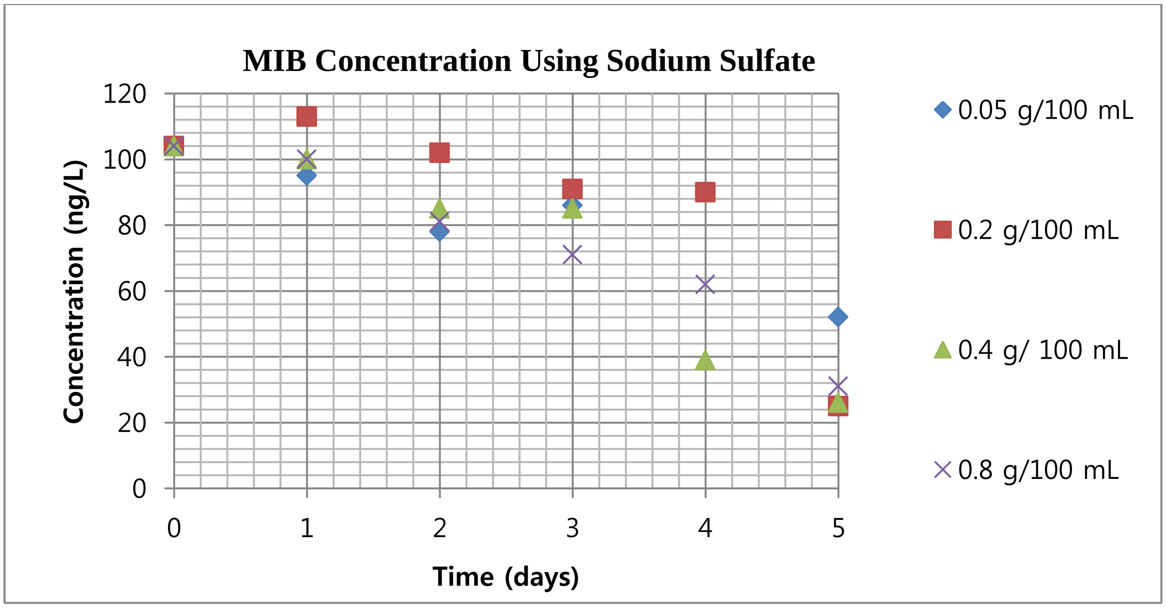


Figure 56 MIB Concentrations at different dosages of Sodium Sulfate

Table 49 2-M-2-B area by different dosages of sodium sulfate

Time (days)	**Sodium Sulfate Dose/Area**			
	0.05 g/100 mL	**0.2 g/100 mL**	**0.4 g/ 100 mL**	**0.8 g/100 mL**
0	179368	179368	179368	179368
1	154863	125956	137234	163509
2	137975	37717	46434	34191
3	139364	49823	29880	28990
4	41111	25868	15222	13412
5	27118	8806	4461	6290

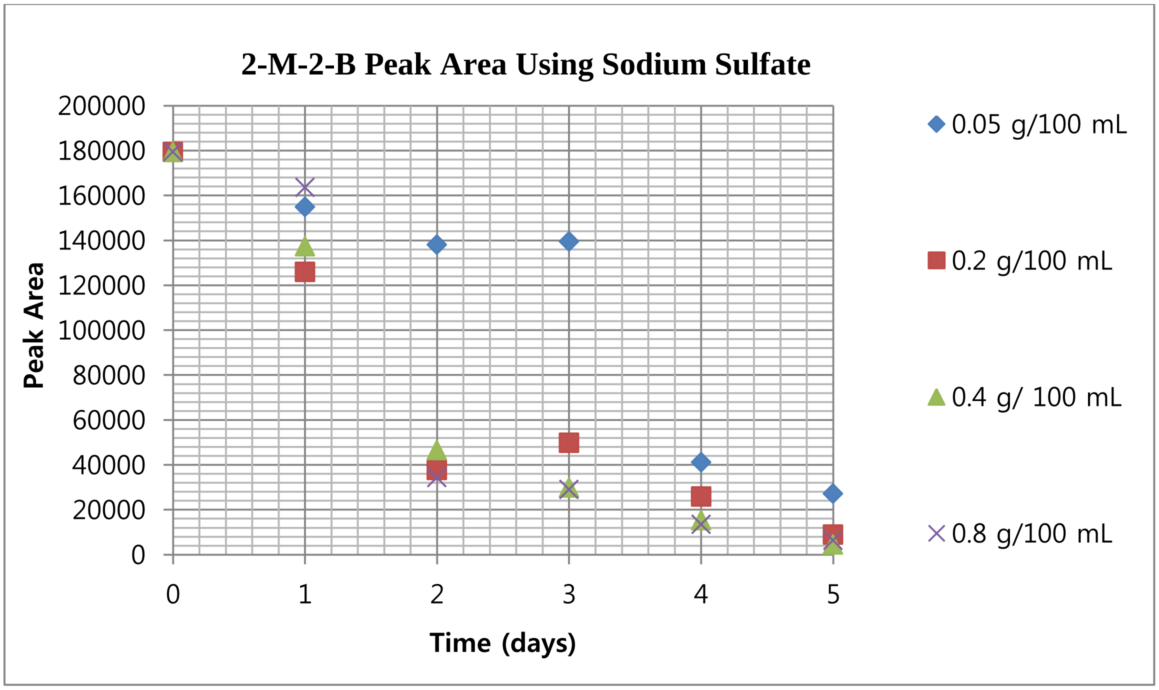


Figure 57 2-M-2-B peak area at different dosages of Sodium sulfate

The initial concentration of 104 ng/L MIB water samples were reduced to 52 ng/L with 0.05 g/100mL , 25 ng/L with 0.2 g/100mL, 26 ng/L with 0.4 g/100mL, 31 ng/L with 0.8g/100mL for 5 days' reaction time. The highest removal efficiency was 76 % with 0.2 g sodium sulfate/100ml MIB water and the lowest removal efficiency was 50 % with 0.05 g sodium sulfate/100mL MIB water. These removal percentages indicate that sodium sulfate removes MIB, though the reaction mechanism is not yet defined.

As shown in Figure 57, the concentrations (peak areas) of the dehydration product of MIB called 2-M-2-B were low with all four dosages of sodium sulfate. This indicates that 2-M-2-B is only generated in dehydration reactions at low pH, and that a drying reaction provides a different aspect of MIB removal.

Overall, sodium sulfate removes both MIB (50-76%) and geosmin (73%-82%) using dosages of 0.05g sodium sulfate/100mL geosmin and MIB water to 0.8g sodium sulfate/100 mL geosmin and MIB water.

4.5.2.2 Low dosages of Sodium Sulfate and Magnesium Sulfate

Sodium sulfate and magnesium sulfate can be used for removal of geosmin and MIB. Both are used as drying agents. Sodium Sulfate is a sodium salt of sulfuric acid and magnesium sulfate contains magnesium, sulfur and oxygen. They are very efficient to absorb water molecules from liquids. In this experiment, low doses of the two salts individually and a combination of sodium sulfate and magnesium sulfate were evaluated to find removal of geosmin and MIB.

Conditions of Sample: Geosmin Concentration: approximately 200 ng/L geosmin, Dosage: sodium sulfate, magnesium sulfate, both of sodium and magnesium sulfate: 0.2g/L geosmin water, pH of sample: 6.8-6.0, Lake Water pH: 7.8

Results and discussion. Results of this set of experiments are shown in Tables 50 and 51 and Figures 58 and 59.

Table 50 Geosmin Concentrations by sodium sulfate, magnesium sulfate and mixture of sodium and magnesium sulfate with dosage of 0.2g/L.

Time (days)	Na_2SO_4 (0.2 g/L)	Na_2SO_4 (0.02 g/L)	$MgSO_4$ (0.2g/L)	Na_2SO_4+$MgSO_4$ (0.2g/L)
0	198	198	194	197
1	175	172	186	185
2	155	170	175	158
3	132	129	173	140
4	125	119	170	130
5	101	115	170	108

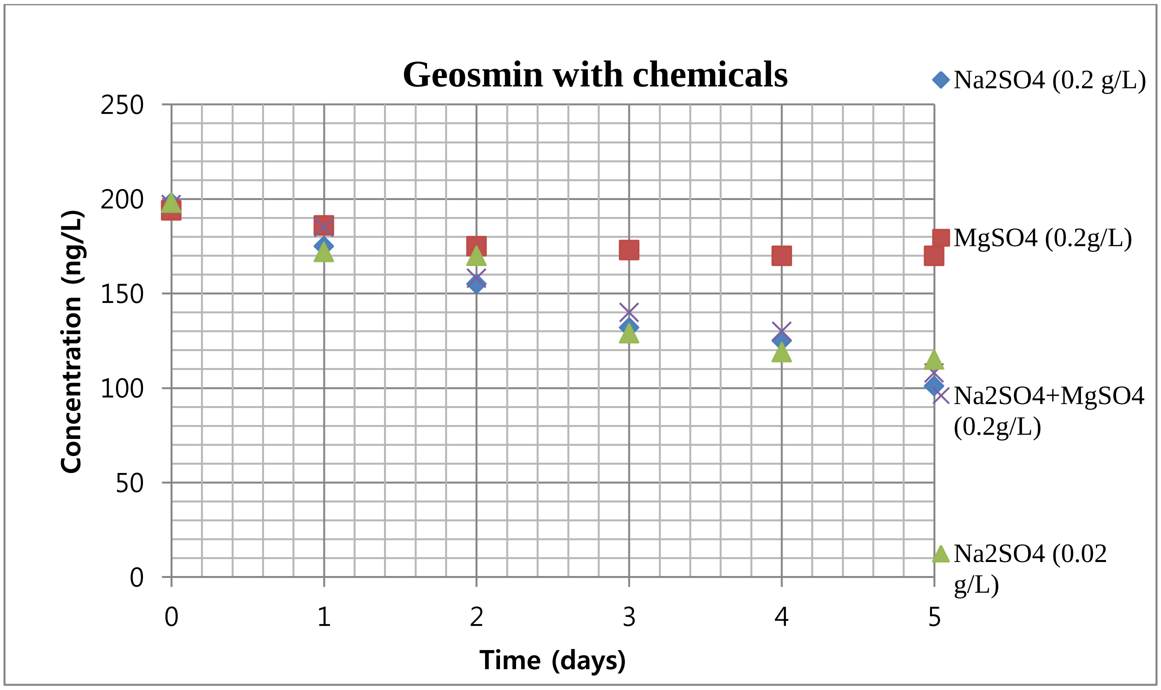


Figure 58 Geosmin concentration plot using sodium sulfate, magnesium sulfate and mixture of sodium and magnesium sulfate

Table 51 Argosmin area by sodium sulfate, magnesium sulfate and mixture of sodium and magnesium sulfate with dosage of 0.2g/L.

Time (days)	$MgSO_4$ (0.2g/L)	Na_2SO_4 (0.02 g/L)	Na_2SO_4 (0.2 g/L)	Na_2SO_4+$MgSO_4$ (0.2g/L)
0	15952	17625	16028	16543
1	33985	28797	15432	36486
2	20986	25769	13980	17809
3	14597	10979	15670	13576
4	8707	9786	13576	9087
5	8987	9265	13898	9564

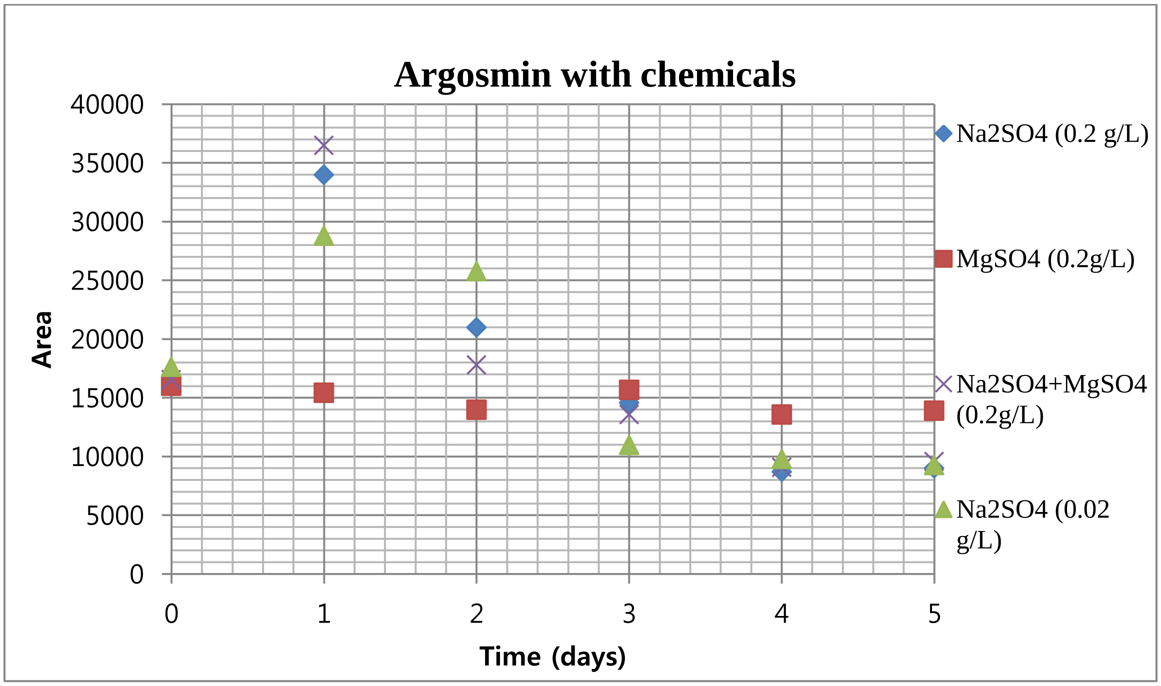


Figure 59 Argosmin area plot using sodium sulfate, magnesium sulfate and mixture of sodium and magnesium sulfate

A low dose of sodium sulfate resulted in approximately 48% geosmin removal, while magnesium sulfate removed approximately 15%. The sodium sulfate and magnesium sulfate mixture provide 47% geosmin removal. Low dosages of sodium and magnesium sulfate do remove some geosmin and MIB, but most of the removal is provided by the sodium sulfate. As a result, sodium sulfate should be investigated further.

Argosmin peaks with sodium sulfate display reduction during 5days' reaction time while argosmin peaks with magnesium sulfate are nearly steady. These results indicate that the drying reaction reacts with geosmin and MIB in a manner different from dehydration.

MIB

Conditions of Sample: MIB Concentration: approximately 200 ng/L, Dosage: sodium sulfate, magnesium sulfate, both of sodium and magnesium sulfate: 0.2g/L MIB water, pH of sample: 6.8-6.0, Lake Water pH: 7.8

Results and discussion. Results of this set of experiments are shown in Tables 42 and 53 and Figures 60 and 61.

Table 52 MIB Concentrations by sodium sulfate, magnesium sulfate and mixture of sodium and magnesium sulfate with dosage of 0.2g/L.

Time (days)	Na_2SO_4 (0.2 g/L)	Na_2SO_4 (0.02 g/L)	$MgSO_4$ (0.2g/L)	Na_2SO_4+$MgSO_4$ (0.2g/L)
0	196	195	201	199
1	175	189	180	172
2	155	170	175	152
3	140	152	155	135
4	125	127	152	130
5	119	120	150	121

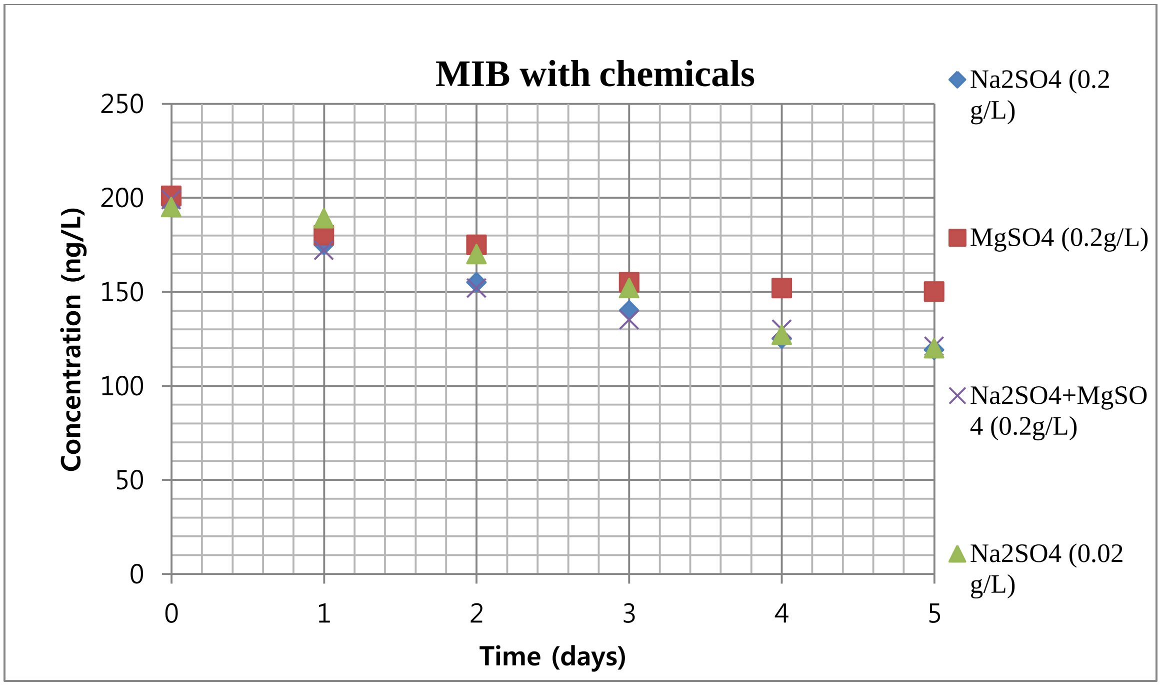


Figure 60 MIB concentration plot using sodium sulfate, magnesium sulfate and mixture of sodium and magnesium sulfate

2-M-2-B

Table 53 2-M-2-B area by sodium sulfate, magnesium sulfate and mixture of sodium and magnesium sulfate with dosage of 0.2g/L.

Time (days)	MgSO$_4$ (0.2g/L)	Na$_2$SO$_4$ (0.02 g/L)	Na$_2$SO$_4$ (0.2 g/L)	Na$_2$SO$_4$+MgSO$_4$ (0.2g/L)
0	64499	63886	65433	69892
1	32069	39786	64753	65453
2	28512	30276	65564	57987
3	25656	29654	62768	47872
4	28859	25654	40820	36757
5	26590	28674	38921	34126

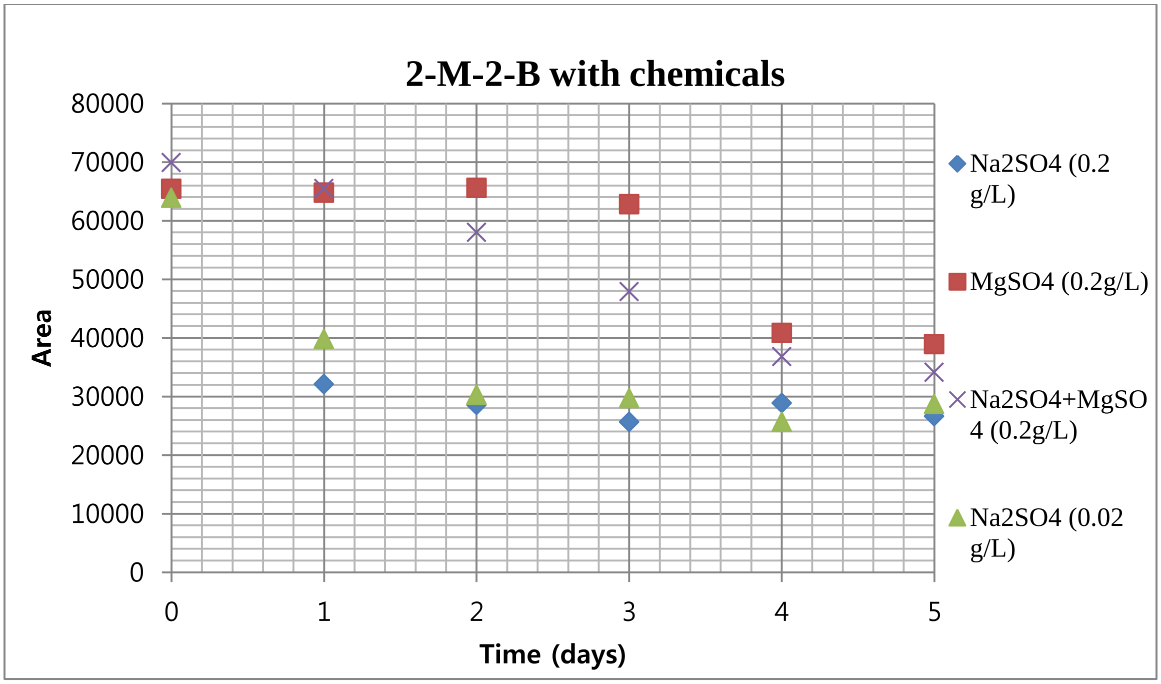


Figure 61 2-M-2-B area plot using sodium sulfate, magnesium sulfate and mixture of sodium and magnesium sulfate

MIB is removed 25% with magnesium sulfate (0.2g/L) and 40% with sodium sulfate and with the combination sodium sulfate plus magnesium sulfate (0.2g/L). Both magnesium sulfate and sodium sulfate have an ability to remove MIB, while sodium sulfate may have better performance than magnesium sulfate. More experiments with sodium sulfate are necessary to develop better mechanisms of MIB removal.

The 2-M-2-B peak area continuously decreased during the five-day reaction time. These results indicate that 2-M-2-B also decreases while MIB is removed. The drying reaction is therefore different from the dehydration reaction.

4.5.2.3 Phosphorous pentoxide

Phosphorus pentoxide (P_4O_{10}) is a white crystalline solid that is the anhydride of phosphoric acid; it is used as a powerful dehydrating agent. In this experiment, phosphorus pentoxide was used to evaluate efficiency for removal of geosmin and MIB.

Geosmin

Conditions of Sample: Geosmin Concentration: 101 ng/L, Phosphorus pentoxide dosage: 0.05 g/100 mL geosmin water to 0.8 g/100 mL geosmin water, pH of samples: 0.05 g/100mL (pH 4.25), 0.2 g/100mL (pH 3.66), 0.4 g/100mL (pH 2.45), 0.8g/100mL (pH 2.24), Lake Water pH: 7.8.

Table 54 Geosmin Concentrations at various dosages of phosphorus pentoxide

Time (days)	Phosphorous pentoxide Dose/Concentration (ng/L)			
	0.05 g/100 mL	0.2 g/100 mL	0.4 g/ 100 mL	0.8 g/100 mL
0	101	101	101	101
1	26	17	8	5
2	18	10	8	3
3	8	7	6	3
4	6	5	3	2
5	7	4	1.5	1.6

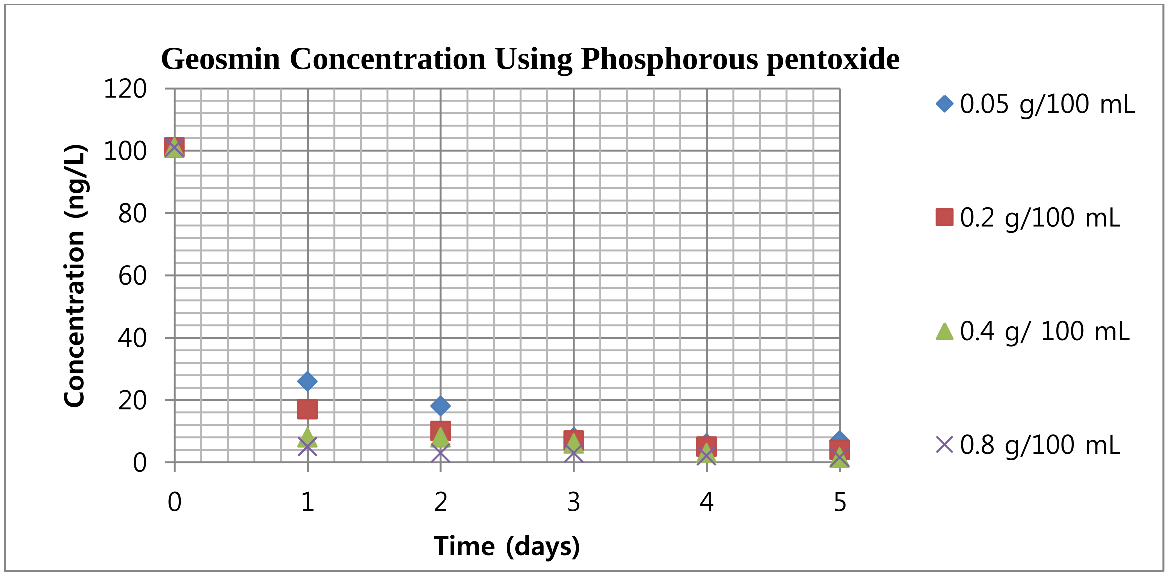


Figure 62 Geosmin Concentrations at different dosages of phosphorous pentoxide

Argosmin

Table 55 Argosmin Area at various dosages of phosphorous pentoxide

Time (days)	Phosphorous pentoxide Dose/Area			
	0.05 g/100 mL	0.2 g/100 mL	0.4 g/ 100 mL	0.8 g/100 mL
0	22320	22320	22320	22320
1	631313	1156884	1256624	1581186
2	531547	848398	785350	476231
3	457727	653879	865380	907544
4	458377	686577	876543	893463
5	379418	136363	72276	53403

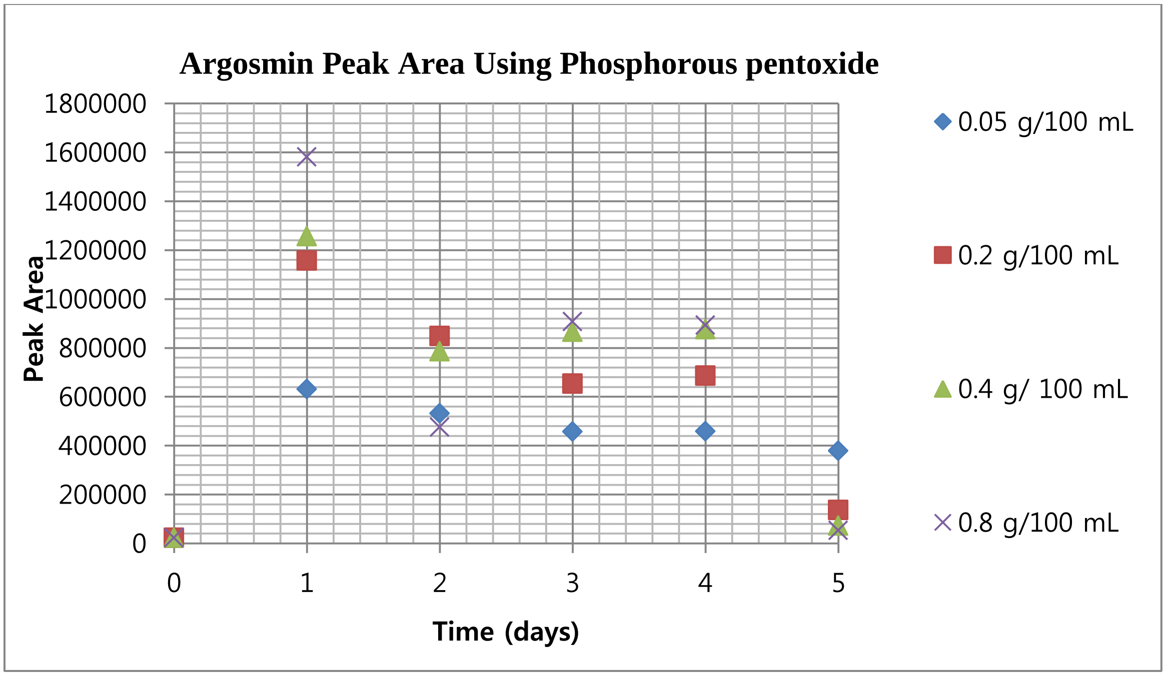


Figure 63 Argosmin Peak Area at various dosages of phosphorous pentoxide

Results and Discussion

Geosmin is removed from 101 ng/L to 7 ng/L with 0.05 g phosphorous pentoxide 100mL, 4 ng/L with 0.2 g phosphorous pentoxide /100mL, 1 ng/L with 0.4 g phosphorous pentoxide 100mL, 1 ng/L with 0.8g phosphorous pentoxide /100mL for 5 days reaction time. From the pH experiment, the starting pH of geosmin removal is approximately 4.5 and the complete removal pH was 2 with 1 day reaction time. In this experiment, it also shows the similar trend as the pH experiment for 1day reaction time. However, argosmin decreased during 5 days reaction time. Thus, phosphorous pentoxide provides dehydration reaction of geosmin in low pH circumstance.

MIB

Conditions of Sample: MIB Concentration: 104 ng/L, Phosphorus pentoxide dosage: 0.05 g/100 mL MIB water to 0.8 g/100 mL MIB water, pH of samples: 0.05 g/100mL (pH 4.25), 0.2 g/100mL (pH 3.66), and 0.4 g/100mL (pH 2.45), 0.8g/100mL (pH 2.24), Lake Water pH: 7.8.

Results and discussion. Results of this set of experiments are shown in Tables 56 and 57 and Figures 64 and 65.

Table 56 MIB Concentrations at various dosages of phosphorus pentoxide

Time (days)	Phosphorous pentoxide Dose/Concentration (ng/L)			
	0.05 g/100 mL	0.2 g/100 mL	0.4 g/ 100 mL	0.8 g/100 mL
0	104	104	104	104
1	3	2	2	3
2	1	1	1	2
3	1	1	0.6	0.4
4	0.6	0.5	0.3	0.3
5	0.2	0.6	1	1

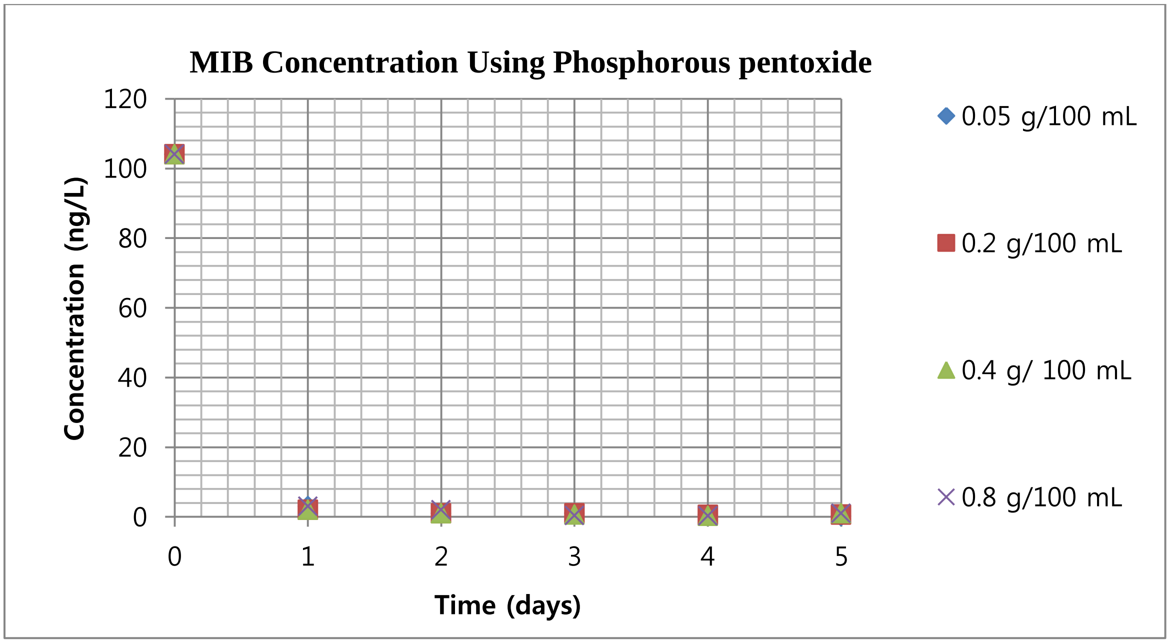


Figure 64 MIB Concentrations at different dosages of phosphorous pentoxide

2-M-2-B

Table 57 2-M-2-B Area at various dosages of phosphorous pentoxide

Time (days)	Phosphorous pentoxide Dose/Area			
	0.05 g/100 mL	0.2 g/100 mL	0.4 g/ 100 mL	0.8 g/100 mL
0	179368	179368	179368	179368
1	760097	843087	769000	426246
2	327007	287363	297123	141340
3	264210	154356	86435	78467
4	24382	47554	51284	49853
5	27558	22322	20867	26000

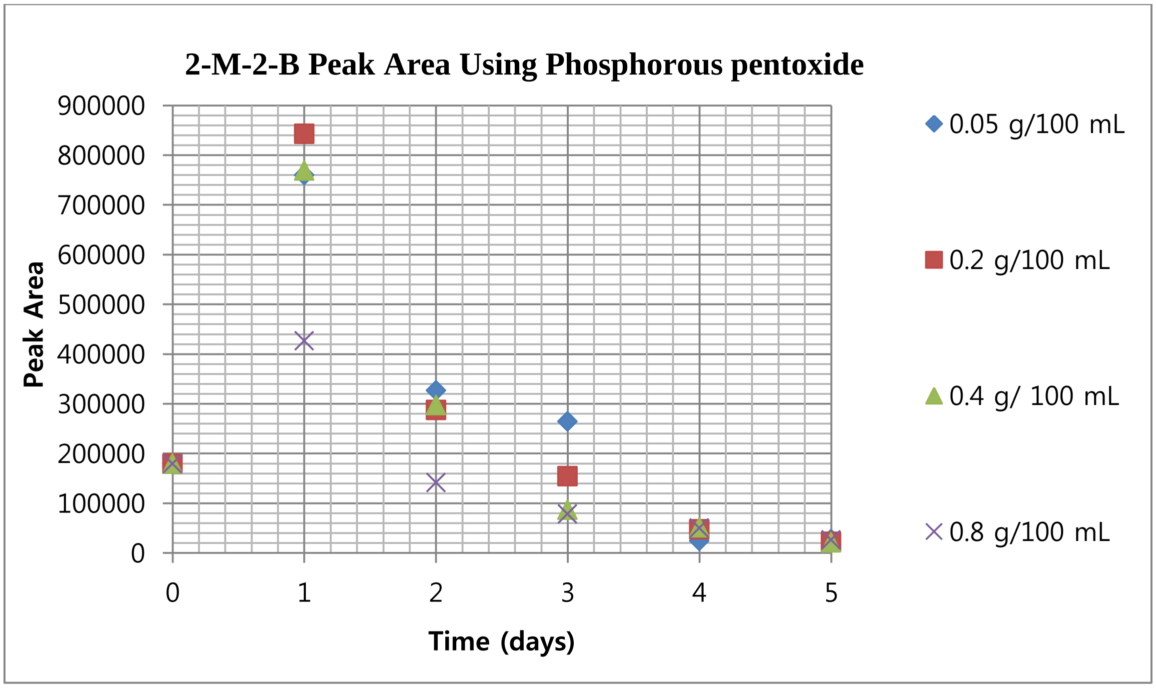


Figure 65 2-M-2-B Area at different dosages of phosphorous pentoxide

MIB is removed almost completely after 1 days’ reaction time by all different dosages (0.05-0.8g phosphorous pentoxide/100mL). The pH of samples were measured 0.05g phosphorous pentoxide/100mL (pH 4.25), 0.2 g/100mL (pH 3.66), 0.4 g/100mL (pH 2.45), and 0.8g/100mL

Although MIB was removed almost 100%, the resulting pH values of samples are too low for drinking water. This experimental result matches with the previous pH experiment results. It is an obvious indication of MIB dehydration.

The 2-M-2-B peak area increased 5 times after 1 day reaction time, the, decreased below 9 times from the initial area. This shows that 2-M-2-B was produced immediately by dehydration of MIB and, then, disappeared when the dehydration process was completed. This indicates that 2-M-2-B is an MIB byproduct, but that is also itself easily changed or decomposed to other compounds.

Overall, phosphorous pentoxide removes MIB by lowering pH.

4.5.3 Conclusions

Table 58 summarized the results of the experiments using different chemicals to remove geosmin and MIB.

Table 58 Summary of different chemical experiments

Product	Dosage	Sample conditions	Result
Cupric Sulfate	1 g/L - 9 g/L geosmin water	Geosmin Concentration: 125 ng/L, MIB Concentration: 118 ng/L, pH of sample: 0.1 g/100mL (pH 6.85), 0.3 g/100mL (pH 6.44), 0.6 g/100mL (6.18), 0.9g/100mL (6.03), Lake Spavinaw water, Reaction time: 5days	Geosmin : 1 g/L (27 % removal), 3 g/L (40% removal), 6 g/ L (35% removal), 9g/1L (30% removal)
			MIB: 1 g/L (54 % removal), 3 g/L (72% removal), 6 g/ 1L (78% removal), 9g/L (78% removal)
Sodium Sulfate	5 g/1L to 8 g/L geosmin water	Geosmin Concentration: 101 ng/L, MIB Concentration: 104 ng/L, pH of samples: 0.02g/L (pH 7.6), 0.2 g/L(pH 7.6), 0.05 g/100mL (pH 7.6), 0.2 g/100mL (pH 7.4), 0.4 g/100mL (7.3), 0.8g/100mL (7.2), Lake Spavinaw water, Reaction time: 5 days	Geosmin : 0.02 g/L (45 % removal) 0.2 g/L (48 % removal) 0.5 g/L (78% removal), 2 g/100L (80% removal), 4 g/ L (81% removal), 8 g/L (80% removal)
			MIB: 0.02 g/L (38 % removal) 0.2 g/L (40% removal) 0.5 g/L (50 % removal), 2 g/L (76% removal), 4 g/ L (75% removal), 8 g/L (70% removal)
Magnesium Sulfate	0.2g/L	Geosmin Concentration: 194 ng/L, MIB Concentration:201 ng/L, pH of samples:7.6, Lake Spavinaw water, Reaction time: 5 days	Geosmin : 13% removal, MIB : 26% removal
Phosphorous pentoxide	0.5 g/L to 8 g/L geosmin water	Geosmin Concentration: 101 ng/L, MIB Concentration: 104 ng/L, pH of samples: 0.05 g/100mL (pH 4.25), 0.2 g/100mL (pH 3.66), 0.4 g/100mL (pH 2.45), 0.8g/100mL (pH 2.24), Lake Spavinaw water, Reaction time: 5 days	Geosmin : 0.5 g/L (93% removal), 2 g/L (96% removal), 4 g/ L (99% removal), 8 g/L (99% removal)
			MIB: 0.5 g/L (99 % removal), 2 g/1L (99% removal), 4 g/ L (99% removal), 8 g/L (99% removal)

The results confirmed that several chemicals could successfully remove geosmin and MIB at reasonable dosages. The experiments showed two distinctive removal processes.

In the geosmin removal experiment, chemicals except magnesium sulfate reduced geosmin by approximately 20% to 99% after 5 days' reaction time. Phosphorous pentoxide displayed the highest removal efficiency, but reduced pH to 4.0r or lower. This would not be acceptable for potable water treatment. Cupric sulfate has 35 % removal and sodium sulfate has 81 % removal at maximum dosages. These removals indicate that these chemicals in low dosage could be useful for removal of geosmin.

According to the MIB removal results, cupric sulfate provided the highest removal at 78% among three chemicals except phosphorous pentoxide. The improvement in reducing MIB with cupric sulfate indicates a possible usage for potable water. Additionally, sodium sulfate is effective at 75 % removal.

However, a concern of this experiment was the high concentration of chemical dosages for potable water use. Further work need to optimize the dosage of chemicals in water treatment systems. The optimization of dosages will be discussed in the conclusions.

CHAPTER V

Conclusions

5.1 Summary of experiments

The problems of off-flavor caused by GSM and MIB persist because the compounds are ineffectively removed by common water treatment systems. The purpose of this dissertation was therefore to investigate alternative treatment technologies for the removal of GSM and MIB from drinking water.. The main approach adopted in this work was the use of EarthTec® and alternative chemicals, and to vary treatment conditions to optimize the removal of geosmin and MIB. This dissertation can be divided into 5 sections.

1. Experiments using EarthTec® and other algaecides using varying chemical dosages.
2. Evaluation of the effects of pH on geosmin and MIB by using Earth Tec® and other acidic treatment chemicals.
3. Evaluation of biodegradation processes of geosmin and MIB in deionized and Lake water.
4. Evaluation of other conditions affecting removal, such as temperature and pipeline turbulence on geosmin and MIB concentrations.
5. Evaluation of other potential chemicals for removal of geosmin and MIB.

Based on these findings, the optimization of chemicals for geosmin and MIB removal were developed.

5.2 Investigate the optimum chemical for removal of MIB and GSM

A lab scale batch reactor was developed to evaluate removal of geosmin and MIB. More than ten chemicals were evaluated to improve geosmin and MIB removal. It became obvious that removal of geosmin and MIB by EarthTec® was insufficient using recommended dosages in any conditions, but that the low pH provided at very high dosages dehydrated geosmin into argosmin and MIB into 2-M-2-B. However, other chemicals experimented (sodium sulfate, copper sulfate, calcium chloride dehydrate) were found to remove large amounts of geosmin and MIB without changing the pH of the water.

For sodium sulfate, the optimum dosage was found to be 0.15g/100mL, which removed both geosmin and MIB in the range of 70-80%. This improvement was clearly observed at pH 6.8.

For copper sulfate, 0.5g/100mL was the most suitable dosage, though it removed MIB up to only 70% and geosmin up to 40%. This removal may not be sufficient for all applications, so more experiments should be accomplished to prove effectiveness of copper sulfate.

For calcium chloride dehydrate, a high dosage of calcium chloride (2.5g/100mL) could remove about 50% of geosmin and 40% of MIB in Lake water. It is not an efficient method for a removal application of geosmin and MIB because it accompanied with high dosages and inefficient removal rates.

The chemicals sodium sulfate, copper sulfate, calcium chloride dehydrate, which were evaluated, were all used in high dosages. Results are plotted in Figure 66 below.

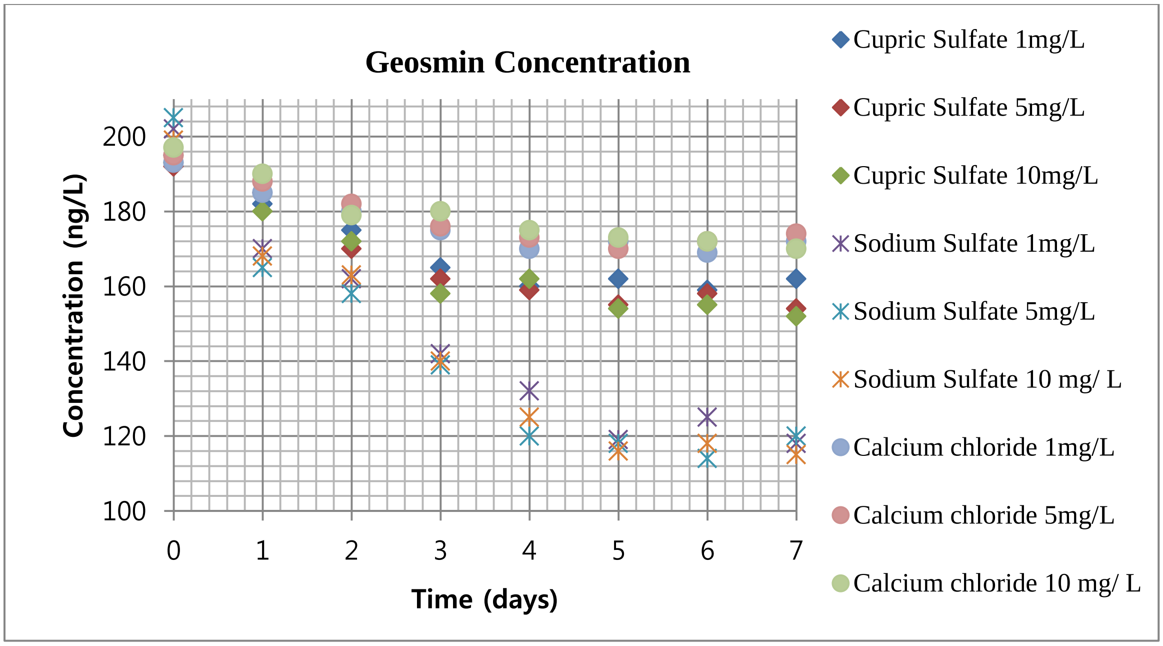


Figure 66 Geosmin concentrations at different dosages of three chemicals

Three different chemicals displayed different removal efficiencies. For cupric sulfate, geosmin concentrations were lowered from 195 to 154 ng/L (approximately 20%). Sodium sulfate produced approximately 40 to 45% removal of geosmin (200 to 115 ng/L) and calcium chloride provided only 10 to 12% geosmin removal (195-170 ng/L). Among these chemicals, sodium sulfate was determined to be the most favorable chemical for geosmin removal with approximately 40% removal efficiency.

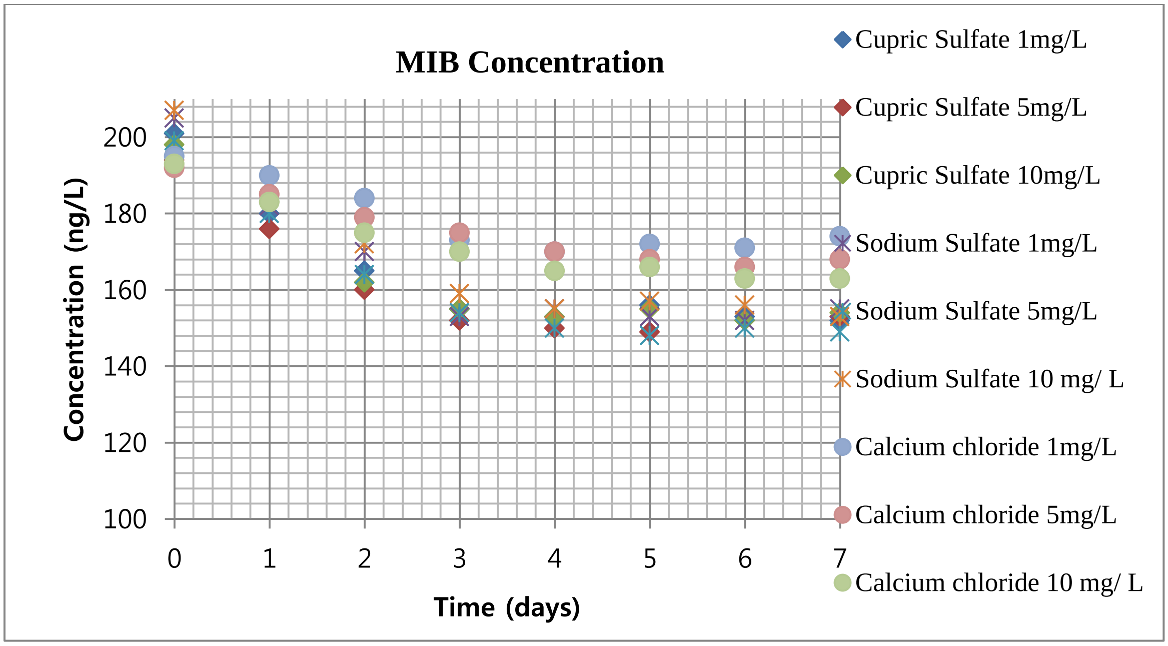


Figure 67 MIB concentrations at different dosages of three chemicals

For MIB removal, sodium sulfate and cupric sulfate exhibited 20 to 27% removal in three different dosages. Calcium chloride only removed less than 15%, which is close to the SPME error range. The results indicate that sodium sulfate and cupric sulfate help in removing MIB, but removal ranges are only approximately 25%.

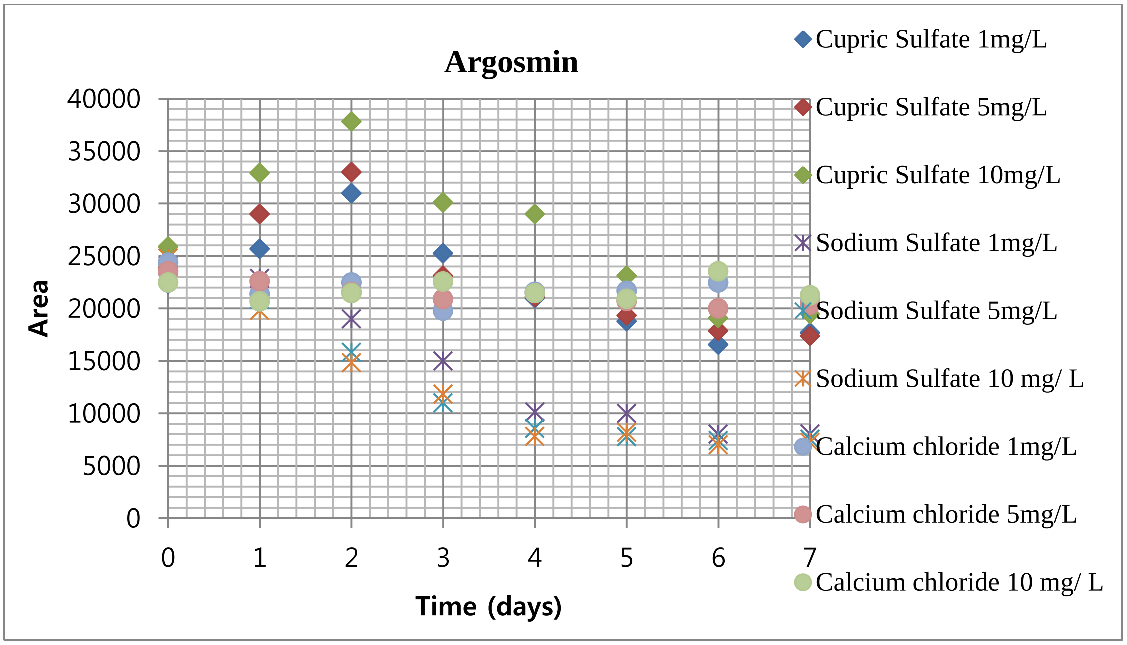


Figure 68 Argosmin Areas at different dosages of three chemicals

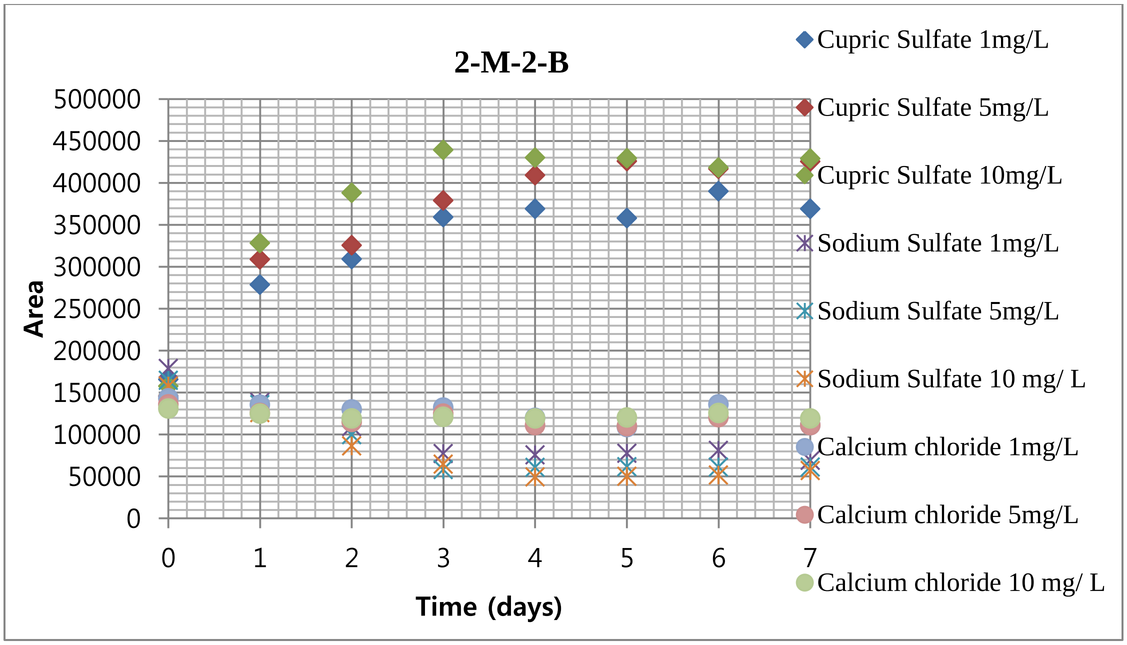


Figure 69 2-M-2-Bs at different dosages of three chemicals

The production of argosmin and 2-M-2-B was investigated to determine what reactions occurred during addition of chemicals. The results are indicated below.

Cupric sulfate

Concentrations of argosmin increased after two days of reaction time, and then, decreased to below the original concentration. 2-M-2-B showed an increase for three days and maintained the concentration on day four. These results are similar to pH experimental results while amounts of argosmin were much smaller. This information provides more concrete evidence that dehydration has occurred.

Sodium sulfate

Both argosmin and 2-M-2-B continuously decreased during a 7-day period. A decrease in these compounds is a common phenomenon for drying reactions. In addition, sodium sulfate is a good drying agent for geosmin and MIB removal.

Calcium chloride

Concentrations of argosmin and 2-M-2-B decreased in a similar manner as sodium sulfate reactions, while calcium chloride decreased less than 25%. It can be concluded that both calcium chloride and sodium sulfate as drying agents result in the same type of drying reactions. Therefore, to conclude overall chemical s removal efficiencies, sodium sulfate is be the best choice for both geosmin and MIB removal of the chemicals tested. However, sodium sulfate only provided 45% removal for geosmin and 25% removal for MIB using an initial concentration of 200 ng/L of geosmin and MIB. These removal efficiencies would be a helpful adjunct, but would not be useful as the main removal technology.

5.3 Development of the effective removal of geosmin and MIB

Five commercially used algaecides and five chemicals were evaluated for their efficiency at geosmin and MIB removal. It became apparent that EarthTec® at the recommended dosage was did not have a significant impact on geosmin and MIB removal. The recommended dosages of five algaecides were found to have little effect on the geosmin reduction. EarthTec® was found to be effective when doses reduced the pH to 4.0 or below; low pH in this range is unacceptable for potable water . The final experiments used other potential chemicals to determine if effective removal of geosmin and MIB could be achieved without unacceptable lowering of pH. Cupric sulfate removed 20% of geosmin and 25% of MIB; calcium chloride removed 12 % of geosmin and 15 % of MIB; and sodium sulfate removed 45% of geosmin and 25% of MIB .

In conclusion, sodium sulfate was demonstrated to be a possible treatment method for the removal of geosmin and MIB from potable waters. However, sodium sulfate provided only 45% removal of geosmin, a reduction which is unlikely to be sufficient for treatment. Further research is required to find the optimal dosage for water treatment. Additionally, sulfate can provide a bitter taste in water if it exceeds a concentration of 250 mg/l. This may make it unacceptable to constituents, and it is not recommended for use for infants. The maximum level of sulfate suggested by the World Health Organization (WHO) in the Guidelines for Drinking-water Quality, set up in Geneva, 1993, is 500 mg/l. The EU standard is more recent (1998), more complete and stricter than the WHO standards, suggesting a maximum of 250 mg/l of sulfate in water intended for human consumption. All these factors require further investigation and would suggest that use of sodium sulfate should not be considered for continuous use, but might be useful as an aid when high geosmin concentrations are detected. This study clearly demonstrated the challenges of working with compounds such as geosmin and MIB using algaecides and chemicals.

5.4 Future work

MIB and geosmin are difficult to remove with conventional water treatment processes and common oxidants. Existing treatment technologies such as activated carbon, oxidation, and biofiltration have several drawbacks, such as cost or undesirable products. The addition of algaecide technology has the potential for cost effectiveness and easy application. This dissertation found that some chemicals can remove geosmin and MIB with efficacies that might be acceptable in water treatment plants. However, several concerns were found which require further study. Potential areas of future work include:

Increase the reactor volume. Bench tests may produce different results from larger-scale tests.

Dose-Response. More experiments to cover a wider range of application quantities and repeated applications could be helpful.

Concentration Issues: high concentrations of geosmin and MIB might provide different results (All experiments were only conducted in 100-200ng/L of geosmin and MIB. High concentrations of geosmin and MIB might result in high or lower removal).

Scale Issues. Evaluate the cost-effectiveness of different points of application of chemicals or of treatment. With supply reservoirs, treatment options include full scale, spot or local treatment. The information gained in the project will directly help the two water treatment utilities in Tulsa and Oklahoma City and potentially other utilities in the U.S. While the small-scale algaecide test did provide insights into methods of algaecide application and potential algae response to treatment, the determination of the efficacy of different algaecide treatments were unclear at the dosages applied. Therefore, extended experiments are recommended and more research is required to determine optimal conditions for a chosen algaecide.

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