DETECTION, ANALYSIS, AND PHOTOCATALYTIC DESTRUCTION OF THE FRESHWATER TAINT COMPOUND GEOSMIN

EDMUND BELLU

A thesis submitted in partial fulfilment of the requirements of The Robert Gordon University for the degree of Doctor of Philosophy.

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By Edmund Bellu for the degree of Doctor of Philosophy

Abstract

A significant issue affecting the aquaculture and water industries is the presence of off-flavour compounds in water, which cause problems by imparting an undesirable earthy/musty flavour and smell to water and fish. Two predominant off-flavour compounds are geosmin (GSM) and 2-methylisoborneol (MIB). These compounds are produced by several varieties of cyanobacteria and actinomycetes as metabolic products and can be detected by humans at concentrations as low as $0.015 \ \mu g \ L^{-1}$.

Removal of GSM and MIB from potable waters has proven to be inefficient using standard water treatment such as filtration, coagulation, flocculation, sedimentation and chlorination. Activated carbon and membrane processes can physically remove GSM and MIB, but do not destroy them, and ozone treatment can be expensive. Titanium dioxide (TiO_2) photocatalysis has recently been demonstrated to rapidly degrade GSM and MIB. When the semiconductor catalyst is illuminated with ultraviolet light simultaneous oxidation and reduction reactions occur. Pollutants are broken down into mineral acids, carbon dioxide and water.

This study was conducted to determine if TiO_2 photocatalysis, using a pelleted form of TiO_2 called Hombikat K01/C, was a suitable method for the treatment of potable water. Additionally an analytical method was developed to rapidily analyse the large number of samples generated.

Two reactors, a bench scale batch reactor and pilot scale flow reactor, were developed and used to evaluate the efficacy of Hombikat K01/C TiO_2 photocatalysis in degrading GSM. The batch reactor, containing Hombikat K01/C, was used to investigate the effect of numerous experimental variables

on the photocatalysis of GSM, including initial substrate concentration, pH, light intensity, aeration rate, the presence of additional reactants, and catalysis conducted in deuterated water.

GSM was rapidly degraded using the TiO_2 batch reactor, with the rate of GSM degradation most affected by light intensity and additional reactants, though pH also had a notable effect. A kinetic isotope effect of 1.61 was observed for the destruction of GSM using Hombikat K01/C TiO_2. The flow reactor was also found to efficiently degrade GSM in raw waters. The rate of GSM destruction was found to be significantly lowered by UV shielding of the catalyst, caused by constituents of raw the water used, and the presence of additional reactants.

The pilot scale flow reactor was also successfully evaluated in Denmark using gesomin contaminated water from an eel farm.

Acknowledgements

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Public Output

Poster Presentations

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Bellu, E., Robertson, P. K. J., and Lawton, L. "The destruction of taint compounds in drinking water by titanium dioxide photocatalysis". Presented at *SURCAT 2005 Conference,* annual conference of the Royal Society of Chemistry surface reactivity and catalysis group, **2005**.

Oral Presentations

Bellu, E. "How to clean water with sweeties and light". Presented at *SETPOINT* annual public lecture series, **2005**.

Bellu, E. "How to clean water with sweeties and light". Presented at *SETPOINT* annual Chemistry at Work series, **2006**.

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AOP	-	Advanced oxidation process
CB	-	Conductance band
CLS	-	Closed-loop stripping
D_{50}	-	50 % pollutant destruction
DAF	-	Dissolved air flotation
DCE	-	Dichloroethane
Eg	-	Band gap energy
ELISA	-	Enzyme-linked immunosorbent assay
FPA	-	Flavour profile analysis
GAC	-	Granular activated carbon
GC-MS	-	Gas chromatography-mass spectrometry
GC-MS-SNIFF	-	Gas chromatography-mass spectrometry-sniffing system
GSM	-	Geosmin
IC_{50}	-	50 % inhibitory concentration
IC	-	Inorganic carbon
MBS	-	Methylbenzimidazoyl sulfide
MIB	-	2-methylisoborneol
MPS	-	Methyl phenyl sulfide
MWCO	-	Molecular weight cut-off
NHE	-	Normal hydrogen electrode
NOM	-	Natural organic matter
PAC	-	Powdered activated carbon
PDMS	-	Polydimethylsiloxane
pH_{zpc}	-	Zero point of charge
RGF	-	Rapid gravity filtration
SIM	-	Selective ion monitoring
SPE	-	Solid phase extraction
SPME	-	Solid phase microextraction
TC	-	Total Carbon
TOC	-	Total organic carbon
UNEP	-	United Nations Environment Programme
VB	-	Valence band
WHO	-	World Health Organisation

Abbreviations

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SIM	-	Selective ion monitoring
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CHAPTER 1 – INTRODUCTION

1.1 OVERVIEW

Potable water is an essential daily requirement for humans, for which there is no substitute. Unlike other important issues facing humanity, which may have multiple solutions, we cannot easily produce more freshwater to meet our various needs. Freshwater accounts for a small proportion (2.5 %) of all water on the planet and only 0.5 % of this is accessible groundwater or surface water (Bernstein, 2002). Enough freshwater exists on the planet for the world's population, however there are a number of ever increasing pressures that are placing rising demands on this finite resource. The three major drivers affecting the increase in the use of freshwater are: (1) population growth; (2) changing standards of living; and (3) expansion of irrigated agriculture (Gleick, 2000). Between 1900 and 2000 the world population has grown from 1,600 million to over 6,000 million people. Land irrigation has increased from 50 million hectares to 267 million hectares. The effect of increased land irrigation is clearly demonstrated by the dramatic decrease of Lake Chad and the Aral Sea, which have had water diverted from them for agricultural use. Since the 1960s Lake Chad has reduced to one twentieth of it's former of size and the Aral sea, which was once the forth largest inland water body in the world, has shrunk by over sixty percent (Crighton *et al.*, 2003). These pressures and a combination of other factors (security of supply, increased usage by industry, and demographic changes) have led to a six-fold increase in freshwater withdrawals (Figure 1-1) (Gleick, 2000). This strain on a finite resource is likely to have a significant effect worldwide with a predicted increase in the number of countries suffering from water stress by 2025 (Figure 1-2) (Gardner-Outlaw *et al.*, 1997). Finally the potential long term effect of climate change on world wide precipitation and subsequent water availability could be severe. Some models predict that rainfall will be significantly more torrential, which may result in less water being absorbed by soil, in turn altering ground and water supplies (Bryden *et al.*, 2006). While some areas, i.e. high latitudes of the northern hemisphere, are likely to have increased precipitation, decreases are predicted for southern Europe, the Middle East, central Asia and Africa. Arid and

semi-arid areas will be particularly vulnerable to the reduced availability of water.
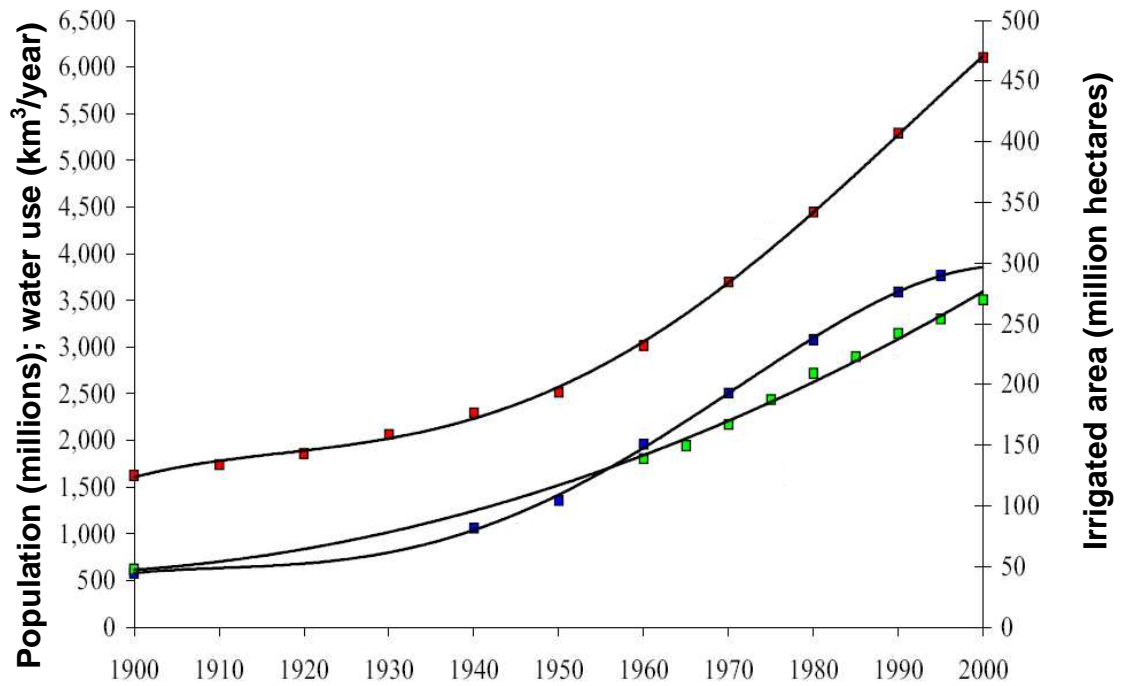
Figure 1-1. World population (■), water withdrawal (■) and irrigated area (■) increases from 1900 to 2000. Reproduced from (Gleick, 2000) with permission.
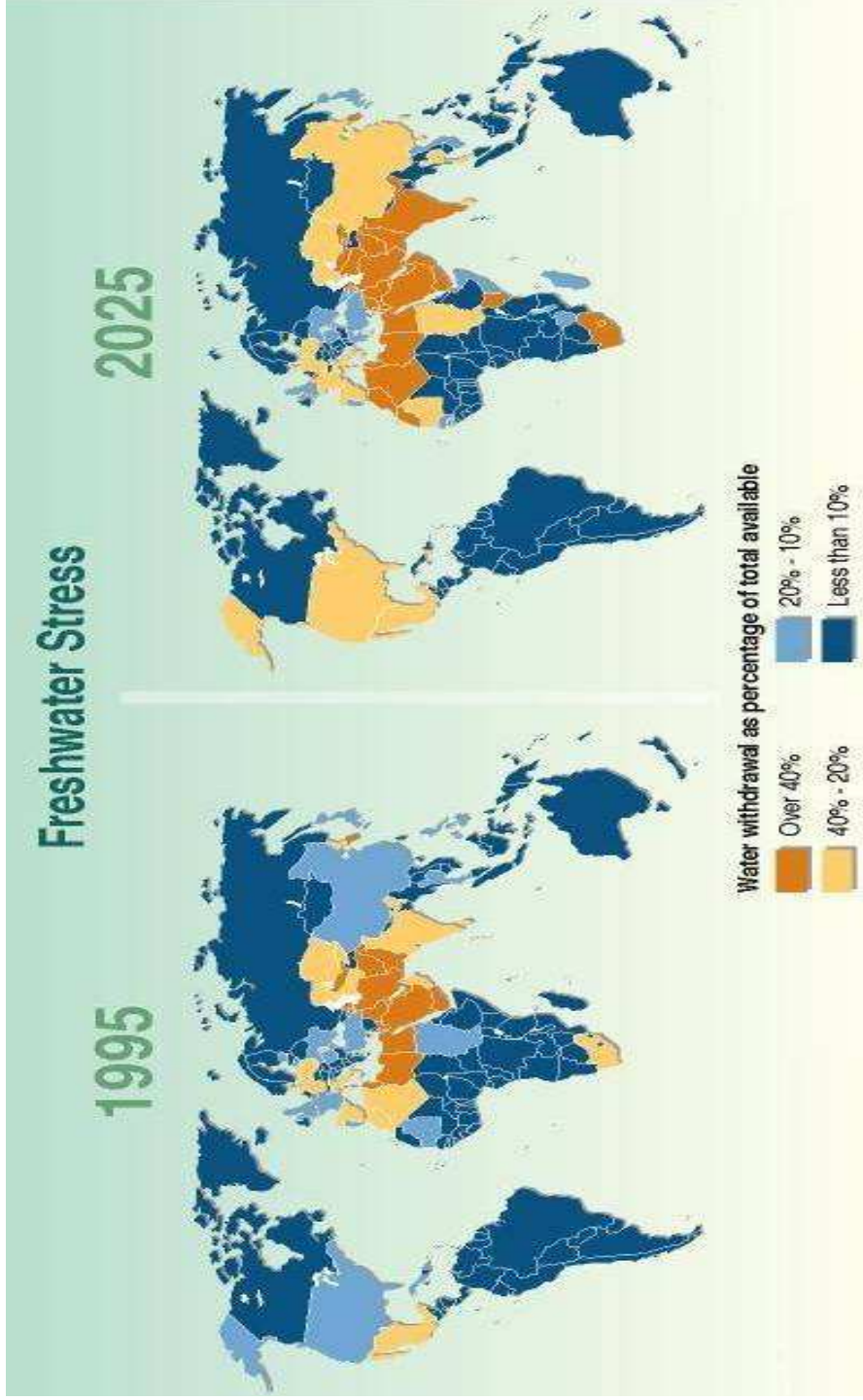
Figure 1-2. Current and predicted freshwater withdrawal as a percentage of total available. By 2025 the number of countries increasing their water withdrawal will have risen significantly, including the United States of America, China and India. Reproduced with permission from the United Nations Environment Programme (UNEP).

1.2 HISTORY OF WATER TREATMENT

The value of safe water has been recognised for millennia. Early Egyptian paintings from the 13th and 15th centuries B.C. depict sedimentation apparatus and wick siphons. Hippocrates invented the "Hippocrates Sleeve", a cloth bag used to filter rain water, in the 5th century B.C. (Baker, 1948). Roman engineers went to great lengths to provide water suitable in both quality and quantity for major cities, yet it was not until 1721 that the first London company began pumping water (Kranzberg et al., 1967). Throughout the 19th century increased volumes of water were pumped from the Thames and Lea rivers, and as London grew, these sources became increasingly polluted. Around the same time in the United States of America (USA), a cholera epidemic in Philadelphia during 1793 instigated the construction of the first major water system. At the beginning of the 1800's, systems using charcoal and sand filtration came into use in Europe and Stein installed one of the first slow sand filters in America at Richmond, Virginia, in 1832 (Kranzberg et al., 1967). The major aim to remove sediment and discoloration. But sand filters did not remove all of the pathogenic bacteria, whose existence were not known at the time, and by the mid 1800's Britain was affected by major epidemics of cholera and typhoid. John Snow and William Bud proved the role water played in the transmission of these two diseases (AWWA, 1996). Their discoveries resulted in improved water treatment, and in 1859 it became a legal requirement for river-derived water in London to be filtered. This practice then proliferated across Europe. The effectiveness of this treatment in reducing deaths from typhoid in London can be exemplified by comparing annual mortality rates between London and Minneapolis. In USA the mortality rate from typhoid of twenty or more people per hundred thousand of population was considered normal, the rate in Minneapolis was 58.7; in London the rate was only 3.3 per hundred thousand (AWWA, 1996). However despite advances in water treatment many people have no access to adequately treated drinking water. The World Health Organisation (WHO) estimate over 1 billion people globally lack access to safe drinking-water supplies, while 2.6 billion lack adequate sanitation. Diseases related to unsafe water, sanitation and hygiene result in an estimated 1.7 million deaths every year (WHO, 2002).

In developed countries water treatment and sanitation has removed the problem of diseases such as typhoid and cholera. These diseases however, among other water related issues, remain a serious problem in developing countries. Modern water treatment processes control the spread of water related disease, remove numerous contaminants, such as organic chemicals and heavy metals, producing safe water. However the presence of pharmaceutical residues, disinfection by-products, and the possibility of pathogens, such as *cryptosporidium*, which are resistant to common water treatment processes, necessitates the investigation of new treatment technologies.

The single largest consumer issue affecting drinking water quality in developed countries is that of off-flavour. Off-flavour is caused by compounds in water that are known for their undesirable taste and odour characteristics. A survey conducted of more than 800 water utilities in the USA and Canada found that 16 % of utilities experience serious taste and odour problems, spending approximately 4.5 % of there total budget on taste and odour control (Westerhoff *et al.*, 2003).

1.3 CYANOBACTERIA AND ACTINOMYCETES

Two groups of microbes have been implicated as significant contributors to the problem of off-flavour episodes in freshwater. Cyanobacteria have been reported to cause off-flavour in freshwater (Slater *et al.*, 1983; Naes *et al.*, 1988; Hayes *et al.*, 1989; van Breemen *et al.*, 1992; Persson, 1996; Izaguirre *et al.*, 1999) and aquaculture (Persson, 1978; Lovell, 1983; van der Ploeg *et al.*, 1992; Schrader *et al.*, 2003; Zimba *et al.*, 2003). Actinomycetes are associated with off-flavour in freshwater (Romano *et al.*, 1963; Persson, 1980; Lovell, 1983; Wnorowski, 1992; Zaitlin *et al.*, 2006).

1.3.1 Cyanobacteria

Cyanobacteria comprise a large and morphologically heterogeneous group of phototrophic bacteria. Existing over a wide range of environments they were first observed and recognised over 250 years ago by the botanist Linné (WHO, 1999). Cyanobacteria represent one of the major phyla within the bacteria domain and cyanobacteria fossils found within Archaean rocks of western Australia date back to 3.5 billion years ago (Madigan *et al.*, 2003). The evolution of oxygenic photosynthesis in cyanobacteria is believed to have contributed to the conversion of the Earth's primitive atmosphere, increasing the concentration of free oxygen from 1 % to the current 21 % (Svrcek *et al.*, 2004). It is also believed that symbiosis between early cyanobacteria and other microbes led to the evolution of the photosynthetic organelles in plants called chloroplasts. Cyanobacteria have only one form of chlorophyll, chlorophyll *a*, and metabolise energy by oxygenic photosynthesis associated with photosystems I and II (Madigan *et al.*, 2003). All cyanobacteria also have characteristic biliprotein pigments, phycobilins, which function as accessory pigments in photosynthesis. One class of phycobilins, phycocyanins, are blue, and together with the green chlorophyll *a* are responsible for the blue-green colour of the bacteria. This explains the common usage of blue-green algae to describe cyanobacteria. However some cyanobacteria produce a red phycobilin, phycoerythrin, resulting in a red or brown colour. Due to similar features that cyanobacteria share with green algae and bacteria, confusion has arisen concerning their taxonomy (WHO, 1999). Algae are photosynthetic and may share similar morphologies to cyanobacteria, but cyanobacteria do not posses nuclei and their cell walls are composed of peptidoglycan and lipopolysaccaride layers as opposed to cellulose (Madigan *et al.*, 2003).

Cyanobacteria are present in a diverse range of environments worldwide, from Antarctic coastal waters to volcanic hot springs. Cyanobacteria are also found in waters with a great range of salinity and temperature, though they are most abundant in water with a neutral or slightly alkaline pH (Svrcek *et al.*, 2004). Cyanobacteria are present in limited numbers in most surface waters at all times, but their presence can cause problems when they form blooms, a dense

accumulation of cyanobacterial cells at the water surface body (Svrcek *et al.*, 2004). Favourable conditions for cyanobacterial growth that lead to blooms are a combination of a number of factors: slow flowing water and little or no wind, resulting in stratified water bodies; warm water temperature (15 to 30 ℃); neutral to alkaline pH (pH 6 to 9); and eutrophic water conditions, i.e. the increased concentration of the nutrients nitrogen and phosphorus (Carmichael, 1994). Certain factors have caused the increase in the occurrence of blooms. These include increased eutrophication of water bodies caused by industrial and agricultural run-off, and increasing temperature caused by climate change (Chorus, 1992; Oskam *et al.*, 1996; Weyhenmeyer, 2001). Several species of cyanobacteria are known to produce off-flavour compounds, two significant off-flavours are geosmin (GSM) and 2-methylisoborneol (MIB). Where these species form blooms they cause considerable problems for water supply utilities and aquaculturists.

1.3.2 Actinomycetes

In natural environments actinomycetes are typically found as soil bacteria or plant pathogenic bacteria, but recent studies indicate that actinomycetes can be abundant microorganisms in freshwater, constituting greater than 60 % of the bacterial community in some cases (Glöckner *et al.*, 2000). Actinomycetes constitute a major group of rod-shaped and filamentous bacteria, including *Streptomyces* and *Actinomyces*. Although these bacteria are predominantly known for producing antibiotics and cytotoxic substances they also produce the off-flavour compounds GSM and MIB (Wood *et al.*, 1985; 2001). Though ubiquitous in aquatic environments their impact on the release of GSM and MIB is unknown and proven cases of off-flavour attributable to actinomycetes are rare (Wnorowski, 1992; Zaitlin *et al.*, 2006). The location of actinomycetes within water systems is of particular interest as they have the ability to colonise areas that greatly magnify off-flavour episodes in water (Zaitlin *et al.*, 2006). Examples of these areas are inlet pipes for raw water collection and indoor aquatic environments such as a closed re-circulatory fish farm. *Streptomyces* that produce GSM have been reported to grow in reservoir bank debris with

relatively high organic matter (Wood *et al.*, 1985). The GSM produced by these bacteria may be washed into the reservoir. Romano *et al.* (1963) reported large numbers of actinomycetes able to produce GSM isolated from mud sampled from the bottom of a number of lakes and rivers. Wood and co-workers (2001) also reported actinomycetes present in reservoir sediments and muds, but at much lower concentrations. In general actinomycetes isolated from reservoir bottom mud have not been linked to off-flavour occurrence, but they may produce GSM or MIB in culture (Yagi *et al.*, 1983). However, benthic actinomycetes, if present in significant numbers and capable of producing GSM and/or MIB in there usual environment, would add considerably to any potential off-flavour episodes in reservoirs.

1.4 OFF-FLAVOUR COMPOUNDS

Adverse off-flavour has been reported in scientific and technical literature since the mid-nineteenth century, with the first report probably that of Horsford and Jackson in 1855. This report was on the strange cucumber odour of the water that supplied the City of Boston in the autumn of 1854 (Persson, 1995). The first reference to cyanobacteria as a source of off-flavours in drinking water supplies was a report by Nicols *et al.* in 1876 (Persson, 1996). The primary source of natural off-flavour in water is caused by certain types of cyanobacteria, and to a lesser extent actinomycetes. Cyanobacteria and actinomycetes, both prokaryotic microorganisms, are believed to produce off-flavour compounds as metabolic by-products, subsequently released into the water in which they are growing. Two major off-flavour compounds are geosmin (GSM) and 2-methylisoborneol (MIB). Cyanobacteria (Persson, 1996; Izaguirre *et al.*, 2004) and actinomycetes (Klausen *et al.*, 2005; Gonçalves *et al.*, 2006) are known to produce both of these compounds. Synthetic off-flavour is also a growing problem, caused by release of chemicals from a number of modern materials, such as plastic pipes, organic coatings, adhesives, and membranes (Rigal *et al.*, 1999; Tomboulian *et al.*, 2004; Wiesenthal *et al.*, 2004).

1.4.1 Geosmin

Geosmin (GSM) (Figure 1-3) is an alicyclic alcohol. It is a semi-volatile compound with a molecular weight of 182 and a boiling point of 270 ℃ (Budavari, 2001). The Henry's Law constant, the ease with which the compound can be transferred from the aqueous phase to the gaseous phase, is 6.66 x 10^{-5} atm m^3 mol^{-1}. At room temperature it exists as a oil and is hydrophobic (aqueous solubility of 150.2 mg L^{-1}) (Pirbazari *et al.*, 1992). GSM has been described as having a earthy/musty/mouldy odour (Suffet *et al.*, 1999) and is produced by a number of cyanobacteria and actinomycetes. GSM is produced by certain species of *Oscillatoriai* (Persson, 1982; Matsumoto *et al.*, 1988), *Anabaena* (Yagi *et al.*, 1983) and actinomycetes (Klausen *et al.*, 2005).

Reported human threshold for detection of GSM in water ranges over 3 or 4 orders of magnitude. This variation is due to a number of interlinked factors including experimental procedure and criterion used to define threshold (Howgate, 2004). Howgate (2004) suggest that a reasonable estimate of odour detection threshold for GSM in water, based on the values gathered from published sources, would be 0.015 μg L^{-1}.
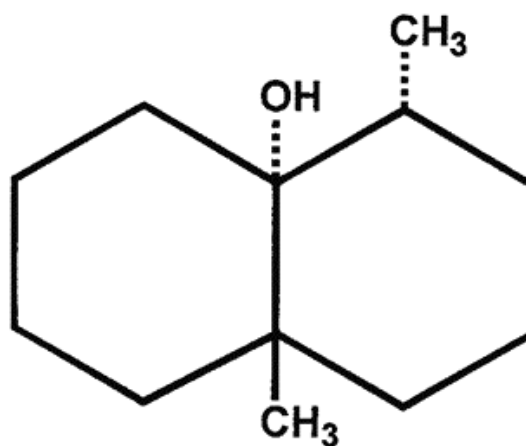
Figure 1-3. Structure of geosmin (GSM).

1.4.2 2-methylisoborneol

2-methylisoborneol (MIB) (Figure 1-4) is a semi-volatile terpene, with a molecular weight of 168. It is less volatile than GSM, its Henry's law constant is 5.76×10^{-5} atm m^3 mol^{-1} and a boiling point of 196.7 ℃ (Pirbazari *et al.*, 1992). MIB exists as a white crystalline solid at room temperature and is also hydrophobic, aqueous solubility of 194.5 mg L^{-1} (Pirbazari *et al.*, 1992). MIB resides in the same odour group of off-flavour compounds as GSM and as such is described with similar terminology as GSM. MIB is also produced by the cyanobacterial species of *Oscillatoriai* (Persson, 1982; Matsumoto *et al.*, 1988) and by *Phormidium* (Negoro *et al.*, 1988). Actinomycetes have also been shown to produce MIB (Klausen *et al.*, 2005). However while certain species of cyanobacteria and actinomycetes produce both GSM and MIB, they tend to produce either GSM or MIB (Persson, 1996).

Howgate (2004) reports that a reasonable estimate of odour detection threshold for MIB in water would be 0.035 µg L^{-1}, approximately double that of GSM.
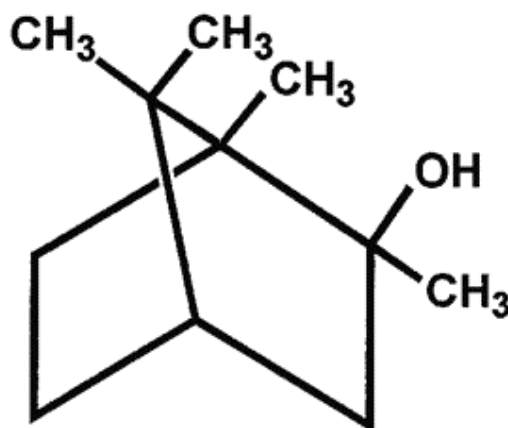
Figure 1-4. Structure of 2-methylisoborneol (MIB).

1.4.3 Toxicology of geosmin and 2-methylisoborneol

Studies of the toxicological properties of GSM and MIB are limited. One study demonstrated that neither GSM nor MIB induced a mutagenic response in the *Salmonella typhimurium* assay up to concentrations reaching cytotoxic levels, approximately six orders of magnitude above odour threshold concentration (Dionigi *et al.*, 1993). Another study using sea urchin embryos estimated IC_{50} (50 % inhibitory concentration) for GSM and MIB as 17 and 69 mg L^{-1} respectively (Nakajima *et al.*, 1996). These concentrations are in the same upper range as those tested by (Dionigi *et al.*, 1993). In both these studies the concentrations of GSM used were far greater than those found naturally in aquatic environments (typically low ng L^{-1}). GSM and MIB in water are degraded by microbial action (Izaguirre, 1992). This degradation is slow with GSM being biodegraded in approximately 3 days (Izaguirre *et al.*, 1988), with MIB appearing more resistant with a degradation time ranging from 5 to 14 days (Izaguirre *et al.*, 1988).

GSM has also been considered as an indicator for other compounds produced by cyanobacteria that may be toxic, such as microcystin (Yagi *et al.*, 1988; Blaha *et al.*, 2004). However, no correlation has been found between the production of GSM and cyanobacterial toxins (Blaha *et al.*, 2004). Current research would suggest that GSM and MIB are non-toxic, however consumers of drinking water believe there is a possible correlation between off-flavour and unsafe water (McGuire, 1995; Jardine *et al.*, 1999). Off-flavour therefore is an important issue for water supply utilities, as it can lead to decreased consumer confidence. Off-flavour in water, along with water colouration, is likely to be the first thing consumers would notice about the water they were drinking. Off-flavour in water is therefore used by the consumer as a judge of water quality, with the presence of an odour suggesting that the water is unsafe to drink, even though it meets guidelines for regulated constituents.

1.5 OCCURRENCE OF CYANOBACTERIA IN AQUATIC ENVIRONMENTS

Cyanobacteria occur in both saline and freshwater worldwide. Ideal conditions for growth such as warm water temperatures and an abundant supply of required nutrients will cause cyanobacteria to multiply and form blooms (Svrcek *et al.*, 2004). In temperate regions these conditions are most likely to occur in the summer months, but in warmer climates ideal growth conditions are extended, increasing the possibility of blooms occurring (Hoffmann, 1996). An increase in eutrophication of water bodies (Oskam *et al.*, 1996) and warming of parts of the planet due to climate change are creating conditions that are more ideal for cyanobacterial growth. Weyhenmeyer (2001) reported that warmer winters during the 1990s caused the early break up of ice covering lakes in Sweden, allowing cyanobacteria to begin growing earlier in the year, instead of only in the summer months. Lake Biwa, a source of water for 14 million people, in Japan is an example of increased cyanobacterial growth due to the effects of eutrophication (Figure 1-5). Lake Biwa is the largest lake (674 km^2) in Japan, consisting of a northern and southern basin. The southern basin has an average depth of 4 m and a volume of 200 million m^3, compared to the average depth of 43 m and a volume of 27.3 m^3 billion for the northern basin (Kajino *et al.*, 1995). Due to its smaller volume and reduced depth the southern basin is very susceptible to eutrophication and there have been many reports of severe episodes of off-flavour caused by GSM and MIB (Yagi *et al.*, 1983; Negoro *et al.*, 1988). Cyanobacteria prefer to grow in water bodies such as slow running rivers or almost static waters, such as reservoirs and lakes (Hayes *et al.*, 1989; Izaguirre, 1992; Seligman *et al.*, 1992; Perschbacher *et al.*, 1995). Cyanobacteria that grow on submerged rocks and sediments have also been reported to produce GSM and MIB. Cyanobacteria growing in these locations were closely associated with off-flavour episodes that occurred in Lake Kasumigaura, Japan (Sugiura *et al.*, 1998). Utkilen *et al.*, (1992) also reported that the benthic cyanobacteria, *Oscillatoria brevis*, produced GSM and suggested that GSM production may increase with depth of the cyanobacteria in the water column.

Figure 1-5. Cyanobacterial blooms in the southern basin of Lake Biwa. Photos courtesy of Kanko Ishikawa (Lake Biwa Environmental Research Institute, Japan).

As raw water required for drinking water is sourced from locations where cyanobacterial blooms occur it is necessary to control the occurrence of cyanobacterial blooms or in the cases where they have already formed action is required to treat the off-flavour compounds that have been released into the water.

1.5.1 Control and treatment of cyanobacterial blooms

A number of environmental factors are known to effect the growth of cyanobacteria including temperature, nutrient availability, and pH. As GSM and MIB are metabolic by-products their incidence increases as cyanobacterial growth increases. Limiting conditions that promote the growth of cyanobacteria prevents bloom formation in the natural environment. The primary cause of blooms in the natural environment is eutrophication (Persson, 1982, 1985; Oskam *et al.*, 1996; Bianchi *et al.*, 2000). Watershed protection, by limiting the input of nitrogen and phosphorus into water from industrial, domestic and farming sources, would be the ideal solution to limiting the occurrence of cyanobacterial blooms. Such a strategy would be dependent on the co-operation of all those who influence discharge in the catchment area. Even with this co-operation significant elimination of excess nitrogen and phosphorus is difficult to achieve and some water bodies are naturally high in nitrogen and phosphorus. However, the cost of eutrophication prevention must be weighed against the restorative expense of large water bodies and the increased expense of treating raw water tainted with off-flavour. Numerous restoration techniques for eutrophied water bodies exist, including dredging of sediments containing phosphorus and nitrogen (Annadotter *et al.*, 1999), and bio-manipulation using microorganisms. These techniques are very expensive when applied on a large scale and combined with long treatment periods restoration is an unattractive option for controlling cyanobacterial blooms.

A unique method that could be applied to controlling cyanobacterial blooms that have already occurred, that has been used to control algal blooms, is the use of vertical curtains in affected waters (Asaeda *et al.*, 1996, 2001). In these studies

two plastic vertical curtains were installed 1335 and 1670 m upstream from the Terauchi dam reservoir, where raw water is extracted for rice field irrigation. The curtains, spanning the width of the reservoir and held in place by floating buoys, were installed close to the riverine zone where the majority of the inflow enters the reservoir. The curtains, which extended to a depth of 5 m, diverted the flow of nutrient rich water from the cyanobacterial growth zone (up to a depth of 4 m) by forcing the water to flow beneath the curtain. This method of controlling the flow of nutrient rich water combined with the ability to withdraw water from the reservoir at various depths ensured that raw water had significantly lowered algal content.

Two simple methods in controlling the occurrence of cyanobacterial blooms is the covering of water bodies (Montiel, 1983) and the addition of barley straw to affected waters (Barrett *et al.*, 1993; Ball *et al.*, 2001). Covering water bodies, stopping light reaching the cyanobacteria, prevents the cyanobacteria photosynthesizing and reduces the production of off-flavour metabolites. This technique is likely to be considerably less practical for larger water bodies. Decomposed barley straw was found to inhibit the cyanobacteria *Microcystis* sp. (Ball *et al.*, 2001). The antialgal activity of rotting barley straw has yet to be elucidated, but it has suggested that that the antialgal inhibitor is, or is derived from, oxidized lignin (Pillinger *et al.*, 1994).

The most common method of preventing or controlling the growth of cyanobacterial blooms in the USA is the application of algicides (this practice is banned in the United Kingdom). These may be used preventatively, or after a bloom has occurred, to disrupt the growth of cyanobacteria in reservoirs (Izaguirre, 1992; Sklenar *et al.*, 1999) and fish ponds used for aquaculture (Perschbacher *et al.*, 1995; Schrader *et al.*, 2005a). Algicides currently being used are 3-[3,4-dichlorophenyl]-1,1-dimethylurea (diuron) and copper-based products such as copper sulphate and chelated copper compounds (Dionigi, 1995; Sklenar *et al.*, 1999; Schrader *et al.*, 2005a). However there are significant drawbacks to the use of copper-based algicides. Wu *et al.* (1988) reported that up to 99 % of GSM produced by *Oscillatoria tenuis* is retained in the cells and Negoro et al. (1988) found 71-90 % of GSM produced by

Anabaena macrospore was retained within the cyanobacterium. As use of copper-based algicides causes lyses of cyanobacterial cells intracellular GSM is released into the water in which the cyanobacteria is residing, exacerbating off-flavour (Bowmer *et al.*, 1992; Dionigi *et al.*, 1995; Sklenar *et al.*, 1999). A further problem is that copper algicides are known to cause the selection of copper tolerant cyanobacteria (Izaguirre, 1992; Koch *et al.*, 1992) and in some cases increase the production of GSM by cyanobacteria (Dionigi, 1995). Finally as copper-based algicides have broad-spectrum toxicity they can upset the ecological balance in water bodies by killing beneficial phytoplankton (Schrader *et al.*, 2005a). Evidence would suggest that long term usage of copper based algicides is ill-advised and counter-productive. It is likely that these algicides will cause the selection of more copper tolerant cyanobacteria while causing wider environmental damage in the environment in which they are used. For this reason their use in the United Kingdom (UK) is banned and in the USA concerns about potential toxicity, particular accumulation of elemental copper in sediments, has led to its use being restricted and in some cases prohibited.

1.6 OFF-FLAVOUR

It is likely that most people have experienced off-flavor caused by the cyanobacterial compounds GSM and MIB. Predominantly the experience of off-flavour will have come from drinking water tainted with off-flavours or from consuming fish that has absorbed off-flavour.

1.6.1 Experience of off-flavour through drinking water

Off-flavour is most likely experienced through drinking tainted water. Complaints of off-flavour in drinking water is a significant issue for water supply companies worldwide (Izaguirre *et al.*, 1995; Jüttner, 1995; Muramoto *et al.*, 1995; Young *et al.*, 1996; Izaguirre *et al.*, 1999).

Due to our low odour detection threshold for both GSM (0.015 μg L^{-1}) and MIB (0.035 μg L^{-1}), monitoring these very low levels that we can detect can be difficult.

An additional problem is caused by the seasonal occurrence of cyanobacterial blooms and their subsequent release of GSM and MIB. This causes sporadic incidences of off-flavour episodes. Conventional water treatment does not always prove effective in removing GSM and MIB, resulting in consumers experiencing off-flavour caused by these compounds (Sklenar *et al.*, 1999).

1.6.2 Off-flavour in tainted fish

Off-flavour is imparted to fish by absorption of odorous compounds from the water in which they reside. Therefore many fish, both freshwater and marine, have a natural tendency to have flesh that tastes of the environment in which they reside. An example of this is wild Atlantic salmon (*Salmo salar*) with muddy or earthy tasting flesh (Farmer *et al.*, 1995). However, strong off-flavour is undesirable and is a foremost concern for the aquaculture industry. Off-flavour has long been recognised as a having an impact on farmed

freshwater fish (Persson, 1978; Lovell, 1983; van der Ploeg *et al.*, 1992; Robertson *et al.*, 2003). Much of the literature focuses on the issue of off-flavour on the production of channel catfish (*Ictalurus punctatus*) in the USA. Farmed rainbow trout (*Onchorhynchus mykiss*) in the UK (Robertson *et al.*, 2003) and France (Robin *et al.*, 2006) are also affected by off-flavour. The problem of off-flavour is not limited to vertebrate fish however, with reports of shrimp (Lovell *et al.*, 1985) and clams (Hsieh *et al.*, 1988) being affected. The majority of off-flavour in aquaculture is associated with compounds produced by microbes, with GSM and MIB the most common (Schrader *et al.*, 2003). As GSM and MIB are lipophilic in nature, fish present in water with these compounds can accumulate these off-flavours in their flesh. Practical experience and laboratory trials have demonstrated that uptake of GSM and MIB is rapid, within hours of exposure, but depuration is slow requiring several days to fully purge the off-flavour from the fish (Howgate, 2004). The accumulation of GSM and MIB in fish flesh imparts a musty/earthy taste to the fish flesh, resulting in a reduction of product quality. Fish processors will reject fish with significant off-flavour. Rejected fish are held, returned to the ponds in which they have grown, until the off-flavour is diminished. This results in harvesting being delayed (Schrader *et al.*, 2003). Typically, the shorter the holding period, the lower the fish mortality due to disease, poor water quality, and bird predation. Preventative measures, such as the application of algicides, are commonly employed to control the growth of cyanobacteria that produce off-flavours to limit the likelihood of marketable fish being rejected by the processor.

Additional production costs, such as harvest delays and algicides, attributed to off-flavour in the USA farm-raised catfish industry ranged from $15 to $23 million annually over the 1997-1999 period (Hanson, 2003). A recent UK survey revealed that 20 % of farms rearing rainbow trout reported incidences of earthy taints on a seasonal basis (Robertson *et al.*, 2003).

1.7 DETECTION AND ANALYSIS OF GSM AND MIB

The importance of off-flavour contamination in drinking water and tainting of fish has led to considerable improvement in the detection and analysis of GSM and MIB. The inherent problem with analysing GSM and MIB is that humans have a very low threshold with regards to these off-flavour compounds, 0.015 μg L^{-1} and 0.035 μg L^{-1} respectively. Further more, no precise boundaries exist for when a person will and will not detect the odour of a chemical. Instead there is a range of concentrations over which a person on repeated exposures will either detect the odour or not. A plot of the proportion of times a person detects the odour at a fixed concentration against the logarithm of the concentration will give the probability of detection (Howgate, 2004). This plot forms a sigmoid-shaped curve and it is conventional in sensory studies to define the threshold as the concentration at which a person will detect the odour in 50 % of the presentations. The variability in odour detection of a chemical combined with the sporadic occurrence of off-flavour episodes is a significant problem when developing a reliable method for detecting GSM and MIB at threshold concentrations. Therefore any method used to detect GSM and MIB must be able to do so at the low concentrations (ng L^{-1}) found in raw water used for drinking water and aquaculture.

There are two main methods used for the detection of GSM and MIB, sensory evaluation and analysis by instrumentation. The use of sensory evaluation to detect GSM and MIB is common for both the aquaculture industry (Lovell *et al.*, 1986; van der Ploeg, 1991; Bett, 1997) and water supply companies (Rigal, 1995; Schweitzer *et al.*, 2004; Wiesenthal *et al.*, 2004). However problems exist with sensory evaluation. Trained personnel are expensive to maintain, it is unable to discriminate specific odours in the presence of stronger ones, reproducibility can be an issue and the human aspect of evaluation can affect accuracy (Bett *et al.*, 1997).

Instrumental methods previously used for identification and quantification of GSM and MIB have also had their limitations. Isolation of GSM and MIB by closed-loop stripping (CLS) followed by analysis by gas chromatography-mass spectrometry (GC-MS) suffers from being time consuming, resulting in low sample throughput (Palmentier *et al.*, 1998). Liquid-liquid extraction requires large sample volumes and intensive sample concentration (Johnsen *et al.*, 1987; Rashash *et al.*, 1997). Purge and trap and steam distillation though effective are also time consuming and labour intensive (Lloyd *et al.*, 1998).

Another technique, chromatographic sniffing and gas chromatography-mass spectrometry (SNIFF-GC-MS), combines instrumental and sensory analysis (Khiari *et al.*, 1992). The effluent from the GC capillary column is divided into two, the first portion going to a GC detector with the second portion going to an olfactory port where it is smelt by a trained operator. Upon detecting an odour the operator triggers an electronic signal which is superimposed on the chromatographic signal. This allows the GC peaks from the chromatographic signal to be related to odours detected by the operator (Hochereau *et al.*, 2004). A disadvantage of this method is the requirement of an operator that has had specific training for odour recognition.

A new analytical technique devised to extract volatile organic carbons from water called solid phase microextraction (SPME) was developed in 1989 (Belardi *et al.*, 1989). SPME coupled with gas chromatography-mass spectrometry was used by Lloyd and co workers to successful detect and quantify GSM and MIB (Lloyd *et al.*, 1998).

Analysis of GSM and MIB by SPME involves the use of a silica fibre coated with a suitable absorbent phase (polydimethylsiloxane - PDMS), which is bound to the tip of a syringe plunger (Supelco, 2002). The plunger is retracted, keeping the delicate fibre protected within the syringe needle. The needle is used to pierce the septum of a sealed vial containing the sample, the plunger is then extended exposing the fibre (Fig. 1-6). The fibre can either be immersed into a liquid sample or more commonly, especially for GSM and MIB analysis, placed in the headspace above the sample. Analyte molecules are absorbed onto the

coating and after equilibration the fibre is retracted into the needle. Sodium chloride may be added to the sample, stirred, and then heated to increase volatilisation of analytes onto the fibre. Finally the needle is extended into the heated injection port of a gas chromatograph where the analytes are thermally desorbed onto a capillary column for separation and subsequent detection (Lloyd *et al.*, 1998).
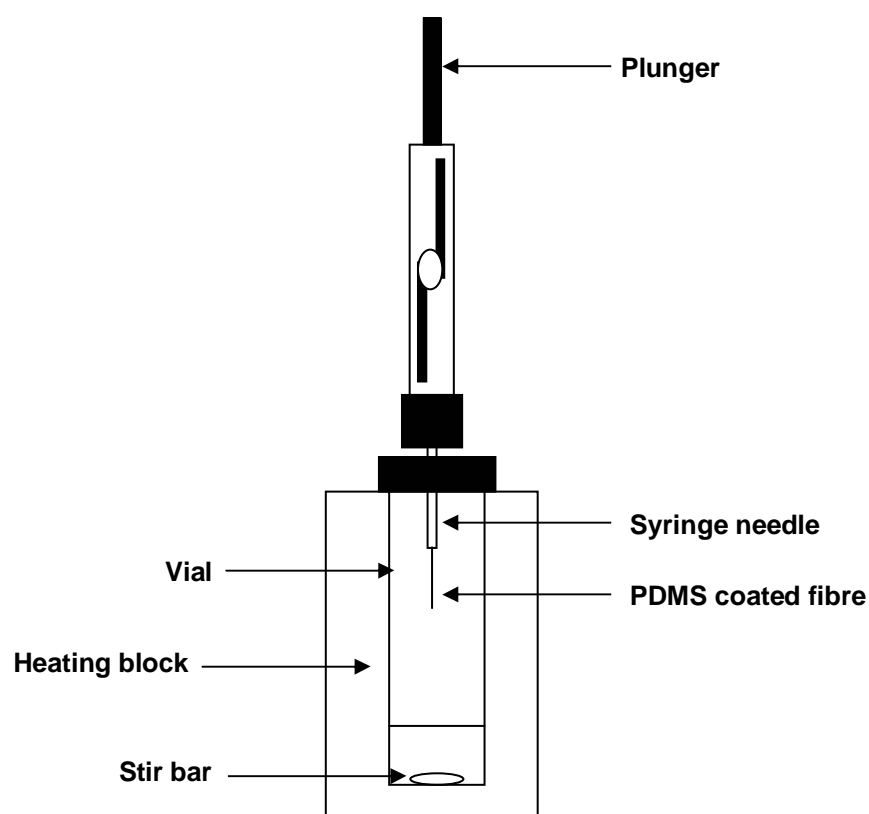
Figure 1-6. SPME assembly pierced through vial septum, plunger extended, resulting in extension of the SPME fibre into the headspace above the sample.

1.8 REMOVAL OF GSM AND MIB FROM DRINKING WATER

When off-flavours enter a drinking water supply their removal during the water treatment process requires the application of costly and sometimes ineffective methods by water supply companies. Drinking water treatment is dependant on

the initial quality of the raw water and the distance between the source and the user. For example a rural family dwelling extracting water from a borehole would require little or no treatment. Water sourced from lowland rivers or reservoirs would commonly undergo treatment as depicted in Figure 1-7, internationally known as standard water treatment (Kiely, 1998). In general the processes in this treatment include pre-treatment, primary and secondary treatment, disinfection and possibly fluoridation.

Pre-treatment may include; screening to remove debris; storage to equalises flow; aeration to release unwanted volatile gases and increase oxygen content; chemical pre-treatment such as pre-chlorination; and addition of activated carbon to remove undesirable water properties. Sedimentation is the separation of a solid-liquid, using gravity settling to remove suspended solids. Sedimentation may be combined with a coagulation and flocculation in a single step. Coagulation involves the addition of a chemical, typically aluminium sulphate or ferrous sulphate, which changes the electric charge of particles in the raw water making them more amenable to aggregation. Flocculation is the process of getting the 'coagulated mix' to form larger flocs. Filtration is the next step and involves the process of passing the water through a filtration system, slow sand filters and rapid gravity filters being examples, containing a porous medium to further improve the water quality. Generally the final step is disinfection by chlorination (Kiely, 1998).

Known techniques deal with off-flavour either by decomposition of the off-flavour compound or by actual removal of the compound from the water. However, standard treatment does not efficiently remove off-flavour, especially earthy/musty off-flavour, from water (Wnorowski, 1992; Sklenar *et al.*, 1999). For this reason, and to deal with other water associated problems, standard water treatment can be supplemented with the use of advanced treatment (Fig. 1-7).

Treatment Categorization	Standard Water treatment
	Intake
Pre-treatment	Coarse screening Fine screening Pumping Storage Equalization Neutralization Aeration Chemical pre-treatment
Primary treatment	Coagulation and mixing Flocculation Sedimentation
Secondary treatment	Filtration
Disinfection	Disinfection
Advanced treatment	Adsorption Activated Carbon Membrane processes Advanced Oxidation Processes
Fluoridation	Fluoridation
Distribution network	Yes

Figure 1-7. Flow chart outline of standard water treatment for water sourced from lowland rivers and reservoirs. Advanced treatments are only selectively used (Kiely, 1998).

1.8.1 Removal of GSM and MIB by physical treatment

Standard water treatment (Fig. 1-7) using coagulation/sedimentation/filtration is primarily conducted to remove solids from treated water and does not efficiently remove off-flavour from water (McGuire *et al.*, 1988; Ando *et al.*, 1992; Wnorowski, 1992).

Aeration can be used as a pre-treatment of raw water and it is accepted that aeration removes volatile compounds that may be present in raw or treated waters. Air stripping is effective for compounds that have a Henry's Law constant greater than 10^{-3} m^3 atm mol^{-1}. GSM and MIB have Henry's Law constants in the range of 10^{-5} m^3 atm mol^{-1}, therefore these compounds are not readily stripped without exceptional measures (Lalezary *et al.*, 1984).

The use of slow sand filtration to remove GSM and MIB has however been successfully demonstrated (Yagi *et al.*, 1983). A slow sand filter is typically a rectangular open box structure containing: a supernatant layer of raw water, a bed of fine sand supported on a thin layer of gravel, a system of under drains and inlet and outlet structures. The raw water flows onto a schmutzdecke layer, a layer on top of the sand that is composed of living and dead microorganisms. The water is drawn through the schmutzdecke layer and the sand and gravel bed below, by gravity. Removal of impurities is by both physical and biological mechanisms. Microorganisms present in the schmutzdecke layer can degrade many organic compounds and bacteria, and the sand bed acts as a filter. The bacterial decomposition of MIB using a pilot gravel sand filter has been reported by Sumitomo and co-workers (1992). However, new gravel in the filter required a period of up to 20 days to build a schmutzdecke layer that could attain 50 % MIB removal. During this lag, the schmutzdecke layer was supplemented with powdered activated carbon to improve MIB removal. While slow sand filtration is effective in removing off-flavour from raw water it has almost exclusively been superseded by rapid gravity filtration (RGF).

RGF has significantly enhanced filtration rates, approximately 50 times greater, when compared to slow sand filtration (Kiely, 1998). This enhanced filtration rate allows for far greater volumes of raw water to be treated. RGF is used to filter chemically coagulated water, with suspended particles removed by a combination of settlement, straining, adhesion, and attraction. RGF operates in a mode where water filters vertically down through the filter, with the filter consisting of single, dual, or multimedia. The media types tend to be sand, gravel, and anthracite. In comparison to slow sand filtration biological activity is limited in RGF. This difference in biological activity may account for the slow sand filtration being more effective in removing off-flavour from raw water. Microorganisms present in the Schmutzdecke layer of the slow sand filter are the likely cause of GSM and MIB degradation. However, slow sand filtration is only practical on a relatively small scale and there have been numerous reports of off-flavours persisting in water after treatment by RGF (Yagi *et al.*, 1983; Hattori, 1988).

Activated carbon in either powdered (PAC) or granular (GAC) form is an effective method for the physical removal of GSM and MIB and is widely used by water supply companies. PAC is generally added to raw source water as a slurry and allowed to react before the addition of either oxidants or coagulants. It has been demonstrated that PAC has removed GSM and MIB from raw water to acceptable levels for human consumption (Gillogly *et al.*, 1999; Cook *et al.*, 2001; Ng *et al.*, 2002; Jung *et al.*, 2004). GAC is also used for treating water containing GSM and MIB (Vik *et al.*, 1988; Chen *et al.*, 1997a; Orr *et al.*, 2004). Filtration by GAC usually occurs after coagulation/sedimentation treatment processes (McGuire *et al.*, 1988), or may be added as an additional layer to a rapid gravity filter.

Yagi *et al.* (1983) reported on the effectiveness of four water treatment plants in removing off-flavour sourced water from Lake Biwa. PAC doses of 10 to 25 mg L^{-1} significantly reduced GSM and MIB in raw water, but a PAC dose of 100 mg L^{-1} was required to remove 100 ng L^{-1} of GSM. In comparison GAC filter depths of 40 cm and 110 cm were required to remove GSM and MIB respectively. Hattori (1988) also demonstrated the effectiveness of GAC

treatment in removing off-flavour from raw water. Removal of GSM and MIB were dependant on the depth of the GAC bed and the flow rate of raw water through the GAC bed, with a clear correlation between increased flow rate and decreased GSM and MIB removal. GSM and MIB concentrations decreased as the depth of the GAC bed increased (both off-flavours were undetectable at 1.4 m). There are numerous examples of successfully installed GAC filters in full-scale plants (Terashima, 1988; Vik *et al.*, 1988).

GAC and PAC remain the two most common methods of dealing with off-flavour episodes in raw water, but they are not without their disadvantages. Both GAC and PAC suffer from decreased efficiency in raw waters with a high organic loading because of their non-selectiveness. This is caused by low molecular weight organic compounds directly competing with MIB and GSM for adsorption sites. (Newcombe *et al.*, 2002; Hepplewhite *et al.*, 2004; Ho *et al.*, 2005). Another important factor is that the effectiveness of GAC and PAC is strongly associated with the type of activated carbon used (Cook *et al.*, 2001; Tennant *et al.*, 2007). PAC is expensive, up to £1000 per ton, and not recoverable after addition to raw water. Due to its expense, the addition of PAC to raw water containing off-flavour compounds will be kept to a minimum. This necessitates the use of modelling to accurately describe the competitive adsorption between background matter and the compound of interest, in this case GSM and MIB, to ensure that an effective PAC dose is added to the raw water (Gillogly *et al.*, 1999; Cook *et al.*, 2001). Finally the efficacy of PAC and GAC reduces as active adsorption sites decrease, this results in significantly reduced performance with regards to removing off-flavours (Hattori, 1988). Once exhausted of their adsorption capacity, spent carbons must be landfilled, incinerated or in the case of GAC thermally regenerated (this requires an inert atmosphere and temperatures of 800 ℃). All these options can result in significant cost (San Miguel *et al.*, 2001; Chestnutt *et al.*, 2007).

There has been research into the use of membrane processes, particularly nano filtration membranes, as a means to remove GSM and MIB (Robert Reiss *et al.*, 1999). Membrane processes can be divided into two distinct groups, sophisticated filtration techniques and reverse osmosis.

Reverse osmosis is a solubilization diffusion technique that makes use of a semi-permeable membrane which acts as a barrier to dissolved salts and inorganic molecules. Filtration techniques exclude particulates and compounds above a certain molecular weight (dependant on the membrane used). Traditionally membrane processes have been used for desalination, but interest in them for drinking water treatment is being revived due to increased impurities in water. Smith *et al.* (2003) demonstrated that NF 90 polyamide nanofilteration membranes removed 95 % of GSM and 91 % MIB from post-filter water sourced from a water treatment plant. NTR 7450 sulfonated polyether sulfone nanofiltration membranes performed poorly with 78 % or more GSM and MIB remaining after filtration. There was a clear correlation between the molecular weight cut-off (MWCO) of the membrane material and GSM and MIB removal. GSM and MIB have molecular weights of 182 and 169 Daltons respectively, which are substantially smaller than the 200-400 Dalton MWCO of the NTR 7450 filter. The NF90 filter had a MWCO of 100 Daltons, much closer to the molecular weights of GSM and MIB. Robert Reiss et al. (1999) also reported a similar trend with CALP and LCF1 nanofilters, MWCO of 300 and 200 respectively. CALP removed 40 – 65 % of GSM and MIB after pre-treatment, but detectable concentrations remained. LFC1 performed better, by virtue of its lower MWCO, by reducing GSM and MIB to less than 1 ng L^{-1}. The GSM and MIB concentrations in this study were much lower, 9 and 18 ng L^{-1} respectively, than the Smith et al. (2003) study, approximately 200 ng L^{-1} for both MIB and GSM. Algal blooms can severely affect filtration membranes, fowling the membrane, resulting in a drastic increase in transmembrane pressure. This causes a loss of performance and will eventually require the membrane to be cleaned (Kwon *et al.*, 2005).

1.82 Biological treatment of GSM and MIB

GSM and MIB are susceptible to biological degradation (biodegradation) with several studies having implicated a number of microorganisms responsible for their removal from water (Ho *et al.*, 2007). Examples of microorganisms capable of degrading MIB are *Pseudomonas* spp. (Izaguirre *et al.*, 1988),

Bacillus spp. (Lauderdale *et al.*, 2004) and for GSM *Bacillus subtilis* (Yagi *et al.*, 1988) and *Arthrobacter atrocyaneus* (Saadoun *et al.*, 1998). MIB and GSM susceptibility to biodegradation can be attributed to their structures which are similar to biodegradable alicyclic alcohols and ketones. As yet no definite pathways have been elucidated for the biodegradation of MIB and GSM. However, Tanaka *et al.* (1996) were able to identify two possible MIB dehydration products, 2-methylcamphene and 2-methyleneborane and Saito *et al.* (1999) identified four possible biodegradation products of GSM. Two of these, enone and 1,4 a-dimethyl-2,3,4,4a,5,6,7,8-octahydronaphthalene, have also been used in the chemical synthesis of (-)-geosmin (Saito *et al.*, 1996).

The majority of studies conducted on the biological treatment of MIB and GSM have used sand or GAC media (Lundgren *et al.*, 1988; Yagi *et al.*, 1988; Elhadi *et al.*, 2004b). The use of porous media such as GAC in evaluating the biodegradation of GSM and MIB is problematic. GAC can act as a solid support for biofilm formation, but will also remove off-flavour by adsorption. Therefore it is difficult to determine the mechanism of removal for GSM or MIB in such systems.

Westerhoff *et al.* (2005) determined MIB and GSM biodegradation as a pseudo-zero order reaction in batch studies of lake water, with biodegradation rates in the range of 0.96±0.15 ng L^{-1} day. Based on these biodegradation rates, MIB concentrations in a reservoir would decrease by approximately 30 ng L^{-1} over a period of 1 month. Ho *et al.* (2007) concluded that MIB and GSM were readily removed through bench-scale sand filters, with removal caused predominantly through biodegradation processes. The biodegradation of GSM and MIB was determined to be pseudo-first order reaction, with rates influenced by the initial concentration of microbes in the biofilm, but not the initial concentration of the off-flavour compounds. Elhadi *et al.* (2003) studied the effects of temperature and media effects on the biofilteration of GSM and MIB from water using GAC and anthracite as media. Both media removed GSM and MIB, but GAC was the most effective. GAC and anthracite were also evaluated at 8 ℃ and 20 ℃, both media had increased rates of removal at evaluated temperature. The increase in temperature is likely causing a increase in microbiological activity.

However this is a negligible advantage as the majority of water treatment processes do not operate at this temperature and considerable energy would be required to raise the temperature to ~20 °C.

1.8.3 Removal of GSM and MIB by oxidation

Previous work has demonstrated that the oxidants commonly used in water treatment, chlorine, chloramines, chlorine dioxide, and potassium permanganate are not effective in removing GSM or MIB (Lalezary *et al.*, 1986). Table 1-1 gives the oxidation potentials of oxidants commonly used in the water industry. Chlorine and chloramines are not powerful enough to oxidise GSM and MIB even at high doses (McGuire, 1999). Lalezary *et al.* (1986) reported that chlorine doses as high as 20 mg L^{-1} (a usual dose is 1 mg L^{-1}) removed less than 60 % of GSM and 35 % of MIB. Chlorine has the added disadvantages that over-chlorination can lead to complaints of water that is unpalatable (Wnorowski, 1992) and that pre-chlorination of raw water containing algal cells can result in their lyses, releasing their intracellular GSM and MIB into the water, exacerbating off-flavour episodes (Ashitani *et al.*, 1988; Levi *et al.*, 1988; Wu *et al.*, 1988; Peterson *et al.*, 1995). Furthermore chlorine derivatives can produce trihalomethanes which are a potential health hazard (Gracia *et al.*, 2000). There are conflicting reports that chlorine dioxide can oxidise GSM and MIB. Lalezary *et al.* (1986) reports that chlorine dioxide is capable of reducing GSM and MIB to levels between 40 and 60 %, whereas McGuire (1999) reports that chlorine dioxide is not a powerful enough oxidant to degrade GSM and MIB.

Potassium permanganate has also been used to attempt the removal of off-flavour problems. Its selection is due to the fact it is a cheaper alternative when compared with chlorine dioxide and advanced oxidation processes (AOPs) such as ozone. Unfortunately it is not a very powerful oxidant, only slightly more oxidising than chlorine and chlorine dioxide, and will not oxidise GSM and MIB (Lalezary *et al.*, 1986; McGuire, 1999; Tung *et al.*, 2004). Dietrich *et al.* (1995) reported on the oxidation of six algal metabolites by potassium

permanganate. After treatment with potassium permanganate four of the algal metabolites retained a detectable odour. Interestingly two of the metabolites that initially had no odour acquired odour after oxidation by potassium permanganate.

Reagent	Standard Reduction Potential (Volts vs. NHE)
Hydroxyl Radical	2.80
Ozone	2.07
Hydrogen Peroxide	1.78
Perhydroxyl Radical	1.70
Permanganate	1.68
Hypochlorous Acid	1.49
Chlorine	1.36
Chlorine Dioxide	1.28

Table 1-1. Reduction potentials of chemical oxidants commonly used by the water industry (Lawton *et al.*, 1999).

1.8.4 Glenfarg water treatment works

Glenfarg reservoir and water treatment works is a facility located in the east of Scotland, approximately 5 miles from Kinross. It is operated by Scottish Water and supplies an average of 50 Megalitres a day (Ml\d) to the Fife and Kinross area. Glenfarg is an excellent example of how algal blooms and off-flavour can seriously affect a water treatment works. High levels of algal activity in Glenfarg reservoir at certain times of the year have historically caused significant problems at the Glenfarg water treatment works (Figure 1-9).

Algal growth in Glenfarg reservoir is exacerbated by two main factors, supplementation of water from the River Earn and the hydrology of the reservoir. When required the reservoir is supplemented with water pumped from the nearby River Earn, usually in the summer months. An evaluation conducted by East of Scotland Water, the operator at the time, concluded that water from the River Earn had significant levels of nutrients that would likely exacerbate the problem of algal blooms.

Figure 1-8. The water draw-off tower at Glenfarg reservoir, with the dam in the foreground (top). One of three DAF tanks at Glenfarg water treatment works with surface sludge clearly visible (bottom).

Glenfarg reservoir is 1,360 m in length and relatively shallow (15.24 m maximum depth), a large surface area to depth ratio. The increase in nutrients, combined with good growth conditions in the summer months, causes significant algal blooms. Intensifying the problem is the location of the water draw-off tower in the reservoir, which supplies the water works. From Figure 1-8 the tower can clearly be seen close to the dam. The prevailing wind blows towards the dam, causing any surface growing algal blooms to be blown towards the draw-off tower.

The algal blooms caused serious physical difficulties during water treatment by clogging rapid gravity filters, resulting in high headlosses and sludge treatment difficulties. Additionally, the types of algal blooms experienced, typically *Anabaena* spp., caused serious GSM and MIB off-flavour problems. This lead to Glenfarg water treatment works adopting numerous techniques in an attempt to solve the issues.

A dissolved air flotation (DAF) pre-treatment plant was installed in 1997 at the cost of £3.7 million. The DAF plant was installed primarily to remove algae before it could reach the rapid gravity filters and is typically in operation during the cyanobacteria growth season (May to November). DAF is a physical separation process, conducted in rectangular tanks, which uses air saturated water to remove colour and particulate material from flocculated raw water (Hargesheimer *et al.*, 1996). Air saturated water is injected into a tank by a bank of nozzles, allowing the controlled release of pressure to form fine bubbles that attach to the floc in the raw water. The floc floats to the surface of the raw flocculated water where it forms a sludge and is removed by a hydraulic scrapper (Figure 1-8). The sludge is subsequently de-watered and land-filled. At Glenfarg DAF has solved the problem of algae disrupting the rapid gravity filters, the next step in the water treatment process. A polyelectrolyte, an alumina coagulant, and PAC are added prior to the DAF process at Glenfarg.

PAC is added to aid adsorption of compounds present in the raw water, but also serves to remove GSM and MIB when present. The usual dose of PAC is 1 ton a day, at the cost of approximately £1000 a ton. This rises to 3 tons a day

during serious off-flavour episodes, a considerable extra expense. PAC usage in response to off-flavour can be seen in Figure 1-9. Due to the severity of off-flavour episodes at Glenfarg treatment works an ozonation facility is available when required to increase GSM and MIB removal, with the dosage point after the DAF process. In addition to the extra treatment facilities an operating strategy for the management of seasonal algal and off-flavour concerns has been developed, dictating when the additional water treatments are used:
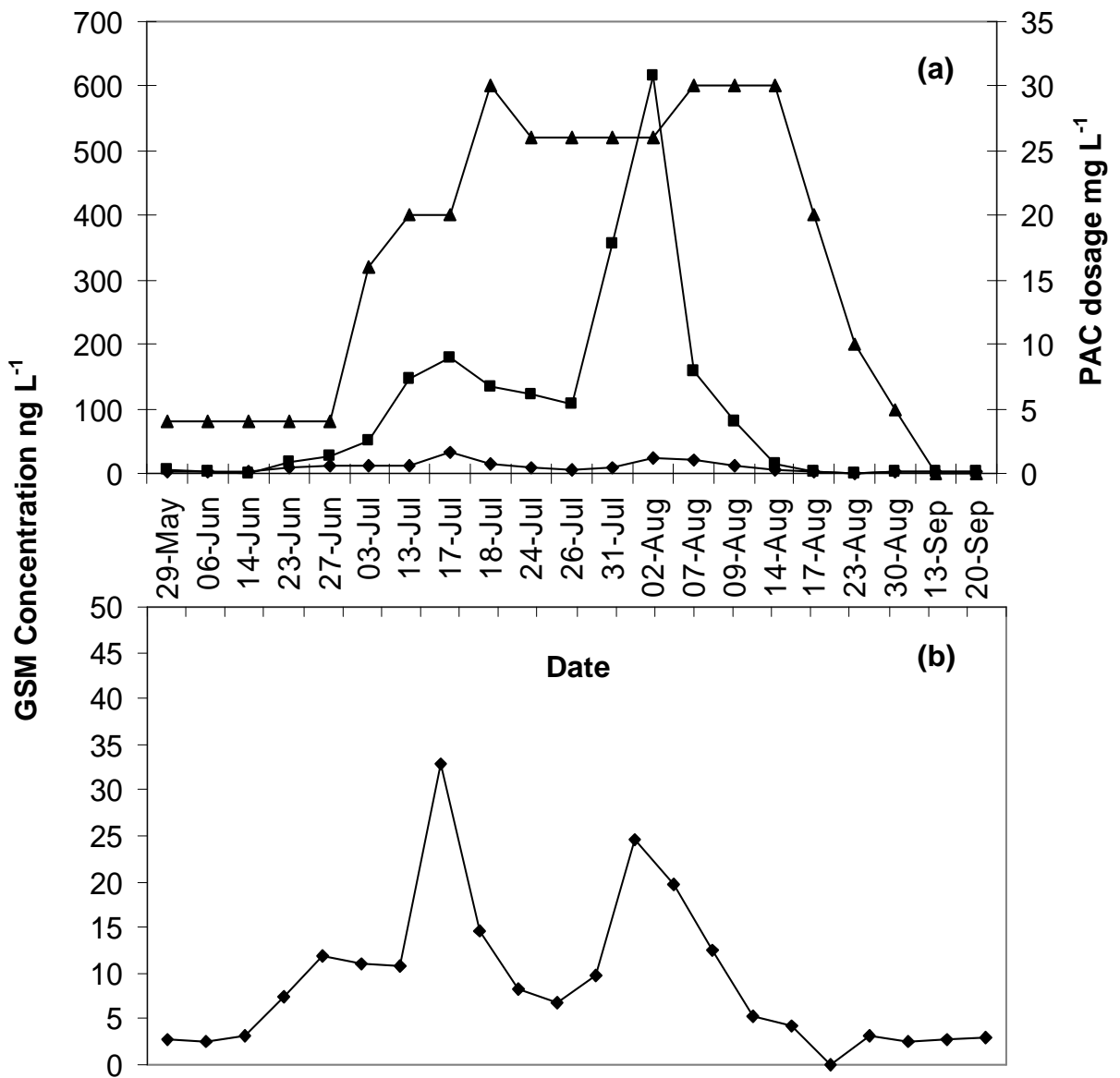
Figure 1-9. (a) the effect of Glenfarg water treatment on GSM concentration (29th May 2006 to 20th September 2006); (b) GSM concentration after treatment. GSM concentrations (ng L^{-1}) in Glenfarg raw water (—■—) and Glenfarg treated water(—◆—). PAC dosage (mg L^{-1}) (—▲—). Data supplied by Scottish Water.

Once routine and non-routine laboratory analysis results, on-line monitoring and physical investigations satisfy any of the following criteria then the DAF unit should be started and the additional chemical dosing and sampling requirements associated with summer algal concerns should begin. Typically these criteria will be satisfied ~May of each year:

- Visible sign of algae in the reservoir, over a period of 2 weeks.

- Raw water pH, colour and turbidity averaging greater than 8.0, 35$^{\text{o}}$ Hazen and 2 NTU (nephlometric turbidity units) respectively, over a period of 2 weeks. Hazen units are a measure of the colour of the raw water compared to standard solutions of coloured water and NTUs give a defined value for the suspended solids present in a water sample.

- Raw water chlorophyll a concentration averaging greater than 10 μg L^{-1} over a 2 week period.

- Filter run times significantly reduced/chemical dose rates significantly increased to maintain filtered water quality.

- Earthy / musty taste or odour in the treated water or smell in the DAF or filter gallery halls.

It is clear that the measures adopted at Glenfarg treatment works to limit the problems of algal blooms and off-flavours are considerable, with high capital costs and significant operational costs. Despite the additional treatments used at Glenfarg, off-flavour in produced drinking water is still a significant problem when the reservoir water contains very high levels of GSM (Figure 1.9). Therefore, more effective and ideally cheaper technologies are desirable. Advanced oxidation processes may offer a solution to the problem of water tainted with GSM and MIB.

1.8.5 Advanced oxidation processes for the removal of GSM and MIB

Advanced oxidation processes (AOPs) are defined as those which involve the generation of hydroxyl radicals ($^{\bullet}$OH) in sufficient quantity to effect water purification via the oxidation of organic solutes (Cooper *et al.*, 1999). AOPs are

a relatively new advancement in water treatment and can be used to control off-flavours. AOPs consist of a combination of oxidants to optimise the production of hydroxyl radicals. These radicals, though short lived, are much more powerful oxidants than chlorine or ozone alone, especially towards aliphatic molecules such as GSM and MIB (Wnorowski, 1992).

Ozone is one of the most implemented off-flavour control technologies when other oxidants will not solve the off-flavour problem (McGuire, 1999). A typical ozone treatment plant consists of three basic subsystems: feed-gas preparation; ozone generation; and ozone/water contacting. The high reactivity and instability of ozone requires immediate usage, necessitating on-site generation. The percentage ozone generated is dependent on the feed-gas employed, either air, oxygen, or oxygen-enhanced air. The maximum concentration of ozone economically produced from air is approximately two percent, while that generated from pure oxygen is six percent (Cheremisinoff, 2002). Selection of the feed-gas depends on economics, the quantity of ozone required, and whether the feed-gas is recycled. Ozone, for water treatment purposes, is produced by the electric discharge or corona method. In principle, an ozone generator consists of a pair of electrodes separated by a gas space and a layer of glass insulator. The feed-gas is passed through the gap and a high voltage applied (between 5 and 25 kV). A corona discharge takes place across the gas space and ozone is generated when a portion of the oxygen is ionized and then becomes associated with non-ionized oxygen molecules. After the ozone has been generated it is mixed with the water stream being treated in a device called a contactor. Substantial energy is required to split stable oxygen bonds to form ozone, only ~10 percent of the input energy is effectively used to produce the ozone, resulting in high energy consumption for the production of ozone. For the typical dosage rate of 1 to 5 g m^3, 10 to 20 kWh of energy per kg of ozone is required. The costs of ozonation are two to three times higher than the costs of chlorination (Kiely, 1998).

Ozone is unstable in water and the decay of ozone in natural waters is characterized by a fast initial decrease of ozone, followed by a second phase in which ozone decreases with first order-kinetics. Depending on water quality,

the half-life of ozone is in the range of seconds to hours. The major secondary oxidant formed from ozone decomposition is the $^\bullet OH$ radical (von Gunten, 2003). The stability of ozone depends largely on the water matrix, especially its pH. The pH of water is important because hydroxide ions initiate ozone decomposition which involves the following reactions:

$$O_3 + OH^- \longrightarrow HO_2^- + O_2 \qquad \text{(Equation 1-1)}$$

$$O_3 + HO_2^- \longrightarrow {}^\bullet OH + O_2^{\bullet -} + O_2 \qquad \text{(Equation 1-2)}$$

$$O_3 + O_2^{\bullet -} \longrightarrow O_3^{\bullet -} + O_2 \qquad \text{(Equation 1-3)}$$

$$O_3^{\bullet -} + H^+ \rightleftharpoons HO_3^\bullet \ (pH < 8) \qquad \text{(Equation 1-4a)}$$

$$HO_3^\bullet \longrightarrow {}^\bullet OH + O_2 \qquad \text{(Equation 1-4b)}$$

$$O_3^{\bullet -} \rightleftharpoons O^{\bullet -} + O_2 \ (pH > 8) \qquad \text{(Equation 1-5)}$$

$$O^{\bullet -} + H^+ \longrightarrow {}^\bullet OH \qquad \text{(Equation 1-5)}$$
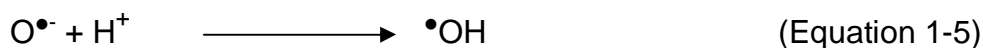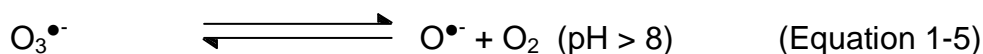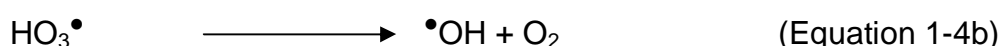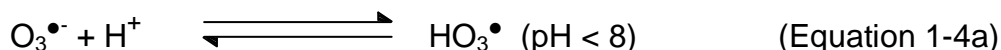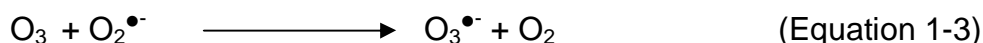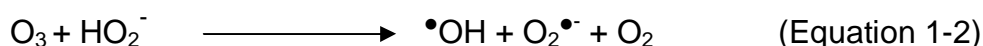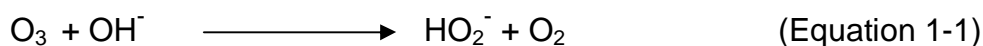
Terashima (1988) reported the reduction of GSM and MIB using a 60 m^3/day water treatment pilot-plant with an ozone dose rate of 2 to 5 mg L^{-1}. This dosage reduced GSM (33 - 89 ng L^{-1}) and MIB (55 - 250 ng L^{-1}) by 75 – 100 %. Initial GSM and MIB concentration had negligible effect on the rate of destruction. Numerous other examples exist of ozone being used to remove GSM and MIB from water (Hattori, 1988; Koch *et al.*, 1992).

According to reactions (Equation 1-1) and (Equation 1-2) the initiation of ozone decomposition can be artificially accelerated by the addition of hydrogen peroxide. This is known as the peroxone process, an AOP using a combination of ozone and hydrogen peroxide (Equation 1-6).

$$^\bullet OH + O_3 \longrightarrow HO_2^\bullet + O_2 \qquad \text{(Equation 1-6)}$$
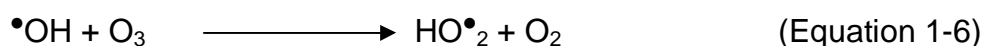
The peroxone process has been studied extensively and is capable of oxidising GSM and MIB. Koch *et al.* (1992) reported on the evaluation of a pilot-scale water treatment plant (22.8 L min^{-1} flow rate; GSM and MIB concentration 100 ng L^{-1}) using ozone for the removal of GSM and MIB. MIB and GSM removal increased with higher applied ozone dosage with 80 – 90 percent removal achieved in two different raw waters with an ozone dose of approximately 4.0 mg L^{-1}. Degradation of both GSM and MIB was increased with the addition of H_2O_2 (H_2O_2/O_3 ratio of 0.2). Treatment with O_3/H_2O_2 allowed the lowering of the ozone dosage to approximately 2.0 mg L^{-1} for the same level of GSM and MIB removal. The use of Peroxone could result in significant cost savings due to the reduction in ozone required. Interestingly, MIB was significantly more resistant to degradation than GSM when treated with ozone alone, with approximately 10 % less degradation across all ozone dosages.

Other AOPs include the combinations of UV/H_2O_2 and O_3/UV (Camel *et al.*, 1998; Ikematsu *et al.*, 2004; Goslan *et al.*, 2006). In a UV/hydrogen peroxide system the production of hydroxyl radicals ($^{\bullet}OH$) is due to the direct photolysis of hydrogen peroxide:

$$H_2O_2 \xrightarrow{h\nu} 2^{\bullet}OH \qquad \text{(Equation 1-7)}$$

$$HO_2^{-} \xrightarrow{h\nu} {}^{\bullet}OH + O^{\bullet-} \qquad \text{(Equation 1-8)}$$

$$HO_2^{-} + O^{\bullet-} \longrightarrow O_2^{\bullet} + OH^{-} \qquad \text{(Equation 1-9)}$$
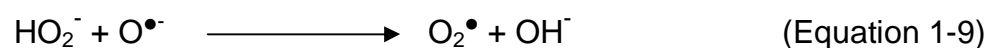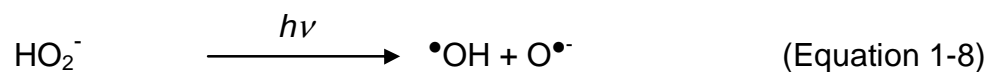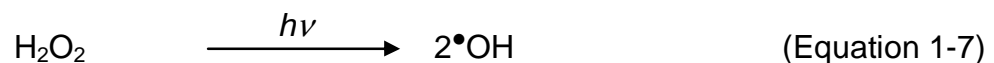
In a O_3/UV system the photolysis of ozone by UV radiation in the UV-C range (254 nm) initiates the production of $^{\bullet}OH$ radicals (Equation 1-10).

$$O_3 + H_2O \xrightarrow{h\nu} {}^{\bullet}OH + O_2^{\bullet-} + O_2 \qquad \text{(Equation 1-10)}$$
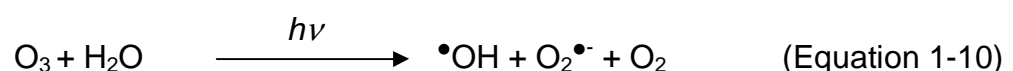
Lawton *et al.*, (2003) demonstrated that a titanium dioxide photocatalyst in the presence of UV light effectively removed GSM and MIB at concentrations higher than those found in the environment after 30 and 60 minutes respectively. This initial study demonstrated that this method has excellent potential for the treatment of water and warrants further investigation.

1.9 SEMICONDUCTOR PHOTOCATALYSIS

When a semiconductor is illuminated with photons of a higher energy than the band gap of the semiconductor the photons can be absorbed (Figure 1-10). This in turn leads to a promotion of electron to the conductance band, leaving a hole in the valence band. This excited electron can either be used directly to create electricity in a photovoltaic cell or drive a chemical reaction, which is called photocatalysis (Carp *et al.*, 2004).

Electron energy
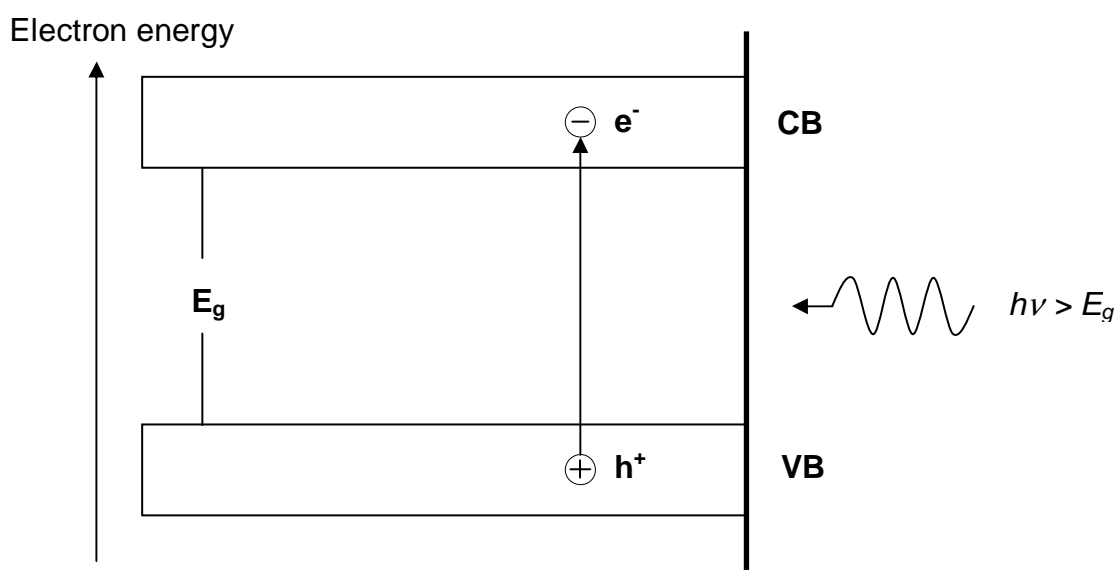
**Figure 1-10. Promotion of an electron from the valence band (VB) to
The conductance band (CB) on illumination of a semiconductor.**

1.9.1 Mechanism of photocatalytic oxidation

Semiconductors can act as sensitisers for light-induced redox processes due to their electronic structure, which is characterised by their band structure. The overlapping of two atomic orbitals gives rise to the formation of bonding and antibonding molecular orbitals separated by an energy gap. The formation of additional atomic orbitals causes the number of bonding and antibonding molecular orbitals to increase. The interaction of a very large chain of atomic orbitals results in a band forming, with many bonding and antibonding orbitals of differing energy. Semiconductor bands therefore constitute closely spaced

molecular orbitals formed by the overlap of atomic orbitals. The numerous molecular orbitals, and their close spacing, effectively form continuous bands. Orbitals which are occupied form what is known as the valence band, with the vacant orbitals referred to as the conductance band. Both the valence and conductance bands have definite band edges, separated by a forbidden region or band gap.

When a photon with an energy that matches or exceeds the band gap energy (E_g) of the semiconductor, an electron, e^-, is promoted from the valence band (VB) into the conductance band (CB) leaving a hole behind (Fig 1.10) (Hoffmann *et al.*, 1995). There are three major process that can occur following electronic excitation:

$$e^- + h^+ \longrightarrow heat \qquad \text{(Equation 1-11)}$$

$$D + h^+_{surface} \longrightarrow D^{\bullet+} \qquad \text{(Equation 1-12)}$$

$$A + e^-_{surface} \longrightarrow A^{\bullet-} \qquad \text{(Equation 1-13)}$$
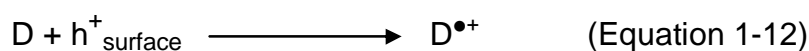
Electron hole recombination can occur at the surface or in the bulk of the semiconductor (Equation 1-11). Alternatively, at the surface of the semiconductor photogenerated electrons can reduce an electron acceptor (Equation 1-12) and photogenerated holes can oxidize an electron donor (Equation 1-13). These processes are illustrated in Figure 1-11. The combination of reactions given in Equation 1-12 and Equation 1-13 represent the semiconductor sensitization of the general redox reaction (Equation 1.14).

$$A + D \xrightarrow[\text{light} \geqslant E_{bg}]{\text{semiconductor}} A^- + D^+ \qquad \text{(Equation 1-14)}$$
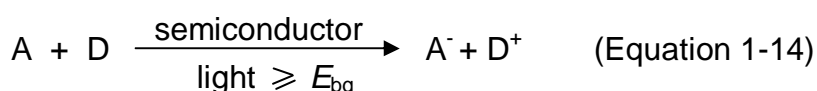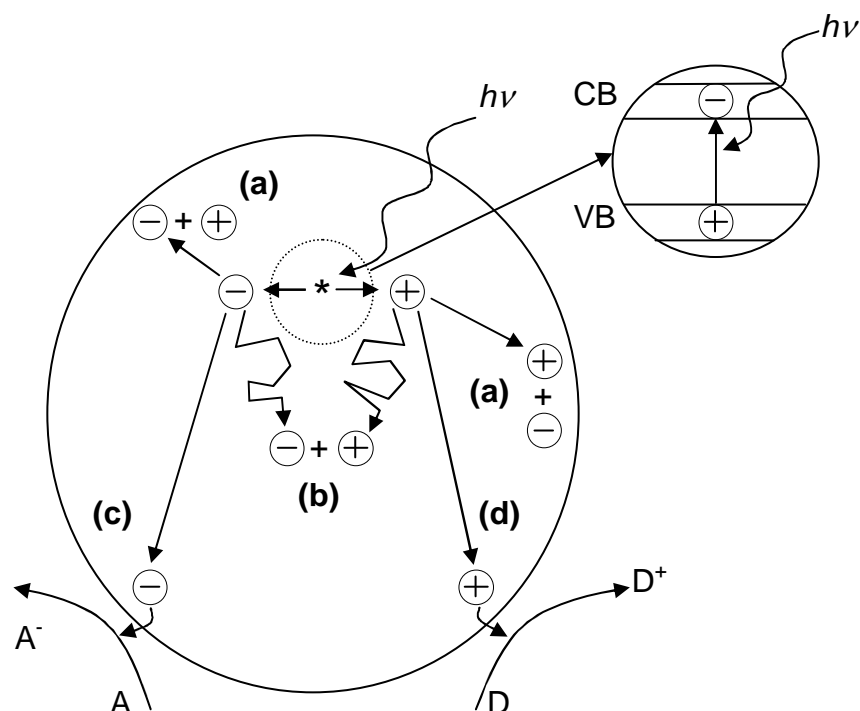
Fig 1-11: Illustration of the major process occurring on a semiconductor particle following electron excitation. Electron hole recombination can occur at the surface (a) or in the bulk (b) of the semiconductor. At the surface, photogenerated electrons can reduce an electron acceptor A (c) and photogenerated holes can oxidize an electron donor (d) (Mills *et al.*, 1997).

The valence band holes are powerful oxidants, while the conductance band electrons are good reductants. Different semiconductors have varying oxidation and reduction potentials for their conductance and valence bands (Table 1-2). The redox potentials for these semiconductors range between 4.1 and -2.3 volts versus Normal Hydrogen Electrode (NHE). For a semiconductor photocatalyst to be efficient the different interfacial electron processes involving e^- and h^+, reactions c and d (Fig. 1-11), must compete effectively with the major deactivation processes involving e^--h^+ recombination, reactions a and b (Fig. 1-11).

Semiconductor	Valence Band Reduction Potential (V *vs.* NHE)	Conductance Band Reduction Potential (V *vs.* NHE)
TiO_2	+3.2	-0.1
SnO_2	+4.1	+0.3
ZNO	+3.0	-0.2
ZnS	+1.4	-2.3
WO_3	+3.0	+0.2
CdS	+2.1	-0.4
CdSe	+1.6	-0.1
GaAs	+1.0	-0.4
GaP	+1.3	-1.0

Table 1-2. Oxidising and reducing potentials of the valence and conductance bands of a selection of common semiconductor materials in aqueous solution at pH 1 (Robertson, 1996).

The ideal semiconductor for photocatalysis would have the following properties:

1. photoactive;

2. able to utilise visible and/or near-UV light;

3. biologically and chemically inert;

4. photostable (i.e. not liable to photocorrosion);

5. inexpensive.

The semiconductor titanium dioxide (TiO_2) is close to being the ideal photocatalyst, satisfying these criteria, with the exception that it does not absorb visible light. The properties of TiO_2 have lead to its wide use in mediating photocatalytic reactions. The band gap of titanium dioxide is 3.2 V (Table 1-2), allowing photooxidation to occur with adsorption of light in the near ultra violet region (~ 380 nm).

Mills *et al.* (1997) and co-workers summarised published articles in the field of semiconductor photocatalysis, demonstrating the very large number of uses for semiconductor photocatalysis. Uses include photoelectrochemical cells for

water splitting and for electricity production, semiconductor particles and films for the photocatalytic destruction of gaseous pollutants and semiconductor particles for the photodestruction of cancer cells, bacteria and viruses. However, the majority of articles on semiconductor photocatalysis are in the area of photocatalysis for the oxidation of organic pollutants by oxygen (Hoffmann *et al.*, 1995; Honglay Chen *et al.*, 1998; McMurray *et al.*, 2004). It has also been demonstrated that the use of TiO_2 as a photocatalyst for the destruction of pollutants in water is an effective process (Hoffmann *et al.*, 1995; Li *et al.*, 1996; Mills *et al.*, 1997; Byrne *et al.*, 1998; Ray, 1998).

The detailed mechanism of the photocatalytic process involving the destruction or transformation of pollutants on the TiO_2 surface is still not completely clear. It is generally assumed that both photocatalytic oxidative and reductive reactions occur simultaneously, otherwise a charge would build up on the TiO_2 particle. In most cases, the electron transfer to oxygen, the primary electron acceptor, is rate-determining in photocatalysis. Hydroxyl radicals are formed on the surface of TiO_2 by the reaction of holes in the valence band (h^+_{VB}) with adsorbed H_2O, hydroxide or surface titanol groups (>TiOH) (Figure 1-12) (Hoffmann *et al.*, 1995). Photogenerated electrons (e^-_{CB}) are capable of producing superoxide (O_2^-), an effective oxidising agent that can attack neutral substrates, surface-adsorbed radicals and/or radical ions (Figure 1-12). The redox potential of the electron-hole pair theoretically permits H_2O_2 formation by either water oxidation or by reduction of adsorbed oxygen by two conduction band electrons, the latter representing the main pathway of H_2O_2 formation (Carraway *et al.*, 1994). H_2O_2 can act as an electron acceptor or as a source of $^\bullet OH$ radicals due to homolytic scission. In summary the holes, $^\bullet OH$ radicals, O_2^-, H_2O_2, O_2, play important roles in the photocatalytic reaction mechanism depending on the reaction conditions. These processes are summarised in Figure 1-12.
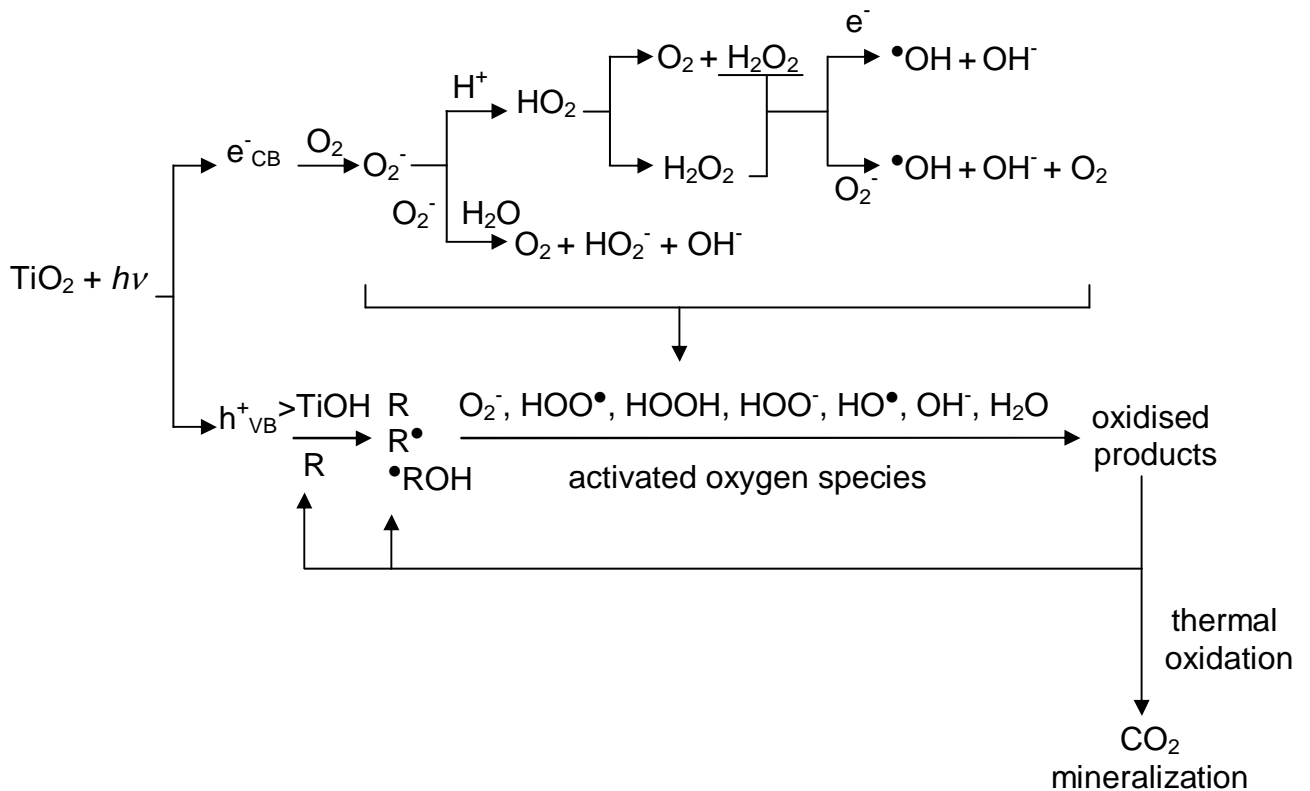
Figure 1-12. Secondary reactions with activated oxygen species in the photoelectrochemical mechanism (Hoffmann *et al.*, 1995).

Mills and co-workers (1993) proposed that in order for a semiconductor to be photochemically active for the destruction of organic compounds in water (Equation 1.15) the redox potential of the photogenerated valence band hole must be sufficiently positive to generate absorbed $^\bullet OH$ radicals. These radicals can subsequently oxidise the organic pollutant. The redox potential of the photogenerated conductance band must be sufficiently negative to reduce absorbed O_2 to superoxide. These processes are represented in Figure 1-13.

$$\text{organic pollutant} + O_2 \xrightarrow[\text{light} \geqslant E_{bg}]{\text{semiconductor}}$$

$$CO_2 + H_2O + \text{mineral acids} \qquad \text{(Equation 1-15)}$$

Electron energy

Semiconductor

Semiconductor/solution
surface reactions
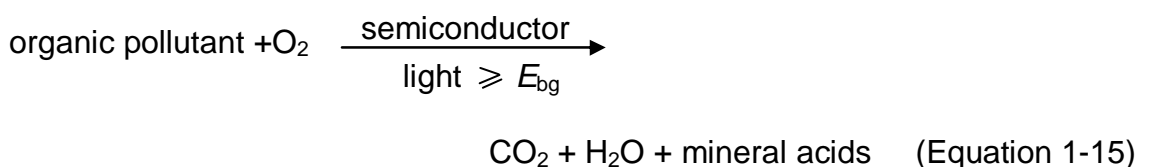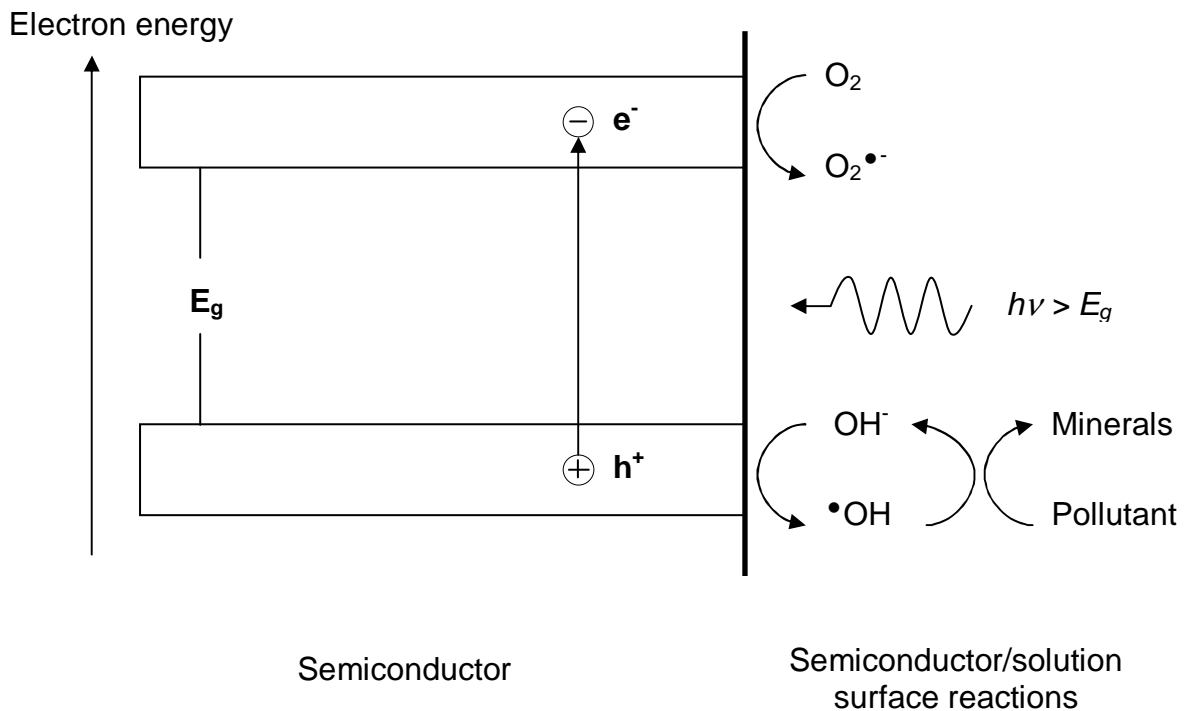
**Figure 1-13. Mechanism of pollutant mineralization in water
using semiconductor photocatalysis (Mills _et al._, 1993)**

Regardless of the mechanism, the oxidation potential for the conductor valence band (3.1 V) or the hydroxyl radical (2.8 V) is greater than that of oxidizing agents commonly used in conventional water treatment, for example chlorine (1.36 V), hydrogen peroxide (1.78 V), and ozone (2.07 V).

1.9.2 The kinetics of titanium dioxide photocatalytic degradation

Many studies of the photocatalysis of organic pollutants by TiO_2 have reported that the initial rate (r_i) of photodegradation of the pollutant (P) fits a Langmuir-Hinshelwood model (Equation 1-6) (Turchi _et al._, 1989; Honglay Chen _et al._, 1998):

$$r_i = \frac{-d[P]_i}{dt} = \frac{k(P)K(P)[P]_i}{1 + K(P)[P]_i} \qquad \text{Equation (1-6)}$$

Where, $[P]_i$ = initial concentration of the pollutant P; $K(P)$ the adsorption coefficient of the reactant P on the TiO_2 surface; and $k(P)$ is the proportionality constant which provides a measure of the intrinsic reactivity of the photoactivated surface with P. It is found that $k(P)$ is proportional to I_a^θ, where I_a is the rate of light absorption and θ is a power term which is equal to $^1/_2$, or 1, at high, or low, light intensities, respectively (Mills *et al.*, 1993). The constants k and K may be determined from a plot of $1/r_i$ *vs.* $1/P_i$. If a catalytic system obeys the Langmuir-Hinshelwood model the plot should be linear. The intercept of the line provides $1/k$ with the slope equal to $1/kK$.

1.9.3 Titanium dioxide photocatalysis for water treatment

There is some dispute as to who first demonstrated the degradation of an organic compound using TiO_2. An early example was published by Mashio et *al.* in 1956 entitled "Autooxidation of TiO_2 as a photocatalyst". The research involved dispersion of TiO_2 powder into various organic solvents, such as alcohols and hydrocarbons, while being irradiated by a mercury lamp (Hashimoto *et al.*, 2005). This research along with other work started the interest in the use of TiO_2 as a means to degrade pollutants from both waste and potable water. There are many examples of pollutants successfully treated using TiO_2 photocatalysis: disinfection of municipal wastewater (*Li et al.*, 1996); destruction of cyanobacterial toxins (Robertson *et al.*, 1997); and the removal of trace organics from drinking water (Honglay Chen *et al.*, 1998).

Ollis (1988) conducted a preliminary comparison of the economics associated with the removal of PCBs from waste water using activated carbon, UV-ozone and a near UV semiconductor photocatalysis system. The calculated costs given in Table 1-3 were updated from 1987 to 1993 by Mills et al. (1993). As can be seen, the calculations indicate that semiconductor photocatalysis could

be economically comparable with activated carbon for water purification systems on an intermediate to large scale. Additionally, semiconductor photocatalysis is significantly cheaper than UV/O$_3$ even at a small scale.

Capacity MGD	Cost, US $		
	Activated Carbon	UV/O$_3$	Photocatalysis
0.03	7.79	13.00	9.85
0.12	4.25	6.32	4.36
0.23	3.19	4.92	3.21
0.92	2.21	3.83	2.23
2.44	1.95	3.10	2.00

Table 1-3. Estimated costs for different water purification systems (1993). MGD = million of gallons per day (Mills *et al.*, 1993)

TiO$_2$ photocatalysis has also been combined with oxidation technologies, TiO$_2$/H$_2$O$_2$ and TiO$_2$/O$_3$ (Dominguez *et al.*, 2005). The main draw backs of these techniques is the required use of expensive additional reagents like H$_2$O$_2$ or the use of a reagent that must be generated on site and strictly monitored in the case of O$_3$.

Photocatalysis is also effective in the treatment of pollutants in potable water. Mills *et al.* (1996) demonstrated the destruction of bromate ions to bromide and oxygen with a platinised titanium dioxide illuminated with ultraviolet light. Eggins *et al.* (1997) demonstrated the removal of humic acid from potable water using titanium dioxide semiconductor photocatalysis. It took approximately 12 min to reduce the humic acid concentration by half; however 50% complete mineralization took 60 min. The ability of TiO$_2$ to remove humic substances has been confirmed by other workers (Bekbolet *et al.*, 2002; Wiszniowski *et al.*, 2002). Another study by (Gracia *et al.*, 2000) used TiO$_2$ supported on alumina, in conjunction with O$_3$, to successfully remove a number of organic compounds from raw river water.

Kim *et al.* (2005) demonstrated the use of TiO$_2$-coated glass beads for the inactivation of the cyanobacteria *Anabaena* spp. and *Microcystis* spp. The

glass beads were deployed into eutrophied water containing the respective cyanobacteria, irradiated with UV-A light, and the effect of their photocatalytic action observed. The two cyanobacterial species lost their photosynthetic ability and became separated into individual cells. These cyanobacterial species are implicated in the production of GSM and MIB and this method could be applied to limit their growth.

Lawton and co workers (Lawton *et al.*, 2003b) in an initial study reported that Geosmin (GSM) and 2-methylisoborneol (MIB) were completely destroyed within 60 min using TiO_2. Further work is required to elucidate and optimize the mechanism of photocatalysis. However, the initial results are extremely encouraging demonstrating a novel approach to the destruction of GSM and MIB.

1.9.4 Photocatalytic reactor types

Photocatalytic reactors are essentially designed around how the semiconductor catalyst is deployed within the reactor, either in colloidal form or as an immobilised film. In reactors that deploy the catalyst as a slurry the rate of pollutant destruction is predominantly determined by light intensity, the quantum efficiency of the catalyst and the adsorbent properties of the reacting and non-reacting components in solution. The major disadvantage of reactors that utilise the catalyst as a slurry or suspension is that post treatment the ultra-fine catalyst must be separated from solution, which can be a time consuming and expensive process (Ray *et al.*, 1998). An additional problem is that light penetration of UV light is limited due to UV shielding and absorption by catalyst particles and natural organic matter. These two problems have lead to the majority of research investigating the use of immobilised semiconductor catalysts for pollutant degradation as it avoids these issues. Immobilisation of the catalyst creates a different problem however, with pollutant destruction occurring at the liquid-solid interface and mass transfer from the bulk of the liquid to the catalyst surface can now be the limiting factor in pollutant degradation.

A scaled up reactor therefore must deliver efficient illumination of the semiconductor catalyst as well as conventional chemical reactor scale-up complications such as mixing and mass transfer, reactant catalyst contacting, flow patterns, and reaction kinetics (Ray, 1999a). Ray (1998) reports that light illumination is of the utmost importance for scaled up photocatalytic reactors as it activates the catalyst, therefore determining the water treatment capacity of the reactor. He also classifies photocatalytic reactors by arrangement of the light source and reactor vessel; immersion type, with lamp(s) immersed within the reactor; external type with lamps outside the reactor (like the reactors in used in Chapter 4 and 5); or distributive type (Figure 1-14) with the light distributed from the source to the reactor by optical means such as reflectors or optical fibres.
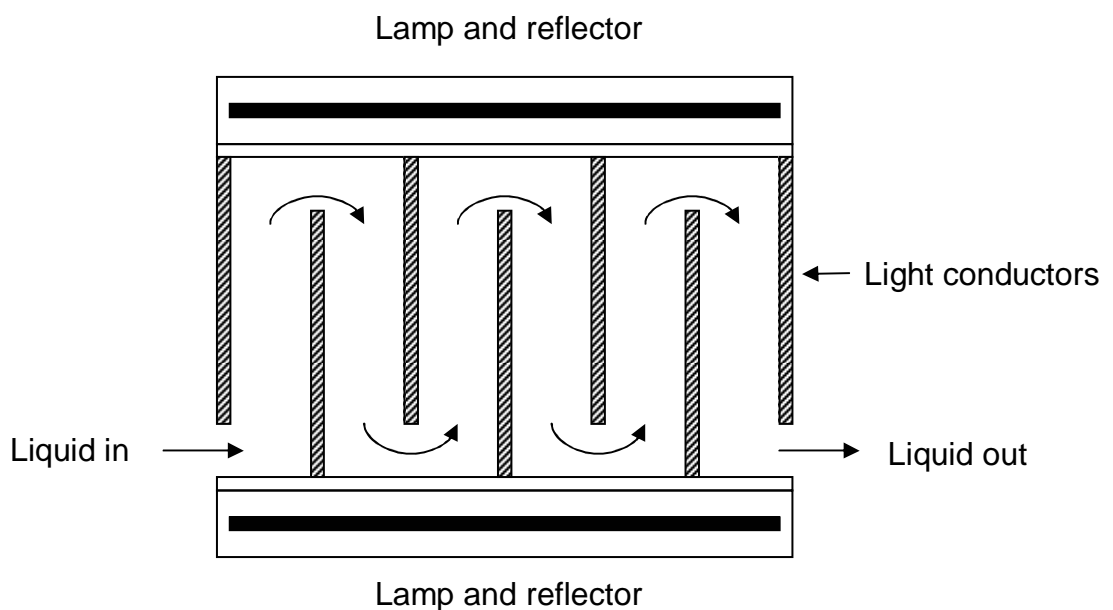
Figure 1-14. Plan view of a distributive type photocatalytic reactor (Ray *et al.*, 1998).

The distributive reactor (Figure 1-14) is a rectangular vessel in which light conductors, such as glass slabs or rods, coated with the photocatalyst, are

embedded vertically. The lamps, with reflectors, are placed on two sides of the reactor with the liquid entering and exiting the other two sides. Light entering the conductors are repeatedly internally reflected down the length of the conductor and at each reflection come in contact with the catalyst present on the surface of the conductors (Ray *et al.*, 1998). Mukherjee *et al.*, (1999) reported the degradation of special brilliant blue (SBB) dye using a distributive reactor (Figure 1-15). The reactor consists of a cylindrical vessel, within which quartz glass tubes coated with catalyst are placed. The light from the light source is focussed down the tubes via a lense and reflector.
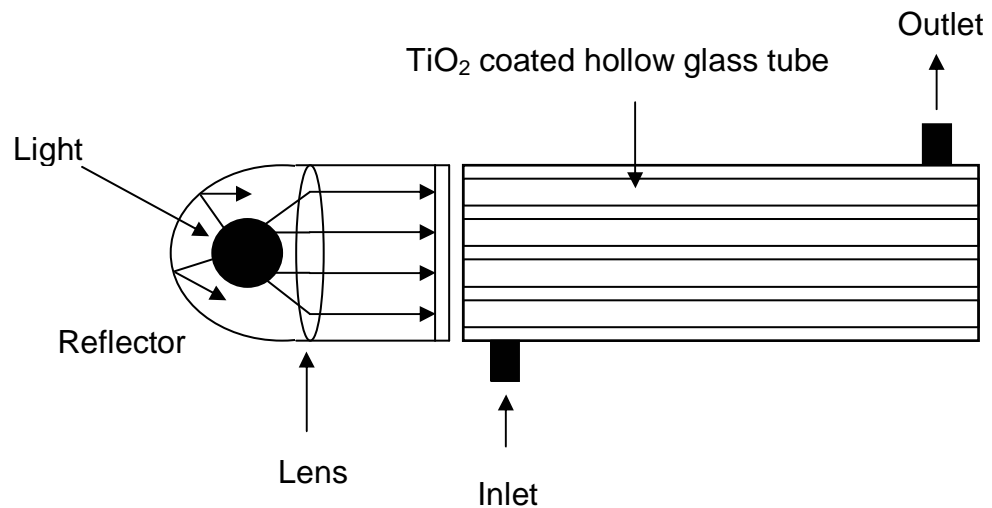
Figure 1-15. Bench-scale multiple tube photocatalytic reactor (Mukherjee *et al.*, 1999).

Another factor that can dictate the design of photocatalytic reactors is the cost of artificial generation of photons required to activate the catalyst and destroy the pollutant. This has lead to a number of reactors utilising solar energy to activate the catalyst (Bahnemann, 2004; Robertson *et al.*, 2005). Current reactors frequently used include, thin-filmed-fixed-bed reactors (TFFBR) (Goslich *et al.*, 1997), compound parabolic collecting reactor (CPCR) (Rodriguez *et al.*, 2005; Perez *et al.*, 2006) and double skin sheet reactor (DSSR) (van Well *et al.*, 1997).

TFFBR reactors were one of the first solar reactors not applying a light-concentrating system, thus being able to utilize diffuse as well as the direct portion of solar UV-A irradiation for the photocatalytic process. A TFFBR pilot plant has been installed at the site of a textile factory in Tunisia (Figure 1-16) (Bahnemann, 2004). The reactor treated waste water from a textile plant and could be operated with a suspended or fixed catalyst. The waste water was pumped up to the top of the thin film and flowed across the surface of the thin film. The water was then collected in a tank at bottom and returned to original tank.
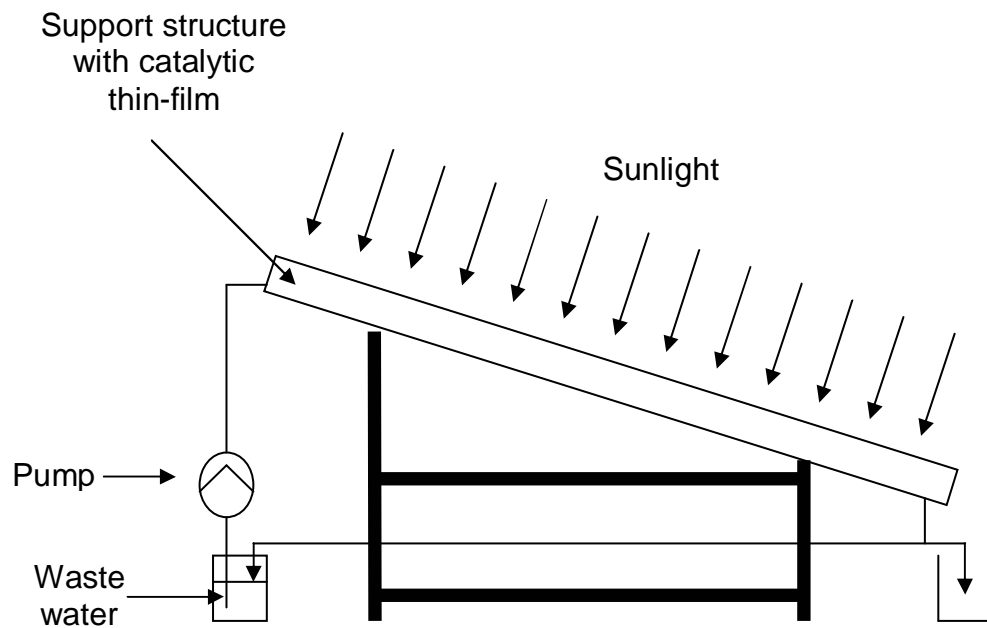
Figure 1-16. Thin-Film-Fixed-Bed Reactor (TFFBR) (Bahnemann, 2004).

Another non-concentrating reactor is the DSSR. The reactor consists of a flat and transparent structured box made of PLEXIGLAS (van Well *et al.*, 1997). The inner structure can be seen in Figure 1-17, the suspension containing the photocatalyst and waste water is pumped through the channels. This reactor can also utilise both direct and diffuse portions of solar radiation. Dillert *et al.* (1999) used a DSSR to treat biologically pre-treated industrial waste waters from Volkswagen AG factories in Wolfsburg (Germany) and Tatbaté (Brazil).
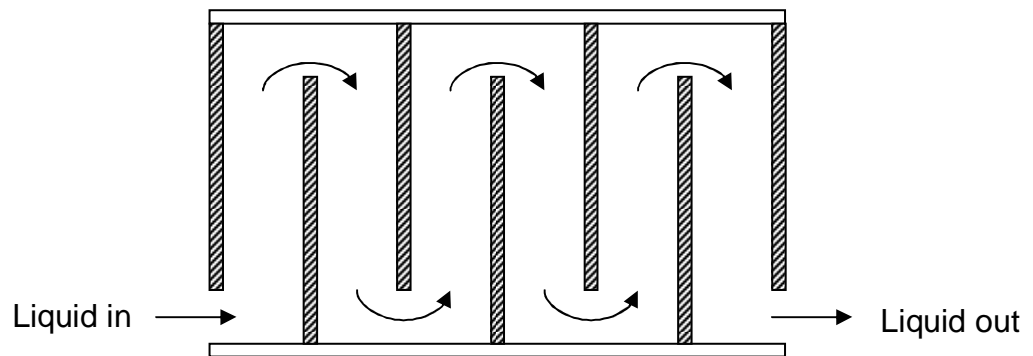
Figure 1-17. Plan view of a Double Skin Sheet Reactor (DSSR) showing the inner structure of the transparent structured box made of PLEXIGLAS.

1.10 PROJECT AIMS

The aim of this thesis is to determine the effectiveness of the TiO_2 photocatalytic process for the oxidation of GSM and MIB. The processes investigated here will utilise a pelleted TiO_2 semiconductor photocatalyst called Hombikat K01/C, produced by Sachtleben, Germany. It is proposed that this catalyst will not suffer from the problems encountered when using powdered P-25 to photocatalyse GSM and MIB. These aims will be achieved through the following objectives:

- Development of a rapid analytical technique, using SPE and GC-MS, to allow trace analysis of large numbers of samples

- Evaluation of GC-MS instrument for the analysis of GSM and MIB

- Design of a bench scale reactor to evaluate Hombikat K01/C in degrading GSM and MIB

- Optimisation of bench scale reactor to minimise the large system losses encountered when investigating the photocatalysis of GSM

- Investigation of the factors effecting the photocatalytic destruction of GSM, including initial substrate concentration, pH, light intensity, and aeration rate.

- Investigation of any potential kinetic istope effect by conducting photocatalysis of GSM in deuterated water.

- Development of a pilot photocatalytic flow reactor to evaluate Hombikat K01/C in degrading GSM in raw waters

CHAPTER 2 - ANALYSIS OF 2-METHYLISOBORNEOL AND GEOSMIN

2.1 INTRODUCTION

2.1.1 Analysis of geosmin and 2-methylisoborneol

In 2005 all drinking water supplied in the UK had to be wholesome and comply with the standards set in the Water Supply (Water Quality) Regulations 2000. These regulations incorporate the European Community Drinking Water Directive (98/83/EC) into British Law. Taste and odour was one parameter that was regulated in this legislation with a maximum dilution number of 3 for both taste and odour at 25°C, the higher the dilution number the more pronounced the taste and odour in the water. These standards were set for aesthetic reasons. Therefore water companies in the UK supplying drinking water have a regulatory requirement for taste and odour levels in water. At this time there is no specific regulatory requirement for levels of geosmin (GSM) and 2-methylisoborneol (MIB) in drinking water, however many water companies do monitor for GSM and MIB (Table 2-1). Of the 28 water companies contacted, 22 replied, with 8 (36 %) monitoring for GSM and MIB, usually at specific times of the year or in response to off-flavour complaints. Whether companies monitored for GSM or MIB was strongly dependant on where they sourced their raw water for drinking water from. A typical management strategy would involve a risk assessment of a source, where historical data of past off-flavour would be taken into account. Routine sampling would begin at high risk times, i.e. during ideal cyanobacterial growth conditions. It is clear from the correspondence received, that despite it not being a regulatory requirement to monitor for GSM and MIB, certain water companies regard off-flavour as a major issue.

Water Company	GSM/MIB Analysis	Method
Anglian Water Services Ltd [d]	-	-
Bournemouth & West Hampshire Water plc	-	-
Bristol Water plc [b]	GSM+MIB	GC-MS
Cambridge Water plc	-	-
Cholderton & District Water Company [a]	-	-
Dee Valley Water plc [b]	GSM	GC-MS
Dwr Cymru / Welsh Water [b]	GSM+MIB	GC-MS
Essex & Suffolk Water [c]	-	-
Folkestone & Dover Water Services Ltd	-	-
Jersey Water [a]	-	-
Mid Kent Water plc	-	-
Northern Ireland Water Service	GSM+MIB	HPLC
Northumbrian Water Ltd	-	-
Portsmouth Water plc	-	-
Scottish Water	GSM+MIB	GC-MS
Severn Trent plc [b]	GSM+MIB	SPE-GC-MS
South East Water Ltd	-	-
South Staffordshire Water plc [a]	-	-
South West Water Ltd	GSM+MIB	SPE-GC-MS
Southern Water	-	-
States of Guernsey Water Board [a]	-	-
Sutton & East Surrey Water plc	-	-
Tendring Hundred Water Services Ltd [a]	-	-
Thames Water Utilities Ltd	-	-
Three Valleys Water plc	-	-
United Utilities Water plc [a]	-	-
Wessex Water Services Ltd	GSM+MIB	SPE-GC-MS
Yorkshire Water Services Ltd	-	-

Table 2-1. Analysis of GSM/MIB by water companies in the UK
[a] no response   [b] analysis conducted at Severn Trent laboratories
[c] part of Northumbrian Water Ltd   [d] part of Anglican Water Group plc
Non-entry (-) indicatses that no specific analysis exists for GSM/MIB.

Current methods for detection of GSM and MIB fall into two distinct categories, sensory analysis and instrumental analysis. Both analyses must be able to detect GSM and MIB at the nano gram per litre level since humans have a very low threshold for these odours, in the order of 35 ng L^{-1} or less (Howgate, 2004).

Sensory analysis, such as flavour profile analysis (FPA), are capable of detecting volatile organic compounds (VOCs), a group which includes GSM and MIB (Morran *et al.,* 2004). However it is difficult to identify and quantify these

compounds quantitatively using sensory analysis (Bett *et al.*, 1997). Limits of detection for GSM and MIB in water can vary depending on the sensory panellist conducting the flavour profile analysis. Rashash *et al.* (1997) reports limits of detection of 6 – 10 ng L^{-1} for GSM and MIB using FPA.

Two other methods of GSM and MIB analysis which may have promise for the development of a simple colorimetric test are an Enzyme-linked immunosorbent assay (ELISA) method developed by (Chung *et al.*) (1990, 1991) and another method developed by Perschbacher *et al.* (1995).

Chung *et al.* (1990, 1991) reported an ELISA method, in which antibodies to GSM and MIB are linked to colorimetric development, to detect GSM and MIB in water samples. Although rapid the reported sensitivity (1000 μg L^{-1}) is too low to be useful for detecting of GSM and MIB. Samples would have to be pre-concentrated before analysis with these ELISA assays. Perschbacher *et al.* (1995) also reports a colorimetric method to quantify GSM and MIB. One litre of filtered water is pumped through a SPE (solid phase extraction) device and then eluted with toluene. The toluene is then combined with a 1 % vanillin and concentrated sulphuric acid solution. This solution is then agitated and the colour change observed. The severe limitation of this technique is that the colour change for GSM requires approximately 20 hours. The sensitivity (1000 ng L^{-1}) is an improvement on the Chung and co-workers method but is still not sensitive enough for the detection of off-flavour that can be detected by humans. While neither of these methods have the necessary sensitivity required to detect GSM and MIB at low environmental concentrations, the development of a simple, rapid colorimetric method would be off great value to unskilled persons requiring information on off-flavour in water. This would apply particularly to aquaculturists who cannot afford expensive instrumentation or do not have the technical ability for complex analytical methods.

Instrumental analysis also has its advantages and disadvantages. Traditional methods of detection and quantification in the nano gram per litre range require large sample volumes (100 – 1000 mL) and substantial sample concentration

procedures such as liquid-liquid extraction (Rashash *et al.*, 1996; Ridal *et al.*, 1999) or relatively complex equipment, e.g., closed loop stripping analysis (Palmentier *et al.*, 1998).

A relatively new analytical technique devised to isolate volatile organic carbons from sample matrices called solid phase microextraction (SPME) was developed in 1989 by Belardi *et al.* This method of extracting volatile samples was combined with GC-MS for analysis and there has been growing interest in this combined technique. SPME eliminates most of the drawbacks in the preparation of aqueous samples, integrating sampling, extraction, concentration and sample introduction in a simple process. The technique has been used to measure the concentration of a number of important odour-causing VOCs in surface waters, with detection limits in the nano gram per litre levels (Sung *et al.*, 2005). GSM and MIB have also been detected in algal cultures at micro gram per litre levels (Lloyd *et al.*, 1998; Watson *et al.*, 1999) and at nano gram per litre levels under optimal conditions. SPME is predominantly coupled with gas chromatography-mass spectrometry for separation and analysis (Watson *et al.*, 2000; Lin *et al.*, 2002; Robertson *et al.*, 2003).

A new analytical method developed by Zhang *et al.* (2006) reported detection limits of 50 pg L^{-1} and 0.34 ng L^{-1} levels respectively for GSM and MIB. These very low detection limits were achieved by a lengthy two-stage sample preparation step, with analysis conducted using a specialised GC-MS.

Although the previous methods have their advantages and disadvantages for the identification of GSM and MIB a method was required for this research that could rapidly separate and identify GSM and MIB. SPME represents an improvement on older techniques but still has limitations, including slow sampling speeds and limited lifetime of the SPME fibres. Furtula *et al.* (2004) reported throughputs of 20 samples a day with an automated SPME-GC-MS system and that over 100 injections were performed with one SPME fibre. The main analytical criteria for this work was the ability to analyse a large number of samples on a regular basis. Although SPME-GC-MS automation is possible, specialised auto samplers are required and these tend to have limited capacity,

making them unsuitable for processing large numbers of samples. Additionally parallel processing of samples is impossible using SPME and one GC-MS.

Solid-phase extraction (SPE) is a process of sample preparation that concentrates and purifies analytes from solution by sorption onto a disposable solid-phase cartridge, followed by elution of the analyte with a solvent appropriate for instrumental analysis. Mechanisms of retention include normal phase, reverse phase, and ion exchange. Liquid-liquid extraction was traditionally used for sample preparation, but this technique has many disadvantages including the use of large volumes of organic solvents, cost and the tendency to create emulsions. These difficulties were overcome with SPE (Figure 2-1) which was invented in the mid-1970s as an alternative to liquid-liquid extraction. The SPE column is first conditioned by passing a solvent through the sorbent (Figure 2-1a). This wets the packing material, solvates the functional groups of the sorbent and replaces the void spaces of air in the sorbent with solvent. The sample containing the analyte is applied to the column resulting in the concentration of the analyte onto the sorbent (Figure 2-1b). Other components from the sample matrix may also be retained, while others may pass through. Those interferences that are retained on the sorbent may be removed with the appropriate solvent (Figure 2-1c). The final step is to elute the analyte from the column with a specifically chosen solvent that will disrupt the analyte-sorbent interaction (Figure 2-1d). The eluted analyte can then be analysed for quantification of GSM and MIB, e.g. by GC-MS.

SPE of MIB, GSM, and other odour compounds has been reported in the literature. Conte *et al.* (1996) reported extraction efficiencies for MIB in channel catfish pond water averaging 89 % at 101 ng L^{-1} and 84% at 202 μg L^{-1} using a C18 solid-phase. The detection limit of the method was calculated to be 11.5 ng L^{-1}. Cole *et al.* (2003) reported successful extraction of GSM and MIB from water using C-18 solid phase disks. Extracted samples were analysed by GC-MS and the detection limits were in the same range as found by Conte *et al.* (1996), 2.37 and 2.34 ng L^{-1} for GSM and MIB respectively. These methods

described by Conte *et al.* and Cole *et al.* offer rapid, simple and sensitive techniques with high recoveries for both GSM and MIB water samples.
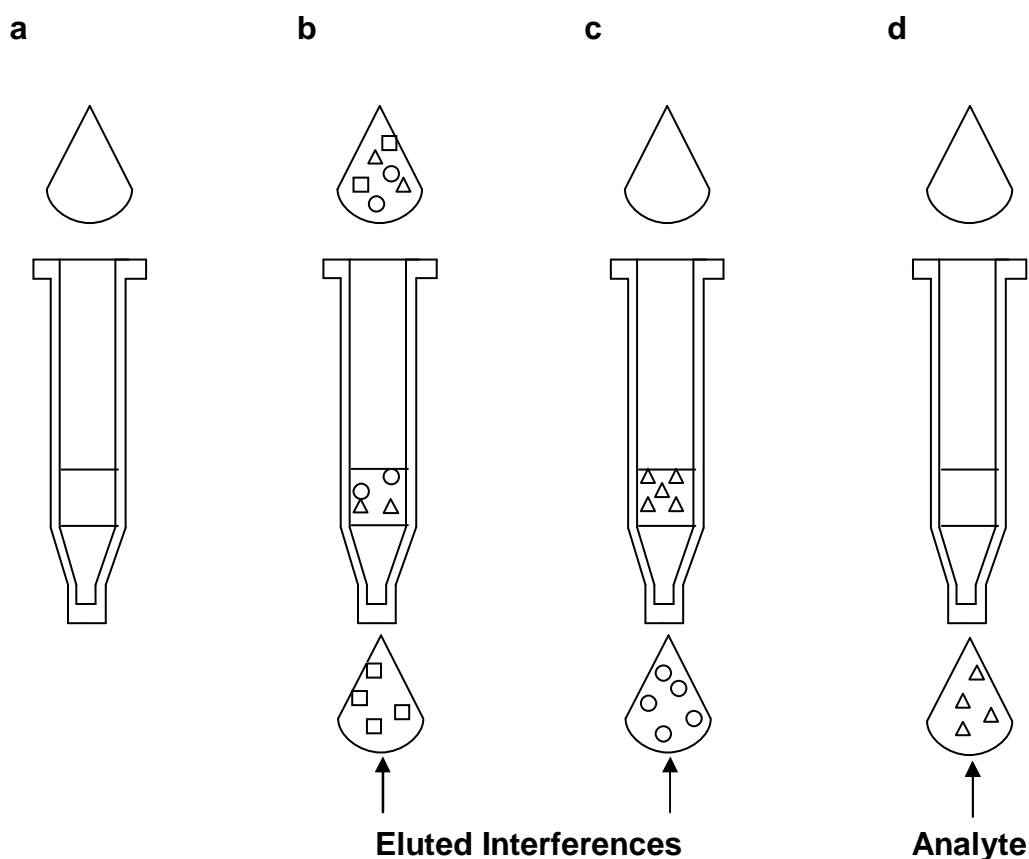
Figure 2-1. The process of solid-phase extraction, (a) solid-phase is conditioned with appropriate solvent, (b) sample containing analyte and interferences applied to the cartridge, (c) cartridge is rinsed with solvent to remove interferences, (d) analyte is eluted from the cartridge with appropriate solvent.

2.1.2 SPE-GC-MS analysis of geosmin and 2-methylisoborneol

Gas chromatography mass spectrometry (GC-MS) has been used by many researchers for the analysis of the off-flavour compounds GSM and MIB, but it was not until the mid-nineties that GC-MS was coupled with SPE for the extraction and analysis of GSM and MIB (Perschbacher *et al.*, 1995; Conte *et al.*, 1996). Cole *et al.* (2003) also reported the use of SPE-GC-MS for analysis

of GSM and MIB. Both these methods used SPE cartridges with a C-18 phase, which is a reversed phase sorbent that is very hydrophobic. Reverse phase sorbents are typically used when aqueous samples are used, and in the case of C-18, when it is required to isolate hydrophobic species from solution. Therefore, it is a phase that can be used to removed GSM and MIB from aqueous samples. As the primary mechanism of interaction for reversed phase sorbents is by van der Waal's forces, the elution of analytes from the sorbent is a simple process of selecting a nonpolar solvent to disrupt these forces. One solvent compatible with reversed phase sorbents is methanol. Therefore, SPE allows samples to be removed from the water phase and subsequently eluted in a solvent that is better suited to analysis by GC-MS. This ability to change solvent is critical if GC-MS is to be used for analysis of GSM and MIB samples taken from water.

In summary the selection of SPE for the separation of GSM and MIB from water samples, coupled with GC-MS for analysis, has a number of key benefits. SPE is rapid in comparison to SPME and other separation methods and most importantly it allows parallel processing of samples, with up to 10 samples capable of being accommodated in a Vacmaster^{TM} Vacuum Manifold system (Figure 2-2). After the samples are processed by SPE they can be analysed by GC-MS, which if equipped with an autosampler and using the method developed here, will allow over 60 samples to be analysed in a 24 hour period. Additionally, the use of SPE will allow small sample volumes (1 mL) to be used, an important factor when a bench-scale reactor with a small volume is to be evaluated. This chapter presents the methods that were developed to isolate and analyse GSM and MIB. It also presents studies which were conducted to compare different types of SPE cartridge and determine whether they were suitable for trace analysis of GSM and MIB.

2.2 METHODS

2.2.1 GC-MS analysis of GSM and MIB

The method described by Watson *et al.* (2000) with the following modifications was used to conduct analysis. Two GC-MS instruments were used throughout the study, a Perkin-Elmer Clarus 500 GC-MS and an Agilent 6890 GC coupled with a 5975 MS. Both instruments were used in conjunction with auto samplers. A Zebron ZB-5 (30 m x 0.25 μm x 0.25 mm, Phenomenex, UK) and DB-5 MSD (30 m x 0.25 μm x 0.25 mm, J&W Scientific, UK) columns were used with the Clarus 500 GC-MS and Agilent GC-MS respectively. The injection volume was 1 μL. A GC temperature gradient was programmed from 60 ℃ (held for 2 min) followed by an increase to 130 ℃ (20 ℃ min^{-1}), then an increase to 152 ℃ (7.5 ℃ min^{-1}) and finally an increase to 300 ℃ (45 ℃ min^{-1}), held for 0.5 min. A 4 minute solvent delay was also in place. For the Clarus GC-MS the mass data was obtained in positive ion mode and Selective Ion Monitoring (SIM) mode by scanning for m/z 112 with a dwell time of 0.2 s The Agilent GC-MS was operated in simultaneous full scan/SIM mode, with the mass range for full scan set between 50 and 300 and the same ion selected for SIM (m/z 112). TurboMass software workstation was used for the GC-MS control, data acquisition and data processing for the Clarus GC-MS and for the Agilent GC-MS Chemstation software was used.

A set of samples were prepared from a GSM-methanol stock solution. This GSM-methanol stock solution was prepared by exhaustively re-suspending approximately 10 mg of (±)-Geosmin (Ultrafine, UK) in analytical grade methanol (10 mL). This solution, with an approximate concentration of 1 mg mL^{-1}, was prepared in a glass airtight container and stored in a freezer. The same process was repeated for 2-methylisoborneol (Ultrafine, UK) of the same approximate weight. These GSM-methanol and MIB-methanol stock solutions were used to prepare the test solutions required for experimentation through the course of this research. Extensive evaluation by Korth *et al.* (1992) proved that GSM and MIB could be stored in methanol for long periods, with no decomposition detected after 250 days at both -15 ℃ an d 22 ℃.

The GSM-methanol stock was diluted to give a range of GSM in methanol samples with approximate concentrations of 1, 10, 50, 100, 500, and 1000 ng mL^{-1}. The concentration of these samples would be compared to GSM standards (1, 10, 50, 100, 500, and 1000 ng mL^{-1}) prepared from a 100 μg mL^{-1} (±)-GSM in methanol standard (Sigma-aldrich, UK). Using the above method to analyse the two sets of samples would achieve two objectives. Firstly it would allow calibration of the two GC-MS systems and establish a method detection limit (MDL) for GSM. Secondly the concentration of the GSM-methanol stock solution could be calculated by comparing the data generated from the analysis of GSM-methanol stock dilutions with the data for the GSM standards. This second point is crucial as it will ensure that all solutions prepared for this work are within a known concentration range. A range (1, 10, 25, 50, 100, 500, and 1000 ng mL^{-1}) of GSM in methanol standards, prepared from a (±)-GSM standard (Sigma-aldrich, UK), were analysed each day that the GC-MS was used for GSM analysis.

As the Clarus 500 GC-MS had poorer sensitivity when compared with the Agilent GC-MS, only the Agilent was used to analyse MIB. Method 2.2.1 was adapted to analyse MIB. All variables were maintained apart from the GC temperature program and the ion selected for SIM mode. The temperature programme was changed to the following, 60 °C (held f or 2 min) followed by an increase to 100 °C (20 °C min^{-1}), then an increase to 175 °C (7.5 °C min^{-1}) and finally an increase to 300 °C (held for 0.5 min). The Agilent GC-MS was again operated in simultaneous full scan/SIM mode, with the mass range for full scan set between 50 and 300 and the same ion selected for SIM (m/z 95).

Each day that the GC-MS was used for MIB analysis a range of MIB in methanol samples, with an approximate range of 1, 10, 25, 50, 100 ng mL^{-1}, were analysed. The samples were prepared from the MIB-methanol stock solution.

2.2.2 SPE of GSM and MIB

The efficacies of three different SPE sorbent phases were evaluated for the recovery of GSM. Reverse phase SPE was carried out using C2, C8, and C18 SPE cartridges; 1 mL reservoir capacity and 25 mg of sorbent (Biotage, UK). For MIB only the C8 and C18 cartridges were evaluated. Triplicates of each sorbet phase were prepared by conditioning with 4 mL of methanol followed by 4 mL of Milli-Q water (Millipore, Waterford, UK). A 1 μg mL^{-1} solution of GSM in Milli-Q water was prepared and 1 mL of the solution was applied to each SPE cartridge. The SPE procedure was carried out using a VacMaster^{TM} Vacuum Manifold System (Figure 2-2). Initially the negative pressure on the manifold was set at -0.05 bar. Upon the sample passing through the cartridge the pressure was then increased to -3.4 bar for 20 s to remove any remaining water. The GSM or MIB was then eluted directly into a GC-MS vial with 1 mL of methanol. A further two elutions of 1 mL of methanol were collected in new vials, three 1 mL elutions for each cartridge. Only one 1 mL elution was collected for MIB. The recovery of GSM and MIB by the different SPE sorbents was then determined by GC-MS.
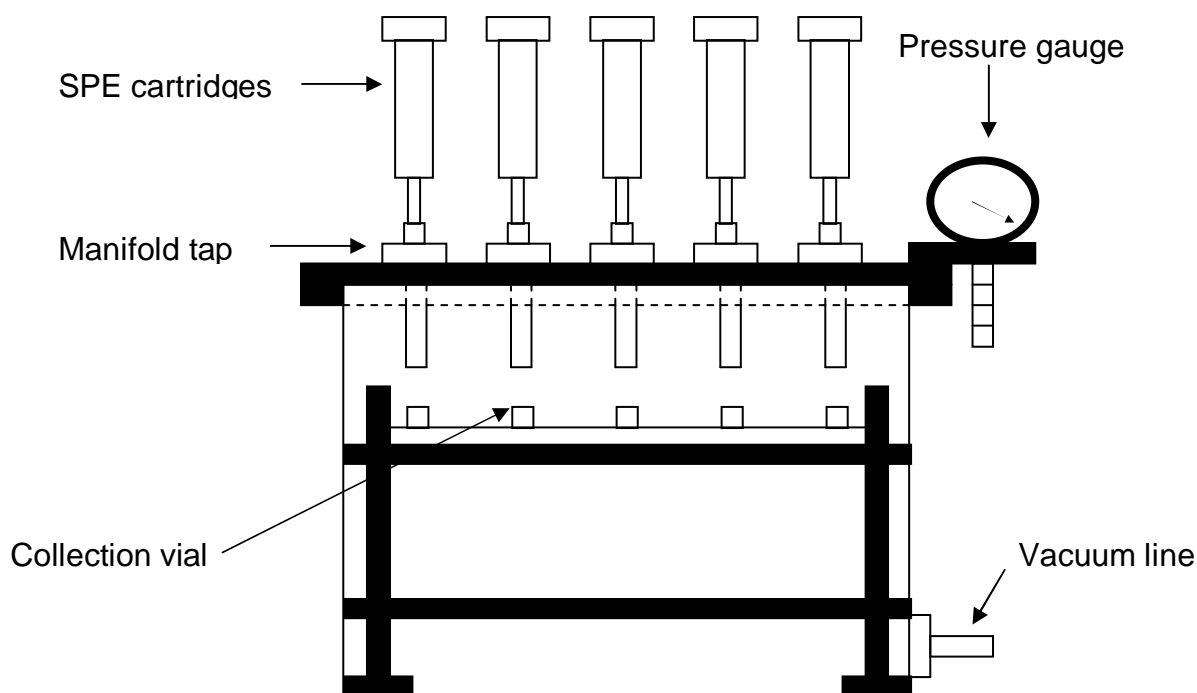
Figure 2-2. Schematic of the Vacmaster^{TM} Vacuum Manifold system.

2.2.3 Evaporation of methanol from GSM and MIB stock solutions

It was noted that the GSM and MIB stock solutions were prepared in methanol, which would subsequently be added along with either GSM or MIB when preparing solutions to evaluate photocatalysis. In this scenario methanol would undergo competitive oxidation, consequently reducing the rate of GSM destruction.   As it was necessary to remove methanol, and its effect as a competing oxidant from GSM and MIB solutions that where to undergo photocatalysis, a method was developed to remove methanol from the GSM and MIB stock solutions.   This method would allow the removal of methanol from small volumes of the GSM or MIB stock solutions as required.

A Techne sample concentrator (Techne, N.J., USA), with a nitrogen supply, was used to evaporate methanol from the GSM and MIB stock solutions using the following method. GSM-methanol or MIB-methanol stock solution was pipetted into a 4 mL glass vial, the pipetted volume dependant on the desired concentration of the final solution. In this instance the volumes pipetted were 50 μl GSM-methanol stock and 10 μl MIB-methanol stock. The needle from the sample concentrator was lowered into the glass vial so as the needle was positioned approximately 2-3 mm above the GSM-methanol or MIB-methanol solution. The flow of nitrogen through the sample concentrator was turned on and maintained at 80 mL min^{-1}. The vial, containing either the GSM-methanol or MIB-methanol solution, was left positioned under the needle for 1 minute, after which the nitrogen was turned off.   This resulted in the methanol being evaporated from the vial. The GSM or MIB was then exhaustively re-suspended by addition of 1 mL of Milli-Q into the vial which was vortexed for 20 s. This solution was transferred from the vial to a volumetric flask using a new glass Pasteur pipette. Milli-Q was then taken up into the pipette and emptied into the volumetric flask after each transfer. This process was repeated twenty times. The re-suspended GSM and MIB solutions were processed as in method 2.2.2 together with comparable solutions of GSM and MIB prepared by direct dilution of the GSM-methanol and MIB-methanol stocks. The recovery of GSM was determined by GC-MS and the re-suspended GSM and MIB solutions compared with the direct dilution solutions for GSM and MIB.

2.2.4 Trace analysis of GSM Using SPE

2.2.4.1 Evaluation of C8 SPE cartridges for trace analysis

Environmental levels of GSM that can cause off-flavour episodes in water can have concentrations in the low ng L^{-1} range. Concentrations in this range are too low to analyse using method 2.2.3. However, SPE can be used for the trace enrichment of GSM in a water sample. For example a 100 mL sample of water containing a trace concentration of GSM could be applied to a SPE cartridge and the cartridge eluted with 1 mL of methanol. Theoretically this would give a enrichment factor of 100, increasing the concentration of GSM in the eluent to a level that can be analysed by GC-MS.

The C8 SPE cartridges used in method 2.2.3 were evaluated to determine if they could be used to concentrate GSM from larger sample volumes. The addition of a 100 mL sample to a SPE cartridge and subsequent elution with 1 mL of methanol would create a concentration step required to investigate samples with a concentration in the environmental range.

Six C8 cartridges were prepared as in method 2.2.3. A 1 mL sample of 1 μg mL^{-1} GSM in Milli-Q was applied to a C8 cartridge, this was repeated to give three cartridges with a 1 mL sample applied. The remaining three C8 cartridges each had a 100 mL sample of 10 ng mL^{-1} GSM in Milli-Q applied to it. The 100 mL samples were contained in individual sample bottles. The samples were transferred from the bottles to the cartridges by Teflon feed lines, the feed lines were attached to the cartridges with adapters that created an air tight seal. All C8 cartridges were eluted with 1 mL of methanol. The SPE procedure was carried out using a VacMaster^{TM} Vacuum Manifold System and the recovery of GSM determined by GC-MS.

2.2.4.2 SPE of waters spiked with GSM

Water samples collected from Aberdeen (tap water) and the River Cowie, Stonehaven (raw water) were spiked with GSM to evaluate SPE for the trace

enrichment of GSM from these waters. These waters will be appreciably different from the Milli-Q water used in previous experiments, with significantly more complex matrices, this is especially noticeable for the River Cowie raw water which has a dark humic colour. Both waters could contain substances which may interfere with the extraction and elution of GSM. Additionally the presence of compounds that may be eluted with GSM could interfere with analysis.

The two collected waters were filtered using GF/C filter disks (110 mm, Whatman International Ltd., Maidstone, UK) to remove particulates. Two solutions were prepared from each water by spiking them with GSM to obtain solutions with concentrations of 10 ng mL^{-1} and 1 μg mL^{-1}. These solutions were applied to C8 cartridges as described in method 2.2.5.1. The SPE procedure was carried out using a VacMaster^{TM} Vacuum Manifold System and the recovery of GSM determined by GC-MS.

2.2.4.3 Use of aqueous methanol wash to remove matrix interferences

Using SPE to concentrate GSM from larger volumes of water could cause the problem of compounds being eluted in addition to GSM that could interfere with the quantification of GSM. Therefore the use of an aqueous methanol wash to remove matrix interferences was proposed. This aqueous methanol wash would be applied to the C8 cartridge after the initial sample had been applied and eluted. The effect of aqueous methanol washes, with 90, 80, 70, 60, 50, 40, 30, and 20 % methanol, were investigated to determine whether they would elute GSM from C8, This would establish if GSM would be lost by using an aqueous methanol wash step.

SPE cartridges were prepared as in method 2.2.3 and 1 mL of 1 μg mL^{-1} GSM in Milli-Q solution applied to a C8 SPE cartridge and eluted. The aqueous methanol wash being investigated was then applied (1 mL) to the same cartridge and eluted into a collection tube. This sample cannot be quantified by GC-MS as it is an aqueous mixture. To solve this problem 9 mL of Milli-Q was

first added to the collection tube containing the eluted aqueous methanol wash (1 mL). This 10 mL solution was then applied to a new C8 cartridge and eluted, 1 mL of 100% methanol was then applied to the same C8 cartridge and eluted into a vial for analysis by GC-MS. All aqueous methanol washes investigated were performed in triplicate. The SPE procedure was carried out using a VacMaster^{TM} Vacuum Manifold System and recovery of GSM determined by GC-MS.

2.2.4.4 SPE of GSM spiked water with aqueous methanol wash

Having determined that a 40% aqueous methanol wash could be applied to C8 cartridges without any significant loss of GSM, the effect of the wash on removing matrix interferences was investigated. The effect of the wash step on the recovery of GSM in the spiked water samples was also investigated

SPE cartridges were prepared as in method 2.2.2. Triplicate samples (1 mL of 1 μg mL^{-1}) of GSM in Milli-Q, Aberdeen tap water and river water from the Cowie in Stonehaven were applied to C8 SPE cartridges. A 40 % aqueous methanol solution (1 mL) was applied to the cartridge and eluted, followed by the addition of 1 mL of 100 % methanol which was eluted into a collection vial for analysis. The SPE procedure was carried out using a VacMaster^{TM} Vacuum Manifold System, with recovery of GSM determined by GC-MS.

2.3 RESULTS AND DISCUSSION

2.3.1 GC-MS analysis of GSM and MIB

GC-MS analysis of a 1000 ng mL^{-1} ($\pm$)-GSM in methanol standard, prepared from a GSM standard (Sigma-aldrich, UK), indicates that GSM was successfully detected in both full scan (Figure 2-3) and SIM mode (Figure 2-4). A 1000 ng mL^{-1} MIB in methanol solution, prepared from a MIB-methanol stock, was also successfully analysed by GC-MS, resulting in detection of MIB in full

scan (Figure 2.3) and SIM mode (Figure 2-4). The identities of GSM and MIB were verified using a National Institute of Standards and Technology (NIST) mass spectral library. The full scan chromatograms in Figure 2-3 contain peaks other than GSM and MIB. These peaks can be attributed to the methanol used to prepare the GSM and MIB standards and silanol compounds from the column which had been recently replaced. These additional peaks were present when only methanol was injected and analysed, and did not interfere with the analysis of GSM and MIB.

GSM in methanol solutions, with the approximate concentrations of 1, 10, 50, 100, 500, and 1000 ng mL^{-1}, were prepared from a GSM-methanol stock solution (section 2.3.1) were detected by both the Clarus and Agilent GC-MS's. A good linear relationship was observed between GSM concentration and peak area for both instruments in SIM, with correlation coefficients for the Clarus and Agilent GC-MS's 0.9934 and 0.9999 respectively (Figure 2-5).

The GSM in methanol standards prepared from the (±)-GSM standard (Sigma-aldrich, UK) were detected by both GC-MS's in SIM mode. The Agilent detected all concentrations (Figure 2-6), with the calibration having a correlation coefficient of 0.994. However, the Clarus was unable to detect any of the standards with a concentration lower than 500 ng mL^{-1}.

MIB in methanol solutions, with the approximate concentrations of 1, 10, 50, 100, 500, and 1000 ng mL^{-1}, were prepared from a MIB-methanol stock solution (section 2.3.1) were detected the Agilent GC-MS. Again a good linear relationship was observed between MIB concentration and peak area in SIM, with a correlation coefficients of 0.991 (Figure 2-7). MIB concentrations below 10 ng mL^{-1} were not detected.
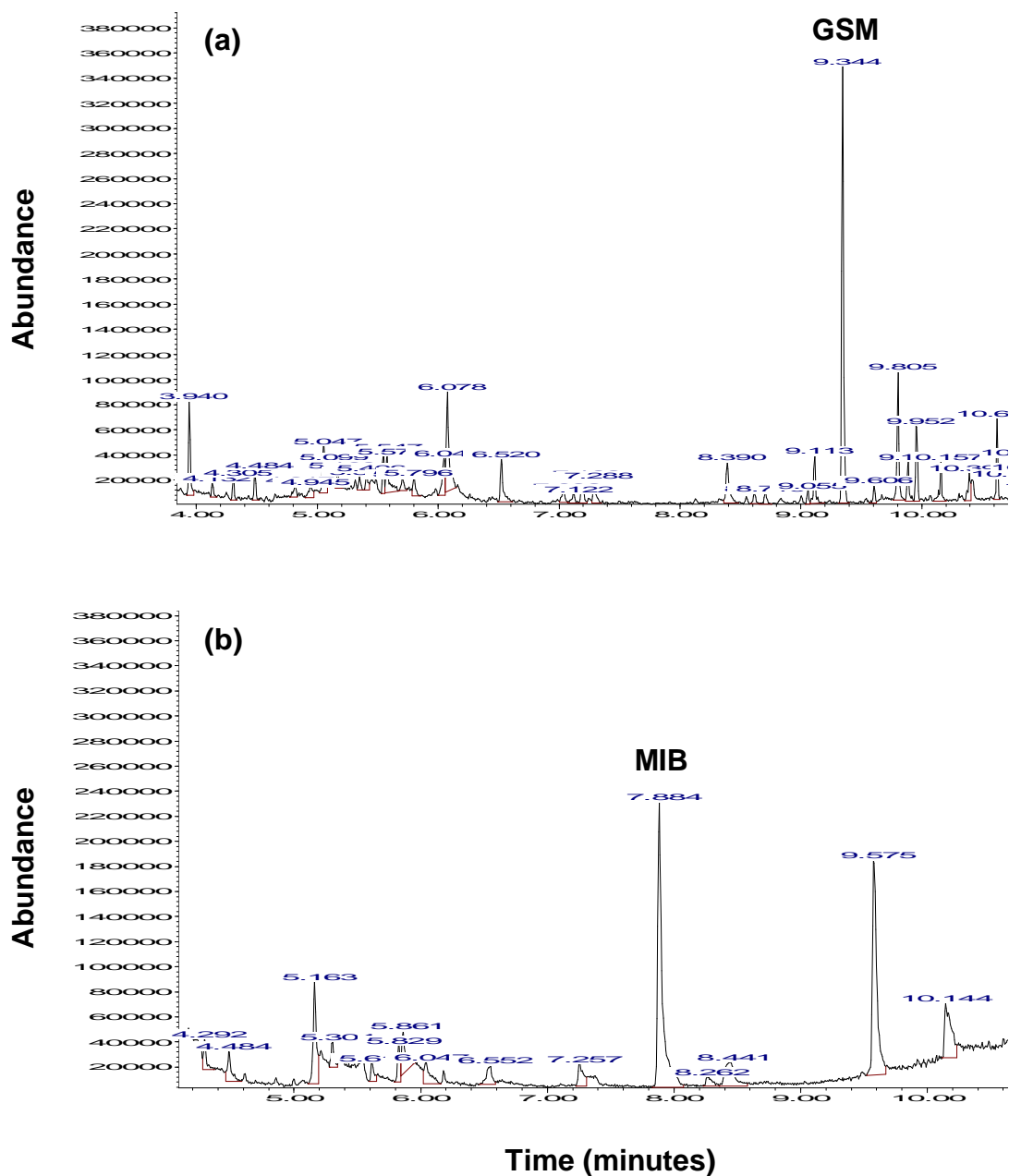
Figure 2-3. Full scan chromatograms of Agilent GC-MS analysis of (a) 1000 ng mL^{-1} (±)-GSM standard (dilution of Sigma-aldrich GSM standard) and (b) 1000 ng mL^{-1} MIB standard (dilution of MIB stock dilution).
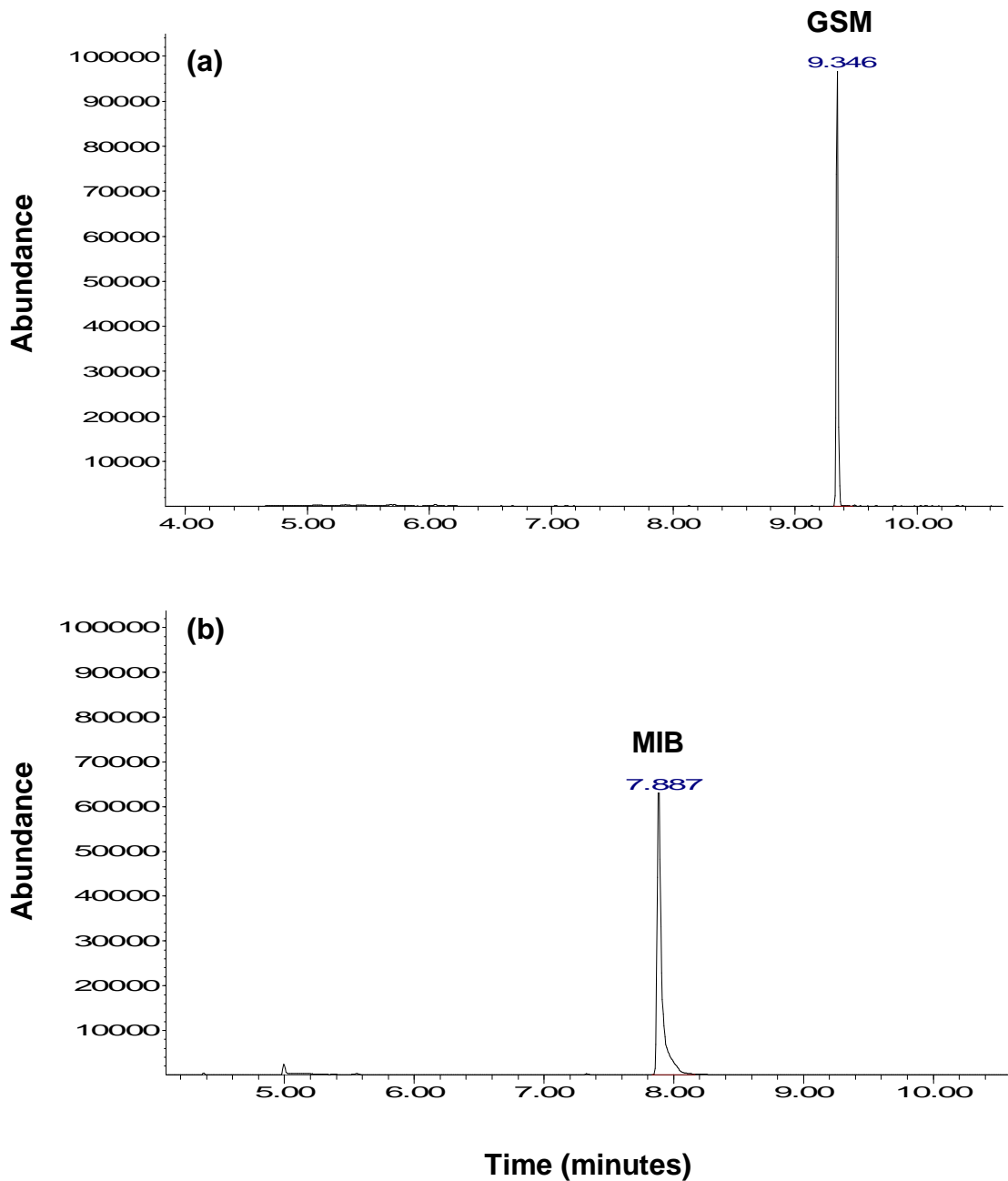
Figure 2-4. SIM (m/z 112 and 95 for GSM and MIB respectively) chromatograms of Agilent GC-MS analysis for (a) 1000 ng mL^{-1} (±)-GSM standard (dilution of Supelco GSM standard) and (b) 1000 ng mL^{-1} MIB standard (dilution of MIB stock dilution).
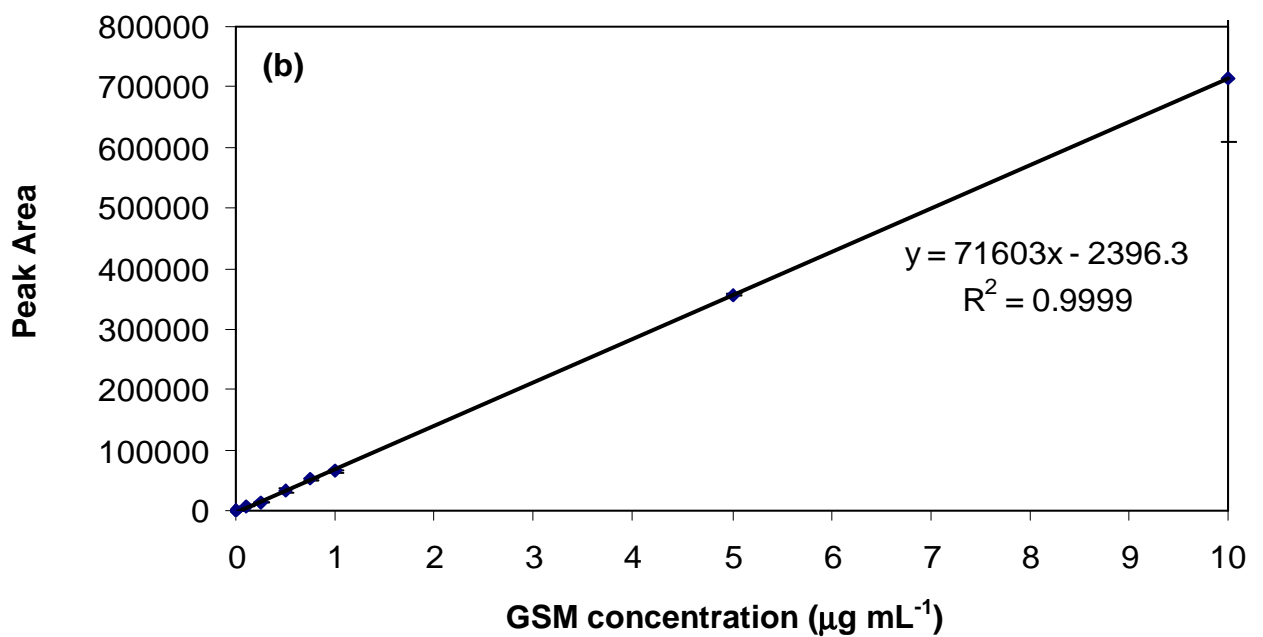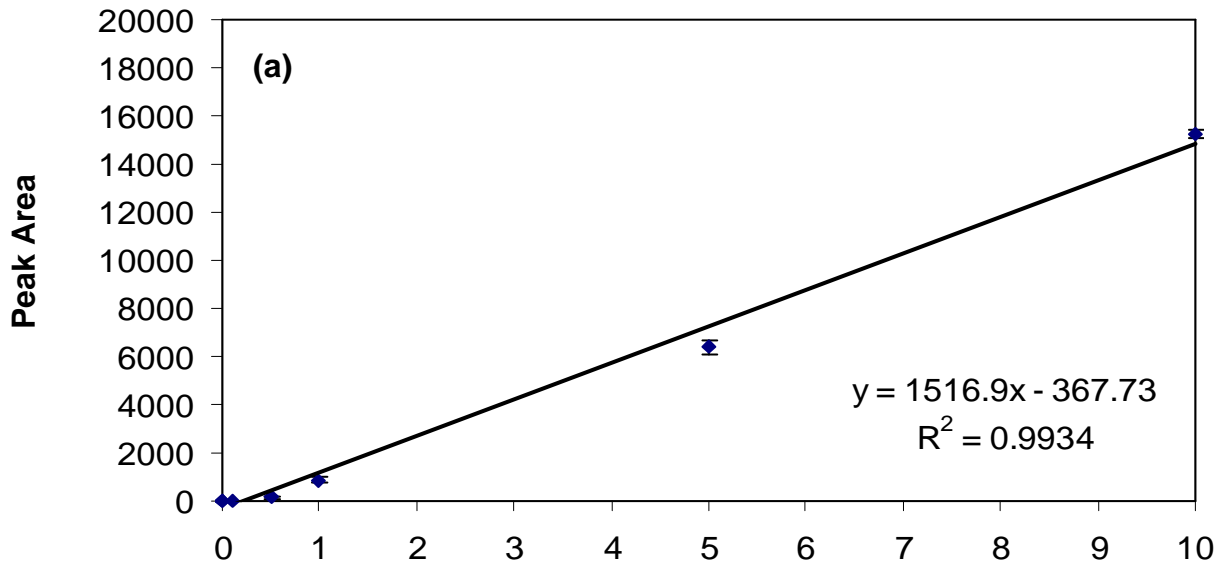
Figure 2-5. Analysis of GSM in methanol solutions using (a) Clarus (b) Agilent GC-MS's. Solutions, concentrations 0.01, 0.1, 0.5, 1, 5, and 10 μg mL^{-1}, prepared from the GSM-methanol stock solution. Data collected in SIM mode.
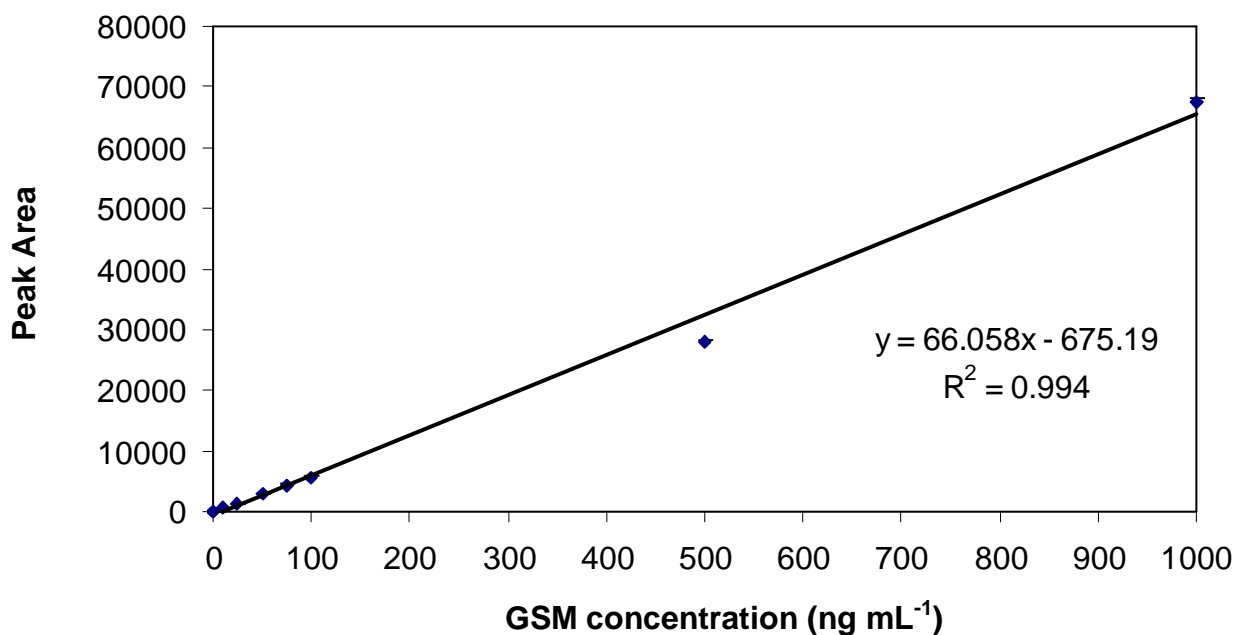
Figure 2-6. Calibration of Agilent GC-MS using GSM in methanol standards (1, 10, 50, 100, 500, and 1000 ng mL^{-1}) prepared from a (±)-GSM standard (Sigma-aldrich, UK). Data collected in SIM mode.
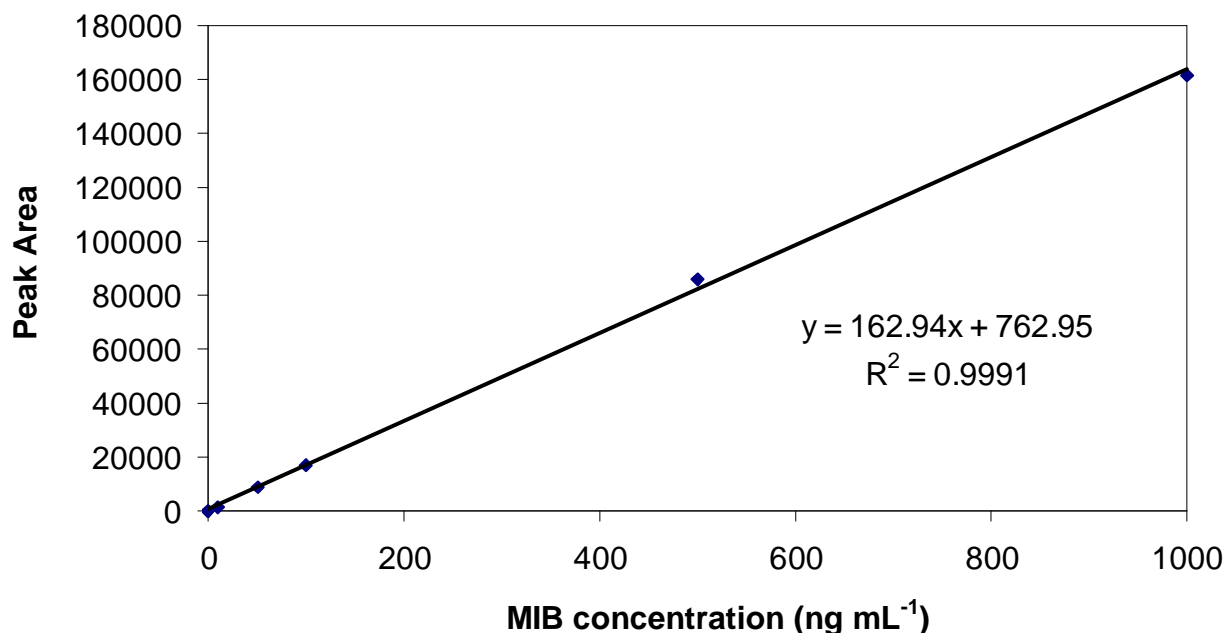
Figure 2-7. Analysis of MIB in methanol solutions by Agilent GC-MS. Solutions, approximate concentrations (1, 10, 50, 100, 500, and 1000 ng mL^{-1}), prepared from the MIB-methanol stock solution. Data collected in SIM mode.

The two data sets (Figures 2-5 and 2-6) show that samples prepared by dilution of the GSM-methanol stock have peak areas approximately ten times higher, across all concentrations, when compared with the standards prepared from the (±)-GSM standard (Sigma-aldrich, UK). This difference in concentration was taken into account when preparing future GSM test solutions. The method detection limit (MDL) for analysis of (±)-GSM in methanol standards using the Clarus was 500 ng mL^{-1}, the Agilent GC-MS performed significantly better with a MDL of 1 ng mL^{-1}. As the Agilent GC-MS had significantly better sensitivity, it alone was used to analyse dilutions of the MIB-methanol stock solution, with a MDL of 10 ng mL^{-1} observed. The Clarus GC-MS was used for the initial development of the GSM and MIB GC-MS analytical method and in the development of the bench-scale photocatalytic reactors in Chapter 3. Neither of these research elements required high sensitivity so the Clarus GC-MS's limitations were not an issue. However, for the majority of the work conducted good sensitivity was required and for this reason the Agilent was used for analysis.

2.3.2 SPE of GSM and MIB

GC-MS analysis of the fractions obtained from the extraction of 1 mL of 1 μg mL^{-1} . GSM shows that total recovery for the three elutions (Table 2-2) was greatest for C18 (97.5 %), followed by C8 (93.2 %), and finally C2 (79.6 %). As expected the first 1 mL elution for each sorbent type was shown to contain the highest concentration of GSM. C8 had the highest recovery (92.8 %) of GSM in the first elution and also the best reproducibility when compared to the next best SPE sorbent C18, 2.25 % RSD compared to 8.75 %. In the case of C2 and C8 the second fraction contained less than 1 % of the total GSM extracted, C18 contained over 6 %. For all sorbent types the third fraction contained residual or no detectable level of GSM (>0.3 %). These results clearly demonstrate the effect of the polarity of the SPE sorbent in retaining GSM, with GSM retention decreasing from the most polar sorbent (C18) to the least polar (C2).

SPE Sorbent	% Recovery Eluent 1	% RSD (n=3)	% Recovery Eluent 2	% RSD (n=3)
C2	78.9	6.51	0.6	29.65
C8	92.8	2.25	0.4	8.66
C18	90.9	8.75	6.3	1.64

Table 2-2. Recovery of 1 μg mL^{-1} GSM using C2, C8, and C18 SPE cartridges as determined by GC-MS.

As reported by Cole *et al.* (2003) extraction of MIB and GSM using SPE followed by GC-MS analysis allows rapid and inexpensive quantification. The SPE method used by Cole *et al.* (2003) used C18 disks to extract GSM from 1 L of water containing 50 ng L^{-1} of GSM, with a reported recovery of 91 % (± 6.3 %). Although the GSM concentration used in the Cole *et al.* study was significantly lower than used here, and the volume higher, the recoveries using C18 are very similar. The SPE method reported by Cole *et al.* (2003) was considerably more complex than the method described in 2.2.2. As in method 2.2.2, methanol and water were used to prepare a C18 disk, however three 5 mL elutions were made to extract the GSM. These eluents were pooled, then dried and concentrated.

To ensure that the method to extract GSM using SPE was as rapid as possible only one elution would be made from the cartridges used. Pooling three 1 mL eluents, without a concentration step, and analysing by GC-MS would decrease the detection of GSM. Therefore, C8 cartridges were selected to extract GSM from water solutions in this study. Although C18 gave better overall recovery, the recovery and the reproducibility in the first eluent was greatest for C8.

The analysis of the MIB fractions obtained from the extraction of 1 mL of 1 μg mL^{-1} MIB proves recovery and reproducibility for MIB (Table 2.3) was greatest for C8 cartridges, with 82 % MIB recovered in the first fraction with an RSD of 5.01 %, compared with 72% recovery and an RSD of 13.15 % for the C18 cartridges. Cole *et al.* (2003) reported the recovery of MIB by C18 disks from 1 L of water containing 50 ng L^{-1} of MIB as 97.5 % (±16.2 %). This

recovery of MIB with C18 is higher than found in this study, however the variability of MIB recovery in this study and that by Cole *et al.* is similar. Conte *et al.* (1996) also reported on the extraction of MIB from 1 L of water using C-18, with recoveries of MIB from water containing 101 and 220 ng L^{-1} of MIB 85.3 (±16.2 %) and 82.2 (±6.5 %) % respectively. The greater recoveries for MIB using C18 in both studies can be attributed to the use of more than one elution to extract the MIB.

SPE Sorbent	% Recovery	% RSD (n=3)
C8	82.0	5.01
C18	72.3	13.15

Table 2-3. Recovery of 1 μg mL^{-1} MIB using C8, and C18 SPE cartridges as determined by GC-MS.

Only one 1 mL methanol elution was made from each C8 and C18 cartridge loaded with the MIB solution. Again this is to ensure that the SPE method is as rapid as possible and that the sensitivity of the MIB analysis by GC-MS is not compromised. C8 cartridges were selected to extract GSM from water solutions in this study as they gave the highest recovery for MIB from water with one elution.

2.3.3 Evaporation of methanol from GSM and MIB stock solutions

Removal of methanol from the GSM-methanol and MIB-methanol stock solutions was achieved by evaporating the methanol using a sample concentrator with a nitrogen gas supply. GC-MS analysis of the 5 μg mL^{-1} re-suspended GSM solution shows that recovery of GSM using the method described in method 2.3.3 gave 89 (± 0.66) % recovery. For the re-suspended 1 μg mL^{-1} MIB solution recovery was extremely poor with only 2.3 (± 0.18) % of MIB recovered. This difference in recovery is possibly due to the different volatilities of GSM and MIB. The boiling points of MIB and GSM are reported as 196.7 and 165.1 °C by Pirbazari *et al.* (1992). This would suggest that MIB is

less volatile than GSM. However, the manufacturers (Ultrafine, UK) of the GSM and MIB used in this work stated the boiling points of MIB and GSM as 165 and 270 °C. The Merck Index (Budavari, 2001) also states the boiling point of GSM as 270 °C. The experiment conducted here would suggest that MIB is more volatile than GSM when dissolved in methanol. If the boiling point of GSM is 270 °C, then MIB will have a boiling point (165.1 °C) almost 40 % lower than GSM. This would suggest that GSM is considerably less volatile than MIB explaining why GSM was not volatilised during the evaporation of methanol by nitrogen gas.

Another possible explanation may be the adhesive properties of GSM. After the evaporation of methanol from the GSM-methanol stock, present in glass 4 mL vials, bands of small globules were observed, adhering to the inside lower portion of the vial. The number of globules and bands were dependant on the volume of GSM-methanol stock used, with the number of globules and bands increasing as volume increased. The interaction between the GSM and the glass may be a factor in limiting its volatilization during methanol removal. GSM is an oil at room temperature, compared to MIB which is a crystalline solid, increasing the likelihood of GSM adhering to the glass vial over MIB. Evaporation of methanol from the MIB-methanol stock by nitrogen, at the flow rate investigated, and subsequent re-suspension in Milli-Q is not a viable option for preparation of methanol free MIB solutions.

2.3.4.1 Evaluation of C8 SPE cartridges for trace analysis

The concentration of GSM in a 100 mL solution using C8 SPE was achieved. The recoveries of the 100 mL 10 ng mL^{-1} GSM solution and the 1 mL 1 μg mL^{-1} GSM control are very similar, with recoveries of 91.3 (± 9.4) % and 94.4 (± 12.9) % respectively. This clearly demonstrates that C8 cartridges are capable of accepting the increased volume of water and that the recovery of GSM is good with little effect on performance. This success allowed the progression to investigating GSM concentration in other water types.

2.3.4.2 SPE of waters spiked with GSM

Following the success of C8 SPE cartridges in concentrating GSM from Milli-Q water, the enrichment of GSM from tap water and river water using C8 was evaluated. Aberdeen tap water and River Cowie water spiked with GSM will provide a significantly more robust test of SPE for concentrating GSM. The River Cowie water will provide a water type similar to that which may contain GSM in the natural environment. Both waters were filtered prior to spiking with GSM, a significant covering of small pieces of organic matter were observed on the filter used for the River Cowie water.

	% Recovery			
	1 mL Control	RSD % (n=3)	100 mL solution	RSD % (n=3)
Aberdeen Tap Water	52.7	10.7	91.7	13.5
River Cowie Water	86.0	16.3	92.6	16.2

Table 2-4. Recoveries of 100 mL 10 ng mL^{-1} re-suspended GSM and 1 mL 1000 ng mL^{-1} re-suspended GSM solutions using C8 cartridges for (a) Aberdeen tap water and (b) Cowie river water

The recovery of GSM from the 100 mL tap water sample that had been concentrated and eluted with 1 mL was significantly higher, 91.7 (± 13.5) %, than the recovery for the 1 mL tap water control 52.7 (± 10.7) % (Table 2-4). The 1 mL control and 100 mL samples for River Cowie water show similar recoveries for GSM (Table 2-4), with recoveries of 86.0 (± 16.3) % and 92.6 (± 16.2) % respectively. The correlation between recoveries of GSM for control and 100 mL samples were considerably closer for the River Cowie samples than for the tap water samples. The variation in recoveries and the decrease in reproducibility is probably caused by the presence of compounds in the sample matrix that have been co-eluted with GSM. These compounds have clearly interfered with the perceived amount of GSM present in the spiked tap and river water samples. A chromatogram of Aberdeen tap water spiked with 10 ng mL^{-1} GSM (Figure 2-8a) indicates interferences in the GSM elution area (~9.35 min).
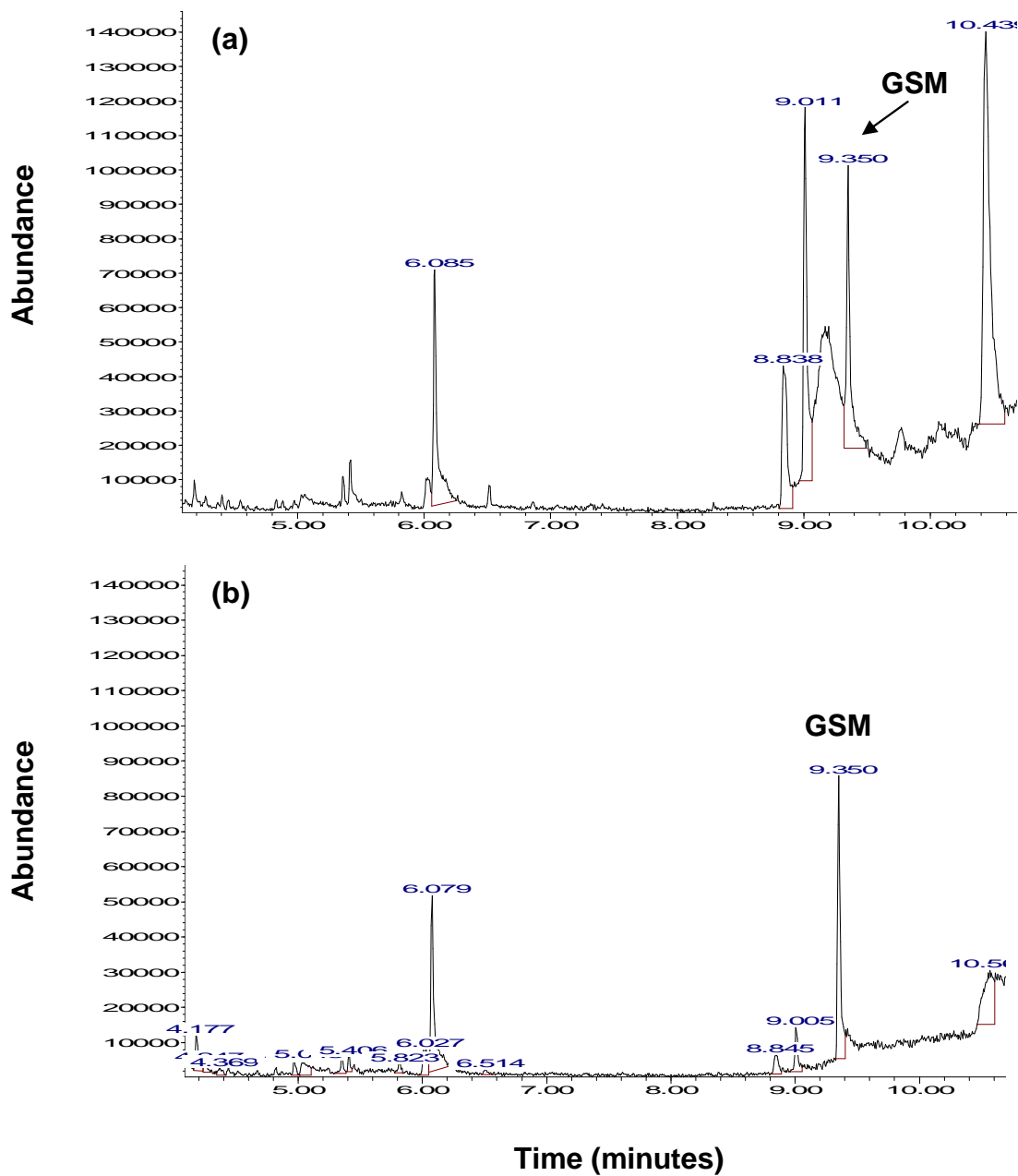
Figure 2-8. GC-MS chromatograms of GSM recovered from waters (100 mL) spiked with 10 ng mL^{-1} GSM (a) spiked Aberdeen tap water (b) spiked River Cowie water.

The interferences are less pronounced for the River Cowie water spiked with 10 ng mL^{-1} GSM (Figure 2-8b). Blanks for both tap and river water samples (no spiked GSM) showed no detectable GSM present.

Interferences caused by the SPE trace-enrichment process are common (Thruman *et al.*, 1998). For environmental samples the typical interferences include particulate matter that can accumulate on the head of the sorbent phase within the SPE cartridge and natural organic substances that are removed by sorption to the SPE cartridge. While these factors are the probable cause of the interferences for the River Cowie water analysis, specifically humic compounds, it is improbable that they are causing the analytical interference for the Aberdeen tap water. The tap water has undergone water treatment and subsequently should contain very little organic matter, this is verified by TOC analysis conducted in Chapter 5 (pg 160). It is possible that inorganic compounds present in both sample matrices are causing interferences. These interferences can be removed by a rinse or wash step prior to final elution of GSM from the SPE cartridge. The wash involves the use of a suitable solvent to remove any interferences. Therefore the use of a wash step prior to elution with 100% methanol was investigated.

2.3.4.3 *Use of aqueous methanol to remove matrix interferences*

The effect of interferences on the quantification of GSM using SPE-GC-MS may be resolved by the use of a wash step to remove these interferences. The method used by Conte *et al.* (1996) used a deionised water wash step before elution with ethyl acetate. Cole *et al.* (2003) did use a wash step, eluting first with ethyl acetate and then with methylene chloride. Ethyl acetate will remove the majority of hydrophobic substances, such as GSM, sorbed to a C-8 or C-18 SPE phase while the majority of humic substances will be retained (Thruman *et al.*, 1998). However, interferences in the tap water sample spiked with GSM are not caused by organic substances so the use of ethyl acetate would not remedy this problem. As the interferences are clearly eluted by 100 % methanol the use

of an aqueous methanol wash may help reduce the problem. However, the elution of GSM from using an aqueous methanol wash must first be quantified.

The results (Figure 2-9) clearly demonstrate the effect aqueous methanol has on elution of GSM from C8 cartridges, with GSM extraction decreasing as the proportion of methanol in the aqueous methanol solution used for elution decreases. The on/off effect of SPE is also visibly demonstrated by the notable difference in GSM extraction for 100 and 40 percent methanol elutions (Figure 2-10), with no visible sign of GSM in the chromatogram for the 40 % aqueous methanol wash. The results clearly show that an aqueous methanol wash, containing 50 % methanol or less, could be used to remove interferences without significant loss of GSM (Figure 2-9). The higher the percentage of methanol in the aqueous methanol wash the increased probability of interferences being removed. However, a compromise had to be made between the increased probability of removing interferences and reducing loss of GSM. Therefore the choice was between the aqueous methanol washes containing 40 and 50 % methanol. The aqueous methanol wash, containing 50 % methanol, eluted a small proportion of GSM from C8 SPE cartridges. The amount of GSM eluted was equal to 4.5 (± 0.4) % of that eluted with 100 % methanol. For the aqueous wash containing 40 % methanol this value was considerably lower, 0.4 (± 0.2) %.

Therefore, the selection of an aqueous methanol wash, containing 40 % methanol, achieves the best balance between reduction of GSM loss and maximised interference removal. For future experiments involving raw waters spiked with GSM an extra wash step was introduced to the SPE process. After the raw water sample is loaded the cartridge will be washed with 1 mL of a 40 % aqueous methanol.
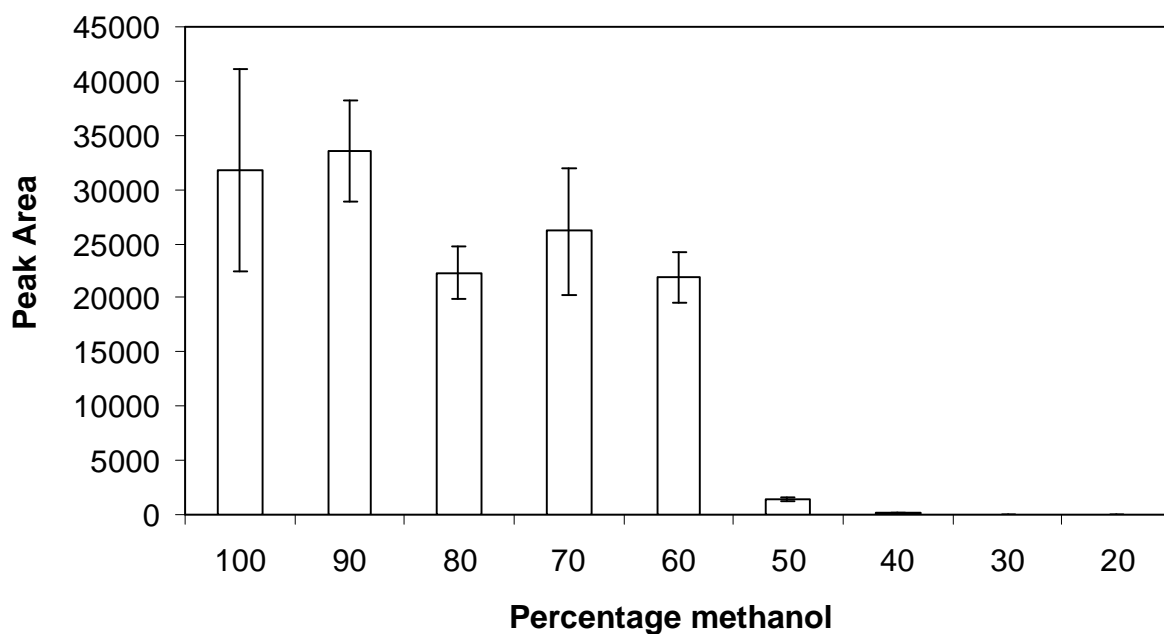
Figure 2-9. GC-MS analysis of GSM elutions from C8 cartridges with additional aqueous methanol step. Bars are equivalent to one standard deviation (n=3).
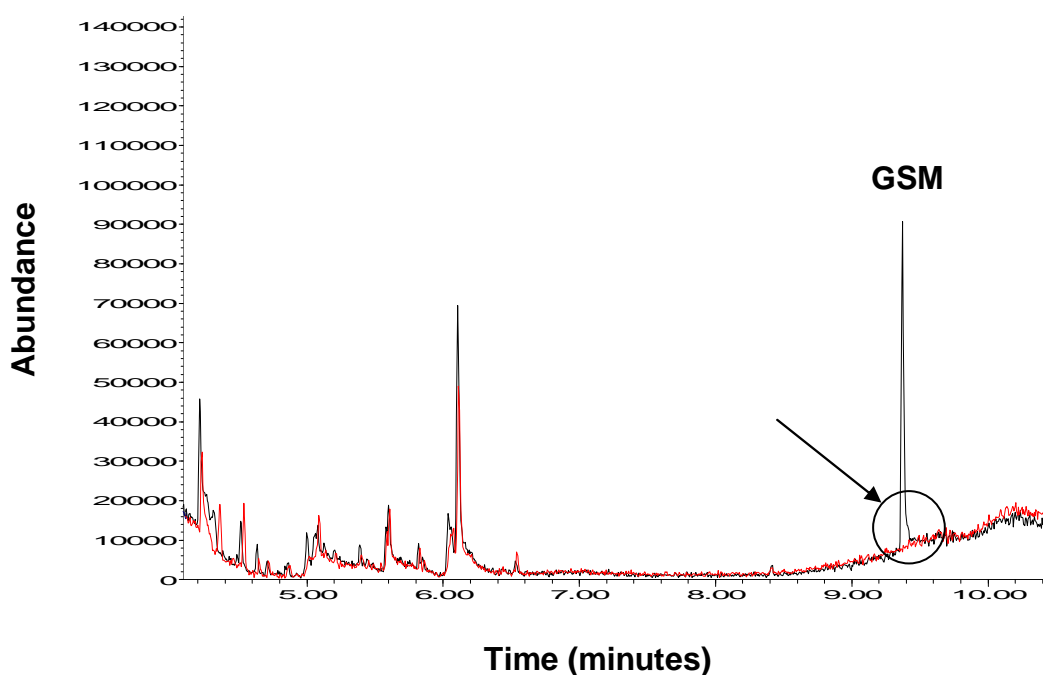
Figure 2-10. Overlayed GC-MS chromatograms of GSM quantification, eluted with(▬▬) 100% methanol and (▬▬) 40% aqueous methanol. Note the difference in GSM eluted (circled).

2.3.4.4 SPE of GSM spiked raw water with additional methanol wash

The improvement in the quantification of GSM in Aberdeen tap and River Cowie water due to the use of a 40% aqueous methanol wash can be seen in Figures 2-11 and 2-12. The addition of a wash step had the desired effect of removing unwanted retained compounds on the SPE cartridges, which were interfering with the quantification of GSM.

The GSM recoveries for Milli-Q and tap water were lower when compared to the unwashed samples, 17.5 and 13.4 % respectively, but GSM recovery for the washed River Cowie sample was slightly higher (3.6 %) than the unwashed sample (Table 2-5 and Figure 2-12).   The reproducibility for the washed samples was higher than the unwashed samples. Although there is a slight loss in GSM recovery with the addition of an aqueous methanol wash, the wash is necessary for reproducible results when using water types other than Milli-Q.

	% Recovery			
	No Wash	RSD % (n=3)	Wash	RSD % (n=3)
Milli-Q	90.9	24.2	73.4	5.3
Aberdeen tap water	90.1	11.5	76.7	5.0
River Cowie water	92.3	11.8	95.9	10.8

Table 2-5. Recoveries of 100 mL 10 ng mL^{-1} re-suspended GSM and 1 mL 1000 ng mL^{-1} re-suspended GSM solutions using C8 cartridges for Milli-Q, Aberdeen tap water, and Cowie river water
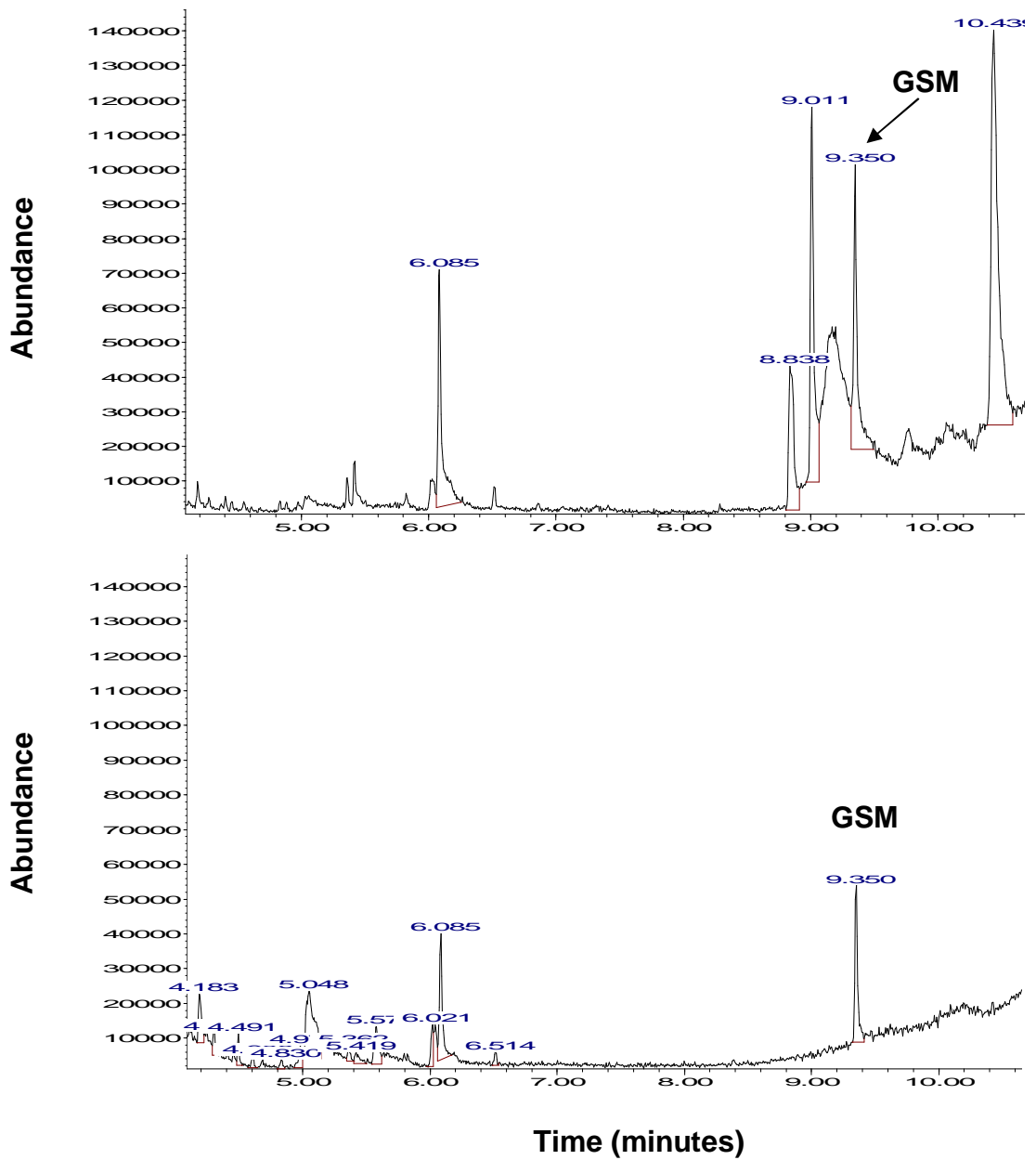
Figure 2-11. GC-MS chromatograms of Aberdeen tap water spiked with GSM (a) without 40% aqueous methanol step (b) with 40% aqueous methanol step
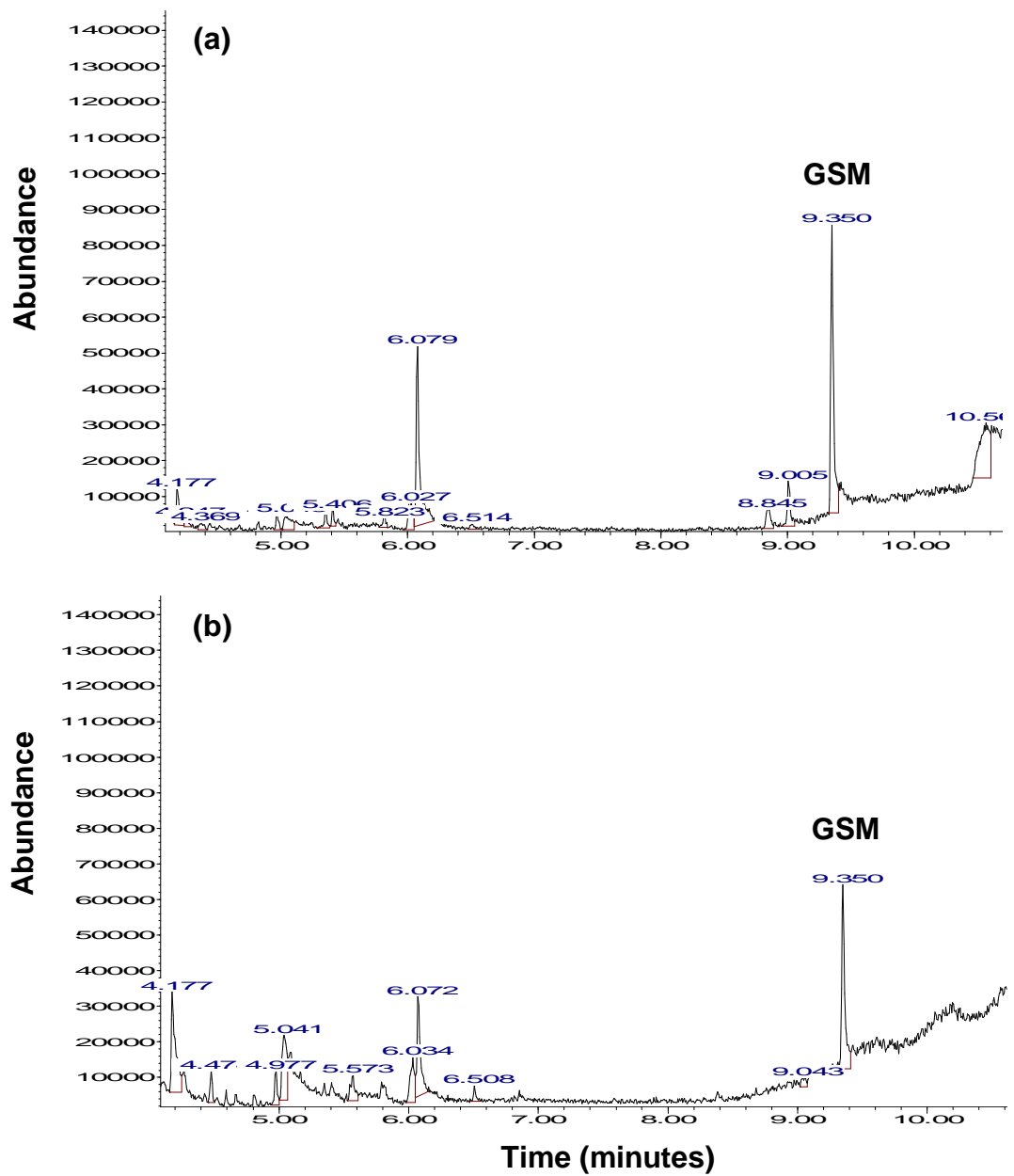
Figure 2-12. GC-MS chromatograms of River Cowie water spiked with GSM (a) without 40% aqueous methanol step (b) with 40% aqueous methanol step
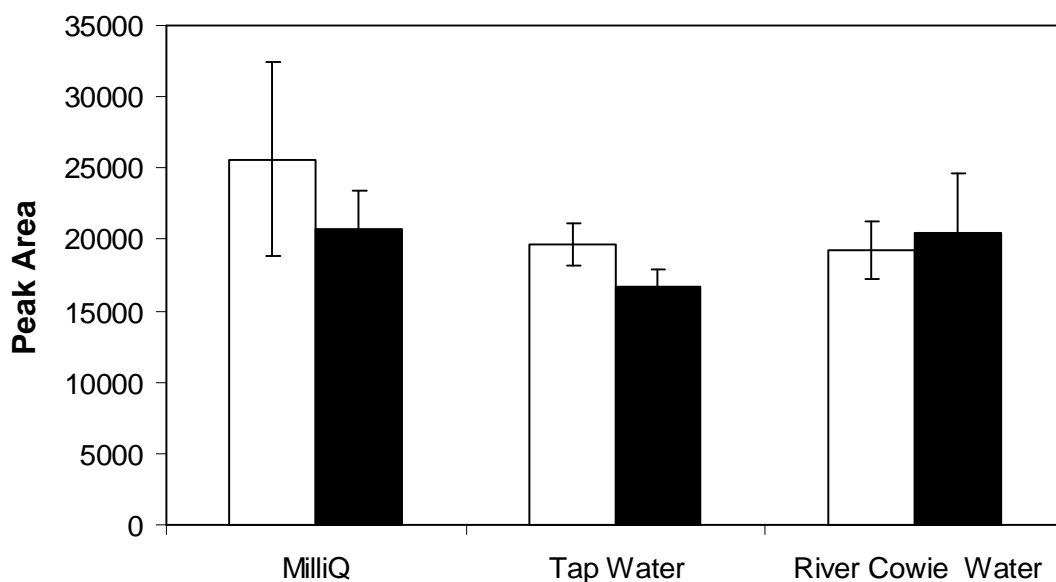
Figure 2-13. GC-MS analysis of Milli-Q, Aberdeen tap water and River Cowie water samples (1 mL) spiked with GSM (1 μg mL^{-1}); No 40 % aqueous methanol wash (□), 40 % aqueous methanol wash (■). Bars equivalent to one standard deviation (n=3).

2.4 CONCLUSIONS

This chapter established that SPE is a viable means of isolating GSM and MIB from water. The C8 sorbent phase represents the best compromise between recovery and reproducibility with recoveries of 93 (± 2.25) % and 82 (± 2.25) % respectively for GSM and MIB from Milli-Q. The C8 cartridges also proved effective in trace analysis of GSM, essential for analysis of samples containing environmental concentrations of GSM. Therefore the decision to use C8 SPE cartridges for isolation of GSM and MIB, with subsequent analysis by GC-MS, in this study was made because it allowed high sample throughput with acceptable limits of detection (1 ng mL^{-1}).

Also in this chapter a technique for the concentration of low levels of GSM in large water volumes was established. Chromatograms obtained for GSM concentrated from spiked raw water by C8 cartridges (Figures 2-11 and 2-12) show interferences near the area where GSM is eluted from the GC column. The introduction of a 40 % aqueous methanol wash step improved quantification of GSM (Figures 2-11 and 2-12), with a slight reduction in GSM recovery.

Finally the evaporation of methanol from the GSM-methanol stock was achieved, with good recovery of GSM 89 (± 0.66) %. Unfortunately, the evaporation of methanol from the MIB-methanol stock was not achieved using the method developed. This represented a significant problem as removal of the methanol from the MIB-methanol solution prior to re-suspension in Milli-Q was critical. As discussed later methanol present in aqueous GSM solutions undergoing semiconductor photocatalysis causes a reduction in the rate of GSM destruction. This is caused by the methanol acting as a competing reactant, this effect was also observed when aqueous solutions of MIB underwent semiconductor photocatalysis.

The issue of evaporation of methanol from the MIB-methanol stock solution by the use of nitrogen gas was unresolved due to time constraints. This resulted in the study focusing on the semiconductor photocatalysis of GSM.

CHAPTER 3 - BENCH SCALE PHOTOCATALYTIC REACTOR

3.1 INTRODUCTION

The treatment of water contaminated with toxic or undesirable compounds is a common problem throughout the world and as standards for water quality become evermore stringent the need for new treatment methods increases. A major issue for water treatment utilities is the problem of off-flavour. Suffet *et al.* (1996) reported that 22 % of municipal water suppliers in the USA using surface water encounter off-flavour problems. Two compounds responsible for off-flavour are geosmin (GSM) and 2-methylisoborneol (MIB), produced by certain cyanobacteria and actinomycetes.

For many years engineers have relied on traditional water treatment processes as diverse as sedimentation, filtration, coagulation, adsorption, and chemical oxidation. However the majority of these technologies are non-destructive, relying on the physical separation of the pollutant from one phase to another, leaving the problem of the final and ultimate disposal of the transferred material. Conventional water treatment does not efficiently remove off-flavour from water (McGuire *et al.*, 1988; Ando *et al.*, 1992; Wnorowski, 1992).

Photocatalysis using titanium dioxide (TiO$_2$) has been investigated for treating contaminated water. The literature contains a very large number of references concerning research into titanium dioxide photocatalytic degradation of various compounds, with over 500 publications a year in this field since 1999 (Carp *et al.*, 2004). Much of this work has been conducted using P-25 TiO$_2$, manufactured by the Degussa company.

Previous work by Lawton *et al.* (2003) demonstrated the efficiency of P-25 titanium dioxide in the removal of GSM and MIB. However, processing was difficult due to the problems separating the catalyst from the GSM and MIB at the end of the reaction. Also non-specific adsorption made it difficult to differentiate catalytic activity and the loss of GSM and MIB to contactable surfaces within the reaction vessels. Non-specific adsorption of GSM and MIB

during evaluation of technologies for their removal or destruction is not commonly discussed in the literature, but Elhadi *et al.* (2004) demonstrated system losses of GSM and MIB in bench-scale filtration apparatus could be substantial. The use of P-25 dispersed in an aqueous solution for the photocatalysis of GSM and MIB has an additional problem, post treatment the P-25 must be removed prior to analysis of the water. Numerous methods of isolating P-25 from solution were attempted by Lawton *et al.* (2003) including centrifugation and filtration but no ideal method was found.

Using P-25 would also be unsuitable for use on a larger scale as it would have to be removed from solution post treatment, involving a filtration, coagulation, sedimentation or centrifugation step (Dijkstra *et al.*, 2001). A commercial system utilizing TiO_2 to degrade pollutants in water is more likely to have the TiO_2 immobilized, i.e. thin film reactor, and the contaminated water flowed over it (Mills *et al.*, 1993).

Due to the issues associated with using a powdered type of titanium dioxide it was decided that it would be more effective to use a pelleted form of titanium dioxide. This would eliminate the need to conduct removal of the catalyst prior to sample analysis. A commercially available titanium dioxide photocatalyst was selected, Hombikat K01/C (Sachtleben, Germany). This is a new titanium dioxide photocatalyst and previous studies have shown the catalyst to be robust and have high efficiency in degrading microcystin-LR (Lawton *et al.,* 2004).

With the catalyst selected the reactor design was considered. A borosilicate glass tube was selected for the reaction vessel (140 mm in length and 20 mm in diameter; 44 cm^3 volume) in which the catalyst would be deployed. Elhadi *et al.* (2004) reported losses of GSM (200 ng L^{-1}) to two litre glass feed bottles as 8 ($\pm$ 5.0) % after four days. If the rate of GSM adsorption to the glass reaction vessel is relatively slow, GSM loss in experiments conducted in this work will likely be limited due to their short duration. The glass vessel with the catalyst deployed within it, in conjunction with a xenon UV lamp (400 W UVASpot 400 lamp, Uvalight Technology Ltd; spectral output 330 – 450 nm), would constitute the main components of a number of reactor designs evaluated in this chapter.

The geometry of this vessel, small in volume and elongated, should allow efficient exposure of the catalyst by the irradiation source. Inefficient illumination of a catalyst is an issue which can affect larger reactors (Ray, 1999b). The light absorbance of the glass reaction vessel was tested using a Perkin-Elmer Lambda 950 UV/Vis spectrophotometer (Perkin-Elmer, UK). This established that the vessel absorbed light in the 260-320 nm region (Appendix 1), although the glass filters out the higher energy UV-C and UV-B (200-315 nm) light, it will allow UV-A (315-400 nm) to reach the catalyst. The band gap of titanium dioxide allows photooxidation to occur with adsorption of light in the near ultra violet region (~ 380 nm), therefore the light entering the vessel should be capable of activating the photocatalyst. The problems associated with the design of larger reactors will be discussed in Chapter 5.

Lawton *et al.*, (2003) previously demonstrated photocatalysis using TiO_2 effectively removed GSM and MIB at concentrations higher (~2000 ng L^{-1}) than those found in the environment, typically 20 – 100 ng L^{-1}. Both GSM and MIB were rapidly degraded with over 99 % decomposition of both compounds achieved within 60 minutes. The rate of GSM and MIB destruction increased with increasing GSM and MIB concentration.

Research is necessary to optimise the conditions for the photocatalytic destruction of GSM and MIB and to elucidate the mechanism for destruction of GSM and MIB. The following chapter presents work conducted to develop a bench scale reactor that will allow the evaluation of the Hombikat K01/C TiO_2 photocatalyst and minimise system losses of GSM.

The band gap of titanium dioxide is 3.2 eV (Table 1-2), allowing photooxidation to occur with adsorption of light in the near ultra violet region (~ 380 nm).

3.2 METHODS

3.2.1 Photocatalysis of GSM – Reactor V.1

An aqueous solution of geosmin (100 mL; ~1 µg mL^{-1}) was prepared and transferred to a 150 mL glass beaker, which would act as a reservoir. The Hombikat K01/C titanium dioxide catalyst (15 g) was deployed within a glass borosilcate vessel (140 mm in length and 20 mm in diameter) that tapered towards one end, with a small glass insert placed into the bottom of the tapered end to restrict the flow through the reactor (Figure 3-1). The 15 g of catalyst, which filled the majority of the vessel, was selected to maximise potential surface area for photocatalysis, while allowing space for 25 mL of test solution. This volume of solution would allow a number of samples to be taken from the vessel through the course of an experiment. A peristaltic pump (Watson-Marlow 101U, Fisher Scientific, UK) with *Marprene* tubing (Fisher Scientific, UK; 1.6 mm wall, 4.8 mm bore) was used to circulate the solution, pumping it from the reservoir to the top of the reactor at a rate of 70 mL min^{-1}. The *Marprene* tubing is made from thermoplastic elastomers giving wide chemical compatibility and resistance to oxidising agents. The solution flows through the vessel and over the catalyst, exiting the bottom of the vessel and into the reservoir. The reactor was illuminated in the presence of air using a xenon UV lamp (400 W UVASpot 400 lamp, Uvalight Technology Ltd; spectral output   330 – 450 nm) situated 30 cm from the reactor. Samples (1 mL) were taken from the reservoir at timed intervals of 0, 20, 40, 60, 80 100, 120, 140, and 160 minutes of illumination then analysed by SPE-GC-MS (see section 2.2.2).

The reactor was also evaluated under two different control conditions, with samples taken at the same time intervals as the photocatalytic reaction. Firstly with the catalyst loaded and the xenon lamp off and secondly without the catalyst loaded and the xenon lamp off.

GSM losses observed under control conditions were considerable so the reactor was evaluated for the effect of non-specific adsorption of GSM. The reactor was set up as in method 3.2.1. A GSM solution (100 mL; ~1 µg mL^{-1})

was circulated through the reactor for 160 minutes, the reactor was then drained and the catalyst removed. Any residual solution within the reactor was removed. To determine non-specific adsorption of GSM within the reactor, methanol (100 mL) was placed into the reservoir and circulated for 120 minutes, with samples (1 mL) taken from the reservoir at timed intervals of 0, 40, 80, 120 minutes. These samples were analysed by SPE-GC-MS (see section 2.2.2). The methanol should extract adsorbed GSM within the reactor and allow non-specific binding to be quantified.
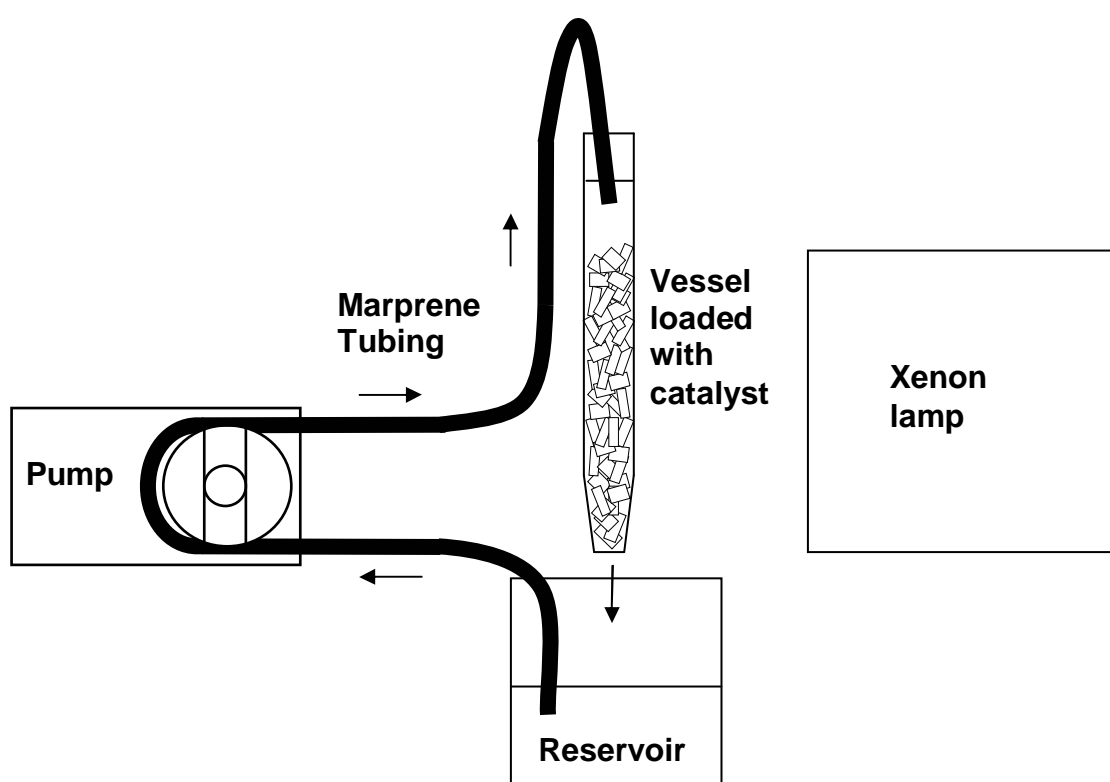
Figure 3-1. Bench scale re-circulatory photocatalytic reactor V.1. Solution pumped from the reservoir by the peristaltic pump, through *Marprene* tubing (indicated above by the thick black lines), to the top of the glass vessel. The solution flows through the vessel and over the catalyst, returning to the reservoir ready for recirculation.

After the methanol had been circulated through the reactor for 120 minutes the two ends of the *Marprene* tubing, still attached to the peristaltic pump, were placed into a beaker containing 100 mL methanol. The methanol in the beaker

was circulated through the *Marprene* tubing for 120 minutes. Samples (1 mL) were taken from the beaker at timed intervals of 0, 40, 80, 120 minutes then analysed by SPE-GC-MS (see section 2.2.2).

3.2.2 *Photocatalysis of GSM – Reactor V.2*

The reactor design was modified to eliminate non-specific adsorption of GSM. Where possible the majority of the *Marprene* tubing was removed and replaced with borosilicate glass tubing (Figure 3-2). A section of tubing approximately 20 cm in length remained as this was required to allow the continued use of the peristaltic pump. Reactor conditions as described in method 3.2.1 were evaluated. However, the reactor was not evaluated with the catalyst loaded and the xenon lamp off as the catalyst would adsorb GSM, making it more difficult to attribute GSM loss to non-specific adsorption within the reactor alone.
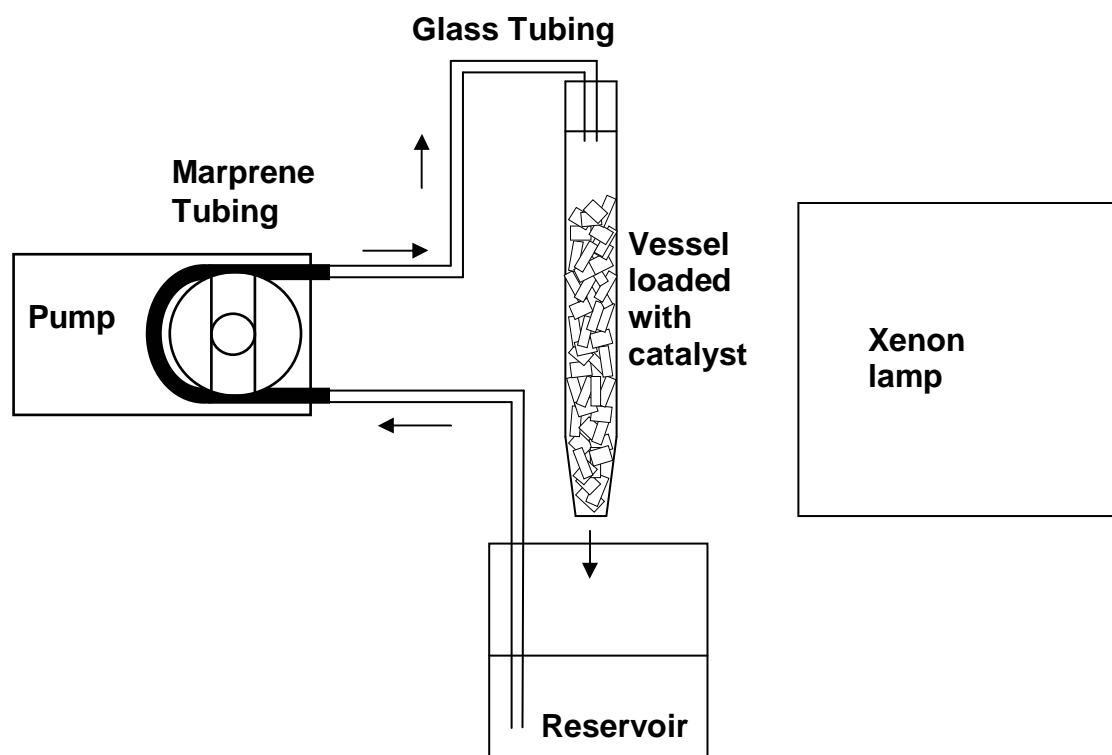
Figure 3-2. Bench scale re-circulatory photocatalytic reactor V.2. Solution pumped from the reservoir by a peristaltic pump, through a combination of *Marprene* tubing (indicated above by the thick black line) and glass tubing (indicated above by the clear tubing), to the top of the glass tube. The solution flows through the vessel and over the catalyst, returning to the reservoir ready for recirculation.

Post experiment the *Marprene* tubing from the peristaltic pump was removed, cut into 8 sections and placed into a 50 mL glass bottle. Methanol was added (50 mL) to the bottle and the bottle capped with an air-tight cap. The immersion of the tubing sections in methanol should desorb any GSM that was adsorbed to the tubing during the control experiment for the 100 mL; ~1 μg mL^{-1} GSM solution. Samples (1 mL) were taken at 20, 120, 300 minutes, and 120 hours. All samples were analysed by SPE-GC-MS (see section 2.2.2).

3.2.3 Photocatalysis of GSM – Reactor V.3

The design of the reactor was once again modified, this time to exclude the use of *Marprene* tubing as it was found to be the cause of a significant proportion of the losses of GSM observed. With non-specific adsorption of GSM onto the remaining tubing still a significant issue and with other types of tubing likely to suffer the same problem, the new design had to ensure that no *Marprene* tubing was present. Where tubing was required, measures were taken to minimise contact with the GSM solution. Teflon tubing (Teflon FEP, Nalgene 890, Fisher, UK) was selected as Elhadi *et al.* (2004) had concluded that it minimised non-specific adsorption of GSM. A consequence of this was that a new method of pumping/mixing the test solutions was required as a peristaltic pump could no longer be used because of the rigidness of the Teflon tubing. V.3 of the reactor (Figure 3-3) incorporated an air pump (Jun aquarium pump, Jun-Air, UK; Maximum air output 4.2 L) to suspend the GSM solution within the reactor, allowing the removal of the remaining *Marprene* tubing. Unlike V.1 and V.2 of the reactor this version is not a re-circulatory batch reactor. The design change simplified the reactor considerably, reducing the length of tubing required and rendering the beaker used as a reservoir redundant. Teflon tubing was used to connect the pump to a rotameter which was included to regulate the air flow from the pump. The rotameter was connected to the bottom of the reactor with Teflon tubing. The tubing was then secured to the bottom of the reactor by using a sleeve that attached to the reactor and passed over the outside of the Teflon tubing. This ensured a tight seal and as the air from the pump suspended the solution within the reactor, contact between the Teflon tubing

and the solution within the reactor was minimal. An added advantage of this design is that the test solution is aerated, supplying required oxygen necessary for photocatalysis (Mills *et al.*, 1993).
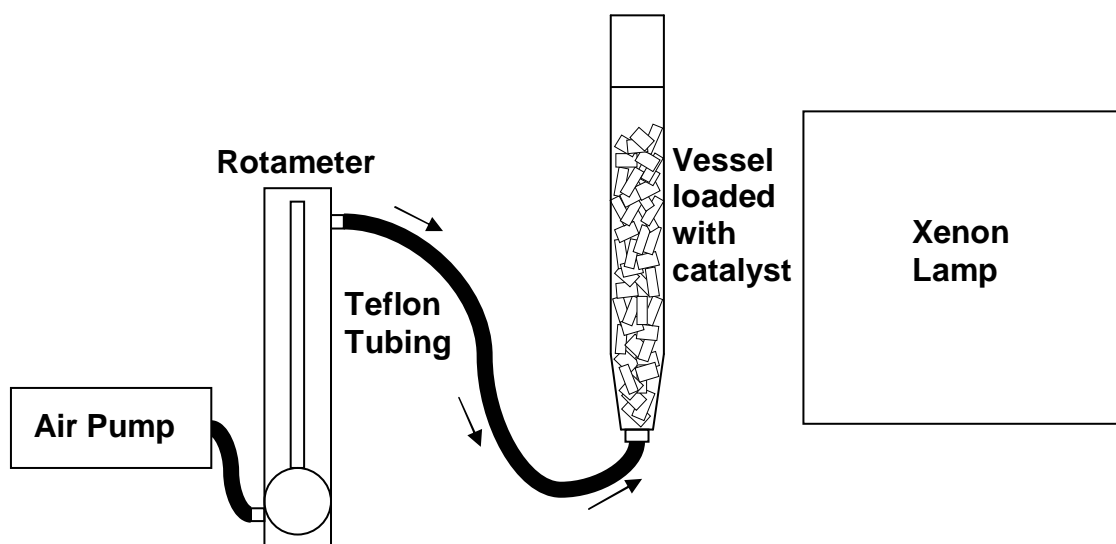
Figure 3-3. Bench scale batch photocatalytic reactor V.3. The arrows indicate the air flow, moving from the air pump, through the Teflon tubing and into the bottom of the glass vessel. The solution within in the vessel is suspended by the air entering the bottom of the reactor. A rotameter maintains the aeration rate.

The reactor was filled with 15 g of Hombikat K01/C. The air flow, passing through the rotameter, and exiting the tubing to be connected to the bottom of the reactor, was maintained at 32 mL min^{-1}. The air flow was verified by a flow meter (CS1 6000 solid state flow meter, Cambridge Scientific Instruments Ltd., England). This Teflon tubing was then connected to the bottom of the reactor and the integrity of the seal checked. An aqueous solution of geosmin (100 mL; ~1 μg mL^{-1}) was prepared, of which 20 mL was added to the reactor. After addition of the solution checks were conducted to ensure that there were no leaks.

The reactor was then illuminated, in the presence of air, using a xenon UV lamp (400 W UVASpot 400 lamp, Uvalight Technology Ltd; spectral output 330 – 450 nm) situated 30 cm from the reactor. Samples (1 mL) were taken at timed intervals of 0, 20, 40, and 60 minutes of illumination then analysed by SPE-GC-MS (see section 2.2.2). The reactor was also evaluated with no catalyst loaded and the xenon lamp switched off for a period of 60 minutes with samples taken at 0, 20, 40, and 60 minutes.

3.3 RESULTS AND DISCUSSION

3.3.1 Photocatalysis of GSM – Reactor V.1

Analysis of the loss of GSM due to photocatalysis indicated a substantial reduction in concentration (Figure 3-4), with approximately 15 % of GSM remaining after 40 minutes. However, the reduction of GSM under the two different control conditions, catalyst with the xenon lamp off and no catalyst with the xenon lamp off, were also significant with only 30 % GSM remaining after 40 minutes (Figure 3-4). From the results shown in Figure 3-4 it is not possible to conclude that the loss of GSM is due to TiO_2 photocatalysis. GSM was being lost in the absence of photocatalytic conditions, possibly due to non-specific adsorption of GSM within the reactor and/or volatilisation of GSM to the atmosphere.

Methanol (100 mL) was re-circulated through the reactor to desorb any GSM that may be present in the reactor, therefore determining the extent non-specific adsorption of GSM. Prior to the methanol being pumped through the reactor a control experiment (the no catalyst, xenon lamp off control from Figure 3-4) involving the re-circulation of a 100 mL ~1 µg mL^{-1} GSM solution had been conducted. As 90 % of the GSM had been lost under this control it ensured that if non-specific binding was the cause of the GSM loss then the reactor would contain adequate GSM to extract with methanol. There was a 50 % reduction in volume of the initial 100 mL methanol after 120 minutes of re-circulation due to evaporation. Analysis of the re-circulated methanol resulted in the detection of

GSM (Table 3-1). The 120 minute sample contained 21.7 % of the GSM lost in the no catalyst, xenon lamp off control, a significant portion of the total GSM lost.
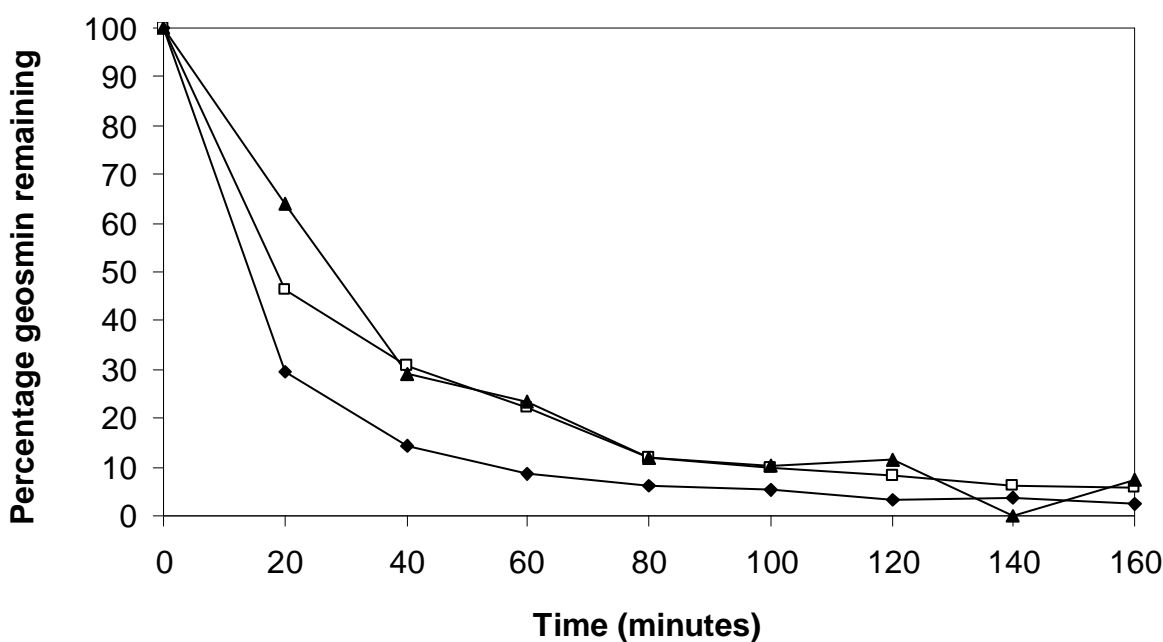
Figure 3-4. Photocatalytic destruction of GSM in re-circulatory reactor V.1 using Hombikat K01/C. Catalyst present, xenon lamp on (—◆—); Catalyst present, xenon lamp off (—□—); xenon lamp off, no catalyst (—▲—). GSM loss monitored by GC-MS.

The *Marprene* tubing was disconnected from the reactor, but left attached to the peristlatic pump. Methanol (100 mL) that had been re-circulated through the *Marprene* tubing only was also found to contain GSM. After 120 minutes of re-circulating the 100 mL methanol through the *Marprene* tubing there was a 10 % reduction in methanol volume. Analysis of the re-circulated methanol again resulted in the detection of GSM. The 120 minute sample contained 23.4 % of the GSM lost in the no catalyst, xenon lamp off control. This represented a significant portion of the GSM lost.

Sample time (minutes)	Percentage GSM extracted	
	Reactor	Tubing
40	7.1	7.8
80	17.1	15.2
120	23.4	22.2

Table 3-1. GSM extracted from reactor V.1 using methanol after the control experiment (no catalyst, xenon lamp off).

The GSM extracted from both the reactor and the tubing totalled 55.6 % of the GSM lost in the control experiment (no catalyst, xenon lamp off). This represented over half of the 90 % GSM lost under these control conditions. From the results in Table 3-1 it is clear that GSM extraction increases as the extraction time in methanol increases. If extraction times had been increased it is likely that more GSM would have been extracted from the reactor and tubing.

The *Marprene* tubing used in this reactor was undoubtedly the major cause of non-specific binding of GSM. From Figure 3-4 it is evident that the rate of non-specific adsorption of GSM to the tubing is relatively rapid. For the TiO_2 photocatalysis of GSM, using Hombikat K01/C, to be demonstrated with this reactor a re-design would be required.

3.3.2 Photocatalysis of GSM – Reactor V.2

V.2 of the reactor reduced GSM with approximately 40 % remaining after 40 minutes (Figure 3-5). The control (no catalyst, with the xenon lamp off) had 70 % GSM remaining after 40 minutes, indicating that a reduction in the amount of peristaltic tubing significantly reduced the loss of GSM in the system.
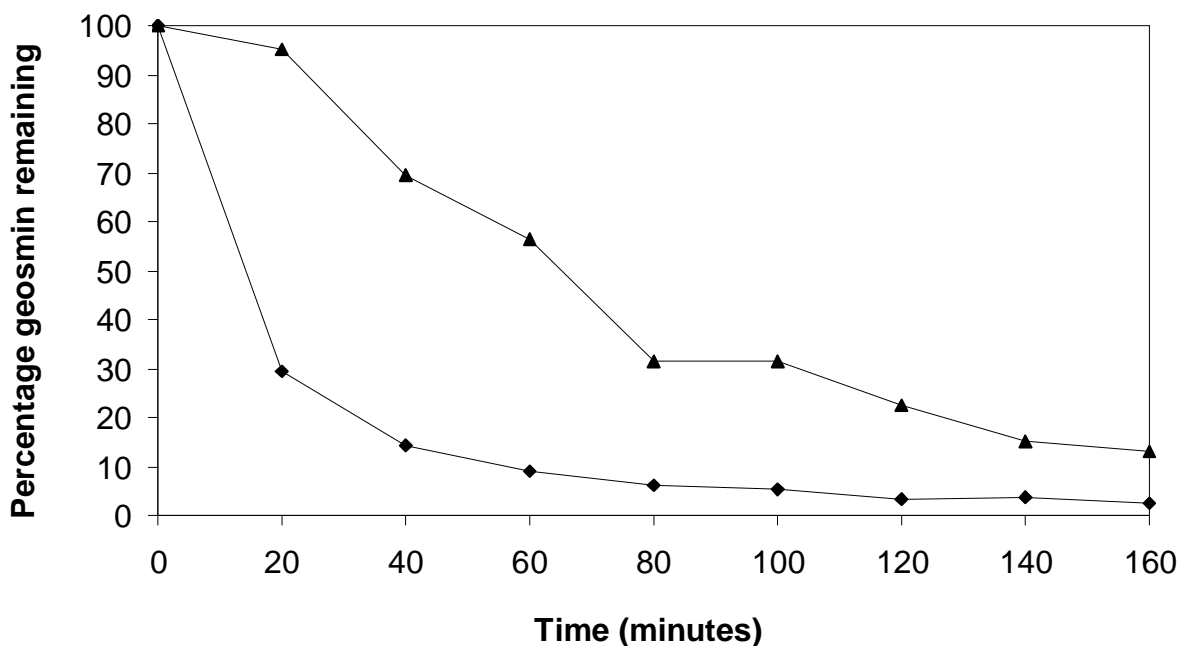
Figure 3-5. Photocatalytic destruction of GSM in re-circulatory reactor V.2 using Hombikat K01/C. Catalyst present, xenon lamp on (—◆—); xenon lamp off, no catalyst (—▲—). GSM loss monitored by GC-MS.

As the *Marprene* tubing used in reactor V.1 had been the cause of major GSM loss it was prudent to check the tubing used in reactor V.2 as a possible cause of non-specific adsorption of GSM. The *Marprene* tubing used in the control (xenon lamp off, no catalyst) (Figure 3-5) was removed from the pump post experiment. The tubing was cut into 8 sections and immersed in methanol to desorb GSM that may have attached to the tubing during the previous control experiment. Analysis of the methanol containing the tubing was found to contain GSM (Figure 3-6). The GSM extracted from the tubing was calculated as a percentage of the 87 % total GSM lost in the xenon lamp off, no catalyst control from Figure 3-5. After 20 and 120 minutes of immersion in methanol the GSM detected was equal to approximately 24 and 38 % respectively of the 87 % loss of GSM observed in the control. This value rose to 90 % after 120 hours of immersion in methanol, indicating that the vast majority of GSM system losses in reactor V.2 can be attributed to non-specific binding of GSM to the *Marprene* tubing. To further reduce system losses caused by non-specific adsorption of GSM it was clear that the *Marprene* tubing would have to be completely removed from the reactor design.
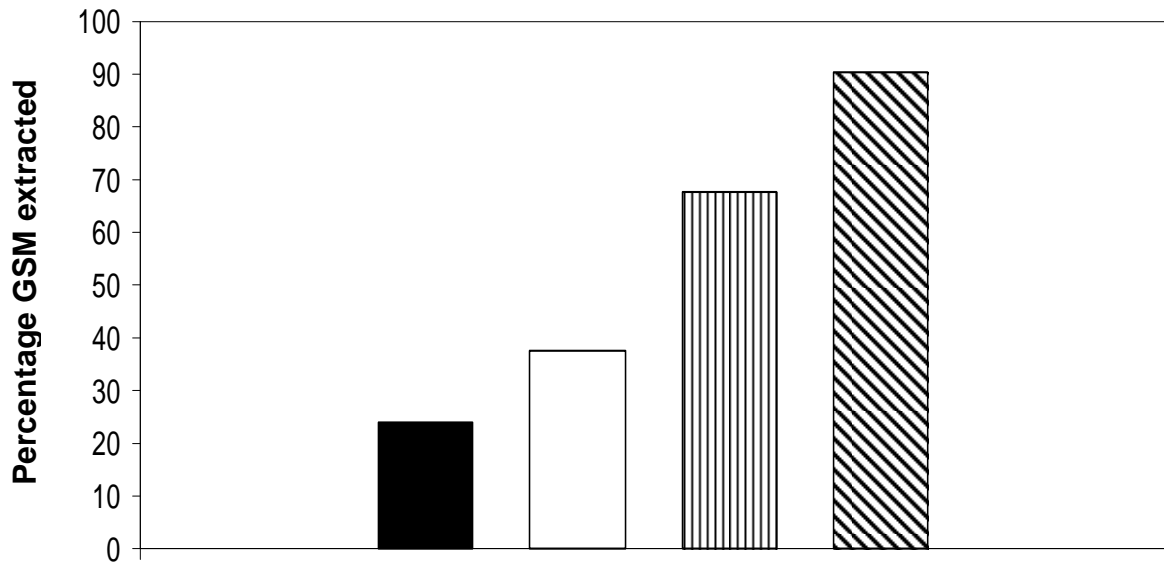
Figure 3-6. GSM extraction from peristaltic tubing used in a control experiment. Extraction time of *Marprene* tubing in methanol; 20 minutes (■); 120 minutes (□); 300 minutes (▥); 120 hours(▨). GSM extraction monitored by GC-MS.

Through the course of this work it became clear that a significant inadequacy of the majority of studies concerning GSM, and its removal, is a disregard for losses of GSM by non-specific adsorption within systems like the one evaluated here. Work conducted by Huck *et al.* (1995) and Elhadi *et al.* (2004) are the only studies that were found in the literature that discuss this issue.

Huck *et al.* (1995) reported that the two major limitations of previous studies in evaluating the removal of GSM and MIB are: lack of study at realistic off-flavour concentrations; and the disregard for the adsorption or loss of these compounds by mechanisms other than the one being investigated. The study of GSM at ng L^{-1} concentrations is exacerbated by these losses, as small absolute losses can be substantial on a percentage basis. Additionally analysis of GSM at environmental concentrations (ng L^{-1}) can be at the limit of detection for some analytical methods, therefore any substantial system loss of GSM during experimentation can impact on this analysis. Finally, losses in systems designed for the removal of GSM must be documented so that the removals attributed to a given treatment can be reliably assessed (Elhadi *et al.*, 2004a).

This last factor has proven absolutely critical in evaluating the efficacy of TiO_2 photocatalysis for the destruction of GSM. Without proper evaluation of the control conditions, GSM loss could have been attributed to photocatalysis rather than to non-specific adsorption of GSM within the reactor.

Huck *et al.* (1995) reported GSM system losses of 38 % for a glass bio-reactor containing glass beads. The other components of the bio-reactor were an influent reservoir, which was connected to the glass column containing the beads by Teflon tubing, and a peristaltic pump (equipped with Pharmed[TM] tubing) placed between the reservoir and the glass column to provide pumping. The losses attributed to the Pharmed[TM] tubing alone was 30 %, with the remaining 8 % loss of GSM attributed to the glass beads and Teflon tubing. The method of calculating the system loss is not stated, but the loss associated with the Pharmed[TM] tubing is similar to that found in this study for Marpene tubing used in reactor V.1 after 120 minutes of extraction (22 %). This is not surprising as both Pharmed[TM] and *Marprene* tubing are both made from thermoplastic elastomers. Elhadi *et al.* (2004) reported on system losses of GSM (200 ng L^{-1}) in five different versions of a bench scale apparatus for the removal of GSM and MIB. The apparatus consisted of a feed bottle that was connected with tubing, via a feed pump, to a glass filter column. The study focussed on GSM losses in this system over an extended period, up to 20 days. Elhadi *et al.* (2004) reported an average 56 % GSM loss to Pharmed[TM] tubing over 4 days, lower than the GSM loss to *Marprene* tubing for reactor V.2 obtained in this study (80 %). Elhadi *et al.* (2004) found the ideal system to consist of a Teflon feed bottle, a valueless stainless steel piston metering pump, Teflon tubing and a glass filter column. The materials which Elhadi *et al.* (2004) and Huck *et al.* (1995) found to limit non-specific adsorption of GSM, namely glass and Teflon, has been verified here by the performance of reactor V.3.

3.3.3 Photocatalysis of GSM – Reactor V.3

The V.3 reactor rapidly reduced GSM, with approximately 10 % GSM remaining after 40 minutes. D_{50} (time taken for 50 % of GSM to be destroyed) was 13 minutes. The control (no catalyst, no xenon lamp) clearly demonstrates the improvement over the previous rector versions in minimising GSM loss caused by non-specific adsorption (Figure 3-7)   Reactor V.3 has approximately 90 % GSM remaining after 40 minutes, compared with 30 and 70 % for reactors V.1 and V.2 respectively. The improvement in minimising non-specific adsorption of GSM in the reactor and the fact that only the treatment of GSM in the presence of titanium dioxide and UV illumination efficiently eliminates the organic contaminant from water, thus indicating the photocatalytic nature of the process. This initial result demonstrates the ability of the Hombikat K01/C photocatalyst to rapidly degrade GSM in aqueous solution.
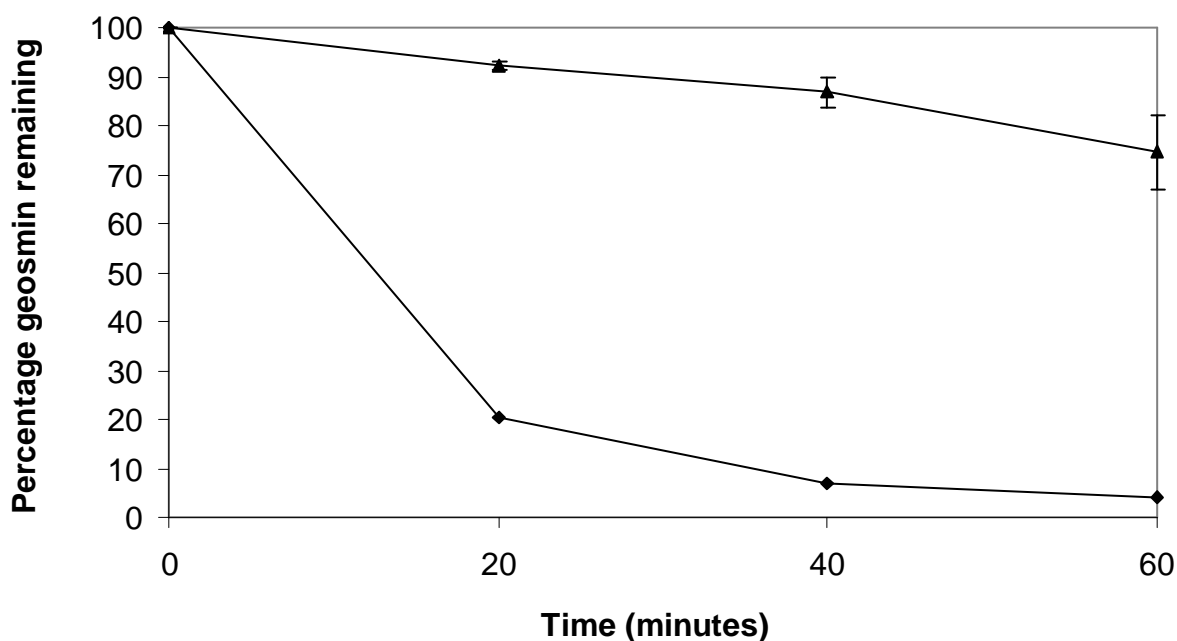
Figure 3-7. Photocatalytic destruction of GSM in batch reactor V.3 using Hombikat K01/C. Xenon lamp on (——◆——); no catalyst and xenon lamp off (——▲——). GSM loss monitored by GC-MS. Bars equivalent to one standard deviation (n=2).

The design of reactor V.3 was very different from the two previous versions using an air pump, controlled by a rotameter, to suspend the solution within the glass vessel. The primary reason for this re-design was that it allowed the removal of *Marprene* tubing from the reactor. However there was added benefits of aerating, and thus supplying O_2, the solution in this manner. Firstly it delivered a constant supply of oxygen during photocatalysis of GSM. Another benefit from using this reactor version is that the addition of air via the bottom of the reactor aids mass transfer within the reactor. Dijkstra *et al.* (2001) reported a comparable enhanced mass transfer effect using a two-phase immobilized reactor that was of similar design. This reactor variable is important as mass transfer can affect the kinetics of adsorption of the reactant, therefore having a possible affect on photodegradation kinetics. In the limiting case, where the irradiation is sufficiently high to eliminate readily all the adsorbed reactant, the rate of the reaction will be equal to the rate of adsorption from solution (Chen *et al.*, 1995). However, a concern of this reactor version was the possibility of increasing GSM volatilisation from the test solution. To minimise this possible problem an air flow rate was selected that provided enough pressure to suspend the test solution within the reactor, but did not aerate the solution to such a degree that it bubbled violently. A flow rate of 30 mL min^{-1} proved to be acceptable. Further work showed that volatilisation is a negligible factor of GSM loss within the system at this flow rate. This is verified by Pirbazari *et al.* (1992) who reported that the Henry's Law constant (*H*) for GSM was 6.66 x 10^{-5} atm m^3 mol^{-1}. The higher the magnitude of *H* the higher the potential is for a compound to volatilize into the atmosphere from solution. The value of *H* for GSM is two orders of magnitude lower than that of chloroform (3.28 x 10^{-3} atm m^3 mol^{-1}). This indicates that air stripping which is considered a viable method for the removal of volatile compounds from water, such as chloroform, is not likely to be feasible in the case of GSM (Lalezary *et al.*, 1984).

3.4 CONCLUSIONS

The results confirmed that a reactor (V.3) had been successfully developed that minimised the considerable problem of non-specific adsorption of GSM. This reactor allowed the rapid destruction of GSM using Hombikat K01/C TiO$_2$ photocatalysis to be observed successfully.

The reactor design evolved considerably through three distinct versions. The first (Figure 3-1) had the limitation of very high GSM loss within the reactor under control conditions, 70 % after 40 minutes. This was mitigated in the second variant (Figure 3-2) by replacing the majority of the *Marprene* tubing with borosilicate glass tubing. This aided in distinguishing the difference between control and photocatalytic data. However, despite improvement there was still considerable system losses with 30 % GSM lost after 40 minutes. Analysis of the *Marprene* tubing (washed with methanol) used in the course of the experiment found that GSM was adhering to this remaining tubing. This necessitated a redesign to remove the tubing, and consequently the peristaltic pump, from the reactor design. This culminated in version three of the reactor (Figure 3-5). The improvements made to V.3 of the reactor resulted in a GSM system loss of approximately 10 % after 40 minutes. The loss of GSM under control conditions for the three reactor versions is summarised in Figure 3-8.

The conclusions of the Elhadi *et al.* (2004) and Huck *et al.* (1995) studies are similar to those found through the course of the work conducted in this chapter. Both studies advocate the use of components constructed of Teflon, glass, or stainless steel for all wetted surfaces to minimise loss of GSM within a test system.

This chapter has revealed that GSM is a very challenging compound to work with. However, the rapid destruction of GSM using the Hombikat K01/C photocatalysis has been demonstrated and a reactor has been developed that has minimised non-specific adsorption. This reactor will allow the evaluation of various factors affecting titanium dioxide photocatalysis, which are reported in subsequent chapters.
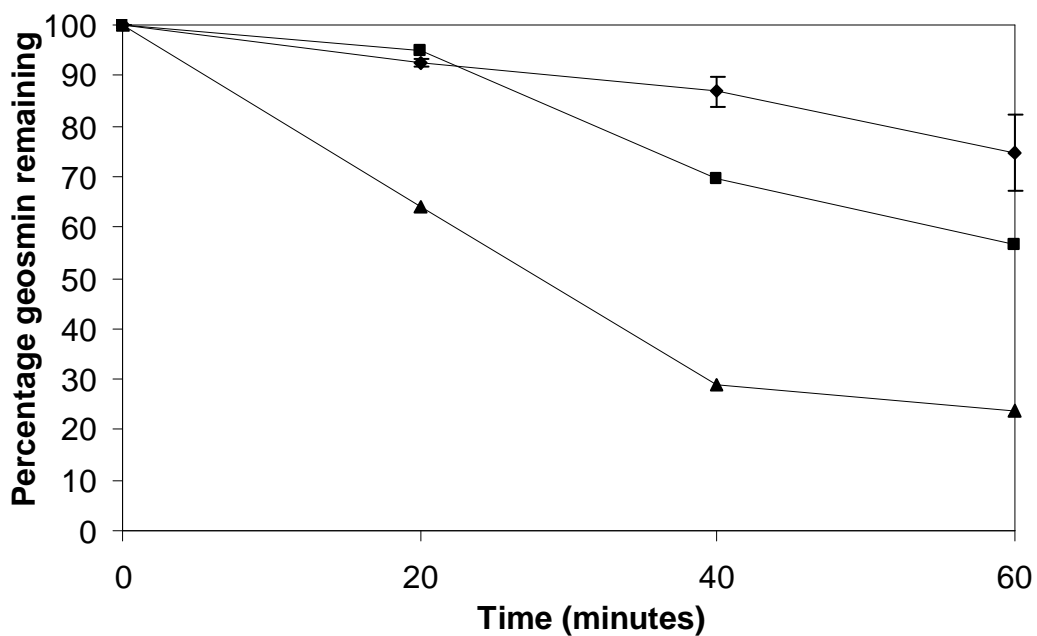
Figure 3-8. Comparison of reactor controls, GSM adsorption with no catalyst and the xenon lamp off; (—▲—) reactor v1.0, Re-circulation with peristaltic pump and *Marprene* tubing; (—■—) reactor v2.0, Re-circulation with peristaltic pump, reduced *Marprene* tubing; (—♦—) reactor v3.0, Batch, no *Marprene* tubing. GSM loss monitored by GC-MS. Bars equivalent to one standard deviation (n=2).

CHAPTER 4 - PHOTOCATALYSIS OF GSM

4.1 INTRODUCTION

The focus of this chapter is the optimisation of the TiO_2 photocatalysis of GSM. A number of factors affecting the photocatalysis of GSM will be investigated using reactor V.3 (Chapter 3).

The first clear implementation of semiconductor photocatalysis for the destruction of an organic compound in water was reported by Carey *et al.* in 1976. Biphenyl and chlorobiphenyls in the presence of TiO_2 were successfully degraded, though complete mineralization of the compounds was not observed. In 1983 Ollis et al., reported the first complete materialisation of a compound in water (Hsiao *et al.*, 1983; Turchi *et al.*, 1989). The destruction of a number of halogenated hydrocarbons, including carbon tetrachloride, chloroform and trichloroethane, was achieved using a TiO_2 photocatalyst. TiO_2 photocatalysis has since proven to be a viable alternative for treating contaminants in potable water. Examples include bromate, typically caused by the oxidisation of bromide ions during water treatment (Mills et al., 1996) and naturally occurring humic substances (Eggins *et al.*, 1997). Bromate is a potential carcinogen while humic substances discolour water and may solubilise pesticides. Raw river water has also been treated (Gracia *et al.*, 2000) with a reduction in 66 observed organic compounds reported. The detailed mechanism of the photocatalytic process on the TiO_2 surface is not completely clear, but the basis of pollutant degradation is believed to be the generation of highly reactive and oxidizing hydroxyl radicals ($^\bullet OH$) produced upon illumination of TiO_2 with UV. The oxidising strength of the hydroxyl radicals (2.8 eV) is greater than that of other reagents currently used in water treatment; Ozone (2.0 eV) and chlorine (1.4 eV).

It has been demonstrated previously that GSM and MIB can be effectively removed from aqueous solution by TiO_2 photocatalysis (Lawton *et al.*, 2003). This initial investigation using P-25 TiO_2 demonstrated that over 99% decomposition was achieved for GSM (2.0 ng mL^{-1}) and MIB (2.0 ng mL^{-1})

within 60 minutes. GSM was found to be significantly more resistant to degradation than MIB, with D_{50} for GSM ~13 minutes compared to ~3 minutes for MIB. Linear plots of ln C_0/C versus time indicated pseudo first-order kinetics, i.e. it is only dependadent on the concentration of one reactant, for both processes, with rate constants determined as 0.1979 and 0.0633 min^{-1} for MIB and GSM respectively. Investigation of the kinetics found the rate of destruction increased with increasing concentration for both compounds.

Further research is required to determine factors that effect photocatalysis of GSM and MIB and to establish the possibility of TiO_2 photocatalysis as a viable water treatment method. Factors which will have an effect on the photocatalysis of GSM within the developed reactor include, reactant-catalyst contact, flow patterns, mixing, mass transfer, pH and illumination of the catalyst (Mukherjee *et al.*, 1999). The factors influencing the photocatalysis of GSM investigated in this chapter include initial concentration of the reactant, the effect of a competing oxidant, pH, light intensity, aeration rate and catalysis in deuterated water.

Many studies have proposed that the photomineralization for organic pollutants by TiO_2 fit a Langmuir-Hinshelwood kinetic scheme (Chen *et al.*, 1995; Robertson *et al.*, 1999) and that the rate of pollutant destruction increases with pollutant concentration (Mills *et al.*, 1993).

Mills et al. (1993) reported that the pH of the aqueous solution significantly affected TiO_2, including, the charge on the particles, the size of the aggregates it forms, and the positions of the conductance and valence bands. The rate of photocatalysis was not usually found to be strongly dependant upon pH, typically varying by less than an order of magnitude from pH 2 to pH 12. The initial rate of destruction microcystin, a toxic cyanobacterial metabolite, was found to be strongly influenced by pH (Robertson *et al.*, 1999), with pH 4 found most effective for destruction for a range of microcystins (Lawton *et al.*, 2003a).

Illumination of the TiO_2 is a very important factor as the amount of TiO_2 that can be activated will determine the capacity of the Hombikat K01/C to degrade GSM. As the reactor developed in Chapter 3 is small the catalyst illumination should not be a problem as this is usually only associated with larger scale reactors (Mukherjee *et al.*, 1999). A number of studies have shown that the degradation of various solutes in the presence of a TiO_2 suspension is directly proportional to light only at light intensities corresponding to one sun or less (Matthews, 1993). As the light intensity increases, the proportionality merges into square root dependence (Kormann *et al.*, 1991; Robertson *et al.*, 1999). This effect has consequences for high intensity sources since the photons are not being used as effectively as possible.

Photomineralization will not proceed without the presence of oxygen (Mills *et al.*, 1993), but an increase of oxygen concentration from air saturated (21 % oxygen) to oxygen saturated (100 % oxygen) only increased the rate by 1.7. Reactor V.3 (Chapter 3) is aerated by the introduction of air from the bottom of the reactor and a increase in the aeration rate should therefore increase the rate of oxygen delivery to the reactor. This also will have the added effect of increasing mass transfer within the reactor by increasing mixing. As reactors utilizing immobilized TiO_2 often suffer from mass transfer limitation (Ollis *et al.*, 1991; Ray *et al.*, 1997), the increase in mass transfer is likely to increase the rate of GSM photomineralization.

Photocatalysis of GSM in heavy water (D_2O) will allow the observation of the kinetic effect on the rate of photocatalysis, aiding the elucidation of a photocatalytic mechanism. If a reduced rate of photocatalytic decomposition of GSM is observed it may suggest that the formation of hydroxyl radicals ($^\bullet OH$) is the rate limiting process in the photocatalytic process. It has been proposed that the reduced rate in D_2O is due to the lower quantum efficiency for the formation of $^\bullet OD$ radicals on the TiO_2 surface (Cunningham *et al.*, 1988). This lower surface concentration of $^\bullet OD$ radicals on the TiO_2 surface will result in fewer radicals for attack on target molecules.

4.2 METHODS

4.2.1 Photocatalysis of geosmin

An aqueous solution of geosmin (100 mL; ~1 μg mL^{-1}), with methanol removed, was prepared using Milli-Q high purity water (see section 2.2.3). The reactor (Figure 3-3; Chapter 3) was filled with 15 g of Hombikat K01/C and the air flow from the pump, passing through a rotameter, adjusted and maintained at 32 mL min^{-1}. The air flow rate was verified by a flow meter (CS1 6000 solid state flow meter, Cambridge Scientific Instruments Ltd., England). The Teflon tubing from the rotameter was then connected to the bottom of the reactor. The GSM solution (20 mL) was then added to the reactor.

The reactor was illuminated in the presence of air using a xenon UV lamp (400 W UVASpot 400 lamp, Uvalight Technology Ltd; spectral output 330 – 450 nm) situated 30 cm from the reactor. Samples (1 mL) were taken at timed intervals of 0, 5, 10, 15, 20 and 25 minutes of illumination then analysed by SPE-GC-MS (see section 2.2.2).

GSM solutions (~1 μg mL^{-1}) were also evaluated in the reactor with catalyst and aeration, and the xenon lamp switched off over the same time period. GSM solutions (~1 μg mL^{-1}) were also illuminated without catalyst over the 25 minute time course.

4.2.2 Effect of concentration on the photocatalysis of GSM

A range of GSM concentrations were prepared to evaluate the effect this had on the efficacy of photocatalysis. Method 4.2.1 was used with the following modifications. A range of 4 test solutions was prepared with the following concentrations of GSM, 5, 1, 0.5 and 0.1 μg mL^{-1}. GSM solutions at each concentration were also aerated with catalyst present and the xenon lamp switched off.

4.2.3 Dark adsorption of GSM onto Hombikat K01/C

A range of GSM concentrations 10, 5, 1, 0.5, and 0.1 μg mL^{-1} were prepared to evaluate the dark adsorption of GSM onto Hombikat K01/C over 24 hours. Glass vials (40 mL) were filled with 20 mL of GSM solution for each concentration and   15 g of catalyst added. The vials were capped, wrapped in aluminium foil and placed onto a 3-D rocking platform (Model STR9, Stuart Scientific, VWR, UK) in the absence of light for 24 hours. The rocking platform ensured that mixing of the catalyst and solution was adequate. Samples (1 mL) were taken for each concentration prior to addition of the catalyst and after 24 hours. Analysis was conducted by SPE-GC-MS (see section 2.2.2).

4.2.4 Methanol as a competing reactant

The experiment in method 4.2.2 was repeated without the removal of methanol from the GSM-methanol stock prior to preparation of the four test solutions. The same GSM concentration range was evaluated, 5, 1, 0.5 and 0.1 μg mL^{-1}. As GSM was dissolved in methanol when the GSM-methanol stock solution was first prepared, and taking into account the difference in concentration observed in Chapter 2 between the dilutions of the GSM-methanol stock solution and actual GSM standards, the methanol/GSM ratio was 100:1. For the GSM concentrations of 5, 1, 0.5 and 0.1 μg mL^{-1}, the methanol present for each concentration was 24.75, 9.90, 4.95, and 0.99 μg respectively.

Total organic carbon (TOC) analysis was conducted for all test solutions, prior to photocatalysis, with a Shimadzu TOC-V$_{CPH}$ analyzer, equipped with ASI-V auto sampler (Shimadzu, UK). The TOC analyzer was operated in the combustion/non-dispersive infrared gas analysis mode. The standard TOC catalyst was used for combustion of the samples and TOC calculated by subtraction of inorganic carbon (IC) from total carbon (TC). TC and TOC standard solutions were used to calibrate the instrument.

4.2.5 Influence of pH on the photocatalysis of GSM

The destruction of GSM was investigated as in method 4.2.1, but with different initial pH (1, 3, 5, 7, 9 and 11). The pH of solutions was altered by the addition of either sodium hydroxide or nitric acid to attain the desired pH. A pH meter (Delta 320, Mettler-Toledo Ltd., England) was used to monitor the pH of solutions and determine when the necessary pH had been reached. For each pH, GSM solutions were also aerated with catalyst and the xenon lamp switched off.

4.2.6 Effect of light intensity on the photooxidation of GSM

Photocatalysis of GSM was investigated with different irradiation intensities, 199, 319, 690, and 1735 μmol s^{-1} m^{-2}. Method 4.2.1 was used with the following alterations. The irradiation strength of the light falling on the reactor was altered prior to the start of each experiment by altering the distance between the reactor and the xenon lamp. The distance was altered to 60, 45, 30 and 15 cm, with irradiation intensity increasing the closer the xenon lamp was to the reactor. Standard conditions for photocatalysis of GSM used a distance of 30 cm (light intensity 690 μmol s^{-1} m^{-2}). A light meter (LI-250A light meter with LI-190SA quantum sensor, Li-COR Bioscience, USA) was used to measure photonic intensity and to attain the desired light intensities.

4.2.7 Influence of aeration rate on the photooxidation of GSM

The effect of aeration rate during photocatalysis was investigated. The reactor was used as described in method 4.2.1 with the following alterations. The aeration rate (30, 60, 120, and 150 mL min^{-1}) into the reactor was altered prior to the start of each experiment and verified with a flow meter. Aeration rates were also investigated with catalyst present and the xenon lamp switched off.

4.2.8 Photocatalysis of GSM and microcystin-LR in D_2O

The destruction of GSM was observed for GSM prepared in D_2O (99.9 % atom %D, Sigma-Aldrich, UK), as an alternative to Milli-Q, to investigate the effect of D_2O on the rate of GSM destruction. This kinetic isotope study will aid understanding of the mechanistic aspects of the photocatalytic reaction. Observation of a reduced rate of photocatalytic decomposition of GSM may suggest that the formation of hydroxyl radicals ($^{\bullet}OH$) is the rate limiting process in the photocatalytic process. Photocatalysis was performed as in section 4.2.1 with the exception that GSM solutions were prepared in D_2O. GSM solutions in D_2O were also aerated, with catalyst present, and the xenon lamp switched off.

To confirm the kinetic isotope effect of D_2O in the photocatalysis of GSM another cyanobacterial metabolite was selected for photocatalysis in D_2O, microcystin-LR (MC-LR). MC-LR was selected as a model compound as its mechanism of photocatalytic degradation has been well elucidated and the kinetic isotope effect of D_2O in the photocatalysis of MC-LR has been demonstrated for P-25 (Robertson *et al.*, 1998).

A ~100 $\mu g\ mL^{-1}$ MC-LR in D_2O solution was prepared by exhaustive re-suspension of freeze-dried MC-LR. The reactor (Figure 3-3; Chapter 3) was prepared as in method 4.2.1 and the MC-LR solution (20 mL) added to the reactor. The reactor was illuminated in the presence of air using a xenon UV lamp (400 W UVASpot 400 lamp, Uvalight Technology Ltd; spectral output 330 – 450 nm) situated 30 cm from the reactor. Samples (200 μl) were taken at timed intervals of 0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90 and 100 minutes of illumination and placed into inserts in 4 mL vials and analysed by high performance liquid chromatography (600E powerline gradient module pump with WISP auto sample and 996 photodiode array detector; Waters Ltd., UK) (Lawton *et al.*, 1994).

The degradation of MC-LR in Milli-Q (~100 $\mu g\ mL^{-1}$) was also investigated using this method. Samples (200 μl) were taken at timed intervals of 0, 5, 10, 15, 20,

25, 30, 40, 50, 60, 70, 80, 90 and 100 minutes of illumination and analysed by high performance liquid chromatography.

4.3 RESULTS AND DISCUSSION

4.3.1 Photocatalysis of geosmin

Results confirm that GSM was rapidly degraded on exposure to TiO_2 and UV light (Figure 4-1). Approximately 30 percent reduction of GSM was observed under control conditions after 25 minutes; aeration, catalyst absent and the xenon lamp switched off. Losses can be attributed to non-specific binding of GSM within the reactor and possible volatilisation of GSM from the reactor.
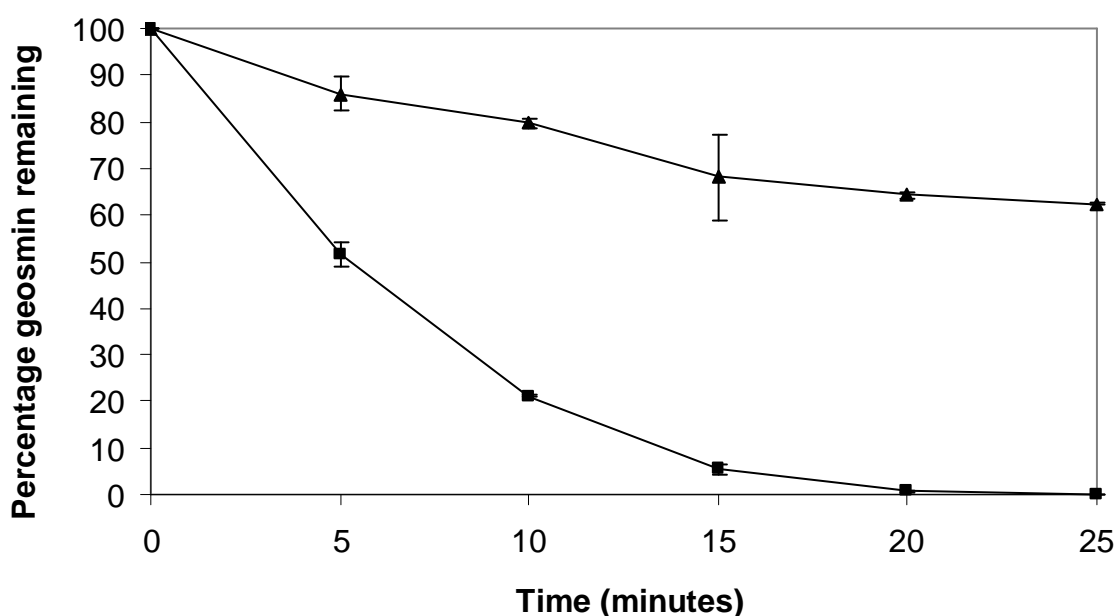
Figure 4-1. Photocatalytic destruction of geosmin (1 µg mL^{-1}) using Hombikat K01/C. Xenon lamp on (─■─); catalyst present and xenon lamp off (─▲─). Photocatalysis monitored by GC-MS. Bars equivalent to one standard deviation (n=2).

4.3.2 Effect of concentration on the photocatalysis of GSM

Initial concentration of GSM was found to have only a slight influence on the rate of GSM destruction (Figure 4.2). The rate of destruction was similar for 5, 1, and 0.5 μg mL^{-1} concentrations with approximately 50 % GSM remaining after 5 minutes. Only the lowest concentration 0.1 μg mL^{-1} displayed a faster degradation rate with approximately 25 % GSM remaining after 5 minutes. Under control conditions (aeration, catalyst absent and xenon lmap switched off) approximately 70 % GSM was remaining after 25 minutes for all concentrations.
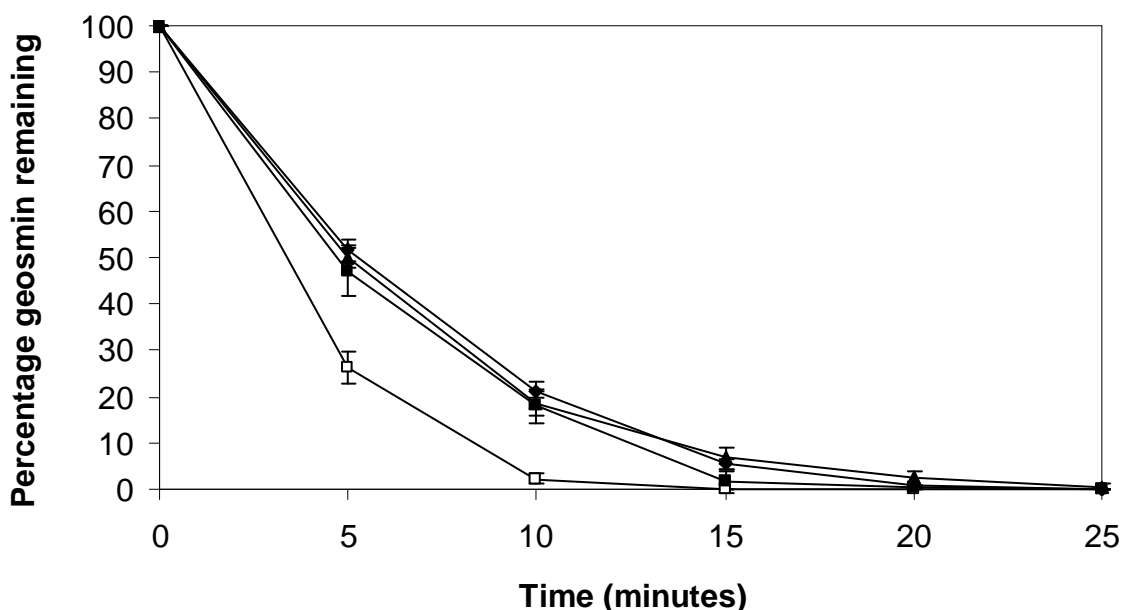
Figure 4-2. Destruction of geosmin by Hombikat K01/C TiO$_2$ photocatalysis at various concentrations; 5 μg mL^{-1} (—▲—); 1 μg mL^{-1} (—■—); 0.5 μg mL^{-1} (—♦—); 0.1 μg mL^{-1} (—□—). Photocatalysis monitored by GC-MS. Bars equivalent to one standard deviation (n=2).

The exact nature of the main oxidizing species formed on the surface of the semiconductor particles following the absorption of a photon is yet unclear and there is debate whether the •OH radical and/or pollutant react as absorbed species, as summarized by Turchi *et al.* 1990. The most commonly suggested

mechanism is the reaction between adsorbed species, leading to classical Langmuir-Hinshelwood rate expression (Childs *et al.*, 1981). This rate expression has been successfully applied to the heterogeneous photocatalytic degradation of a wide variety of organic compounds (Turchi *et al.*, 1990; Hoffmann *et al.*, 1995; Honglay Chen *et al.*, 1998), describing the relationship between initial degradation and initial concentration. Plotting In (C/C_0) against time gives a clearer indication of the effect of initial GSM degradation on degradation rate (Figure 4.3). The degradation profiles are similar for 5, 1, and 0.5 μg mL^{-1} GSM concentrations, with only 0.1 μg mL^{-1} showing a significantly different profile, though it is more scattered. By plotting reciprocal initial rate, determined after 5 minutes of photocatalysis for each GSM concentration, against reciprocal initial concentration a linear expression can be obtained (Chen *et al.*, 1998). A reasonable fit is achieved (R^2 = 0.9902) with values of 1.56 μM min^{-1} and 0.099 μM^{-1}, for *k* and *K* respectively (Figure 4-4). This would suggest that degradation of GSM obeys the Langmuir-Hinshelwood model and that GSM degradation occurs on the TiO$_2$ surface. However, as the effect of initial concentration on GSM degradation is not pronounced it would suggest that degradation may also be taking place in solution.
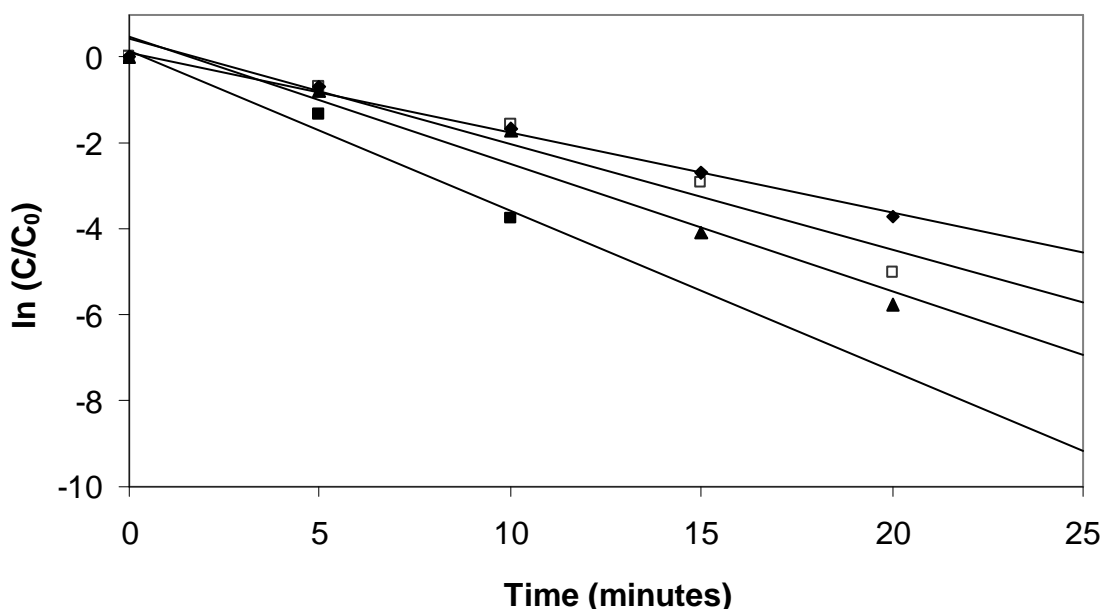
Figure 4-3. Effect of initial GSM concentration on degradation rate;
0.1 μg mL^{-1} (—■—); 0.5 μg mL^{-1} (—□—); 1 μg mL^{-1} (—▲—); 5 μg mL^{-1} (—◆—).
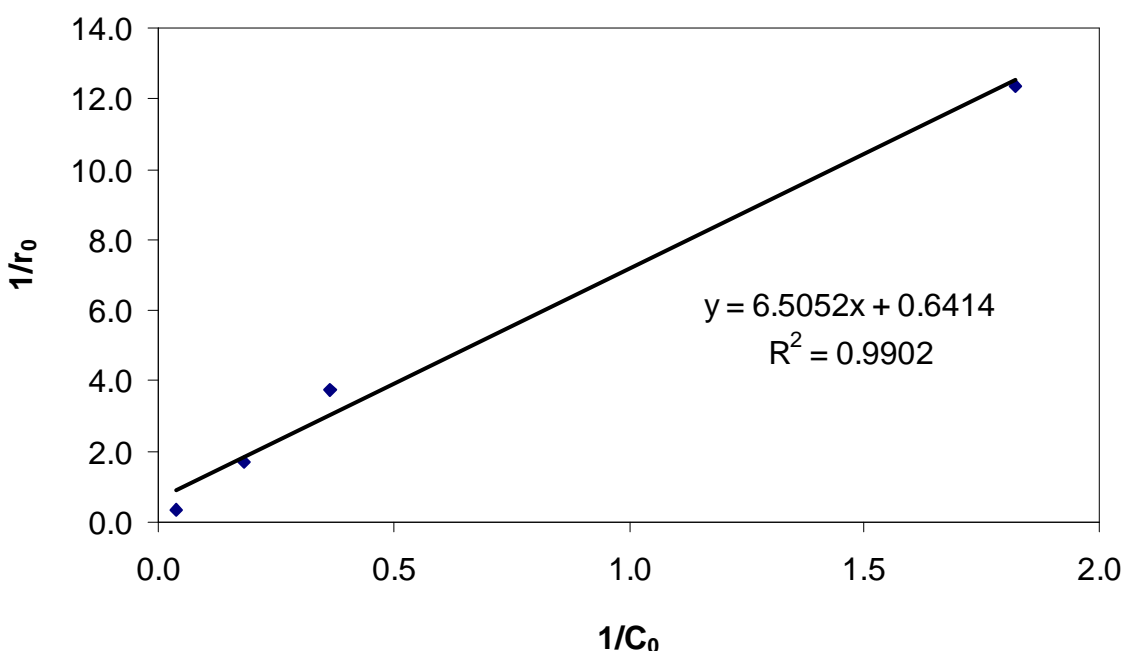
Figure 4-4. Reciprocal initial rate (1/r_0) of GSM destruction vs. reciprocal initial concentration (1/C_0) of GSM.

Despite the concentrations of GSM used in this study being considerably higher than those found in the environment, a typical environmental concentration being 10,000 times smaller than the lowest concentration investigated here, GSM was rendered undetectable by SPE-GC-MS after 25 minutes.

Table 4-1 presents the values determined for k and K for the destruction of GSM using the Langmuir-Hinshelwood model and also contains the values for GSM destruction using P-25 titanium dioxide (Lawton *et al.*, 2003b). The rate of GSM degradation is considerably faster than previously found with P-25 (Table 4-1) with D$_{50}$ ~5 minutes, compared with ~12 minutes for P-25. Table 4.2 shows data reported for other compounds using the Langmuir-Hinshelwood model, however it is difficult to make direct comparisons between k and K values for photocatalytic systems as they are greatly affected by experimental conditions including light intensity and initial substrate concentration (Xu *et al.*, 2000). The values obtained for GSM using Hombikat K01/C are significantly

different from those reported in other studies (Table 4-2), with the exception of *K* value reported by Robertson *et al.* (1997).

TiO$_2$ Catalyst	*k* (μM min^{-1})	*K* (μM^{-1})
Hombikat K01/C	1.56	0.099
P-25, Degussa	4.80 x 10^{-3}	24.55

Table 4-1. Comparison of rate and adsorption constants for the photocatalytic destruction of GSM by two different TiO$_2$ catalysts. Constants *k* and *K* determined using simple Langmuir-Hinshelwood model for photocatalytic destruction. P-25 data from Lawton and co-workers (Lawton *et al.*, 2003b).

Compound	*k* (μM min^{-1})	*K* (μM^{-1})	Reference
Microcystin-LR	19.23	0.029	(Robertson *et al.*, 1997)
Phenol	2.19 x 10^{-2}	12.9	(Matthews *et al.*, 1992)
Benzene	1.80 x 10^{-2}	39	(Turchi *et al.*, 1990)
Perchloroethylene	8.60 x 10^{-3}	34	(Turchi *et al.*, 1990)
4-chlorophenol	4.88 x 10^{-3}	79.3	(Matthews, 1988)

Table 4-2. Comparison of rate and adsorption constants of other organic compounds. Simple Langmuir-Hinshelwood model used to determine constants for photocatalytic destruction.

Previous work has demonstrated that organic compounds appear to be more strongly adsorbed to TiO$_2$ dispersions than film forms of TiO$_2$. The Hombikat K01/C catalyst has greater photocatalytically available surface area than a thin film, but less than powdered TiO$_2$, this is reflected in the *K* values in Table 4.1, with adsorption of GSM onto dispersed P-25 250 times greater than adsorption onto Hombikat K01/C. This data would initially suggest that surface adsorption of GSM onto Hombikat K01/C TiO$_2$ is not essential for the degradation of GSM.

4.3.3 Dark adsorption of GSM onto Hombikat K01/C

Dark adsorption of GSM onto Hombikat K01/C appeared to be dependent on GSM concentration with GSM adsorption greatest at the lowest concentration (0.1 μg mL^{-1}) with approximately 60 % of GSM adsorbed after 24 hours

(Figure 4-5). Adsorption of GSM was lower for the higher concentrations with approximately 20 % of GSM adsorbed after 24 hours. Chen *et al.* (1995) reported approximately 20 % adsorption of 1,2-Dichioroethane (DCE) onto P-25 TiO_2. Initial concentration of DCE was not found to greatly affect adsorption suggesting that the kinetics are controlled by other factors such as transport processes.
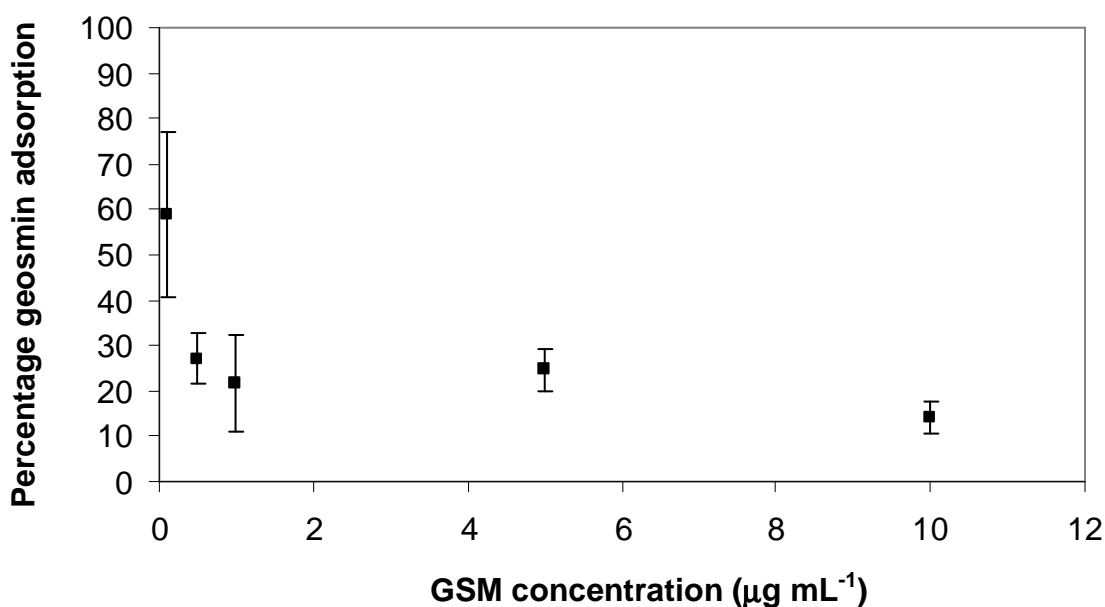
Figure 4-5. Dark adsorption of geosmin onto Hombikat K01/C, after 24 hours, at different concentrations (10, 5, 1, 0.5, and 0.1 μg mL^{-1}). GSM adsorption monitored by GC-MS. Bars equivalent to one standard deviation (n=2).

The amount GSM actually adsorbed was calculated by subtracting final GSM solution concentration from the initial GSM concentration of the aqueous solution. The amount of GSM adsorbed at equilibrium (24 h) was calculated since maximum adsorption occurs at equilibrium. The amount of GSM adsorbed at equilibrium Q_e (mg g^{-1}) was obtained using Equation 4-1:

$$Q_e = \frac{(C_o - C_e)\ V}{W} \qquad \text{(Equation 4-1)}$$

Where C_o and C_e are the initial and equilibrium liquid-phase concentration of GSM (mg L^{-1}) respectively. V is the volume of solution (L) and W is the amount of adsorbent (TiO$_2$) used (g). The results for adsorption of GSM onto the catalyst, with respect to different initial GSM concentrations, can be seen in Figure 4-6.
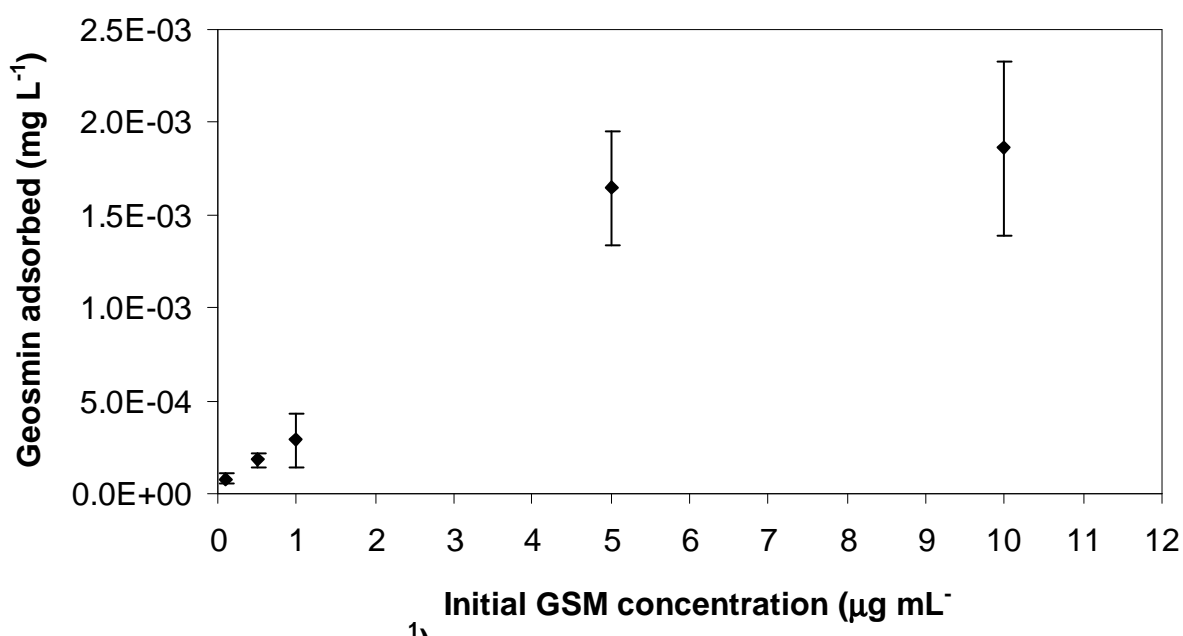
Figure 4-6. Dark adsorption of geosmin onto Hombikat K01/C, after 24 hours, at different concentrations (10, 5, 1, 0.5, and 0.1 μg mL^{-1}). GSM adsorption monitored by GC-MS. Bars equivalent to one standard deviation (n=2).

The results show an initial linear relationship between adsorption of GSM onto the catalyst and GSM concentration. This changes to a curved relationship at the higher GSM concentrations of 5 and 10 μg mL^{-1} suggesting that maximum adsorption has been achieved for this catalyst loading (15 g) at a GSM concentration of 10 μg mL^{-1}. This is a typical Langmuir type adsorption isotherm.

4.3.4 Methanol as a competing reactant

GSM solutions of similar concentrations as found in method 4.3.2 were prepared, but without the prior removal of methanol. These solutions subsequently underwent photocatalysis in the reactor. This allowed the observation of how methanol acted as a competing oxidant with GSM.

The effect methanol has on the destruction of GSM can be clearly seen by comparing the photocatalysis of GSM solutions with and without methanol (Figure 4-7). The reduced rate of GSM destruction was most pronounced for 5 and 1 μg mL^{-1} GSM solutions containing methanol, with GSM reduction after 5 minutes ~30 % lower when compared with comparable GSM solutions containing no methanol. This decrease in the rate of GSM degradation between the solutions containing and not containing methanol became more pronounced after 5 minutes of photocatalysis.

The decrease in the rate of GSM degradation in the 5 and 1 μg mL^{-1} GSM solutions containing methanol is unsurprising as TOC analysis of these solutions (Figure 4-8) demonstrated that organic carbon was highest for the 5 and 1 μg mL^{-1} solutions. TOC analysis of solutions containing only GSM only detected GSM at the highest concentration (5 μg mL^{-1}), with a TOC concentration of 6 ppm.

Bekbolet *et al.* (2002) reported that the presence of 1 % methanol caused significant retardation of the P-25 photocatalysis of methylene blue, with a 50 % reduction in the rate of methylene blue degradation. A mechanism for the effect of methanol within the photocatalytic system was not discussed. The 5 μg mL^{-1} GSM solution contained approximately 0.12 % methanol, this also caused 50 % reduction in the initial rate of GSM destruction. The effect of methanol on the retardation of photocatalysis observed here is significantly greater than that observed by Bekbolet *et al.* (2002).
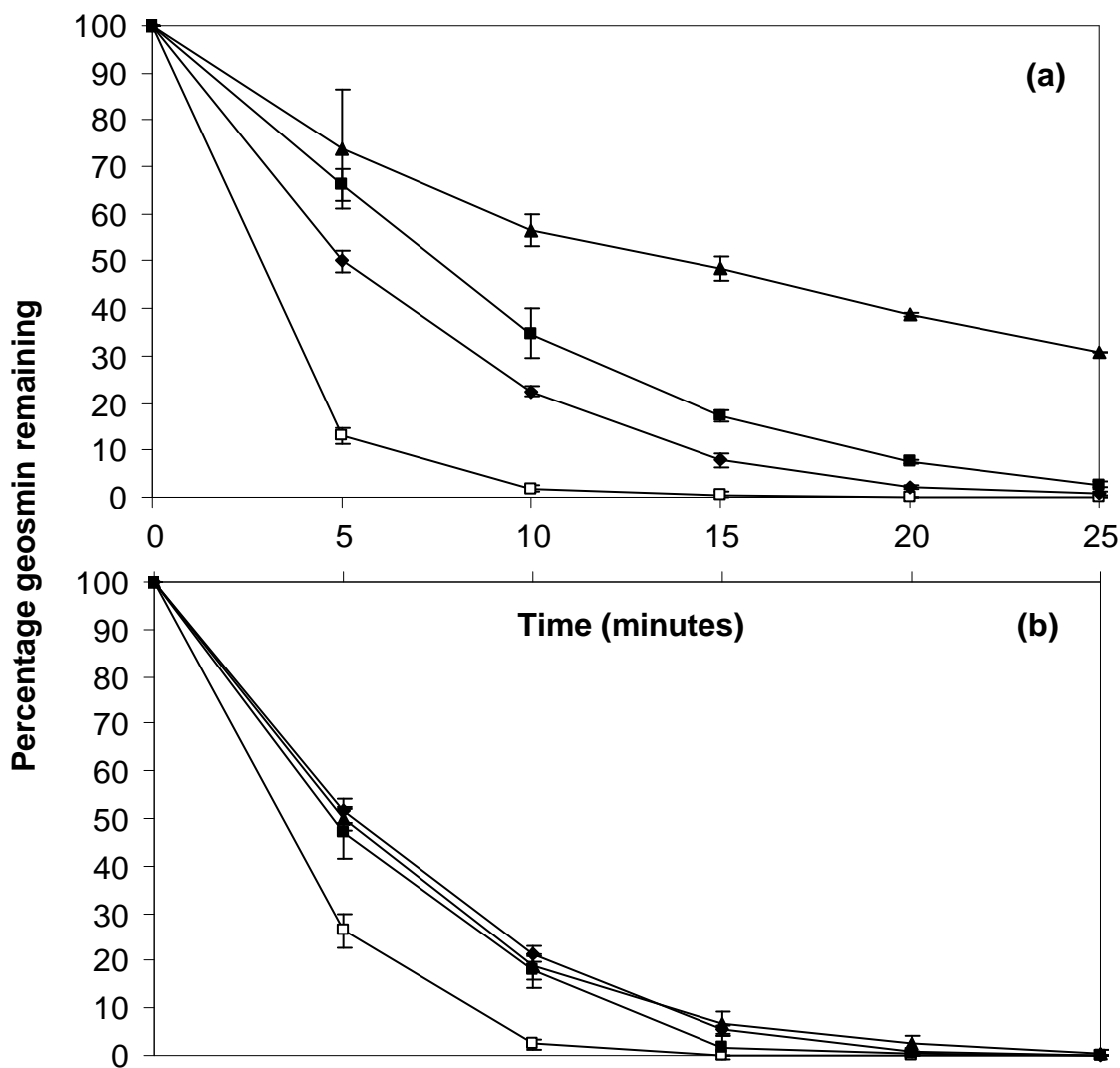
Figure 4-7. Destruction of geosmin by Hombikat K01/C TiO$_2$ photocatalysis at different concentrations with methanol present (a) and methanol absent (b) 5 μg mL^{-1} (—▲—); 1 μg mL^{-1} (—■—); 0.5 μg mL^{-1} (—◆—); 0.1 μg mL^{-1} (—□—). Photocatalysis monitored by GC-MS. Bars equivalent to one standard deviation (n=2).

One of the main factors affecting the degradability of organic compounds by TiO_2 photocatalysis is solution polarity (Guisnet *et al.*, 1993). Brezova *et al.* (1997) investigated the selective photocatalytic reduction of 4-nitrophenol to 4-aminophenol in P-25 titanium dioxide suspensions prepared in aliphatic alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, i-butanol). The photoreduction rate of 4-nitrophenol was found to be significantly affected by the solvent polarity, with the rate of photoreduction increasing with an increase in solvent polarity. Therefore, the best solvent for the reduction of 4-nitrophenol was methanol. However, as water is more polar than methanol, photocatalysis should be greater when using water as a solvent as opposed to methanol.

This fact is supported by the findings of Habibi *et al.* (2005) who reported on the TiO_2 photocatalytic degradation of methyl phenyl sulfide (MPS) and methyl benzimidazoyl sulfide (MBS) using water and methanol as a solvent. The degradation of MPS and MBS in water was 85 and 80 % respectively, compared with 7 and 5 % in methanol. Additionally methanol is an effective hole acceptor and may be competing with GSM for oxidation on the catalyst surface.
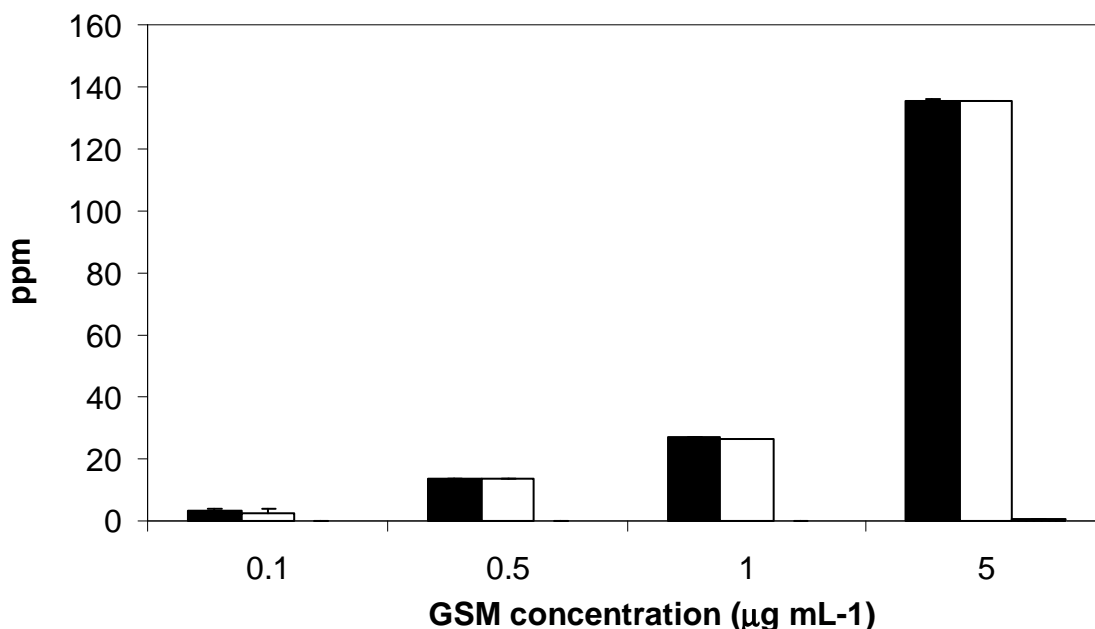
Figure 4-8. TOC analysis of GSM solutions, prepared without the removal of methanol, prior to photocatalysis; total carbon (■); total organic carbon (□); inorganic carbon (▨). Bars equivalent to one standard deviation (n=2).

The GSM reduction rate of the 0.5 μg mL^{-1} GSM solutions, containing methanol and not containing methanol, were very similar (Figure 4-7). However, the initial rate of GSM destruction (after 5 minutes) for the 0.1 μg mL^{-1} GSM solution, containing methanol was 50 % greater than the corresponding GSM solution that did not contain methanol (Figure 4-5).

Clearly the presence of methanol, especially at higher concentrations, has the effect of reducing the rate of GSM degradation by TiO$_2$ photocatalysis. The major contributor to this decrease in the rate of GSM reduction is likely to be the effect of methanol as a competing reactant to GSM.

4.3.5 Influence initial of pH on the photocatalysis of GSM

The pH of solutions was altered by the addition of either sodium hydroxide or nitric acid to attain the desired pH. A pH meter (Delta 320, Mettler-Toledo Ltd., England) was used to monitor the pH of solutions and determine when the necessary pH had been reached. The pH of the reaction was not found to have a major influence on the overall rate of GSM destruction (Figure 4-9 and Figure 4.10). However, there was a general trend, indicating the initial rate of GSM degradation increased at lower pH. Remaining GSM after 5 minutes for pH 1 was 28 ($\pm$ 0.11) %, compared to 43 ($\pm$ 0.24) % GSM remaining at pH 11 (Figure 4-10). Photocatalysis of GSM at pH 7 resulted in the slowest rate of GSM degradation after 5 minutes, with 56 % remaining. There was however, poorer reproducibility, 15.12 % RSD, at this pH. This was also true for photocatalysis of GSM conducted at pH 3, with 14.48 % RSD. The effect on lower pH on the increased rate of GSM destruction is also observed after 10 minutes of photocatalysis (Figure 4-10). Losses of GSM under control conditions for the different pH valuess was within the same range, ~30 % GSM lost after 25 minutes (Figure 4-9), as that typically observed when conducting photocatalysis of GSM in Milli-Q. Slight changes in the pH values after 25 minutes were observed, likely caused by the test solutions being unbuffered.
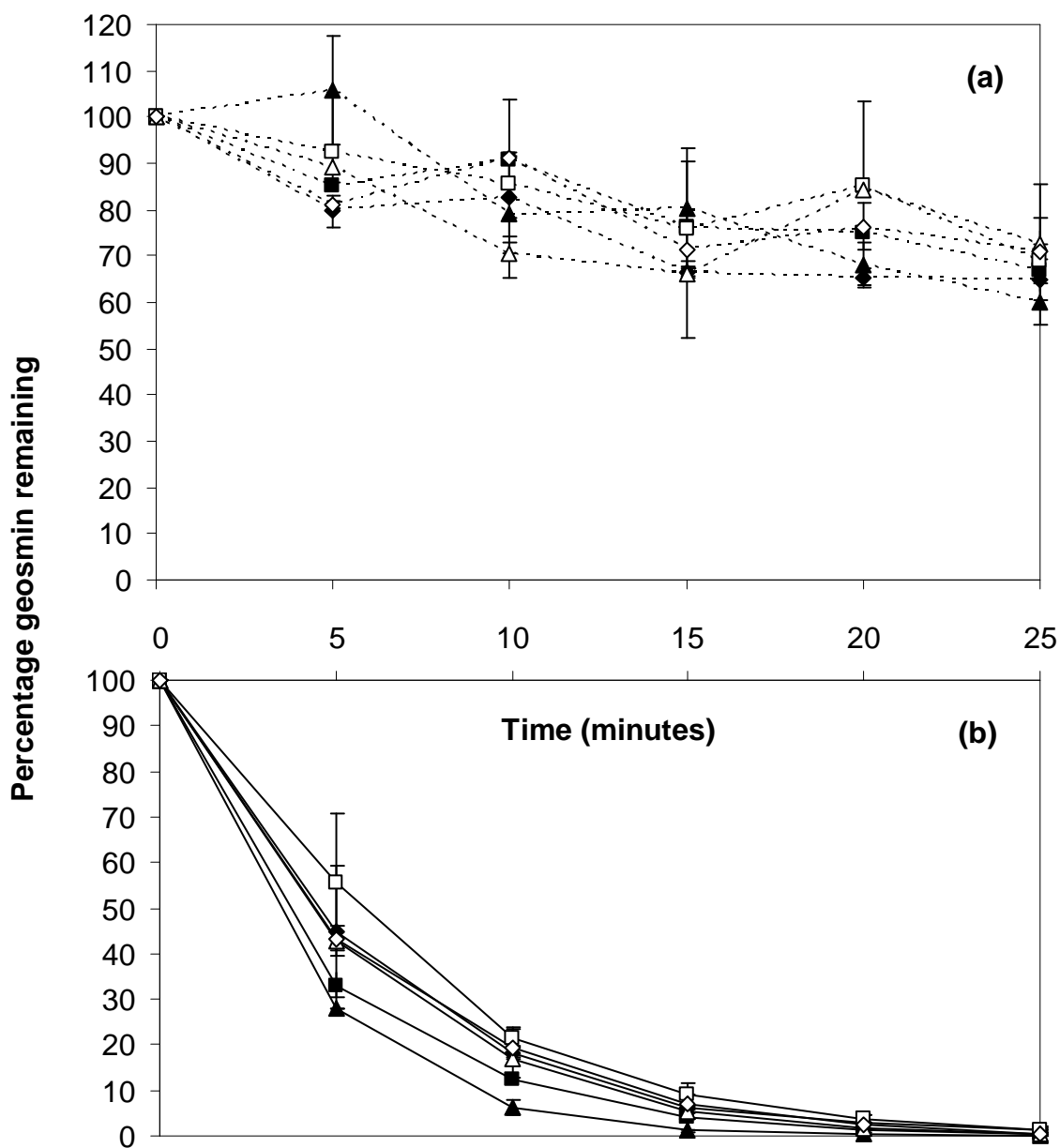
Figure 4-9. Destruction of geosmin by TiO$_2$ photocatalysis at different pH values, (a) pH controls and (b) photocatalysis at different pH values; pH1 (—▲—); pH3 (—◆—);pH5 (—■—); pH7 (—□—);pH9 (—△—); pH11 (—◇—). Photocatalysis monitored by GC-MS.Bars equivalent to one standard deviation (n=2).

Ku *et al.*, (1996) also reported this general trend of increased degradation at lower pH values for the degradation of 2-chlorophenol by TiO_2 photocatalysis, but at a greater magnitude. The complete disappearance of 2-chlorophenol was achieved in 3.5 hours at pH 3, compared to 10 hours at pH 11. It was also reported that the higher removals at acidic conditions were possibly attributed to the increased amounts of undissociated 2-chlorophenol species adsorbed on the TiO_2 surface. The destruction of a number of microcystins, a cyanobacterial metabolite, using P-25 TiO_2 photocatalysis was also found to be pH dependant by Lawton *et al.* (2003). The pH dependence was associated with catalyst surface charge and the altered hydrophobicity and net charge of the microcystin. The two most hydrophobic microcystins (-LW and -LF) were found to have high dark adsorption (98 and 91 % at pH 4) in contrast to microcystin-RR, which was found to have almost no (2- 3 %) dark adsorption across all pH values.
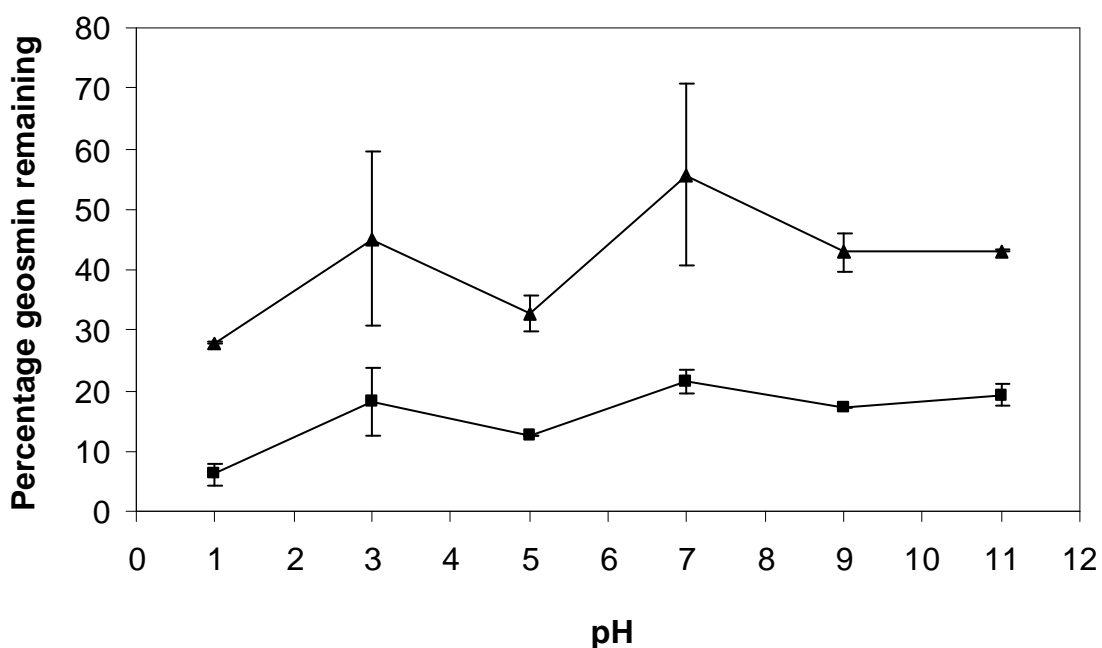
Figure 4-10. Geosmin remaining after 5 (——▲——) and 10 (——■——) minutes of TiO_2 photocatalysis at different pH values, Photocatalysis monitored by GC-MS. Bars equivalent to one standard deviation (n=2).

As GSM appears to be stable at the pH values investigated here (Figure 4-9) the increased rate of GSM destruction at lower pH values must be due to the effect of pH on the surface charge of the catalyst and the charge of the pollutant. The interpretation of the effect of pH on the efficiency of photocatalysis is difficult because of its multiple effects. The ionisation state of the TiO_2 surface is affected by pH according to the following reactions (Habibi *et al.*, 2005):

$$TiOH + H^+ \rightleftharpoons TiOH_2^+ \qquad \text{(Equation 4-2)}$$

$$TiOH + OH^- \rightleftharpoons TiO^- + H_2O \qquad \text{(Equation 4-3)}$$
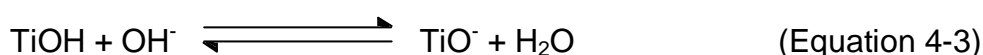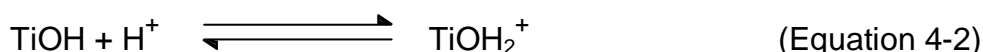
Hydroxyl radicals can be formed by hydroxide ions and positive holes. At low pH the positive holes are considered the major oxidation species, with hydroxyl radicals the predominant species at neutral or high pH (Kormann *et al.*, 1991). Hydroxyl radicals are more readily generated in alkaline solution as more hydroxide ions are available on the TiO_2 surface, The formation of hydroxyl radicals could however be prevented by the Coulombic repulsion between the negatively charged surface of the photocatalyst and the hydroxide anions, decreasing photooxidation (Konstantinou *et al.*, 2004).

The ionisation state of the reactants can also be affected by pH. The combination of the pH effects on the reactant and the catalyst can therefore influence the adsorption of the GSM onto the surface of the TiO_2, an important factor in photocatalysis. The zero point of charge (pH_{zpc}) of the TiO_2 is pH 6.25 (Hoffmann *et al.*, 1995). Therefore, the surface charge of the TiO_2 is positive in acidic media (pH < 6.25), attracting anions, and negative in alkaline media (pH > 6.25), attracting cations.

Another possible explanation for the increased rate of GSM degradation observed at low pH may be due to the presence of HNO_3, nitric acid was used

to adjust test solutions to low pH. Epling *et al.* (2002) reported that the degradation rate of two dyes, methylene blue and methylene green, by P-25 photocatalysis was accelerated in the presence of HNO_3. The photocatalytic degradation of methylene blue and methylene green increased by 24 and 37 % over 1 hour in the presence of 0.01 M HNO_3. This effect was not explained, but the increase observed in the rate of GSM destruction after 5 and 10 minutes in the presence of HNO_3 was 46 and 40 % compared to photocatalysis conducted in its absence (Figure 4-10). The increase in photodegradation of GSM at lower pH is of a similar magnitude to that found by Epling *et al.*, (2002) for the presence of HNO_3.

4.3.6 Effect of light intensity on the photocatalysis of GSM

The rate of GSM destruction was proportional to the light intensity investigated with GSM destruction increasing with increasing light intensity (Figure 4-11). For example GSM remaining, after 5 minutes at the lowest light intensity, was 58 (± 2.5) %, compared to 19 (± 2.6) %, at the highest light intensity.
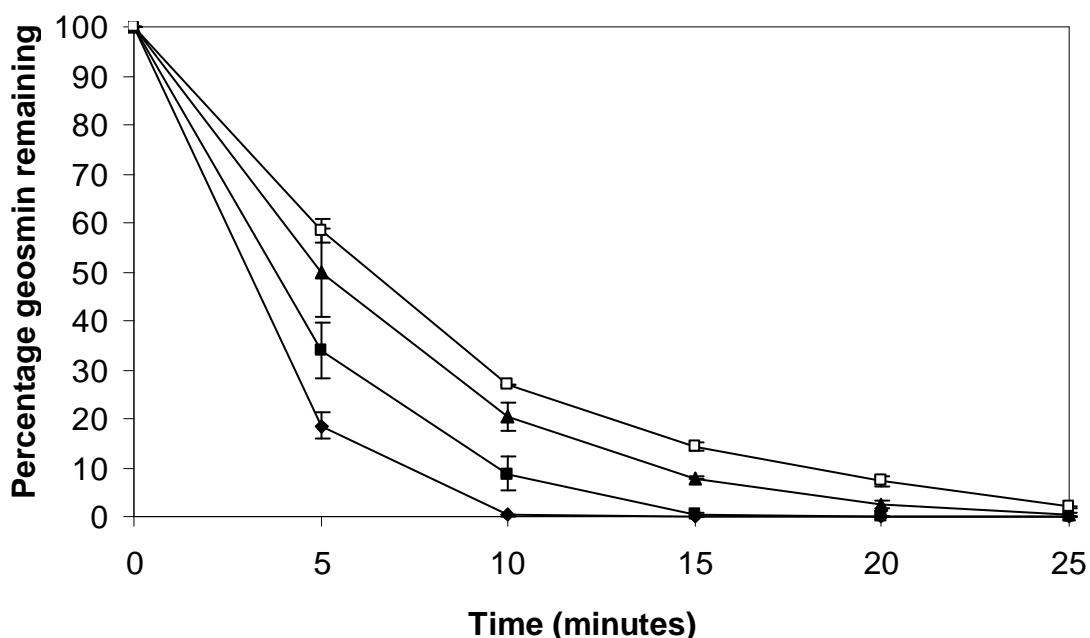
Figure 4-11. Destruction of geosmin by Hombikat K01/C TiO$_2$ photocatalysis at different light intensities (μmol s^{-1}m^{-2}); 1735 (—◆—); 690 (—■—); 319 (—▲—); 199 (—□—). Photocatalysis monitored by GC-MS. Bars equivalent to one standard deviation (n=2).

A plot of the reciprocal initial rate of GSM destruction (R_0) against light intensity demonstrates that the increase in GSM destruction is linear at low light intensities, but reducing at the higher light intensities, possibly moving into a square root relationship between light intensity and GSM destruction (Figure 4-12). A similar relationship has been observed by other workers. A reduction in GSM was observed under control conditions with approximately 70 % GSM remaining after 25 minutes.
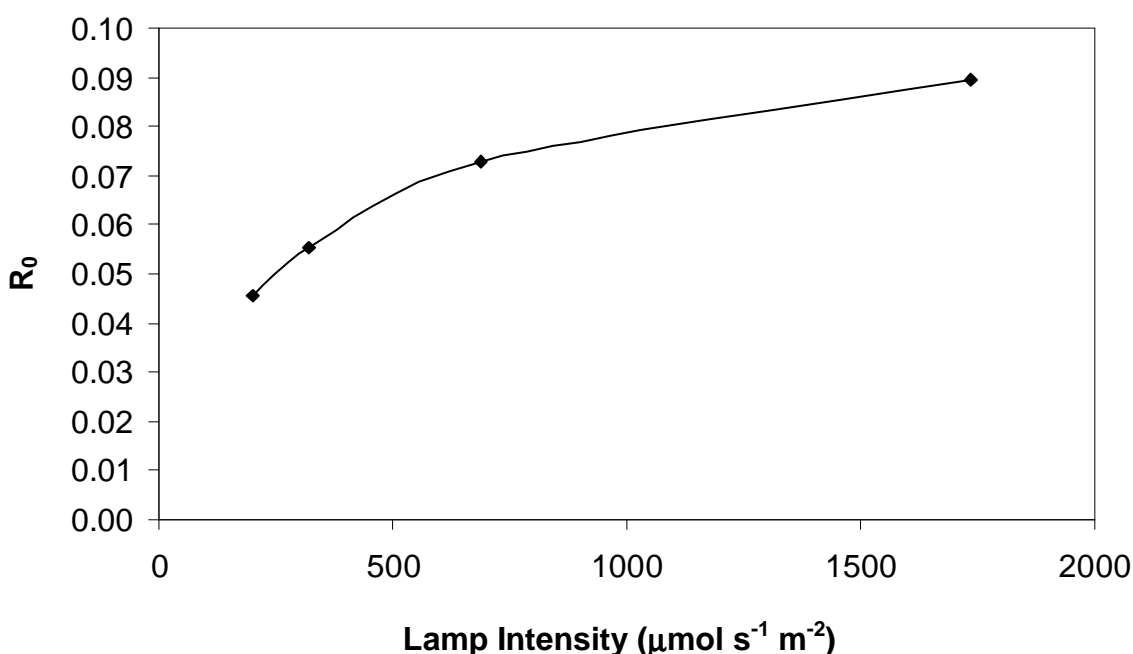
Figure 4-12. Relationship between reciprocal Initial Rate ($1/R_0$) and lamp (400 W UVASpot 400 lamp; spectral output 330 – 450 nm) intensity for destruction of GSM (1 μg mL^{-1}) using Hombikat K01/C.

Previous studies (Egerton *et al.*, 1979; Ollis *et al.*, 1991; Hoffmann *et al.*, 1992; Hoffmann *et al.*, 1995; Chen *et al.*, 1998) of the effect of light intensity on the kinetics of the photocatalysis process indicated that at low light intensities (0-20 W cm^{-2}), and mass transfer dependant, the reaction rate would increase linearly with increasing light intensity (first order). At intermediate intensity levels (~20 W cm^{-2}), the reaction rate increases with the square root of light intensity. At high light intensities the rate is independent of light intensity. This is probably caused by the competition of electron-hole pair separation and recombination, resulting in a reduced effect of light intensity on the reaction rate. At low light intensities electron-hole recombination is negligible. The work

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conducted here clearly demonstrates a similar relationship between the rate of GSM destruction and increasing light intensity.

4.3.7 Influence of aeration rate on the photooxidation of GSM

An increase in aeration rate was found to increase the rate of GSM destruction, with an increase in GSM destruction plateauing at an air flow rate of 150 mL min^{-1} (Figure 4-13). However this increase in GSM loss can be attributed to the increase in system loss of GSM. Adjusting GSM loss, by subtracting GSM loss under control conditions from the GSM reduction under photocatalytic conditions, shows there is negligible difference in the rate of GSM destruction. For the flow rates of 30, 60, 120, and 150 min^{-1}, adjusted GSM loss was 48, 46, 49, and 44 % respectively after 5 minutes.

Although data suggest that air stripping is unlikely to remove GSM from water (Lalezary *et al.*, 1984), results in this study appear to show that an increase in aeration rate does have an effect on the volatilisation of GSM. This effect is most pronounced when comparing the aeration rates of 30 mL min^{-1}, the standard air flow rate used in this study for the photocatalysis of GSM, and the 150 mL min^{-1} flow rate, under control conditions (Figure 4-13). GSM losses under these conditions are 34 and 67 % for the 30 and 150 mL min^{-1} flow rates respectively after 25 minutes. Although a proportion of these losses can be associated with non-specific adsorption of GSM within the reactor and dark adsorption onto the catalyst surface, it is clear that a significant percentage of the GSM loss observed at the 150 mL min^{-1} flow rate is caused by volatilisation.

Dijkstra *et al.* (2001) reported on the photocatalytic efficiency of P-25 in immobilized and suspended reactors in degrading formic acid. Although the reactor was considerably larger (volume 124 x 10^{-6} m^3) than he one used in this study (volume 4.39 x 10^{-8} m^3), 2800 larger, the design was very similar. The reactors were evaluated with and without the addition of oxygen, with addition of oxygen to the suspended system having little effect on degradation of formic acid. In the immobilised system addition of oxygen through the bottom of the
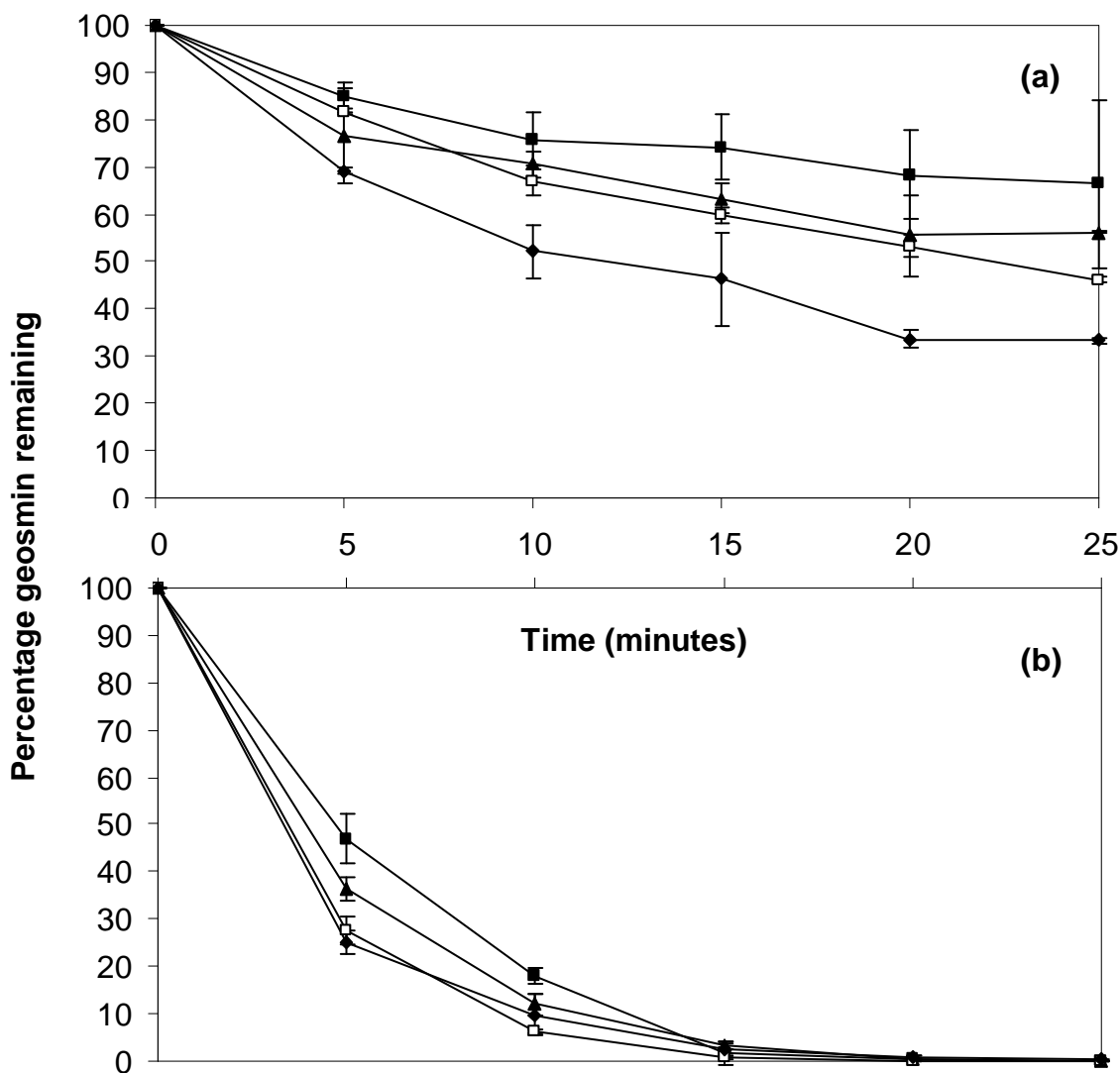
Figure 4-13. Destruction of geosmin by Hombikat K01/C TiO$_2$ photocatalysis at different aeration rates, (a) aeration controls (b) photocatalysis ; 30 mL min^{-1} (—■—); 60 mL min^{-1} (—▲—); 120 mL min^{-1} (—□—); 150 mL min^{-1} (—◆—). Photocatalysis monitored by GC-MS. Bars equivalent to one standard deviation (n=2).

reactor greatly increased the quantum yield of the system from 0.063 to 0.28. The addition of oxygen was believed to increase mass transfer by enhancing agitation.

Increasing the aeration rate, and therefore enhancing mass transfer, did not increase the rate of GSM degradation. This effect has also been noted by other researchers. Chen *et al.* (1995), in a study of P-25 photocatalysis of 1,2-dichloroethane (DCE), reported that the limiting rate of adsorption to be approximately twice the rate of photodegradation in upper concentration ranges. It was concluded that this limiting rate was much higher than the rate of photodegradation in the lower range of concentrations and did not impede the overall kinetics. In these two studies the rate of substrate degradation was not significantly affected by mass transfer. From the results reported here GSM destruction, using the TiO_2 catalyst in this reactor configuration and under the conditions investigated, was also not influenced by mass transport.

4.3.8 Photocatalysis of GSM and Microcystin-LR in D_2O

The destruction of GSM was investigated in both Milli-Q (H_2O) and heavy water (D_2O) solvents (Figure 4-14). The rate of destruction of GSM was significantly reduced when photocatalysis was conducted in the D_2O solvent. GSM was still present after 25 minutes of photocatalytic treatment in D_2O for all concentrations, in contrast to photocatalysis conducted in H_2O under standard conditions where no GSM was detectable after 25 minutes. The degradation profiles of GSM in D_2O displayed the same trend as GSM degradation in H_2O with respect to concentration. The rate of GSM destruction was similar for 5, 1, and 0.5 $\mu g\ mL^{-1}$ concentrations, with only the 0.1 $\mu g\ mL^{-1}$ GSM concentration displaying a faster degradation rate. The typical loss of 30 % GSM after 25 minutes was observed under control conditions.
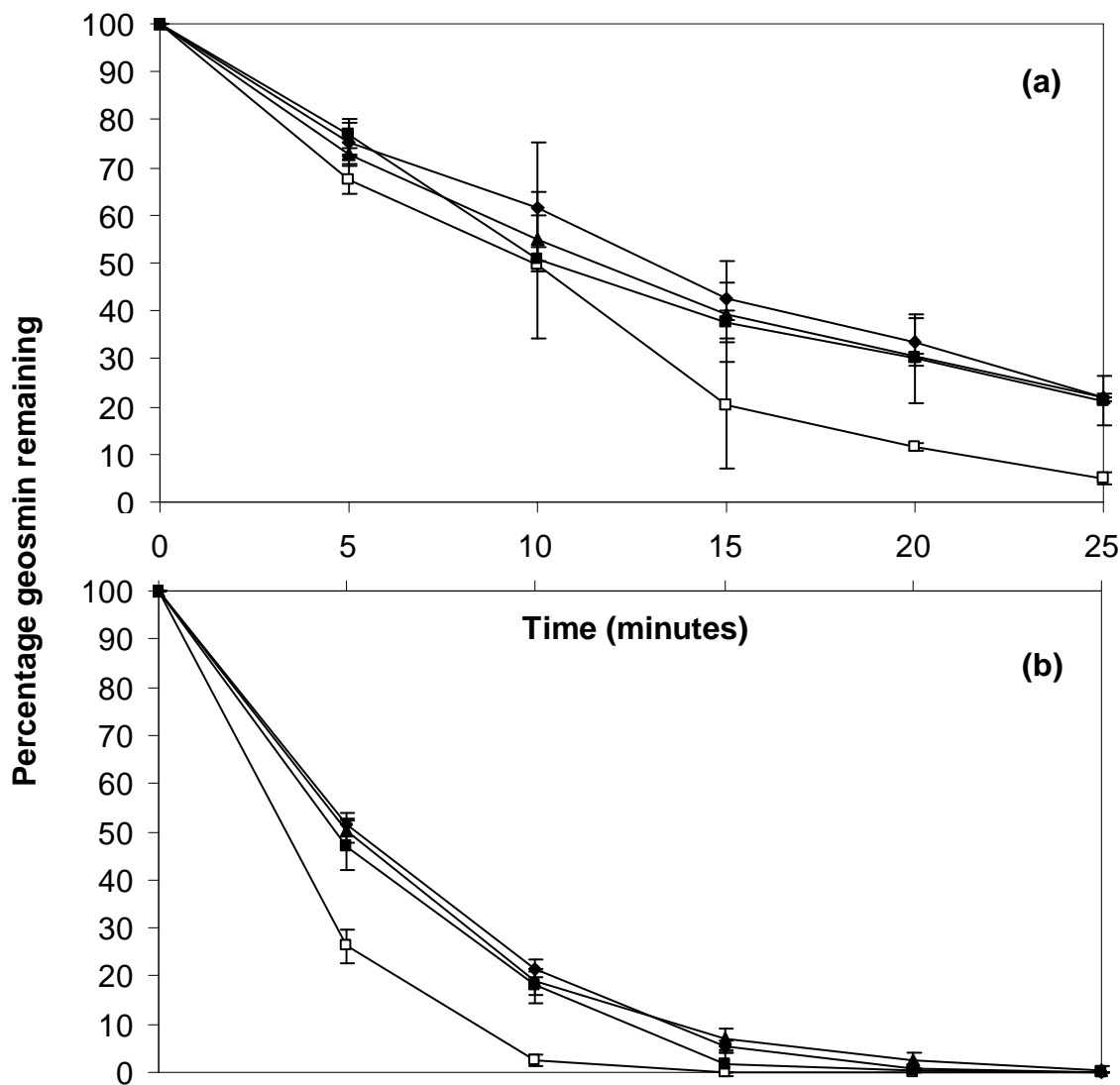
Figure 4-14. The photocatalytic destruction of different geosmin concentrations, 1 µg mL^{-1} (──■──), 0.5 µg mL^{-1} (──♦──), 0.1 µg mL^{-1} (──□──), and 5 µg mL^{-1} (──▲──), using Hombikat K01/C, in D$_2$O (a) and Milli-Q (b). Photocatalysis monitored by GC-MS. Bars equivalent to one standard deviation (n=2).

To confirm the kinetic isotope effect of D_2O in the photocatalysis of GSM, another cyanobacterial metabolite was selected for photocatalysis in D_2O, microcystin-LR (MC-LR). MC-LR was rapidly degraded in H_2O and D_2O using TiO_2 photocatalysis with a D_{50} of approximately 7 and 12 minutes. Again the rate of substrate destruction was reduced considerably when photocatalysis was conducted in D_2O (Figure 4-15), confirming the kinetic isotope effect for Hombikat K01/C.
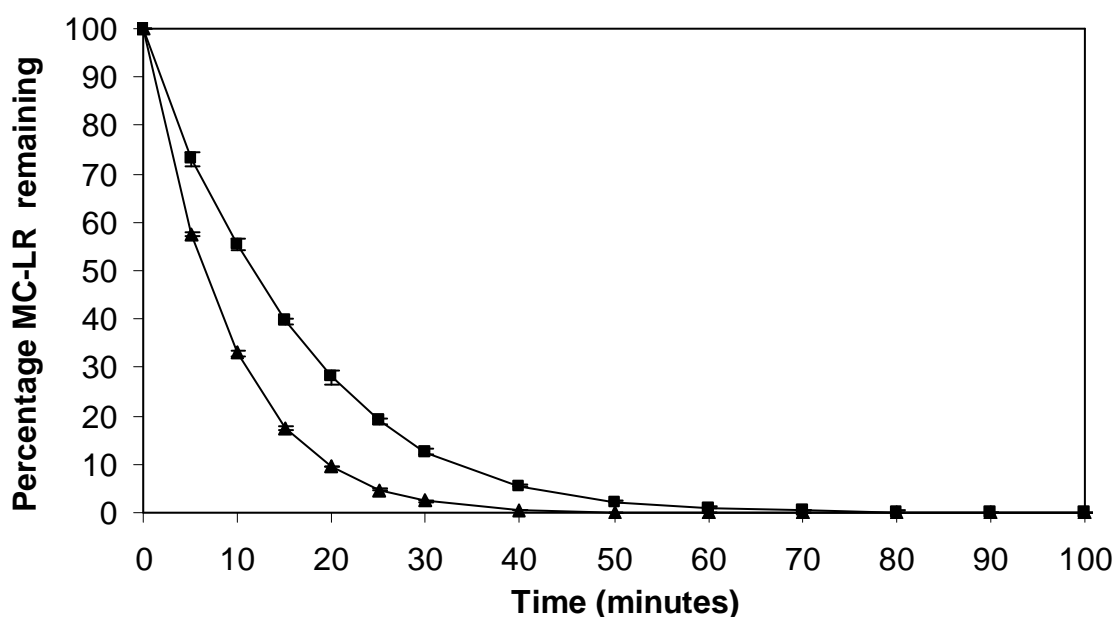
Figure 4-15. Destruction of MC-LR by TiO$_2$ photocatalysis in Milli-Q (—▲—) and D$_2$O (—■—). Photocatalysis monitored by HPLC. Bars equivalent to one standard deviation (n=2).

The primary isotope effect for the destruction of GSM using Hombikat K01/C TiO_2 was calculated to be 1.61 (Table 4.3). Photocatalysis of GSM in D_2O reduced the rate of destruction for GSM. This effect was verified by the photocatalysis of MC-LR in D_2O, where the primary isotope effect was calculated to be 1.56 (Table 4.3). Robertson *et al.* (1998) and Cunningham *et al.* (1988) also reported primary isotope effects for the destruction of microcystin-LR and isopropanol respectively using P-25 TiO_2. The primary

isotope effect of 3 reported by Robertson et al. (1998) was similar to the effect of 3.3 reported by Cunningham *et al.* (1998). The results of both studies suggest that the formation of hydroxyl species is the main agent in substrate degradation and may be the rate limiting factor in the photocatalytic process. It was also proposed that the reduced rate of photocatalytic degradation was due to the lower quantum efficiency for the formation of $^\bullet$OD radicals on the TiO_2 surface, resulting in a reduction of $^\bullet$OD radicals on the TiO_2 surface for subsequent attack on substrate molecules. Alternatively, the lower rate of oxidation rate may be due to the fact that $^\bullet$OD radicals have lowered oxidation potential when compared to $^\bullet$OH radicals.

Solvent	GSM			MC-LR	
	k (μM min^{-1})	K (μM^{-1})	Relative Rate	k (μM min^{-1})	Relative Rate
H_2O	1.56	0.099	1.0	8.55	1.0
D_2O	0.97	0.069	0.62	5.44	0.64

Table 4-3. Kinetic isotope effect based on the photocatalytic destruction of GSM and MC-LR in two different solvents. Constants *k* and *K* determined using simple Langmuir-Hinshelwood model for photocatalytic destruction.

It may be possible that the kinetic isotope effect reported here for GSM (and MC-LR), which is approximately 50 % lower than found in the studies by Robertson *et al.* (1998) and Cunningham *et al.* (1988), is mediated via hydroxyl radicals generated from the superoxide radical anion produced at the conduction band. This is subsequently hydrated or deuterated by the solvent (Mao *et al.*, 1991). This may be rate determining since O_2 has to be generated at the conduction band prior to interaction with the solvent and subsequent formation of $^\bullet$OD or $^\bullet$OH species. Therefore the kinetic isotope effect could be caused by the interaction of the solvent with the superoxide species rather than attack on GSM. Robertson et al. (1998) proposed that if this was the case that a similar kinetic isotope effect should be observed no matter what the substrate being treated. The similarities in the kinetic isotope effect for both GSM and MC-LR would suggest that formation of hydroxyl radicals generated via the superoxide radical anion produced at the conductance band is a rate determining step (Draper *et al.*, 1990).

4.4 CONCLUSIONS

The work conducted in this chapter confirms that TiO_2 photocatalysis using Hombikat K01/C achieves rapid degradation of GSM. Concentrations of GSM used in this study are considerably higher than those found in the environment, but even at the highest GSM concentration of 5 μg mL^{-1}, GSM was rapidly degraded. MC-LR was also found to be rapidly destroyed with Hombikat K01/C, with no MC-LR detectable after 40 minutes.

A number of experimental conditions were altered to investigate the effects on GSM degradation. Using Langmuir-Hinshelwood rate expressions it was found that the effect of initial concentration on GSM degradation is not pronounced. Test solutions with lower pH were found to increase the initial rate of GSM destruction and the addition of methanol to test solutions was observed to significantly retard the rate of GSM destruction. The effect of methanol on the rate of GSM destruction is interesting as it gives a useful indication of what the effect of additional reactants may be in more complex test solutions. The rate of GSM destruction was also found to increase with increased illumination of the catalyst. The reactor and catalyst configuration used was not found to be mass transport limited. Finally the kinetic isotope effect for Hombikat K01/C was determined using GSM and MC-LR, with the primary isotopes calculated as 1.61 and 1.56 respectively. The work conducted on the factors affecting photocatalysis of GSM in this chapter proved valuable for the development of the pilot photocatalytic flow reactor in Chapter 5.

CHAPTER 5 - PILOT PHOTOCATALYTIC FLOW REACTOR

5.1 INTRODUCTION

5.1.1 Photocatalytic reactors

Recent research into larger scale photocatalytic reactors has been carried out in reactors where the photocatalyst is immobilized on a suitable surface (Mills *et al.*, 1993; Dijkstra *et al.*, 2001; Li *et al.*, 2003; Lee *et al.*, 2004). The pollutant of interest is passed over the film in the presence of a UV source. These reactors have the advantage over dispersed or batch style systems utilizing a powdered photocatalyst as they do not require an expensive filtration or sedimentation step required to remove the photocatalyst after treatment (Chen *et al.*, 1988; Mills *et al.*, 1993).

Immobilised catalysts are not without their problems however with two issues predominant. For a given photoactivated volume an immobilized film will have a reduced number of activated sites when compared with the same weight of a freely suspended catalyst (Matthews, 1993). Additionally mass transfer limitation may become rate controlling at low flow rates (Turchi *et al.*, 1988). Most workers have not noticed an appreciable loss in the activity of TiO_2 when used for the photomineralisation of pollutants in water. Indeed, the Hombikat KO1/C catalyst used in this work was repeatedly used without reduction in GSM degradation rates. If semiconductor photocatalysis is to be used extensively as a method of water purification then significant extended wear tests need to be carried out. (Mills *et al.*, 1993). A study by Rao *et al.* (2004) investigated the extended wear of P-25 and PC500 TiO_2 photocatalysts immobilized on organic fibres, pumice and a polymer film. The degradation of a dye, acid orange 7, was used to study the ageing effect on the immobilized TiO_2. Long term use (4 weeks) of the immobilized TiO_2 to degrade the dye resulted in a large reduction in dye removal rates when compared to newly prepared catalyst, with irradiation time extended by up to 5 times to completely remove the dye. The study concluded that two major effects were responsible for the reduction in the rate of dye removal. Firstly the removal of TiO_2 from its support was observed

for all catalyst supports. Secondly fouling of the catalyst by degradation by-products over an extended period was a concern. It was concluded that degradation by-products were formed more rapidly than they could be destroyed, resulting in their accumulation on the catalyst surface. This subsequently caused a reduction in the efficiency of the catalyst to degrade the pollutant, or in this case dye. However, it was also reported that the performance of the immobilised catalyst, which had been used for 4 weeks, could be restored by 50 % by heating at 150 °C for 3 hours. Though the immobilisation supports for TiO_2 used in the Rao *et al.* (2004) study had their problems TiO_2 has been shown to strongly interact with glass (Matthews, 1993). It was suggested that this strong attraction was due to the electrostatic charge on the catalyst surface and the negatively charged surface of the glass.

Several factors limit the efficient design of a photocatalytic reactor; good contact between reactants and the catalysts; efficient exposure of the catalyst by light irradiation, as well as conventional reactor complications such as, flow patterns, mixing, mass transfer and reaction kinetics (Mukherjee *et al.*, 1999).

The development of a pilot photocatalytic flow reactor began with considering the design of the successful V.3 reactor (Figure 3-3, Chapter 3) and how the Hombikat K01/C catalyst could be deployment within a flow reactor. The V.3 reactor was a batch reactor and degradation results proved that the catalyst was not mass transfer limited when deployed in the reactor and also benefited from efficient illumination of light. To have effective destruction of GSM using a flow reactor sufficient contact time between the reactant (GSM) and the catalyst is required. Two main options exist to increase contact time, recirculation of the polluted water though the flow reactor and/or using a combination of reduced flow rate and increased catalyst. A flow reactor comprising a glass tube spiralled around a suitable light source, with Hombikat K01/C pellets deployed within the tube would achieve these required attributes. A similar flow reactor with TiO_2 coated on the inside of a glass tube has been reported (Matthews, 1988). With a design selected a pilot flow reactor was constructed and evaluated as part of this research to evaluate its effectiveness in degrading GSM.

5.1.2 Field testing photocatalytic flow reactor

Off-flavour is a major problem in the aquaculture industry (Schrader *et al.*, 2003). Much of the research is based on cat fish aquaculture in the southern USA (van der Ploeg *et al.*, 1992; King *et al.*, 2003; Zimba *et al.*, 2003; Schrader *et al.*, 2005b), but problems have been reported in European trout aquaculture (Robertson *et al.*, 2003; Robin *et al.*, 2006). Off-flavour in these cases is caused predominantly by cyanobacteria growing in the surface waters of ponds that are used to rear the fish. Less common is the use of indoor ponds to rear fish with a recirculatory system for providing water to the tanks. Off-flavour in these circumstances is believed to be caused by actinomycetes growing within the recirculatory system as there is little or no natural light to allow cyanobacteria to grow.

An opportunity arose to field test the flow reactor using water naturally contaminated with GSM. The source of the water was a Danish eel farm in central Jutland. Eels affected by off-flavour, by being in contact with water contaminated with GSM, has been an ongoing problem for Danish eel farmers for a number of years. The water used in the eel farm is sourced from ground water, which is then recirculated around the various rearing tanks. The eels are cultured in large indoor tanks over two stages, the first stage involves rearing immature glass eels (Figure 5-1), after which they are transferred to larger tanks to mature. This water quickly becomes contaminated with feed, chemicals added during production and waste generated by the eels. The water is treated on a regular basis, with a proportion replaced with fresh groundwater every week. Initial testing of water collected from three different stages of the recirculatory system detected significant concentrations of GSM (~19 ng L^{-1} mean) present. The GSM detected is likely to be caused by actinomycetes (Klausen, *et al.*, 2005) that are growing within the culturing tanks and related aquaculture apparatus. Water samples were collected in stainless steel containers to minimise GSM adsorption. This water was returned to the Royal Veterinary and Agricultural University laboratories in Copenhagen were it was used to evaluate the pilot photocatalytic flow reactor.

Figure 5-1. Eel farm Jutland, Denmark. First stage culturing tanks (top) containing immature glass eels (bottom).

5.2 METHODS

5.2.1 Construction of pilot photocatalytic flow reactor

Borosilcate glass tubing (diameter 10 mm) was selected that had the necessary dimensions to allow Hombikat K01/C pellets to be placed inside the tubing. This glass tubing was then fashioned into a coil approximately 1200 mm in length; external diameter 110 mm; internal diameter 70 mm; internal volume 1150 cm^3 (Vitrum Ltd., Aberdeen, UK). The internal diameter of the coil was sufficient to allow a UV strip lamp to be passed through the centre of the coil (Figure 5-2). Between the lamp and the coil was a borosilcate glass tube that was used to support the coil.
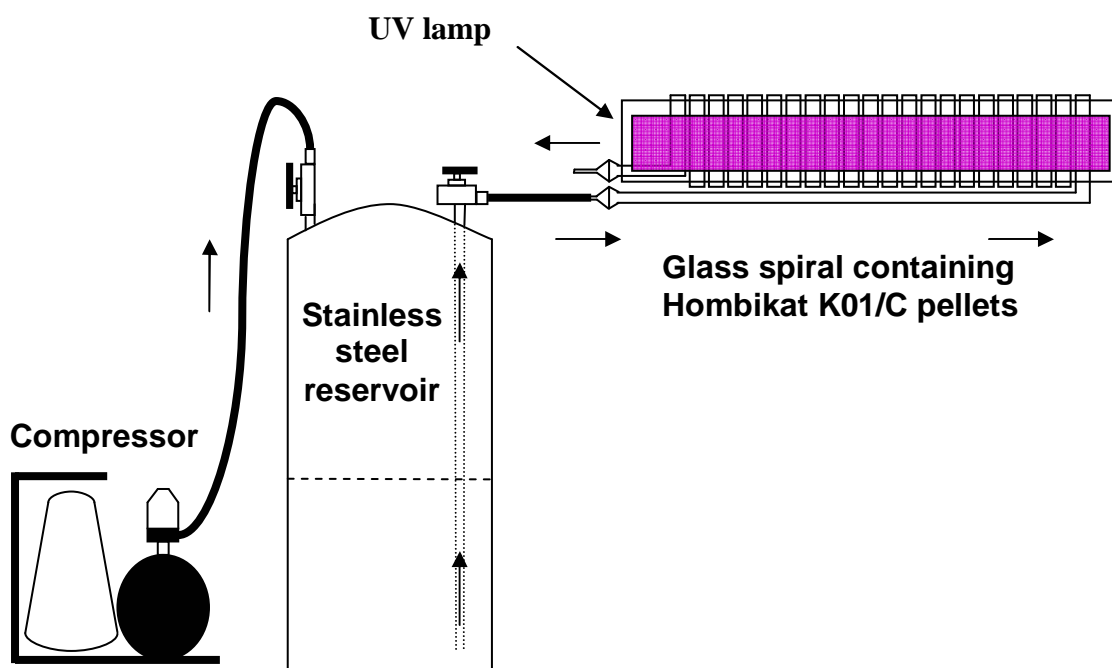
Figure 5-2 Pilot photocatalytic flow reactor. The compressor is used to pressurize the stainless steel reservoir containing the test solution. The valves on the reservoir are used to control the flow (indicated by the arrows) of the solution through the coil. The UV lamp is housed within the centre of the coil and is powered by control gear (not shown). Teflon tubing is used to connect the reservoir to the coil.

Hombikat K01/C pellets (1 kg) were washed with Milli-Q to remove any residual titanium dioxide powder from the manufacturing process. It had been observed previously that new pellets would sometimes split upon immersion in Milli-Q. These split pellets were removed and the pellets placed into a moderately hot oven (50 °C) for 24 hours to remove any residual water. The pellets were then graded to achieve more uniform pellet size. Firstly pellets of similar diameter (approximately 5 mm) were selected and then cut, if required, to produce sections approximately 5 - 7 mm in length. This pellet size was selected to minimise the chance of the glass coil being blocked when it was being filled with the catalyst. Using a combination of compressed air and water to move the pellets, the coil was filled with the catalyst. In total 842 g of Hombikat K01/C pellet was placed into the glass coil. The volume of the coil, with catalyst loaded, was 895 cm^3.

Both the inlet and the outlet of the coil were fitted with Quickfit fittings (Figure 5-3) that reduced the diameter of the coil tubing, by tapering to a smaller aperture. These fittings allowed tubing to be fitted as required and also served to act as a barrier to prevent the pellets from leaving the coil when under pressure. The reactor was completed by placement within a cylindrical plastic housing.

The light source selected for the reactor was a black light UV lamp (40 watt General Electric lamp, the Light Bulb Company, UK; spectral output 300 – 400 nm; Peak emission wavelength 368 nm. Additional information available in Appendix 2). The lamp (1220 mm in length) was passed through the centre of the glass tube supporting the coil. The lamp was aligned centrally within the glass tube with two Perspex discs 80 mm from each end of the lamp (Figure 5-3). The discs were machined to allow them to pass over the lamp and were the same internal diameter as the glass tube.

Figure 5-3. Completed photocatalytic flow reactor. (A) Compressor, reservoir and coil reactor within housing. (B) UV lamp in operation. (C) Inlet and outlet detail.

A 33 L stainless steel pressure vessel (Biotage, UK) was chosen as a reservoir for the test solutions (Figure 5-3). Selection of a stainless steel reservoir would ensure that non-specific adsorption of GSM would be minimised within the reservoir (Huck *et al.*, 1995). The reservoir was connected to the coil with Teflon tubing (Teflon FEP, Nalgene 890, Fisher, UK) which will again minimise loss of GSM (Elhadi *et al.*, 2004a). All valves that came into contact with a wettable surface were constructed from stainless steel (Swaglelok, UK). A compressor (Jun Air Model OF301, Jun Air, Denmark) was connected to the reservoir. This provided the source of compressed air to move the test solution from the reservoir and through the coil.

The absorbance of the glass used to construct the coil was tested using a Perkin-Elmer Lambda 950 UV/Vis spectrophotometer (Perkin-Elmer, UK). This established that the vessel had a very similar absorption profile (Appendix 1) as the glass vessel used in reactor V.3 (Chapter 3), absorbing light in the 260 – 320 nm region.

5.2.2 Photocatalytic destruction of GSM using coil reactor

An aqueous solution of geosmin (100 mL; ~1 μg mL^{-1}) was prepared. The reservoir was filled with 20 L of Milli-Q. The geosmin solution (3 mL) was then added to the reservoir. An additional 10 L of Milli-Q was added to the reservoir. Adding the Milli-Q in two stages ensured that the added GSM solution was mixed. The test solution concentration (100 ng L^{-1}) represents a GSM level that is comparable to that found in the environment. After filling the reservoir three 100 mL samples were taken from the reservoir (control) and the compressor switched on and set to 20 psi pressure. The valves on the reservoir were opened to allow the test solution to pass through the reactor. This continued until the coil was full of the test solution and all large air bubbles had been removed. The flow rate was then altered and maintained at a constant flow rate. The flow rates investigated were 50, 75, 100, and 200 mL min^{-1}. Upon adjustment of the flow rate four 100 mL samples were taken in succession from the outlet on the coil, this would provide the data on adsorption of GSM within

the reactor. The UV lamp was then activated and the solution allowed to flow through the coil until the 895 mL (capacity of the reactor with catalyst loaded) of solution had passed through. Four consecutive 100 mL samples were then taken with the lamp on. All samples were analysed by SPE-GC-MS (See section 2.2.4.4).

5.2.3 Photocatalytic destruction of GSM in spiked tap and raw waters

The procedure was carried out as in section 5.2.2 with two main alterations. Only 10 L of each water type under investigation was required, therefore 1 mL of GSM stock was added to each water to give the required GSM concentration (~100 ng L^{-1}).

The water samples were collected from two lochs and two rivers. Loch Rescobie and Forfar Loch, both located in Angus, Scotland, regularly support cyanobacterial blooms. Forfar loch represented a highly eutrophic water body. Water from the rivers, Carron and Cowie, Aberdeenshire, Scotland, represented water bodies with no previous exposure to cyanobacterial blooms as might be expected for relatively fast flowing waters. Despite the relative proximity of the rivers Cowie and Carron, their catchments and thus their chemistry are diverse. River Cowie passes through forested land and is high in humic compounds whereas the Carron passes through predominantly agricultural land. The tap water was sourced from a cold water tap within the laboratory.

The water was filtered prior to use with GF/C filter disks (110 mm, Whatman International Ltd., Maidstone, UK) to remove particulates. Also only two flow rates were evaluated, 50 and 75 mL min^{-1}. These flow rates were selected on the basis that they were most likely to show significant GSM degradation.

Samples were collected from the reservoir prior to the solution being pumped through the reactor, from the coil outlet after the solution had passed through the reactor (lamp off) and post photocatalysis. These were analysed using TOC (see section 4.2.4). The samples that were taken from the reservoir were also

analysed using a Helios Gamma UV-Vis Spectrophotometer (Thermo Scientific, UK). Their absorbance at 368 nm (the peak emission wavelength of the UV light) was recorded. The analysis was conducted to determine whether any of the waters used absorbed light in the 368 nm region, as this may affect photocatalysis of GSM.

The flow reactor was tested with each GSM spiked raw water at the 75 mL min^{-1} flow rate, with the black light UV lamp substituted for the xenon lamp used with reactor V.3 (Chapter 3), to determine if light intensity was a limiting factor in GSM degradation for this reactor design.

5.2.4 Photocatalytic destruction of GSM in raw water collected from Danish eel farm

The purpose of this procedure was to evaluate the ability of the coil flow reactor in degrading GSM occurring naturally in water. Water from an eel farm in Denmark was used that was known to contain a detectable concentration of GSM (~ 19 ng L^{-1}). The water collected would be passed through the coil multiple times to give an indication of the contact time required to degrade the GSM present completely. Method 5.2.2. was used with the following alterations:

The main consideration was that once the water had passed through the coil it was collected to be returned to the reservoir for the next treatment. Water from the eel farm (8 L) was added to the reservoir. Three 100 mL samples were taken (samples also taken for TOC and UV/Vis analysis) and the reservoir sealed and pressurised to 20 psi. The valve on the reservoir was opened and water allowed to fill the coil until all large air bubbles had been removed. The flow was then adjusted and maintained at 50 mL min^{-1}. Upon adjustment of the flow rate four 100 mL samples were taken in succession, this would provide information on adsorption of GSM within the reactor. The UV lamp was then activated and the solution allowed to flow through the coil until the 895 mL (capacity of the reactor with catalyst loaded) of solution had passed through.

From this point onwards the UV lamp was left on for the remainder of the experiment. Four consecutive 100 mL samples were then taken with the lamp on. The water flowing through the coil was collected in a large glass bottle until the reservoir was empty. The reservoir was then depressurized and refilled with the water which had passed through the reactor. The reservoir was then re-pressurized and the above process repeated with four 100 mL samples collected after each pass through the coil for a total of four passes (1 pass for GSM adsorption and 3 passes with the UV lamp on). Samples were not collected for GSM adsorption on subsequent passes. All samples were analysed by SPE-GC-MS (See section 2.2.4.4).

5.3 RESULTS AND DISCUSSION

5.3.2 Photocatalytic destruction of GSM using flow reactor

The flow reactor was found to degrade GSM across all the flow rates investigated (Figure 5-4). The general trend observed is that GSM degradation is related to the flow rate, as the flow rate was reduced the rate of GSM degradation was observed to increase. This is represented by the GSM remaining after exposure to UV and catalyst for the 50 and 200 mL min^{-1}, with 33 (± 3.1) % and 81 (± 13.0) % GSM remaining respectively.
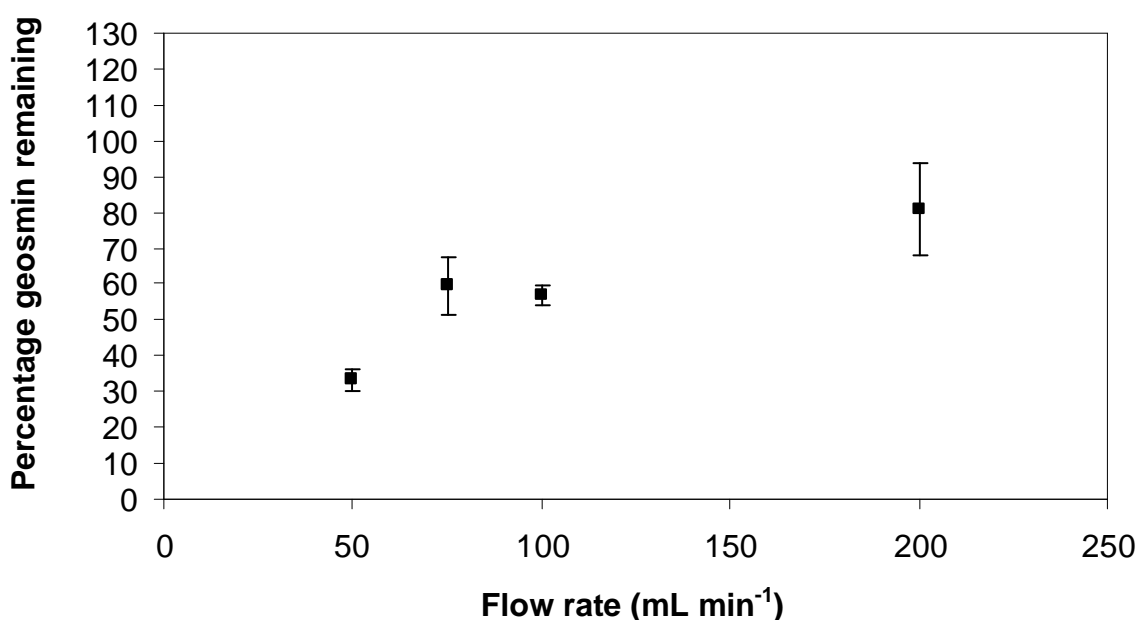
Figure 5-4. Destruction of GSM by Hombikat K01/C photocatalysis in flow reactor, at different flow rates. GSM loss monitored by GC-MS. Bars equivalent to one standard deviation (n=4).

The results confirm that GSM is degraded successfully in the flow reactor. Calculating the molar destruction rate of GSM reveals that the number of moles of GSM destroyed increased slightly at the 100 and 200 mL min^{-1} flow rates, 4.3 and 3.8 mol min^{-1} respectively, as apposed to 3.3 and 3.0 for the 75 and 100 mL min^{-1}. Previous work by Turchi *et al.* (1988) speculated that degradation in fixed film systems is limited to a thin water layer near the catalyst

surface. Therefore, the degradation rate would be controlled by the rate at which the pollutant passed over the catalytic film. The molar destruction rate appears to increase as flow rate increases.

The rate of GSM destruction is considerably lower than that observed using the V.3 batch reactor (Chapter 4). The GSM in Milli-Q degradation data for the flow reactor (50 mL min^{-1} flow rate), demonstrates that after 18 minutes of irradiation approximately 33 percent GSM remained. In comparison the V.3 batch reactor evaluated in Chapter 4 rendered the lowest GSM concentration investigated, 0.1 μg mL min^{-1}, undetectable after 15 minutes. This concentration of GSM is 1000 times higher than the concentration used to evaluate the flow reactor. Table 5-1 compares the catalyst loading and catalyst surface area for the two different reactors. The catalyst loading is slightly higher for the flow reactor, consequently so is the catalyst surface area. The catalyst surface area for the flow reactor is also increased as a result of a greater proportion of the total catalyst used being comprised of smaller pellets. Therefore, the difference in the performance of the two reactors in degrading GSM is not a result of the different catalyst loading. The catalyst surface area was determined by a colleague by nitrogen adsorption and was very similar to the surface are of P-25 (50 m^2 g^{-1}).

Reactor	Catalyst loading (% w/v)	Catalyst surface area (m^2 g^{-1})
Reactor V.3	75	49
Flow	94	49

Table 5-1. Comparison of Hombikat K01/C catalyst loading and catalyst surface areas for Reactor V.3 (Batch reactor) and flow reactor. Catalyst surface area determined by nitrogen adsorption

5.3.3 Photocatalytic destruction of tap and raw waters spiked with GSM using flow reactor

The presence of compounds within the raw waters evaluated, had a clear effect on GSM degradation (Figure 5-5). This is clearly demonstrated when comparing the degradation of GSM in Milli-Q with GSM degradation in the other waters evaluated, with the reduction most pronounced at the 50 mL min^{-1} flow rate. The effect of increasing the flow rate from 50 to 75 mL min^{-1} resulted in a 10 – 20 % decrease in the rate of GSM coversion for all raw waters (including tap water, excluding Milli-Q). The magnitude of the reduction in the rate of GSM conversion between the flow rates was not as high as that observed for the degradation of GSM in Milli-Q at 50 to 75 mL min^{-1} (44%). Substitution of the irradiation source, from the UV tube lamp to the Xenon lamp, did not result in an increase in photocatalytic degradation of GSM (Figure 5.6). The GSM degradation rate when the xenon lamp was used (75 mL min^{-1} flow rate) was slower in all waters when compared to the GSM degradation using the black light UV lamp (75 mL min^{-1} flow rate), with a 10-23 % reduction in GSM degradation observed.

Carbon analysis conducted (Figure 5-7) highlighted the significant difference in the total organic carbon (TOC) and inorganic carbon (IC) for the different waters. The negative TOC value obtained for tap water is due an instrumental error. This was caused by the method used to calculate TOC (TC-IC). If a sample has significantly higher IC content than TOC content this can result in a negative result for TOC detection as detection accuracy decreases with increasing IC concentration. As expected the TC, TOC, and IC levels found in the raw waters were considerably higher than the levels found in Milli-Q and tap water.
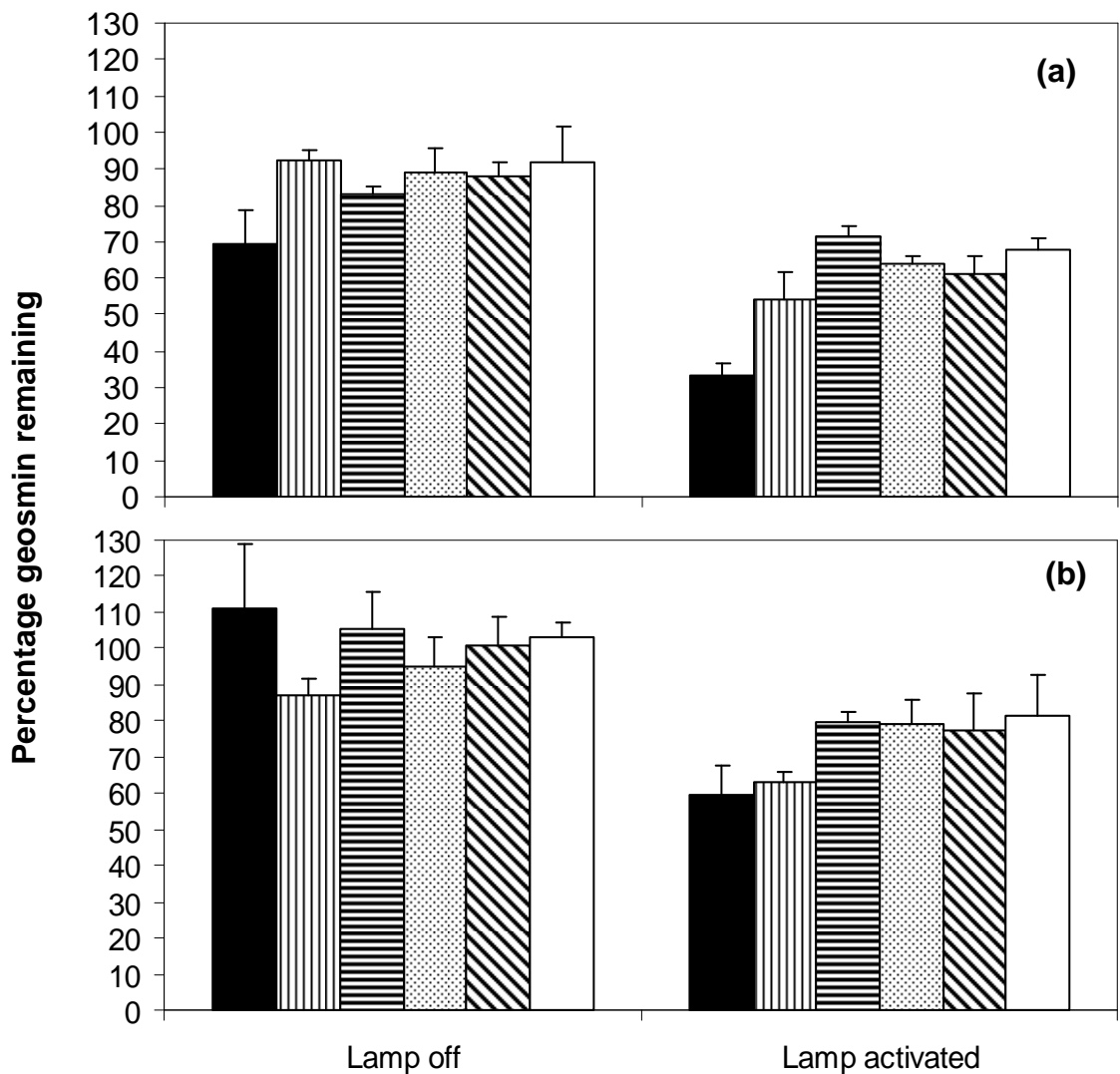
Figure 5-5. Destruction of GSM by Hombikat K01/C in flow reactor, with UV lamp off and lamp activated, at (a) 50 mL min^{-1} (b) 75 mL min^{-1}. Milli-Q (■); Tap (▥); Cowie (▤);Rescobie (▨); Carron (▨); and Forfar (□). GSM loss monitored by GC-MS.Bars equivalent to one standard deviation (n=4).
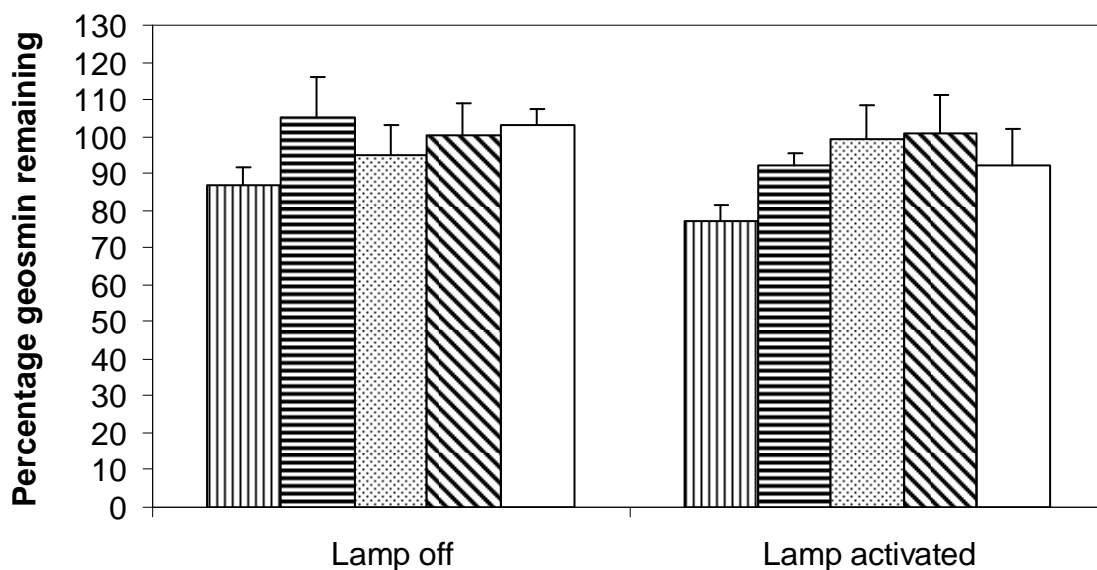
Figure 5-6. Destruction of GSM by Hombikat K01/C in flow reactor, with xenon lamp off and lamp activated, at 75 mL min^{-1}. Tap (▥); Cowie (▤); Rescobie (▨); Carron (◩); and Forfar (□). GSM loss monitored by GC-MS. Bars equivalent to one standard deviation (n=4).

The waters were analysed to determine whether they absorbed light at 368 nm, the peak emission wavelength of the UV light (Figure 5-8). This would give an indication as to whether any of the waters contained compounds that would absorb light that could be utilized by the catalyst. As expected the Milli-Q did not absorb light at 368 nm, Rescobie, Forfar and Tap water did (~0.025), but most noticeable was the absorbance of River Carron (0.138) and River Cowie (0.421) water.

The presence of additional organic and inorganic compounds in the test solution during photocatalysis was found to have a significant effect on the degradation rate of GSM. Photocatalysis is non-selective in its oxidation so it is likely that these compounds present are acting as direct competitors with GSM for binding sites on the catalyst and/or acting as competing reactants in solution. This had the effect of lowering the rate of GSM destruction.
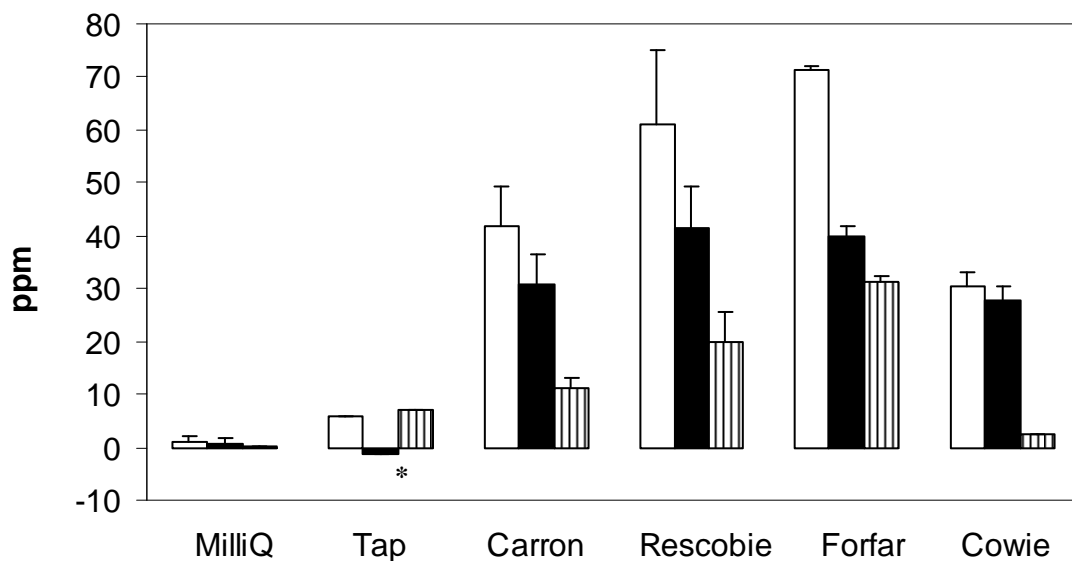
Figure 5-7. Carbon analysis of waters, prior to photocatalysis; total carbon (□); total organic carbon (■); inorganic carbon (▦). The TOC value (*)for tap water is an experimental error. Bars equivalent to one standard deviation (n=2).
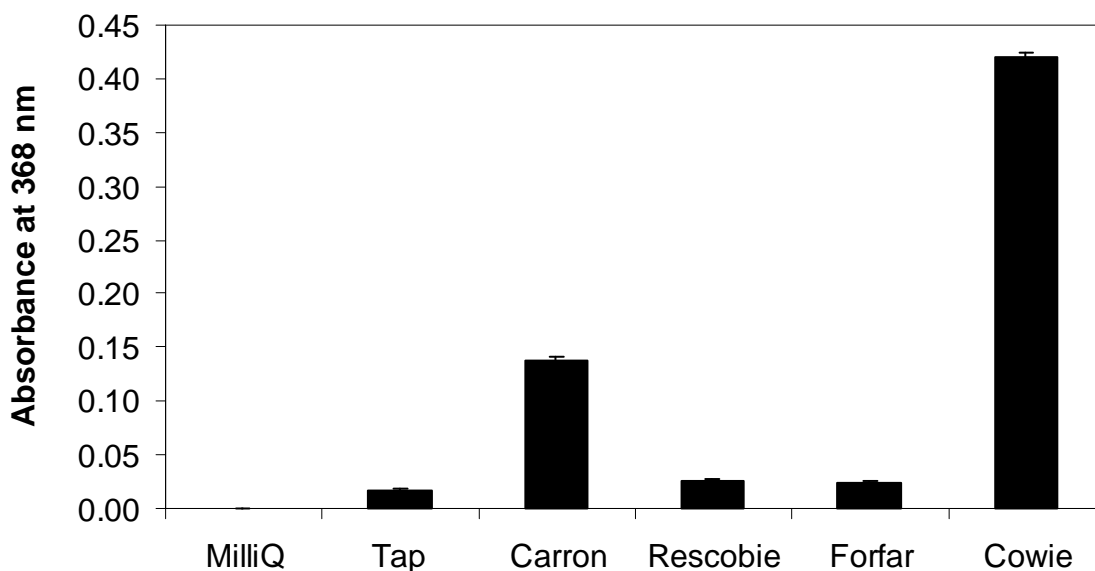
Figure 5-8. Absorbance (368 nm) of waters prior to photocatalysis. Bars equivalent to one standard deviation (n=2).

Photocatalysis of GSM (50 mL^{-1} min flow rate) in Milli-Q, a water with minimal TOC and IC and no absorbance at 368 nm, resulted in 33 % GSM remaining

after one treatment (~18 minutes). Conducting photocatalysis of GSM in tap water reduced the rate of GSM degradation significantly, with 54 % GSM remaining at the 50 mL^{-1} min flow rate. The tap water used had very low TC (~6 ppm) and IC was a very large proportion of the carbon detected. An increase in TOC, by the addition of methanol as a competing reactant, has been shown to effect photocatalysis of GSM, but it did not produce a reduction in the rate of GSM degradation until the TOC concentration was above 14 ppm (Chapter 4). Therefore it is likely that the IC, or perhaps some other constituents of the water that have not been determined, is causing the reduction in the rate of GSM destruction. One of the possible constituents affecting the rate of GSM destruction may be nitrate (NO_3^-). In the UK it is a regulatory requirement for nitrate in drinking water to be below 50 mg L^{-1}, though the tap water is unlikely to have a concentration as high as this it may contain a level high enough to affect photocatalysis. There are conflicting reports in the literature as to whether nitrate retards photocatalysis. Abdullah *et al.* (1990) reports that nitrate has little effect on photocatalysis, but Mills *et al.* (1993) and Chen *et al.* (1997) both reported that nitrate can significantly reduce the rate of substrate destruction. Chen *et al.* (1997) reported on the inhibitory effect of a number of inorganic ions on the photocatalysis of dichloroethane (DCE). Nitrate was found to have a significant effect on the adsorption and rate of destruction of DCE by TiO_2, reducing the rate of DCE destruction by 20 %. Mills *et al.* (1993) also reported that nitrate, albeit at a greater concentration (24.8 g L^{-1}), reduced the rate of TiO_2 photocatalysis, with the rate of 4-chlorophenol degradation reduced by 50 %. It was concluded that the reduction in degradation was caused not by blocking of oxidation sites on the TiO_2, but by UV screening of the catalyst particles. The reduction in the rate of photomineralization of GSM in tap water may be in part a result of UV screening (absorbance at 368 nm was 0.017). The concentration of nitrate (31 mg L^{-1}) used by Chen et al. (1997) is at a level that is possible in tap water. Therefore a proportion of the 38 % reduction observed in the destruction of GSM in tap water when compared to Milli-Q, may be caused by the combination of the presence of nitrate and UV screening. This is complicated by the fact that nitrate, if the cause of the reduction rate of GSM degradation, can also at as an accelerator for photocatalysis by absorbing UV light and forming hydroxyl radicals (Chen *et al.*, 1997b).

The effect of retardation on the rate of GSM destruction in the four raw waters was significantly greater than that observed for tap water. As retardation on GSM destruction had been observed in tap water it was to be expected that the effect would be greater in the raw waters. As the raw waters had been untreated, apart from filtering, they contained a far greater concentration of organic and inorganic matter when compared to the tap water. This resulted in increased concentrations of competitive adsorbents/reactants in the subsequent test solutions prepared using these raw waters. This difference is highlighted by the carbon analysis of the different waters (Figure 5-7). Additional water chemistry information can be found in Table 5-2 for the four raw waters.

	NH_4^+ ($\mu g\ mL^{-1}$)	NO_3^- ($\mu g\ mL^{-1}$)	NO_2^- ($\mu g\ mL^{-1}$)	PO_4^{3-} ($\mu g\ mL^{-1}$)	DOC ($\mu g\ mL^{-1}$)
Carron	0.03	6.47	0.007	0.05	5.94
Rescobie	0.11	8.08	0.041	0.14	7.01
Forfar	0.57	2.43	0.056	0.36	4.00
Cowie	0.03	1.88	0.001	0.01	12.40

Table 5-2. Additional water chemistry information for four raw waters including, ammonium, nitrate, nitrite, phosphate and dissolved organic carbon (DOC) concentrations. Analysis conducted by the Macaulay Institute.

Abdullah *et al.* (1990) reported on the effect of anions on the photomineralization of organic pollutants (salicyclic acid, aniline, and ethanol) by TiO_2. Perchlorates and nitrates were found to have very little effect, but sulfates or phosphates even at millimolar concentrations were rapidly adsorbed by the catalyst and reduced the rates of oxidation by 20-70 %. Chen *et al.* (1997) also reported the inhibitory effect of inorganic ions on the P-25 TiO_2 degradation of dichloroethane. The ions were found to effect adsorption in the order $Cl^- < NO_3^- < [HCO_3^-, CO_3^{2-}] < SO_4^{2-} < [H_2PO_4^-, HPO_4^{2-}]$ and the overall rate of photodegradation in the order $NO_3^- < Cl^- < HCO_3^- < CO_3^{2-} < SO_4^{2-} < H_2PO_4^- < HPO_4^{2-}$. The pH of all test solutions was pH 6, apart from those which contained carbonate (pH 10) and phosphate (pH 8). The effect of inhibition on

the photocatalytic degradation of DCE was approximately half that on the adsorption of DCE. The strong UV screening effect of nitrate observed by Mills *et al.*, (1993), that may have had an effect on the rate of GSM degradation in tap water may also have an effect on GSM degradation in the raw waters.

The reduction in GSM degradation observed in the raw waters is likely caused by a combination of factors including, nitrate and phosphate concentration, total carbon and light absorbance at 368 nm. These factors and their effect on the rate of GSM degradation can be seen in Figure 5.9.
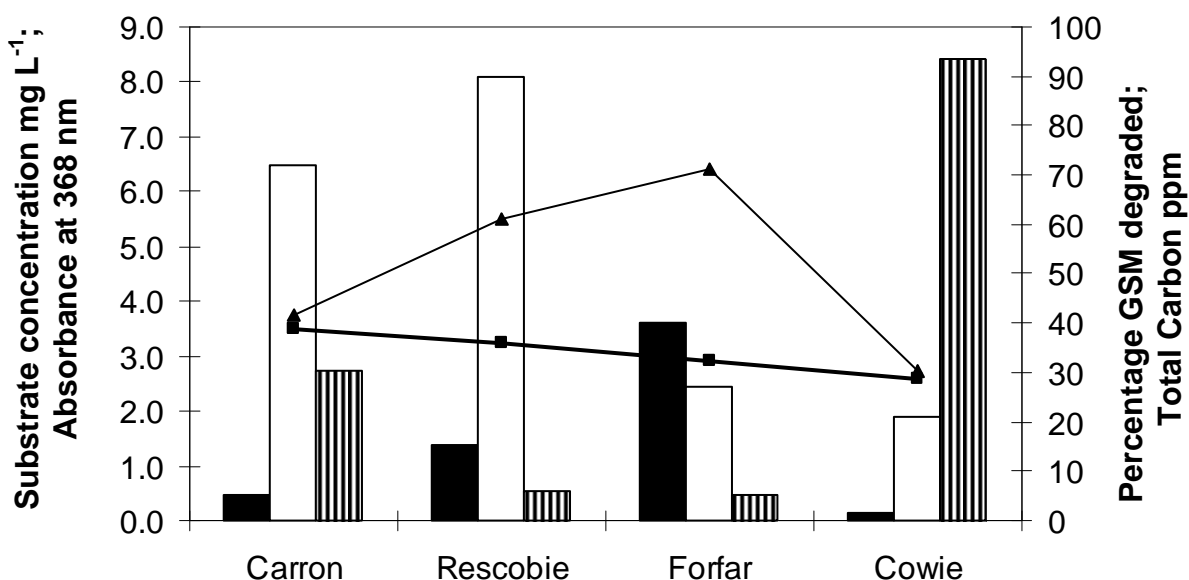
Figure 5-9. The effect of nitrate (□), phosphate (■), light absorbance at 368 nm (▦) and total carbon (—▲—) on TiO₂ photocatalysis of GSM (—■—). A multiplication factor of 10 and 20 has been applied to phosphate and light absorbance respectively.

For the Carron, Rescobie and Forfar raw waters it appears there is correlation of the photocatalytic rate with total carbon (TC) concentrate, with the increasing TC causing a retardation of the photocatalysis of GSM. Nitrate, especially for the concentrations observed in the Carron and Rescobie raw waters, may be causing either the blocking of oxidation sites or UV screening. The concentration of phosphate found in the raw waters, even at the highest concentration (0.36 mg L⁻¹ for Forfar raw water), is not likely to effect the rate of

GSM degradation. Abdullah *et al.* (1990) and Chen *et al.* (1997) did report that phosphate can reduce the rate of substrate degradation during TiO_2 photocatalysis, for the same reasons as nitrate, however the phosphate concentrations used where in the range of 48 – 100 mg L^{-1}.

While high TC and nitrate may account for the retardation of GSM photomineralization in Rescobie and Forfar waters, it does not fully account for Carron and Cowie raw waters. Both these waters were peaty/yellow in colour, indicating the likely presence of humic compounds and had greatly increased absorbance values of 0.138 (Carron) and 0.421 (Cowie) at 368 nm. This is unsurprising as both waters were collected from rivers during late autumn, at which time the rivers experience significant leaf fall along their lengths. The absorbance values obtained for both Carron and Cowie raw waters clearly demonstrate that compounds within the waters are absorbing UV light from the lamp used. This results in screening of the catalyst and stops the light from reaching the catalyst. GSM degradation in both waters is also likely to be effected by the presence of increased concentrations of competitive adsorbents/ reactants, reflected by their respective TC values. However as the TC values for Carron and Cowie are significantly lower than those for the Rescobie and Forfar waters, the effect of UV screening must be considerable. Epling *et al.* (2002) also found, in an extensive study, that humic substances could retard the rate of TiO_2 photocatalysis of a number of dyes. He found that with increasing concentration of humic acids the rate of dye degradation decreased, at the highest concentration of 1000 mg L^{-1}, the degradation rate of methylene blue was reduced by 90 %. It was also reported that the high initial retardation of natural humic substances may be attributed to competition between the more degradable portion of dissolved organic matter (DOM) in the reaction mixture and the less degradable dye. This effect is likely to be partly responsible for the reduced degradation of GSM in Cowie water as the Cowie raw water had the highest dissolve organic carbon (12.4 mg L^{-1}) (Table 5-2). Epling *et al.* (2002) concluded that the presence of humic acid in a reaction mixture could significantly reduce light transmittal and therefore photooxidation rate. Additionally it was suggested that humic acid may also compete with organic dyes for active sites on the TiO_2 surface, and because of their highly oxidized

nature, be more resistant to oxidation than organic dyes, resulting in a longer adsorption to the catalyst surface. A recent study by Lin *et al.* (2007) also found that humic substances caused the retardation of TiO_2 photocatalysis. The rate of 4-chlorophenol degradation was slowed by 12 times in the presence of 50 mg L^{-1} of humic acid. This study concluded that humic acid caused catalyst inhibition (surface deactivation), competition and light attenuation.

A noticeable colour change was observed in Carron and Cowie water post photocatalysis, probably caused by the break down of some of the humic compounds. Other workers have also demonstrated TiO_2 photocatalysis of humic substances (Eggins *et al.*, 1997; Bekbolet *et al.*, 2002; Wiszniowski *et al.*, 2002).

The retardation of substrate degradation by humic acids is not a problem unique to photocatalysis. Ozone and O_3/UV oxidation processes are also considerably affected by the presence of humic acids. The degradation of nitrobenzene by O_3 was significantly retarded (treatment time doubled) by humic acids through radical scavenging and promotion of radical reaction by hydrogen peroxide formation (Latifoglu *et al.*, 2003). Humic acid caused treatment time to be tripled when O_3/UV was used. The effect of humic acids in the O_3/UV system was found to be inhibitive, the inhibition caused by radical scavenging and UV light screening. The occurrence of other natural organic matter (NOM) has been reported to reduce ozonation of GSM and MIB (Sagehashi *et al.*, 2005).

A study by Shon *et al.*, (2005) investigated P-25 TiO_2 photocatalysis coupled with ferric chloride flocculation and PAC adsorption for the treatment of a synthetic wastewater. The synthetic wastewater contained effluent organic matter and NOM. TiO_2 photocatalysis of the wastewater was found to increase organic concentration of the wastewater by breaking larger molecular weight compounds into smaller weight compounds. Pre-treatment of the wastewater by PAC prior to TiO_2 photocatalysis did not alleviate this problem as it did not adsorb the higher molecular weight compounds. However, simultaneous treatment with PAC and TiO_2 photocatalysis was found to remove the problem and increased the rate of organic matter degradation, the PAC likely adsorbing

the smaller molecular weight compounds generated by TiO_2 photocatalysis. Finally, pre-flocculation of the waste water improved the rate of organic matter destruction further. This would be expected as flocculation would remove significant proportions of organic matter present in the wastewater, increasing the efficiency of the TiO_2 photocatalytic treatment.

The presence of NOM also effects water treatment technologies such as activated carbon in removing GSM and MIB. As in TiO_2 photocatalysis, the NOM competes with the GSM and MIB for adsorption sites resulting in a lowered efficiency for removal of GSM and MIB by activated carbon. This has been demonstrated by a number of workers (Graham *et al.*, 2000; Newcombe *et al.*, 2002; Ho *et al.*, 2005).

The use of a xenon lamp instead of the black light UV lamp did not increase the rate of degradation of GSM (Figure 5.6) despite having an output 10 times higher, 400 W compared to 40 W. The glass that the coil was constructed from had an almost identical composition when compared to the glass vessel used for reactor V.3. in Chapter 4 (Appendix 1), so could not be screening any additional light from the xenon lamp. In Chapter 4 GSM degradation was found to have an initial linear relationship with light intensity, moving into a possible square root relationship. It would therefore be expected that the rate of GSM degradation would have increased with the use of the xenon lamp. The black light UV lamp lights the coil more efficiently as it extends the length of the coil and as it is housed inside the coil is likely to illuminate more of the catalyst. However, though the xenon lamp may not illuminate the coil as efficiently, in Chapter 4, at distance of 60 cm (199 μmol s^{-1}m^{-2}), a ~1 μg mL^{-1} GSM solution had 80 % GSM removal after 15 minutes. Mills et al. (1993) reports that the use of black-light UV lamps (365 nm maximum emission) coupled with a borosilicate glass irradiation vessel is a good combination for the destruction of pollutants that do not significantly absorb in the 300 – 400 nm wavelength region. It appears that the rate of GSM degradation is not limited by Hombikat K01/C illumination for this flow reactor.

5.3.4 Photocatalytic destruction of GSM in raw water collected from Danish eel farm

GSM present in water collected from an eel farm was degraded by photocatalysis (Figure 5.10), with 36 % GSM remaining after three passes (approximately 60 minutes exposure to illuminated catalyst). After one pass (20 minutes exposure) 33 % GSM was degraded, comparable to the degradation rate observed for GSM spiked into the other water types (Figure 5.5). The concentration of GSM in the eel farm water prior to photocatalysis was 7.2 ng L^{-1}, considerably lower than the concentration used when spiking the raw waters (~100 ng L^{-1}). Carbon analysis of the eel farm water prior to photocatalysis gave the following results (ppm); TC 24.40 (±0.74); TOC 10.36 (±2.47); IC 14.04 (±1.74). Absorbance at 368 nm was 0.115, comparable to that of Carron river water.

Photocatalysis of naturally occurring GSM in eel farm water was successful, and represented the first time that the flow reactor was used to treat water with naturally occurring taint. It also represented the first time that a solution was treated with multiple passes through the reactor, allowing increased treatment time. Analysis of the GSM in the eel water also provided a robust assessment of the analytical procedure developed in Chapter 2 as the GSM concentration was very low (7.2 ng L^{-1}). GSM degradation after one pass through the reactor (approximately 20 minutes of contact time) was 33 %. Although the GSM concentration in the other spiked raw waters was much higher (~100 ng L^{-1}), the rate of degradation was comparable with that of GSM in Forfar water (32 %). However, from the data available (additional water chemistry data was not available) the eel farm water would appear to be most like the Carron raw water. Though the TC for the eel farm water was lower, 24 ppm as opposed to 42 ppm for Carron raw water, the IC was similar 14 ppm compared to 11 ppm and the absorbance was similar 0.115 and 0.138 for eel farm and Carron water respectively. Though these waters are more similar the GSM degradation rate was slightly higher for Carron 38 %. It is likely that the rate of GSM degradation in eel farm water is effected by the same factors found for the four other raw

waters, namely the effects of UV screening and the competitive effect of adsorbents/ reactants within the reactant solutions.

The curve is labeled with the equation $y = 97.866e^{-0.0172x}$ and $R^2 = 0.9971$. The y-axis is "Percentage geosmin remaining" and the x-axis is "Time (minutes)".
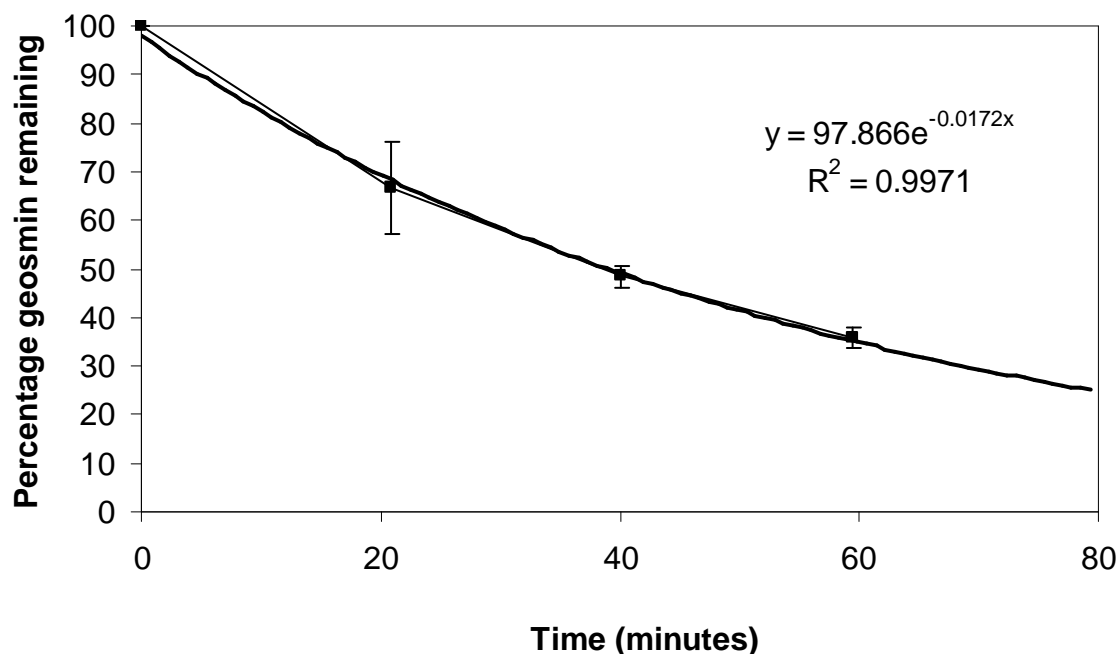
Figure 5.10: Destruction of naturally occurring GSM in eel farm water by Hombikat K01/C photocatalysis. GSM loss monitored over 60 minutes by GC-MS. Bars equivalent to one standard deviation (n=4).

The eel farm water was treated by passing it through the reactor three times to increase treatment time and to determine the length of time to reduce GSM to a suitable level. The degradation of the GSM on subsequent passes through the reactor is reduced. After passes one, two and three, the proportion of GSM destroyed is 33, 52, and 64 % respectively (Figure 5-10). This appears to be an exponential trend (R^2 = 0.9971), with the rate of GSM destruction reducing (Figure 5-10) with each subsequent pass through the flow reactor, actual GSM degraded in pass one, two, three was 33, 21, and 13 % respectively. This data suggest that degradation of GSM in eel farm water follows pseudo-first order kinetics.

5.4 CONCLUSIONS

The work in this chapter has demonstrated the efficacy of the pilot photocatalytic flow reactor, containing Hombikat K01/C, in destroying GSM in Milli-Q and raw water. The reactor was also shown to destroy naturally occurring GSM, which was present in water collected from a Danish eel farm.

The complexity of the raw waters, due to the varied concentration and type of species present, made it very difficult to elucidate which factors were having an effect on the rate of GSM degradation. No obvious trends where discovered, but the overall effect of the raw waters was to reduce the rate of GSM degradation. The likely cause of the reduction of the rate of GSM degradation is the combined effects of an increased number of adsorbents, the increase in degradation by-products and the effect of UV screening by humic compounds and nitrate. Light intensity and mass transfer were not found to be rate limiting for the Hombikat K01/C, when deployed in the flow reactor. The molar destruction of GSM was slightly higher at increased flow rates.

Howgate (2004) suggests that a reasonable estimate of odour detection threshold for GSM in water would be 15 ng L^{-1}. As the average degradation of GSM in the four waters, after one pass. is similar to the degradation of GSM in eel water, 34 % compared to 33 % , it is likely that the same degradation rate after multiple treatments will be followed. Raw water containing 100 ng L^{-1} of GSM would represent a relatively high GSM concentration for potable water treatment. The 50 mL min^{-1} flow rate was found to give optimal performance and at this flow rate a raw water containing 100 ng L^{-1} of GSM would require approximately 110 minutes of Hombikat K01/C TiO_2 treatment to degrade the GSM present below the 15 ng L^{-1} odour detection limit. At this flow rate and treatment time that would equate to an output of 1.6 L hr^{-1}, or 38.4 L in 1 day. Clearly at this flow rate rapidly treating large volumes of contaminated water is not viable with a reactor of this size.

If TiO$_2$ photocatalysis is to be used as a method of water purification the significant draw backs of TiO$_2$ screening, by abundant natural substances such as humic acid, and competitive adsorption/oxidation, caused by species present in the water to be treated, must be resolved. Three approaches could be taken to improve the performance of the flow reactor evaluated in this Chapter, which also apply to TiO$_2$ photocatalysis as a method of water purification. Firstly, treatment time could be increased. This was the major factor in improving GSM degradation within the flow reactor, but this subsequently reduced the flow rate. Therefore, to increase overall treatment time without reducing flow rate, the reactor could be scaled up to a larger size, or a number of smaller units joined together. Secondly pre-treatment, such as coagulation and sedimentation, of the raw water to remove the majority of NOM and inorganic substances, prior to TiO$_2$ photocatalysis, would reduce catalyst inhibition and UV screening. This would result in increased GSM degradation. This has been demonstrated by Shon *et al.*, (2005), with treatment by PAC and coagulation improving the performance of the TiO$_2$ photocatalysis of a synthetic wastewater. The second point is important in comparing TiO$_2$ photocatalysis to other advanced water treatment processes such as activated carbon, membrane processes and ozone. Finally the back-face illumination could be used to reduce the distance between the illumination source and the catalyst, allowing more efficient illumination of the catalyst and limiting the effect of catalyst screening.

These advanced processes are usually applied after primary (coagulation, flocculation and sedimentation) and secondary (filtration) water treatment (Figure 1.7), where the majority of NOM and inorganic matter has been removed. TiO$_2$ photocatalysis treatment conducted on raw water containing GSM, that has undergone primary and secondary water treatment, would see an improvement on GSM degradation rates when compared to GSM degradation in the four raw waters evaluated in this chapter. Therefore, a combination of reactor scale up and judicious placement of TiO$_2$ photocatalytic treatment within the water treatment process, i.e. after primary and secondary water treatment, would give the best performance for GSM degradation using this reactor configuration.

The benefits of this reactor is that it uses a black light UV lamp (40 watt General Electric lamp, the Light Bulb Company, UK; spectral output 300 – 400 nm; Peak emission wavelength 368 nm), which when compared to a higher output lamp is cheaper to run. This is important as a large proportion of costs incurred by the water industry for water treatment is from power consumption. Additionally the flow reactor was made out of glass to minimise GSM adsorption, however future designs could be constructed of cheaper material such as Perspex.

CHAPTER 6 - CONCLUSIONS

6.1 INTRODUCTION

The problems of off-flavour caused by GSM and MIB are well documented and as standard water treatment is inefficient in removing them from potable water, alternative treatment technologies are required.

The aim of thesis was therefore to investigate as an alternative advanced treatment technology for the removal of GSM and MIB from water, TiO_2 photocatalysis. The novel approach adopted in this work was the use of a new TiO_2 catalyst, Hombikat K01/C, a pelleted form of TiO_2, which is substantially different from typical powdered TiO_2 catalysts, such as P-25. The pelleted form of the catalyst removes the need for a filtration step to remove the catalyst from treated water, as would be the case with using a P-25 suspension.

The findings of this thesis can be divided into 3 sections which address the aims outlined in section 1.10:

Those that address the development and optimisation of a rapid analytical method for the separation and detection of GSM and MIB in aqueos samples.

- Development of a rapid analytical technique, using SPE and GC-MS, to allow trace analysis of large numbers of samples.

- Evaluation of GC-MS instrument for the analysis of GSM and MIB.

Those that investigated the design and optimisation of a bench scale batch reactor to degrade GSM and MIB.

- Design of a bench scale reactor to evaluate Hombikat K01/C in degrading GSM and MIB.

- Optimisation of bench scale reactor to minimise the large system losses encountered when investigating the photocatalysis of GSM.

- Investigation of the factors effecting the photocatalytic destruction of GSM, including initial substrate concentration, pH, light intensity, aeration rate and catalysis conducted in deuterated water.

Those that investigated the ability of a pilot flow reactor to degrade GSM in raw water.

- Development of a pilot photocatalytic flow reactor to evaluate Hombikat K01/C in degrading GSM in raw waters

6.2 DEVELOPMENT AND OPTIMISATION OF A RAPID ANALYTICAL METHOD FOR GSM AND MIB DETECTION

Evaluation of SPE for the separation of GSM and MIB from aqueous samples found that C8 cartridges offered the best compromise between recovery and reproducibility. The ability of SPE to act as a trace enrichment and separation step, effectively concentrating GSM from large volumes of water, was also demonstrated. This allowed the evaluation of environmental concentrations of GSM in this study. Subsequent analysis of the isolated GSM and MIB by the developed GC-MS analytical method was successful, with the Agilent GC-MS attaining significantly better limits of detection than the Clarus GC-MS. The combination of parallel processing of aqueous samples containing GSM and MIB by SPE, and subsequent analysis of the samples by GC-MS (with autosampler) allowed large numbers of samples to be processed rapidly. The development of this analytical method was central to this work, as alternative methods of analysis would not allow such a large number of samples to be processed, making this work conducted here unviable.

The GSM and MIB used in this study were prepared in methanol to eliminate the problem of microbial degradation, allowing long term storage of the prepared solutions. However, for the majority of experiments conducted the methanol had to be removed, due to its effect as an additional oxidant during photocatalysis of test solutions. The removal of methanol from the GSM solutions prepared in methanol was achieved by evaporation under nitrogen. Subsequent re-suspension of the GSM in water resulted in test solutions required for this work. Regrettably, this method did not work when applied to MIB-methanol solutions, with the reasons for this not established. The consequence of this was that the study focussed on investigation of the photocatalysis of GSM.

6.3 THE DESIGN AND OPTIMISATION OF A BENCH SCALE BATCH REACTOR TO DEGRADE GSM AND MIB

A bench scale batch reactor was developed to evaluate the Hombikat K01/C TiO_2 photocatalysis of GSM. Three versions of the reactor were evaluated, with each subsequent reactor improving on the last. It became apparent that non-specific adsorption of GSM to certain wettable surfaces within the reactor was a significant issue with the early reactor versions. This non-specific adsorption of GSM within the reactor under control conditions was unacceptable. The problem was traced to the use of peristaltic tubing, which accounted for the majority of GSM system losses. The final reactor design (V.3) was re-designed to dispense with the need for a peristaltic pump, and hence peristlatic tubing. This resulted in greatly reducing system losses of GSM under control conditions. This study clearly demonstrated the challenges of working with a compound such as GSM and calls into question the accuracy of other studies involving the removal/destruction of GSM that do not report on possible system losses.

The improvement in reducing system losses allowed the Hombikat K01/C TiO_2 photocatalysis of GSM to be clearly observed, with GSM being rapidly degraded. A number of experimental variables were altered to observe the

effect on GSM degradation within the batch reactor. The initial concentration of GSM was found to have little effect on the rate of GSM destruction, according to Langmuir-Hinshelwood rate expressions. Low pH of the test solutions during the photocatalysis of GSM was found to increase the initial rate of GSM. The presence of methanol during the photocatalysis of GSM caused the retardation of the rate of GSM destruction. This gave an interesting initial insight into the effect of additional reactants within the photocatalytic system. Increased light intensity was also observed to increase the rate of GSM degradation. A kinetic isotope effect was observed for the degradation of GSM using the Hombikat K01/C catalyst, this effect was corroborated by a similar isotope effect of microcystin-LR. The reactor and catalyst configuration used was not found to be mass transport limited.

6.4 INVESTIGATION OF THE ABILITY OF A PILOT FLOW REACTOR TO DEGRADE GSM IN RAW WATER

The Hombikat K01/C TiO_2 photocatalytic degradation of GSM was observed using the flow reactor. The rate of GSM degradation in Milli-Q solutions was comparable to that observed when using the batch reactor, albeit at a slightly reduced rate. However, the GSM degradation rate reduced significantly when GSM was present in raw waters. This effect was observed in four raw waters spiked with GSM and one raw water from an eel farm in Denmark that naturally contained GSM. Although difficult to elucidate the exact reasons for this decrease in GSM degradation, the major contributors are likely to be the presence of additional adsorbents within the test solution and the effect of UV shielding of the catalyst.

In conclusion Hombikat K01/C TiO_2 photocatalysis has been demonstrated to be a promising treatment method for the removal of GSM from potable waters. However, further research is required to optimise the performance of scaled up photocatalytic reactors. This requires additional work to be conducted on the effects of raw water on the photocatalytic degradation of GSM, which applies to photocatalysis as a whole in regards to water treatment. Investigation of the

affects of additional constituents present in raw water, such as anions, on the rate of photocatlysis is necessary. In particular the long term usage of the catalyst should be observed for alterations in performance and catalyst integrity. Results for the degradation of GSM in the water collected from the eel farm suggested that the rate of GSM destruction decreased with each subsequent treatment in the reactor. This is likely to be caused by a number of factors. The accumulation of degradation by-products on the catalyst surface and/or the poisoning of the catalyst by constituents of the water are a possibility. Additionally there may not have been sufficient oxygen present in the reactor, resulting in a decrease in the rate of photocatalysis. All these factors require further investigation and would suggest that a cleaning step would be necessary after continued use of the catalyst to limit decrease in catalyst performance.

6.5 FURTHER WORK

A pilot plant consisting of several of the reactors evaluated in Chapter 5 would obviously decrease treatment time and allow larger volumes to be treated. The plant would have to be designed to allow the introduction of clean water, and possibly additional cleaning agents, so the catalyst could be cleaned when significant performance reduction was observed. A pilot plant would also be necessary to determine the affects of long term usage on the integrity of the catalyst. Increased flow rates and significant agitation of the catalyst are likely to increase the rate of catalyst degradation.

Investigation of solar energy to activate the catalyst would also be worthwhile as a significant proportion of the treatment cost is associated with the cost of electricity to power the light source. However, this would only be viable in countires with the required sustained periods of sunny weather.

The most realistic use of photocatalysis as a potable water treatment would be as an advanced water treatment method. Therefore it would ideally be used after primary and secondary water treatment, were the majority of organic and inorganic constituents have been removed.

The different raw waters investigated in Chapter 5 significantly reduced GSM degradation, but no factor was found to be individually responsible for the loss in performance. Therefore further scope exists for research into how different water parameters affect the photocatalytic rate of compounds.

CHAPTER 7 - REFERENCES

Abdullah, M., Low, G. K. C. and Matthews, R. W. (1990). "Effects of common inorganic anions on rates of photocatalytic oxidation of organic carbon over illuminated titanium dioxide." Journal of Physical Chemistry **94** (17): 6820-6825.

Ando, M., Miwa, M., Kanjino, M. and Tatsumi, S. (1992). "Removal of musty-odorous compounds in water and retained in algal cells through water purification processes." Water Science & Technology **25** (2): 299-306.

Annadotter, H., Cronberg, G., Aagren, R., Lundstedt, B., Nilsson, P.-Å. and Ströbeck, S. (1999). "Multiple techniques for lake restoration." Hydrobiologia **395-396**: 77-85.

Asaeda, T., Pham, H. S., Nimal Priyantha, D. G., Manatunge, J. and Hocking, G. C. (2001). "Control of algal blooms in reservoirs with a curtain: a numerical analysis." Ecological Engineering **16** (3): 395-404.

Asaeda, T., Priyantha, D. G. N., Saitoh, S. and Gotoh, K. (1996). "A new technique for controlling algal blooms in the withdrawal zone of reservoirs using vertical curtains." Ecological Engineering **7** (2): 95-104.

Ashitani, K., Hishida, Y. and Fujiwara, K. (1988). "Behaviour of musty odorous compounds during the process of water treatment." Water Science and Technology **20** (8/9): 261-267.

AWWA, A. W. W. A. (1996). Australian Drinking Water Guidelines - National Water Quality Management Strategy. A. W. W. Association.

Bahnemann, D. (2004). "Photocatalytic water treatment: solar energy applications." Solar Energy **77** (5): 445-459.

Baker, M. N. (1948). The quest for pure water. New York, American Water Works Association.

Ball, A. S., Williams, M., Vincent, D. and Robinson, J. (2001). "Algal growth control by a barley straw extract." Bioresource Technology **77** (2): 177-181.

Barrett, P. R. F. and Newman, J. R. (1993). "The control of algae with barley straw." Aquatic Weeds Research Unit - Information sheet: 1-9.

Bekbolet, M., Suphandag, A. S. and Uyguner, C. S. (2002). "An investigation of the photocatalytic efficiencies of TiO_2 powders on the decolourisation of humic acids." Journal of Photochemistry and Photobiology A: Chemistry **148** (1-3): 121-128.

Belardi, R. P. and Pawliszyn, J. B. (1989). "Application of chemically modified fused silica fibers in the extraction of organics from water matrix samples and their rapid transfer to capillary columns." Water Quality Research Journal of Canada **24** (1): 179-191.

Bernstein, S. (2002). "Freshwater and human population: A global perspective." Yale F&E's Bulletin: 149 -157.

Bett, K. L. (1997). "Flavor-quality control in freshwater aquaculture." Progressive Fish - Culturist (2): 149-154.

Bett, K. L. and Dionigi, C. P. (1997). "Detecting seafood off-flavors: Limitations of sensory evaluation." Food Technology (8): 70-81.

Bianchi, T. S., Engelhaupt, E., Westman, P., Andren, T., Rolff, C. and Elmgren, R. (2000). "Cyanobacterial blooms in the Baltic Sea: Natural or human-induced?" Limnology and Oceanography (3): 716-726.

Blaha, L., Sabater, S., Babica, P., Vilalta, E. and Marsalek, B. (2004). "Geosmin occurence in riverine cyanobacterila mats: is it causing a significant health hazard?" Water Science & Technology (9): 307-312.

Bowmer, K. H., Padovan, A., Oliver, R. L., Korth, W. and Ganf, G. G. (1992). "Physiology of geosmin production by *Anabaena circinalis* isolated from the Murrumbidgee River, Australia." Water Science & Technology (2): 259-267.

Brezova, V., Blazkova, A., Surina, I. and Havlinova, B. (1997). "Solvent effect on the photocatalytic reduction of 4-nitrophenol in titanium dioxide suspensions." Journal of Photochemistry and Photobiology A: Chemistry **107** (1-3): 233-237.

Bryden, I. G., Robertson, P. K. J. and Bahnemann, D. W. (2006). "Anthropogenic climate change: Issues and Discussions." Journal of Energy and Climate Change **1** (1): 61-73.

Budavari, S. (2001). The Merck index: an encyclopedia of chemicals, drugs, and biologicals, Whitehouse Station, NJ: Merck & Co.

Byrne, J. A., Eggins, B. R., Brown, N. M. D., McKinney, B. and Rouse, M. (1998). "Immobilisation of TiO_2 powder for the treatment of polluted water." Applied Catalysis B: Environmental **17** (1-2): 25-36.

Camel, V. and Bermond, A. (1998). "The use of ozone and associated oxidation processes in drinking water treatment." Water Research **32** (11): 3208-3222.

Carey, J. H., Lawrence, J. and Tosine, H. M. (1976). "Photodechlorination of PCB's in the presence of titanium dioxide in aqueous suspensions." Bulletin of Environmental Contamination and Toxicology **16** (6): 697-701.

Carmichael, W. W. (1994). "The toxins of cyanobacteria." <u>Scientific American</u> **270** (1): 78-86.

Carp, O., Huisman, C. L. and Reller, A. (2004). "Photoinduced reactivity of titanium dioxide." <u>Progress in Solid State Chemistry</u> **32**: 33-177.

Carraway, E. R., Hoffmann, A. J. and Hoffmann, M. R. (1994). "Photocatalytic Oxidation of Organic Acids on Quantum-Sized Semiconductor Colloids." <u>Envirnomental Science and Technology</u> **28**: 786-793.

Chen, D. and Ray, A. K. (1988). "Photodegradation Kinetics of 4-Nitrophenol in TiO_2 Suspensions." <u>Water Research</u> **32**: 3223-3234.

Chen, D. and Ray, A. K. (1998). "Photodegradation kinetics of 4-nitrophenol in TiO2 suspension." <u>Water Research</u> **32** (11): 3223-3234.

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

Chen, H. Y., Zahraa, O. and Bouchy, M. (1997b). "Inhibition of the adsorption and photocatalytic degradation of an organic contaminant in an aqueous suspension of TiO_2 by inorganic ions." <u>Journal of Photochemistry and Photobiology A: Chemistry</u> **108** (1): 37-44.

Chen, H. Y., Zahraa, O., Bouchy, M., Thomas, F. and Bottero, J. Y. (1995). "Adsorption properties of TiO_2 related to the photocatalytic degradation of organic contaminants in water." <u>Journal of Photochemistry and Photobiology A: Chemistry</u> **85** (1-2): 179-186.

Cheremisinoff, N. P. (2002). <u>Handbook of water and wastewater treatment technologies</u>. Boston, MA, Butterworth-Heinemann, 2002.

Chestnutt, J. T. E., Bach, M. T. and Mazyck, D. W. (2007). "Improvement of thermal reactivation of activated carbon for the removal of 2-methylisoborneol." <u>Water Research</u> **41** (1, January 2007): 79-86.

Childs, L. P. and Ollis, D. F. (1981). "Photoassisted heterogeneous catalysis: Rate equations for oxidation of 2-methyl-2-butyl-alcohol and isobutane." <u>Journal of Catalysis</u> **67**: 35-46.

Chorus, I. (1992). Algal metabolites and water quality: toxins, allergens, and taste-and-odor-substances. <u>Strategies for Lake Ecosystems Beyond 2000</u>. R. de Bernardi, R. Pagnotta and A. Pugnetti, Men. Ist. ital. Idrobiol.**:** 257-280.

Chorus, I. and Bartram, J. (1999). <u>Toxic Cyanobacteria in Water: A guide to their public health consequences,monitoring and management</u>. Great Britain, F & FN Spon.

Chung, S.-Y., Johnsen, P. B. and Klesius, P. H. (1990). "Development of an ELISA using polyclonal antibodies specific for 2-methylisoborneol." Journal of Agricultural and Food Chemistry **38**: 410-415.

Chung, S.-Y., Vercellotti, J. R., Johnsen, P. B. and Klesius, P. H. (1991). "Development of an enzyme-linked immunosorbent assay for geosmin." Journal of Agricultural and Food Chemistry **39**: 764-769.

Cole, D., Oman, J., Oman, N. and Chaudhuri, S. (2003). Chemical and microbial sources of taste and odor in water. AWWA Water Quality Technology Conference, Philadelphia, Pennsylvania.

Conte, E. D., Conway, S. C., Miller, D. W. and Perschbacher, P. W. (1996). "Determination of methylisoborneol in channel catfish pond water by solid phase extraction followed by gas chromatography-mass spectrometry." Water Research **30** (9): 2125-2127.

Cook, D., Newcombe, G. and Sztajnbok, P. (2001). "The application of powdered activated carbon for mib and geosmin removal: predicting pac doses in four raw waters." Water Research **35** (5): 1325-1333.

Cooper, C. and Burch, R. (1999). "An Investigation of Catalytic Ozonation for the Oxidation of Halocarbons in Drinking Water Preparation." Water Research **33** (18): 3695-3700.

Crighton, E. J., Elliott, S. J., Upshur, R., van der Meer, J. and Small, I. (2003). "The Aral Sea disaster and self-rated health." Health & Place **9** (2): 73-82.

Cunningham, J. and Srijaranai, S. (1988). "Isotope-effect evidence for hydroxyl radical involvement in alcohol photo-oxidation sensitized by TiO2 in aqueous suspension." Journal of Photochemistry and Photobiology A: Chemistry **43** (3): 329-335.

Dietrich, A. M., Hoehn, R. C., Dufresne, L. C., Buffin, L. W., Rashash, D. M. C. and Parker, B. C. (1995). "Oxidation of odorous and nonodorous algal metabolites by permanganate, chlorine, and chlorine dioxide." Water Science and Technology **31** (11): 223-228.

Dijkstra, M. F. J., Michorius, A., Buwalda, H., Panneman, H. J., Winkelman, J. G. M. and Beenackers, A. A. C. M. (2001). "Comparison of the efficiency of immobilized and suspended systems in photocatalytic degradation." Catalysis Today **66** (2-4): 487-494.

Dillert, R., Vollmer, S., Schober, M., Theurich, J., Bahnemann, D., Arntz, H.-J., Pahlmann, K., Wienfeld, J., Schmedding, T. and Sager, G. (1999). "Photocatalytic treatment of an industrial wastewater in the double-skin sheet reactor." Chemical Engineering and Technology **22** (11): 431-434.

Dionigi, C. P. (1995). "The effects of copper sulfate on geosmin biosynthesis by *streptomyces tendae*, *streptomyces albidoflavus*, and *penicillium expansum*." Water Science and Technology **31** (11): 135-138.

Dionigi, C. P. and Champagne, E. T. (1995). "Copper-containing aquatic herbicides increase Geosmin biosynthesis by *Streptomyces tendae* and *Penicillium expansum*." Weed Science **43** (2): 196-200.

Dionigi, C. P., Lawlor, T. E., McFarland, J. E. and Johnsen, P. B. (1993). "Evaluation of geosmin and 2-methylisoborneol on the histidine dependence of TA98 and TA100 Salmonella typhimurium tester strains." Water Research **27** (11): 1615-1618.

Dominguez, J. R., Beltran, J. and Rodriguez, O. (2005). "Vis and UV photocatalytic detoxification methods (using TiO_2, TiO_2/H_2O_2, TiO_2/O_3, $TiO_2/S_2O_8^{2-}$, O_3, H_2O_2, $S_2O_8^{2-}$, Fe^{3+}/H_2O_2 and $Fe^{3+}/H_2O_2/C_2O_4^{2-}$) for dyes treatment." Catalysis Today **101** (3-4): 389-395.

Draper, R. B. and Fox, M. A. (1990). "Titanium dioxide photosensitized reactions studied by diffuse reflectance flash photolysis in aqueous suspensions of TiO_2 powder." Langmuir **6** (8): 1396-1402.

Egerton, T. A. and King, C. J. (1979). "The Influence of Light Intensity on Photoactivity in Pigmented Systems." Journal of the Oil and Colour Chemists' Association **62**: 386-391.

Eggins, B. R., Palmer, F. L. and Byrne, J. A. (1997). "Photocatalytic treatment of humic substances in drinking water." Water Research **31** (5): 1223-1226.

Elhadi, S. L. N., Huck, P. M. and Slawson, R. M. (2003). Removal of earthy/musty odour compounds by biological filtration: temperature and media effects. AWWA Water Quality Technology Conference, Philadelphia, Pennsylvania.

Elhadi, S. L. N., Huck, P. M. and Slawson, R. M. (2004a). "Determination of system losses of Geosmin and MIB In bench-scale filtration apparatus." Water Quality Research Journal of Canada (3): 207-212.

Elhadi, S. L. N., Huck, P. M. and Slawson, R. M. (2004b). "Removal of geosmin and 2-methylisoborneol by biological filtration." Water Science & Technology (9): 273-280.

Epling, G. A. and Lin, C. (2002). "Investigation of retardation effects on the titanium dioxide photodegradation system." Chemosphere **46** (6): 937-944.

Farmer, L. J., McConnell, J. M., Hagan, T. D. J. and Harper, D. B. (1995). "Flavour and off-flavour in wild and farmed atlantic salmon from locations around northern ireland." Water Science and Technology **31** (11): 259-264.

Fox, M. A. and Dulay, M. T. (1993). "Heterogeneous Photocatalysis." Chemical Reviews **83**: 341-357.

Furtula, V., Davies, J.-M. and Mazumder, A. (2004). "An automated headspace SPME-CG-ITMS technique for taste and odour compound identification." Water Quality Research Journal of Canada **39** (3): 213-22.

Gardner-Outlaw, T. and Engelman, R. (1997). Sustaining Water, Easing Scarcity: A Second Update. Revised Data for the Population Action International Report, Sustaining Water: Population and the Future of Renewable Water Supplies. Washington DC, Population Action International.

Gillogly, T. E. T., Snoeyink, V. L., Newcombe, G. and Elarde, J. R. (1999). "A simplified method to determine the powdered activated carbon dose required to remove Methylisoborneol." Water Science and Technology **40** (6): 59-64.

Gleick, P. H. (2000). "The changing water paradigm - A look at twenty-first century water resources development." Water International (1): 127-138.

Glöckner, F. O., Zaichikov, E., Belkova, N., Denissova, L., Pernthaler, J., Pernthaler, A. and Amann, R. (2000). "Comparative 16S rRNA Analysis of Lake Bacterioplankton Reveals Globally Distributed Phylogenetic Clusters Including an Abundant Group of Actinobacteria." Applied and Environmental Microbiology **66** (11): 5053-5065.

Gonçalves, A. B., Paterson, R. R. M. and Lima, N. (2006). "Survey and significance of filamentous fungi from tap water." International Journal of Hygiene and Environmental Health **209** (3): 257-264.

Goslan, E. H., Gurses, F., Banks, J. and Parsons, S. A. (2006). "An investigation into reservoir NOM reduction by UV photolysis and advanced oxidation processes." Chemosphere **65** (7): 1113-1119.

Goslich, R., Dillert, R. and Bahnemann, D. W. (1997). "Solar water treatment: principles and reactors." Water Science and Technology **35** (4): 137-148.

Gracia, R., Cortes, S., Sarasa, J., Ormad, P. and Ovelleiro, J. L. (2000). "TiO_2-catalysed ozonation of raw Ebro river water." Water Research **34** (5): 1525-1532.

Graham, M. R., Summers, R. S., Simpson, M. R. and MacLeod, B. W. (2000). "Modeling equilibrium adsorption of 2-methylisoborneol and geosmin in natural waters." Water Research **34** (8): 2291-2300.

Guisnet, M., Barbier, J., Barrault, J., Bouchoule, C., Duprez, D., Montassier, C. and Perot, G. (1993). Heterogeneous Catalysis and Fine Chemicals III: Proceedings of the 3rd International Symposium, Poitiers, April 5-8, 1993 (Studies in Surface Science and Catalysis), Elsevier.

Habibi, M. H. and Vosooghian, H. (2005). "Photocatalytic degradation of some organic sulfides as environmental pollutants using titanium dioxide suspension." Journal of Photochemistry and Photobiology A: Chemistry **174** (1): 45-52.

Hanson, T. R. (2003). "Economic Impact of Off-Flavor to the U.S. Catfish Industry." ACS Symposium Series 848 Off Flavours in Aquaculture: 13-29.

Hargesheimer, E. E. and Watson, S. B. (1996). "Drinking water treatment options for taste and odor control." Water Research **30** (6): 1423-1430.

Hashimoto, K., Irie, H. and Fujishima, A. (2005). "TiO_2 Photocatalysis: A Historical Overview and Future Prospects." Japanese Journal of Applied Physics **44** (12): 8269-8285.

Hattori, K. (1988). "Water treatment systems and technology for the removal of odor compounds." Water Science and Technology **20** (8/9): 237-244.

Hayes, K. P. and Burch, M. D. (1989). "Odorous compounds associated with algal blooms in south Australian waters." Water Research **23** (1): 115-121.

Hepplewhite, C., Newcombe, G. and Knappe, D. R. U. (2004). "NOM and MIB, who wins in the competition for activated carbon adsorption sites?" Water Science & Technology **49** (9): 257-265.

Ho, L., Hoefel, D., Bock, F., Saint, C. P. and Newcombe, G. (2007). "Biodegradation rates of 2-methylisoborneol (MIB) and geosmin through sand filters and in bioreactors." Chemosphere **66** (11): 2210-2218.

Ho, L. and Newcombe, G. (2005). "Effect of NOM, turbidity and floc size on the PAC adsorption of MIB during alum coagulation." Water Research **39** (15): 3668-3674.

Hochereau, C. and Bruchet, A. (2004). "Design and application of a GC-SNIFF/MS system for solving taste and odour episodes in drinking water." Water Science & Technology **49** (9): 81-87.

Hoffmann, A. J., Lee, H., Mills, G. and Hoffmann, M. R. (1992). "Photoinduced polymerization of methyl methacrylate using Q-sized zinc oxide colloids." Journal of Physical Chemistry **96**: 5540-5546.

Hoffmann, L. (1996). "Geographic distribution of fresh-water blue-green algae." Hydrobiologia **336** (1-3): 33-40.

Hoffmann, M. R., Martin, S. T., Choi, W. and Bahnemann, D. W. (1995). "Environmental applications of semiconductor photocatalysis." Chemical Reviews **95**: 69-96.

Honglay Chen, P. and Jenq, C. H. (1998). "Kinetics of photocatalytic oxidation of trace organic compounds over titanium dioxide." Environment International **24** (8): 871-879.

Howgate, P. (2004). "Tainting of farmed fish by geosmin and 2-methyl-iso-borneol: a review of sensory aspects and of uptake/depuration." Aquaculture **234** (1-4): 155-181.

Hsiao, C.-Y., Lee, C.-L. and Ollis, D. F. (1983). "Heterogeneous photocatalysis: Degradation of dilute solutions of dichloromethane (CH2Cl2), chloroform (CHCl3), and carbon tetrachloride (CCl4) with illuminated TiO2 photocatalyst." Journal of Catalysis **82** (2): 418-423.

Hsieh, T. C.-Y. Tanchotikul, U. and Matiella, J. E. (1988). "Identification of geosmin as the major muddy off-flavour of Louisiana brackish water clam (*Rangia cuneata*)." Journal of Food Science **53**: 1228-1229.

Huck, P. M., Kenefick, S. L., Hrudey, S. E. and Zhang, S. (1995). "Bench-scale determination of the removal of odour compounds with biological treatment." Water Science and Technology **31** (11): 203-209.

Ikematsu, T., Hayashi, N., Ihara, S., Satoh, S. and Yamabe, C. (2004). "Advanced oxidation processes (AOPs) assisted by excimer lamp." Vacuum **73** (3-4): 579-582.

Izaguirre, G. (1992). "A copper-tolerant *Phormidium* species from Lake Mathews, California, that produces 2-methylisoborneol and geosmin." Water Science & Technology **25** (2): 217-223.

Izaguirre, G. and Taylor, W. D. (1995). "Geosmin and 2-methylisoborneol production in a major aqueduct system." Water Science and Technology **31** (11): 41-48.

Izaguirre, G. and Taylor, W. D. (2004). "A guide to geosmin and MIB producing cyanobacteria in the United States." Water Science & Technology **49** (9): 19-24.

Izaguirre, G., Taylor, W. D. and Pasek, J. (1999). "Off-flavor problems in two reservoirs, associated with planktonic Pseudanabaena Species." Water Science and Technology (6): 85-90.

Izaguirre, G., Wolfe, R. L. and Means, E. G. (1988). "Degradation of 2-methylisoborneol by aquatic bacteria." Applied and Environmental Microbiology **54** (10): 2424-2431.

Jardine, C. G., Gibson, N. and Hrudey, S. E. (1999). "Detection of odour and health risk perception of drinking water." Water Science and Technology **40** (6): 91-98.

Johnsen, P. B. and Kuan, K. C. (1987). "Simplified method to quantify geosmin and 2-methylisoborneol concentrations in water and microbiological cultures." Journal of Chromatography 1987 Nov 13;409:337-42 **409**: 337-42.

Jung, S.-W., Baek, K.-H. and Yu, M.-J. (2004). "Treatment of taste and odor material by oxidation and adsorption." Water Science & Technology **49** (9): 289-295.

Jüttner, F. (1995). "Physiology and biochemistry of odorous compounds from freshwater cyanobacteria and algae." Water Science and Technology **31** (11): 69-78.

Kajino, M. and Sakamoto, K. (1995). "The relationship between musty-odor-causing organisms and water quality in Lake Biwa." Water Science and Technology **31** (11): 153-158.

Khiari, D., Brenner, L., Burlingame, G. A. and Suffet, I. H. (1992). "Sensory gas chromatography for evaluation of taste and odor events in drinking water." Water Science and Technology **25** (2): 97-104.

Kiely, G. (1998). Environmental Engineering, Irwin/McGraw-Hill.

Kim, S.-C. and Lee, D.-K. (2005). "Preparation of TiO_2-coated hollow glass beads and their application to the control of algal growth in eutrophic water." Microchemical Journal **80**: 227- 232.

King, J. M. and Dew, T. (2003). "Catfish off-flavours and their elimination." ACS Symposium Series 848 Off Flavours in Aquaculture: 31-43.

Klausen, C., Nicolaisen, M. H., Strobel, B. W., Warnecke, F., Nielsen, J. L. and Jorgensen, N. O. G. (2005). "Abundance of actinobacteria and production of geosmin and 2-methylisoborneol in Danish streams and fish ponds." FEMS Microbiology Ecology **52** (2): 265-278.

Koch, B., Gramith, J. T., Dale, M. S. and Ferguson, D. W. (1992). "Control of 2-Methylisoborneol and Geosmin by ozone and peroxone: A pilot study." Water Science & Technology **25** (2): 291-298.

Konstantinou, I. K. and Albanis, T. A. (2004). "TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: A review." Applied Catalysis B: Environmental **49** (1): 1-14.

Kormann, C., Bahnemann, D. W. and Hoffmann, M. R. (1991). "Photolysis of chloroform and other organic molecules in aqueous titanium dioxide suspensions." Envirnomental Science and Technology **25** (3): 494-500.

Korth, W., Ellis, J. and Bowmer, K. (1992). "The stability of Geosmin and MIB and their deuterated analogues in surface waters and organic solvents." Water Science & Technology **25** (2): 115-122.

Kranzberg, M. and Pursell, C. W. (1967). Technology in western civilization. New York, Oxford University Press.

Ku, Y., Leu, R.-M. and Lee, K.-C. (1996). "Decomposition of 2-chlorophenol in aqueous solution by UV irradiation with the presence of titanium dioxide." Water Research **30** (11): 2569-2578.

Kwon, B., Park, N. and Cho, J. (2005). "Effect of algae on fouling and efficiency of UF membranes." Desalination **179** (1-3): 203-214.

Lalezary, S., Pirbazari, M. and McGuire, M. J. (1986). "Oxidation of Five Earthy-Musty Taste and Odor Compounds." Journal American Water Works Association **78**: 62-69.

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

Latifoglu, A. and Gurol, M. D. (2003). "The effect of humic acids on nitrobenzene oxidation by ozonation and O_3/UV processes." Water Research **37** (8): 1879-1889.

Lauderdale, C. V., Aldrich, H. C. and Lindner, A. S. (2004). "Isolation and characterization of a bacterium capable of removing taste- and odor-causing 2-methylisoborneol from water." Water Research **38** (19): 4135-4142.

Lawton, L. A., Edwards, C. and Codd, G. A. (1994). "Extraction and high-performance liquid chromatographic method for the determination of microcystins in raw and treated waters." The Analyst **119** (7): 1525-30.

Lawton, L. A. and Robertson, P. K. J. (1999). "Physico-chemical treatment methods for the removal of microcystins (cyanobacterial hepatotoxins) from potable waters." Chemical Society Review **28**: 217-224.

Lawton, L. A., Robertson, P. K. J., Cornish, B. J. P. A., Marr, I. L. and Jaspars, M. (2003a). "Processes influencing surface interaction and photocatalytic destruction of microcystins on titanium dioxide photocatalysts." Journal of Catalysis **213** (1): 109-113.

Lawton, L. A., Robertson, P. K. J., Robertson, R. F. and Bruce, F. G. (2003b). "The destruction of 2-methylisoborneol and geosmin using titanium dioxide photocatalysis." Applied Catalysis B: Environmental **44** (1): 9-13.

Lawton, L. A., Lui, I., Bahnemann, D. W. and Robertson, P. K. J. (2004). Photocatalytic efficiency of selected commercial and synthetic TiO_2 in the destruction of microcystin-LR. Sixth International Conference on Toxic Cyanobacteria, Bergen, Norway.

Lee, J.-M., Kim, M.-S. and Kim, B.-W. (2004). "Photodegradation of bisphenol-A with TiO_2 immobilized on the glass tubes including the UV light lamps." Water Research **38** (16): 3605-3613.

Levi, Y. and Jestin, J. M. (1988). "Offensive tastes and odors occuring after chlorine addition in water treatment processes." Water Science and Technology **20** (8/9): 269-274.

Li, L., Zhu, W., Zhang, P., Chen, Z. and Han, W. (2003). "Photocatalytic oxidation and ozonation of catechol over carbon-black-modified nano-TiO$_2$ thin films supported on Al sheet." Water Research **37** (15): 3646-3651.

Li, X. Z., Chua, H., and Zhang, M. (1996). "Disinfection of municipal wastewater by sensitized photooxidation." Water Science and Technology **33** (3): 111-118.

Lin, C. and Lin, K.-S. (2007). "Photocatalytic oxidation of toxic organohalides with TiO2/UV: The effects of humic substances and organic mixtures." Chemosphere **66** (10): 1872-1877.

Lin, T.-F., Wong, J.-Y. and Kao, H.-P. (2002). "Correlation of musty odor and 2-MIB in two drinking water treatment plants in South Taiwan." The Science of The Total Environment **289** (1-3): 225-235.

Lloyd, S. W., Lea, J. M., Zimba, P. V. and Grimm, C. C. (1998). "Rapid analysis of geosmin and 2-methylisoborneol in water using solid phase micro extraction procedures." Water Research **32** (7): 2140-2146.

Lovell, R. T. (1983). "Off-flavors in pond-cultured channel catfish." Water Science & Technology (6-7): 67-73.

Lovell, R. T. and Broce, D. (1985). "Cause of musty flavor in pond-cultured penaeid shrimp." Aquaculture **50** (1-2): 169-174.

Lovell, R. T., Lelana, I. Y., Boyd, C. E. and Armstrong, M. S. (1986). "Geosmin and musty-muddy flavors in pond-raised channel catfish." Transactions of American Fisheries Society **115**: 485-489.

Lundgren, B. V., Grimvall, A. and Sävenhed, R. (1988). "Formation and removal of off-flavour compounds during ozonation and filtration through biologically active sand filters." Water Science and Technology **20** (8/9): 245-253.

Madigan, M. T., Martinko, J. M. and Parker, J. (2003). Brock Biology of Microorganisms, Pearson Education International.

Mao, Y., Schoeneich, C. and Asmus, K. D. (1991). "Identification of organic acids and other intermediates in oxidative degradation of chlorinated ethanes on titania surfaces en route to mineralization: a combined photocatalytic and radiation chemical study." Journal of Physical Chemistry **95** (24): 10080-10089.

Matsumoto, A. and Tsuchiya, Y. (1988). "Earthy-musty odor-producing cyanophytes isolated from five water areas in Tokyo." Water Science & Technology **20** (8-9): 179-183.

Matthews, R. W. (1988). "Kinetics of photocatalytic oxidation of organic solutes over titanium dioxide." Journal of catalysis **111**: 264-272.

Matthews, R. W. (1993). Photocatalysis in water purification: Possibilities, problems and prospects. Photocatalytic Purification and Treatment of Water and Air. D. F. Ollis and H. Al-Ekabi, Elsevier Science Publishers B. V.**:** 121-138.

Matthews, R. W. and McEvoy, S. R. (1992). "A comparison of 254 nm and 350 nm excitation of TiO2 in simple photocatalytic reactors." Journal of Photochemistry and Photobiology A: Chemistry **66**: 355-266.

McGuire, M. J. (1995). "Off-flavor as the consumer's measure of drinking water safety." Water Science and Technology **31** (11): 1-8.

McGuire, M. J. (1999). "Advances in treatment processes to solve off-flavor problems in drinking water." Water Science and Technology **40** (6): 153-163.

McGuire, M. J. and Gatson, J. M. (1988). "Overview of technology for controlling off-flavors in drinking water." Water Science and Technology **20** (8/9): 215-228.

McMurray, T. A., Byrne, J. A., Dunlop, P. S. M., Winkelman, J. G. M., Eggins, B. R. and McAdams, E. T. (2004a). "Intrinsic kinetics of photocatalytic oxidation of formic and oxalic acid on immobilised TiO_2 films." Applied Catalysis A: Generall **262**: 105-110.

Mills, A., Belghazi, A. and Rodman, D. (1996). "Bromate removal from drinking water by semiconductor photocatalysis." Water Research **30** (9): 1973-978.

Mills, A., Davies, R. H. and Worsley, D. (1993). "Water purification by semiconductor photocatalysis." Chemical Society Reviews: 417-425.

Mills, A. and Le Hunte, S. (1997). "An overview of semiconductor photocatalysis." Journal of Photochemistry and Photobiology A: Chemistry **108** (1): 1-35.

Montiel, A. J. (1983). "Municipal Drinking Water Treatment Procedures for Taste and Odour Abatement - A Review." Water Science and Technology **15** (6-7): 279-289.

Morran, J. and Marchesan, M. (2004). "Taste and odour testing: how valuable is training?" Water Science & Technology **49** (9): 66-74.

Mukherjee, P. S. and Ray, A. K. (1999). "Major Challenges in the Design of a Large-Scale Photocatalytic Reactor for Water Treatment." Chemical Enginnering and Technology **22** (3): 253-260.

Muramoto, S., Udagawa, T. and Okamura, T. (1995). "Effective removal of musty odor in the Kanamachi purification plant." Water Science and Technology **31** (11): 219-222.

Naes, H., Utkilen, H. C. and Post, A. F. (1988). "Factors influencing geosmin production by the cyanobacterium *Oscillatoria Brevis.*" Water Science and Technology **20** (8/9): 125-131.

Nakajima, M., Ogura, T., Kusama, Y., Iwabuchi, N., Imawaka, T., Araki, A., Sasaki, T., Hirose, E. and Sunairi, M. (1996). "Inhibitory effects of odor substances, geosmin and 2-methylisoborneol, on early development of sea urchins." Water Research **30** (10): 2508-2511.

Negoro, T., Ando, M. and Ichikawa, N. (1988). "Blue-green algae in Lake Biwa which produce earthy-musty odors." Water Science & Technology **20** (8-9): 117-123.

Newcombe, G., Morrison, J., Hepplewhite, C. and Knappe, D. R. U. (2002). "Simultaneous adsorption of MIB and NOM onto activated carbon: II. Competitive effects." Carbon **40** (12): 2147-2156.

Ng, C., Losso, J. N., Marshall, W. E. and Rao, R. M. (2002). "Freundlich adsorption isotherms of agricultural by-product-based powdered activated carbons in a geosmin-water system." Bioresource Technology **85** (2): 131-135.

Ollis, D. F. (1988). "Process economics for water purification: a comparative assessment." Photocatalysis and Environment, Trends and Application **237**: 663.

Ollis, D. F., Pelizzett, E. and Serpone, N. (1991). "Photocatalyzed destruction of water contaminants." Envirnomental Science and Technology **25** (9): 1522-1529.

Orr, P. T., Jones, G. J. and Hamilton, G. R. (2004). "Removal of saxitoxins from drinking water by granular activated carbon, ozone and hydrogen peroxide--implications for compliance with the Australian drinking water guidelines." Water Research **38** (20): 4455-4461.

Oskam, G., van Genderen, J., Sladeckova, A., Klein, H.-P., Zimmermann, U., Liu, C.-J. and Tseng, S.-K. (1996). "Eutrophication and development of algae in surface water - a threat for the future?" Water Supply (3-4 (Durban)): 415-437.

Palmentier, J. P. F. P., Taguchi, V. Y., Jenkins, S. W. D., Wang, D. T., Ngo, K.-P. and Robinson, D. (1998). "The determination of geosmin and 2-methylisoborneol in water using isotope dilution high resolution mass spectrometry." Water Research **32** (2): 287-294.

Perez, M. H., Penuela, G., Maldonado, M. I., Malato, O., Fernandez-Ibanez, P., Oller, I., Gernjak, W. and Malato, S. (2006). "Degradation of pesticides in water using solar advanced oxidation processes." Water Research **64** (3-4): 272-281.

Perschbacher, P. W., Miller, D. and Conte, E. D. (1995). "Algal off-flavors in reservoirs." Multidimensional Approaches to Reservoir Fisheries Management, AFS, Bethesda, MD, USA (American Fisheries Society Symposium): 67-72.

Persson, P.-E. (1978). "Muddy off-flavour in bream (*Abramis brama* L) from the Porovo area, Gulf of Finland." Verh Int Ver Theor Angew Limnologie/Proceedings of the International Association of Theoretical & Applied Limnology/Trav Assoc Int Limnol Theor Appl (3): 2098-2102.

Persson, P.-E. (1982). "Muddy odour: a problem associated with extreme eutrophication." Hydrobiologia (1-32): 161-164.

Persson, P.-E. (1985). "Off-flavours in fish from the Gulf of Finland." Finnish Fisheries Research: 112-117.

Persson, P.-E. (1995). "19th century and early 20th century studies on aquatic off-flavours - a historical review." Water Science and Technology **31** (11): 9-13.

Persson, P.-E. (1996). "Cyanobacteria and off-flavours." Phycologia **35** (6): 168-171.

Persson, P. E. (1980). "Muddy odour in fish from hypertrophic waters." Developments in Hydrobiology: 203-208.

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

Pillinger, J. M., Cooper, J. A. and Ridge, I. (1994). "Role of phenolic compounds in the antialgal activity of barley straw." Journal of Chemical Ecology **20** (7): 1557-1569.

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

Rao, K. V. S., Subrahmanyam, M. and Boule, P. (2004). "Immobilized TiO2 photocatalyst during long-term use: decrease of its activity." Applied Catalysis B: Environmental **49** (4): 239-249.

Rashash, D. M. C., Dietrich, A. M. and Hoehn, R. C. (1997). "FPA of selected odorous compounds." Journal of American Water Works Association (4): 131-141.

Rashash, D. M. C., Hoehn, R. C., Dietrich, A. M., Gizzard, T. and Parker, B. C. (1996). Identification and control of odorous algal metabolites. Denver, Colarado, AWWARF. **31:** 165-172.

Ray, A. K. (1998). "A new photocatalytic reactor for destruction of toxic water pollutants by advanced oxidation process." Catalysis Today **44** (1-4): 357-368.

Ray, A. K. (1999a). "Design, modelling and experimentation of a new large-scale photocatalytic reactor for water treatment." Chemical Engineering Science **54** (15): 3113-3125.

Ray, A. K. (1999b). "Design, modelling and experimentation of a new large-scale photocatalytic reactor for water treatment." Chemical Engineering Science **54** (15-16): 3113-3125.

Ray, A. K. and Beenackers, A. A. C. M. (1997). "Novel swirl-flow reactor for kinetic studies of semiconductor photocatalysis." AIChE Journal **43** (10): 2571-2578.

Ray, A. K. and Beenackers, A. A. C. M. (1998). "Development of a new photocatalytic reactor for water purification." Catalysis Today **40** (1): 73-83.

Ridal, J., Brownlee, B. and Lean, D. R. S. (1999). "Occurrence of the odor compounds, 2-Methylisoborneol and Geosmin in Eastern Lake Ontario and the Upper St. Lawrence River." Journal of the Great Lakes Research **25** (1): 198-204.

Rigal, S. (1995). "Odour and flavour in waters: quantitative method for a new european standard." Water Science and Technology **31** (11): 237-242.

Rigal, S. and Danjou, J. (1999). "Tastes and odors in drinking water distribution systems related to the use of synthetic materials." Water Science and Technology **40** (6): 203-208.

Robert Reiss, C., Taylor, J. S. and Robert, C. (1999). "Surface water treatment using nanofiltration--pilot testing results and design considerations." Desalination **125** (1-3): 97-112.

Robertson, P. K. J. (1996). "Semiconductor photocatalysis: an environmentally acceptable alternative production technique and effluent treatment process." Journal of Cleaner Production **4** (3-4): 203-212.

Robertson, P. K. J., Bahnemann, D. W., Robertson, J., M. C. and Wood, F. (2005). Photocatalytic detoxification of water and air, Springer-Verlag.

Robertson, P. K. J., Lawton, L. A., Cornish, B. J. P. A. and Jaspars, M. (1998). "Processes influencing the destruction of microcystin-LR by TiO$_2$ photocatalysis." Journal of Photochemistry and Photobiology A: Chemistry **116** (3): 215-219.

Robertson, P. K. J., Lawton, L. A., Munch, B. and Cornish, B. (1999). "The destruction of cyanobacterial toxins by titanium dioxide photocatalysis." Journal of Advanced Oxidative Technology (1): 215-219.

Robertson, P. K. J., Lawton, L. A., Münch, B. and Rouzade, J. (1997). "Destruction of cyanobacterial toxins by semiconductor photocatalysis." Chemical Communications: 393-394.

Robertson, R. F. and Lawton, L. L. (2003). "Off flavour problems and a potential solution within the U.K. trout industry." ACS Symposium Series 848 Off Flavours in Aquaculture: 55-68.

Robin, J., Cravedi, J.-P., Hillenweck, A., Deshayes, C. and Vallod, D. (2006). "Off flavor characterization and origin in French trout farming." Aquaculture **260** (1-4): 128-138.

Rodriguez, S. M., Galvez, J. B., Maldonado Rubio, M. I., Ibanez, P. F., Gernjak, W. and Alberola, I. O. (2005). "Treatment of chlorinated solvents by TiO_2 photocatalysis and photo-Fenton: influence of operating conditions in a solar pilot plant." Chemosphere **58** (4): 391-398.

Romano, A. H. and Safferman, R. S. (1963). "Studies on actinomycetes and their odors." Journal of American Water Works Association (Feb): 169-176.

Saadoun, I. and El-Migdadi, F. (1998). "Degradation of geosmin-like compounds by selected species of Gram-positive bacteria." Letters in Applied Microbiology: 98-100.

Sagehashi, M., Shiraishi, K., Fujita, H., Fujii, T. and Sakoda, A. (2005). "Adsorptive ozonation of 2-methylisoborneol in natural water with preventing bromate formation." Water Research **39** (16): 3900-3908.

Saito, A., Tanaka, A. and Oritani, T. (1996). "A practical synthesis of enantiomerically pure (-)-geosmin via highly diastereoselective reduction of (4aS,8S)-4,4a,5,6,7,8-hexahydro-4a,8-dimethyl-2(3H)-naphthalenone." Tetrahedron: Asymmetry **7** (10): 2923-2928.

Saito, A., Tokuyama, T., Tanaka, A., Oritani, T. and Fuchigami, K. (1999). "Microbiological degradation of (-)-geosmin." Water Research **33** (13): 3033-3036.

San Miguel, G., Lambert, S. D. and Graham, N. J. D. (2001). "The regeneration of field-spent granular-activated carbons." Water Research **35** (11): 2740-2748.

Schrader, K. K., Dayan, F. E. and Nanayakkara, N. P. D. (2005a). "Generation of reactive oxygen species by a novel anthraquinone derivative in the cyanobacterium Planktothrix perornata (Skuja)." Pesticide Biochemistry and Physiology **81** (3): 198-207.

Schrader, K. K. and Dennis, M. E. (2005b). "Cyanobacteria and earthy/musty compounds found in commercial catfish (*Ictalurus punctatus*) ponds in the Mississippi Delta and Mississippi-Alabama Blackland Prairie." Water Research **39** (13): 2807-2814.

Schrader, K. K. and Rimando, M. (2003). "Off-flavours in aquaculture: An overview." ACS Symposium Series 848 Off Flavours in Aquaculture: 1-29.

Schweitzer, L., Tomboulian, P., Astasi, K., Chen, T. and Khiari, D. (2004). "Utility quick test for analyzing materials for drinking water distribution systems for effect on taste-and-odor." Water Science & Technology **49** (9): 75-80.

Seligman, K., Ewnos, A. K. and Lai, H. H. (1992). "A comparison of 1988-1990 flavor profile analysis results with water conditions in two Northern California reservoirs." Water Science & Technology **25** (2): 19-25.

Shon, H. K., Vigneswaran, S., Ngo, H. H. and Kim, J. H. (2005). "Chemical coupling of photocatalysis with flocculation and adsorption in the removal of organic matter." Water Research **39** (12): 2549-2558.

Sklenar, K. S. and Horne, A. J. (1999). "Horizontal distribution of Geosmin in a reservoir before and after copper treatment." Water Science and Technology **40** (6): 229-237.

Slater, G. P. and Blok, V. C. (1983). "Isolation and identification of odorous compounds from a lake subject to cyanobacterial blooms." Water Science & Technology (6-7): 229-240.

Smith, D. P., Levine, A. D., Mody, A., MacLeod, B. and Simpson, M. (2003). Factors influencing selection of nanofiltration membranes for removal of organics from surface water. AWWA Water Quality Technology Conference, Philadelphia, Pennsylvania.

Suffet, I. H., Corado, A., Chou, D., McGuire, M. J. and Butterworth, S. (1996). "AWWA taste and odor survey." Journal - American Water Works Association **88** (4): 168-180.

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

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

Sumitomo, H. (1992). "Biodegradation of 2-Methylisoborneol by gravel sand filtration." Water Science & Technology **25** (2): 191-198.

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

Supelco (2002). Solid Phase Microextraction of Odors in Drinking Water, for Analysis by GC/MS. Application Note 147**:** 1-2.

Svrcek, C. and Smith, D. W. (2004). "Cyanobacteria toxins and the current state of knowledge on water treatment options: a review." Journal of Environmental Engineering Science **3**: 155-185.

Tanaka, A., Oritani, T., Uehara, F., Saito, A., Kishita, H., Niizeki, Y., Yokota, H. and Fuchigami, K. (1996). "Biodegradation of a musty odour component, 2-methylisoborneol." Water Research **30** (3): 759-761.

Tennant, M. F. and Mazyck, D. W. (2007). "The role of surface acidity and pore size distribution in the adsorption of 2-methylisoborneol via powdered activated carbon." Carbon **45** (4): 858.

Terashima, K. (1988). "Reduction of musty odor substances in drinking water - a pilot plant study." Water Science and Technology **20** (8/9): 275-281.

Thruman, E. M. and Mills, M. S. (1998). Solid-Phase Extraction - Principles and Practice. New York, John Wiley & Sons, Inc.

Tomboulian, P., Schweitzer, L., Mullin, K., Wilson, J. and Khiari, D. (2004). "Materials used in drinking water distribution systems: contribution to taste-and-odor." Water Science & Technology **49** (9): 219-226.

Tung, S.-C., Lin, T.-F., Liu, C.-L. and Lai, S.-D. (2004). "The effect of oxidants on 2-MIB concentration with the presence of cyanobacteria." Water Science & Technology (9): 281-288.

Turchi, C. S. and Ollis, D. F. (1988). "Photocatalytic reactor design: an example of mass-transfer limitations with an immobilized catalyst." Journal of Physical Chemistry **92** (23): 6852-6853.

Turchi, C. S. and Ollis, D. F. (1989). "Mixed reactant photocatalysis: Intermediates and mutual rate inhibition." Journal of Catalysis **119** (2): 483-496.

Turchi, C. S. and Ollis, D. F. (1990). "Photocatalytic degradation of organic water contaminants: Mechanisms involving hydroxyl radical attack." Journal of Catalysis **122** (1): 178-192.

Utkilen, H. C. and Froeshaug, M. (1992). "Geosmin production and excretion in a planktonic and benthic *Oscillatoria*." Water Science & Technology **25** (2): 199-206.

van Breemen, L. W. C. A., Dits, J. S. and Ketelaars, H. A. M. (1992). "Production and reduction of Geosmin and 2-Methylisoborneol during storage of river water in deep reservoirs." Water Science & Technology **25** (2): 233-240.

van der Ploeg, M. (1991). "Testing flavor quality of preharvest channel catfish." Southern Regional Aquaculture Center (SRAC) **431**: 1-8.

van der Ploeg, M., Tucker, C. S. and Boyd, C. E. (1992). "Geosmin and 2-methylisoborneol production by cyanobacteria in fish ponds in the southeastern United States." Water Science & Technology **25** (2): 283-290.

van Well, M., Dillert, R. H. G., Bahnemann, D. W., Benz, V. W. and Mueller, M. A. (1997). "A novel nonconcentrating reactor for solar water detoxification." Journal of solar energy engineering **119** (2): 114-119.

Vik, E. A., Storhaug, R., Naes, H. and Utkilen, H. C. (1988). "Pilot scale studies of geosmin and 2-methylisoborneol removal." Water Science & Technology **20** (8-9): 229-236.

von Gunten, U. (2003). "Ozonation of drinking water: Part I. Oxidation kinetics and product formation." Water Research **37** (7): 1443-1467.

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

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

Westerhoff, P., Nair, B. and Pei, P. (2003). Oxidation of MIB and geosmin by ozone and hydroxyl radicals. AWWA Water Quality Technology Conference, Philadelphia, Pennsylvania.

Westerhoff, P., Rodriguez-Hernandez, M., Baker, L. and Sommerfeld, M. (2005). "Seasonal occurrence and degradation of 2-methylisoborneol in water supply reservoirs." Water Research **39** (20): 4899-4912.

Weyhenmeyer, G. A. (2001). "Warmer winters: Are planktonic algal populations in Sweden's largest lakes affected?" AMBIO (8): 565-571.

WHO (2002). The World Health Report 2002: Reducing Risks, Promoting Healthy Life. Geneva.

Wiesenthal, K. E., Amah, G., Lam, T. and Suffet, I. H. (2004). "The effect of applying a pipe-joint lubricant to connect ductile iron pipe on off-flavors in drinking water distribution systems." Water Science & Technology **49** (9): 233-240.

Wiszniowski, J., Robert, D., Surmacz-Gorska, J., Miksch, K. and Weber, J.-V. (2002). "Photocatalytic decomposition of humic acids on TiO_2: Part I: Discussion of adsorption and mechanism." Journal of Photochemistry and Photobiology A: Chemistry **152** (1-3): 267-273.

Wnorowski, A. U. (1992). "Tastes and odours in the aquatic environment: a review." Water South Africa **18** (3): 203-214.

Wood, S., Williams, S. T. and White, W. R. (1985). "Potential sites of geosmin production by *Streptomycetes* in and around reservoirs." Journal of Applied Bacteriology (3): 319-326.

Wood, S., Williams, S. T. and White, W. R. (2001). "Microbes as a source of earthy flavours in potable water - a review." International Biodeterioration & Biodegradation (1-4): 26-40.

Wu, J. T. and Jüttner, F. (1988). "Effect of environmental factors on geosmin production by *Fischerella Muscicola*." <u>Water Science and Technology</u> **20** (8/9): 143-148.

Xu, Y. and Langford, C. H. (2000). "Variation of Langmuir adsorption constant determined for TiO_2-photocatalyzed degradation of acetophenone under different light intensity." <u>Journal of Photochemistry and Photobiology A: Chemistry</u> **133** (1-2): 67-71.

Yagi, M., Kajino, M., Matsuo, U., Ashitani, K., Kita, T. and Nakamura, T. (1983). "Odor problems in Lake Biwa." <u>Water Science & Technology</u> (6-7): 311-321.

Yagi, M., Nakashima, S. and Muramoto, S. (1988). "Biological degradation of musty odor compounds, 2-methylisoborneol and geosmin, in a bio-activated carbon filter." <u>Water Science & Technology</u> **20** (8/9): 255-260.

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

Zaitlin, B. and Watson, S. B. (2006). "Actinomycetes in relation to taste and odour in drinking water: Myths, tenets and truths." <u>Water Research</u> **40** (9): 1741-1753.

Zhang, L., Hu, R. and Yang, Z. (2006). "Routine analysis of off-flavor compounds in water at sub-part-per-trillion level by large-volume injection GC/MS with programmable temperature vaporizing inlet." <u>Water Research</u> **40** (4): 699-709.

Zimba, P. V. and Grimm, C. C. (2003). "A synoptic survey of musty/muddy odor metabolites and microcystin toxin occurrence and concentration in southeastern USA channel catfish (*Ictalurus punctatus* Ralfinesque) production ponds." <u>Aquaculture</u> **218** (1-4): 81-87.
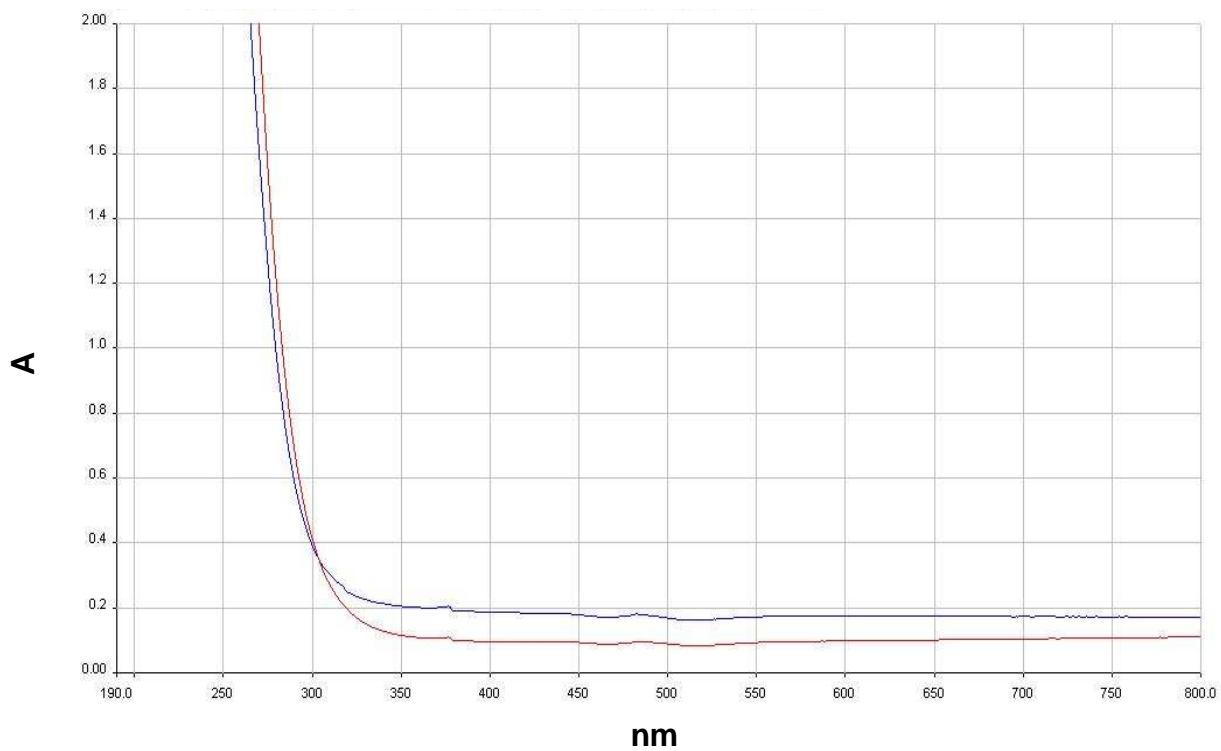
APPENDIX 1 - BATCH AND FLOW REACTOR GLASS SPECTRAS

Figure A-1. Comparison of UV/Vis absorbance for (⎯⎯) glass vessel used in reactors V.1 – V.3 (Chapter 3) and (⎯⎯) glass used to construct coil flow reactor (Chapter 5).

APPENDIX 2 – UV BLACK LIGHT LAMP DATA

10531 – F40BLB 6PK
GE Black Light T12 - Blacklight Blue

• GE Blacklight lamps emit at 368 nm. These lamps are typically used in insect traps and inspection applications.

GENERAL CHARACTERISTICS

Lamp type	Linear Fluorescent - Straight Linear
Bulb	T12
Base	Medium Bi-Pin (G13)
Bulb Finish	Blacklight/blacklight blue
Wattage	40
Voltage	101
Rated Life	20000 hrs
Rated Life (instant start) @ Time	20000 h @ 3 h
Starting Temperature (MIN)	10 °C (50 °F)
Primary Application	Blacklight Blue

ELECTRICAL CHARACTERISTICS

Open Circuit Voltage (rapid start) (MAX)	330 V
Open Circuit Voltage (rapid start) Min @ Temperature	256 V @ 10 °C
Cathode Resistance Ratio - Rh/Rc (MAX)	6.5
Preheat Voltage (MIN)	4 V

DIMENSIONS

Maximum Overall Length (MOL)	48.0000 in (1219.2 mm)
Bulb Diameter (DIA)	1.500 in (38.1 mm)
Bulb Diameter (DIA) (MAX)	1.590 in (40.3 mm)
Face to End of Opposing Pin (B) (MAX)	47.500 in (1206.5 mm)

PRODUCT INFORMATION

Product Code	10531
Description	F40BLB 6PK
Standard Package	BUNDLE
Standard Package GTIN	00043168105316
Standard Package Quantity	24
Sales Unit	Unit
No Of Items Per Sales Unit	1
No Of Items Per Standard Package	24
UPC	043168981637

COMPATIBLE GE BALLASTS

Product Code	Description	# of Bulbs	Power Factor	Ballast Factor
24773	GE240RS-MV-N-DIY	1	99.0	0.89
24107	GE-240-RS-MV-N	1	99.0	0.89
24774	GE340RS-MV-N-DIY	2	99.0	0.89
24109	GE-340-RS-MV-N	2	99.0	0.89
97498	GE240RS120	2	98.0	0.85
46958	GEM240RS120DIY	2	98.0	0.95
89713	GEM240RS277DIY	2	98.0	0.95
89709	GEM140RS120DIY	1	47.0	0.6
86124	GEM240RS277IP	2	98.0	0.95
89710	GEM240HRS120DIY	2	95.0	0.84
89714	GEM140HRS120DIY	1	97.0	1.0
86139	GEM240RS120IP	2	98.0	0.95

⚠ CAUTIONS & WARNINGS

See list of cautions & warnings.

*GE Ecolux Fluorescent lamps contain less than 1/2 the 1994 industry average of mercury for 4 foot Fluorescent lamps and they pass the EPA Toxicity Characteristic Leaching Procedure (TCLP) test.
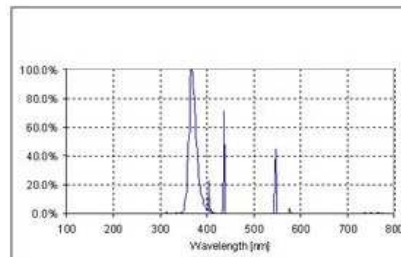
Bulb Base Package
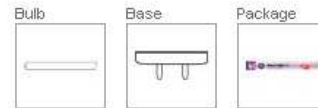
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ADDITIONAL RESOURCES
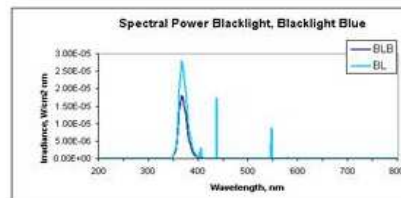
Catalogs
Testimonials
MSDS (Material Safety Data Sheets)
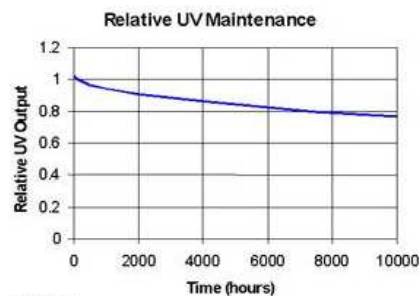Disposal Policies & Recycling Information

GRAPHS & CHARTS

Percent Irradiance

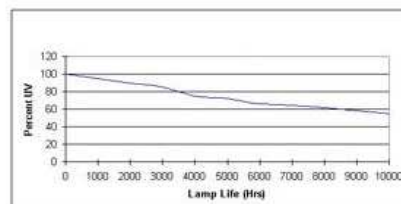**Spectral Power Distribution**

UV Maintenance

UV Maintenance

Figure A-2. UV black light lamp data (Chapter 5).