ORGANIC VOLATILE SULFUR COMPOUNDS

IN

INLAND AQUATIC SYSTEMS

BY

SHIRLEY R. RICHARDS

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

Department of Microbiolgy
University of Manitoba
Winnipeg, Manitoba

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TO

MY MOM AND DAD

for their indefatigable support and encouragement

from

"orange sticker-books"

to

PhD. thesis

ABSTRACT

The speciation, concentration, and fluxes of organic volatile sulfur compounds (VSCs) in a wide variety of inland aquatic systems were studied. Dissolved VSCs were sparged from water samples, trapped cryogenically, and quantified by gas chromatograph equipped with a flame photometric detector.

Species detected and mean surface water concentrations were: carbonyl sulfide (COS), 0.091-7.6 nM; methanethiol (MSH), undetected-180 nM; dimethyl sulfide (DMS), 0.48-1290 nM; carbon disulfide (CS_2), undetected-69 nM; dimethyl disulfide (DMDS), undetected-68 nM. The range in surface water concentrations of over five orders of magnitude was influenced principally by lake depth and sulfate concentration ($[SO_4^{2-}]$). Unstratified lakes had surface water concentrations of DMS, MSH, and DMDS 5-70 times higher than stratified lakes. Salt lakes (Saskatchewan) with more than 20 g (SO_4^{2-}) $litre^{-1}$ contained concentrations of DMS and MSH orders of magnitude greater than freshwater lakes. The sediments were net sources of MSH and DMS, while the water column was both a source and a sink.

Globally, inland aquatic systems are not as significant as the oceans in producing atmospheric sulfur. However, fluxes per unit area were similar to, or greater than, the ocean. Furthermore, lakes can return to the atmosphere a

significant fraction of the SO_4^{2-} precipitated on their surface, and may be regionally significant contributors to atmospheric sulfur.

PREFACE

Chapters in this thesis were written as papers for submission to scientific journals. Chapter 2 has been published (Richards et al. 1991. Limnology and Oceanography 36(3): 468), and Chapter 3 has been accepted by Limnology and Oceanography. The data described in Chapter 5 will be combined with another manuscript (Amaral et al. In prep. The isolation and characterization of ^{35}S-organosulfur from $^{35}SO_4^{2-}$ reduction in a freshwater sediment.) prior to publication.

ACKNOWLEDGEMENTS

The research encompassed in this volume has been supported, aided, and encouraged by many people. My two principal advisors, Drs. Carol Kelly and John Rudd, provided the initial idea for the study, and their approach to biogeochemical cycling is evident throughout the work. Papers arising from this research were improved by their careful and thorough reviews, and I would like to thank them for the advice and encouragement they have given me.

All committee members gave willingly of their expertise and time whenever asked. Dr. Bob Flett was an invaluable source of technical knowledge, and provided both an educated and a friendly ear on many occasions, whether at the lab, in his home, or over the phone. His personal interest and enthusiasm was much appreciated. Dr. Gregg Brunskill was a unique source of ideas and advice. He significantly contributed to the scope of this research by persistent and repeated suggestions to go west to the prairie salt lakes. Dr. Dave McKinnon, having permitted himself to be drawn into the "wilds of biology", was a willing source of advice on all aspects of chemistry.

Many others at the Freshwater Institute were very helpful at different stages of the work. Akira Furutani contributed to initial methods development, and Pat Ramlal, Dr. Ray Hesslein, Len Hendzel and Bruce Townsend are just a

few of the people who helped in many practical and technical aspects of the work. Sharon Berg ensured the proper papers were signed, dated, and submitted, in order to satisfy all administrative obligations.

Throughout the years taken to complete this work, my family has given me much practical and personal support. Their communications helped me to maintain an awareness of life outside the lab. John Amaral, a "co-sulfurfile", was an unexpected "plus" in my choice of graduate work. He provided an introduction to the experimental approach used in this field, including instrumentation and lab techniques. Our many discussions (of microbiology, sulfur, life, and the relative merits of cats and dogs) conducted while driving to ELA at 5:00 AM, drinking one of many cups of coffee, working in the lab, or sinking into the mud at Chaplin Lake, contributed significantly to the enjoyment and progress of this research.

Finally, I would like to acknowledge the financial assistance I received in the form of NSERC postgraduate scholarships, and a Department of Fisheries and Oceans graduate student stipend. Equipment and lab supplies necessary for the research were purchased on NSERC grant No. OGPGP 010.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

Ae	surface area of epilimnetic sediments
A_o	surface area
chl *a*	chlorophyll *a*
Cl_2	chlorine
Cl^-	chloride ion
CO_3^{2-}	carbonate ion
CO_2	carbon dioxide
COS	carbonyl sulfide
CS_2	carbon disulfide
CrII	chromium II
DIC	dissolved inorganic carbon
DMDS	dimethyl disulfide
DMS	dimethyl sulfide
DMSO	dimethyl sulfoxide
DMSP	dimethyl sulfoniopropionate
ELA	Experimental Lakes Area
Eh	redox potential
HBL	Hudson Bay lowland
HCO_3^-	bicarbonate ion
$HgCl_2$	mercuric chloride
H_2O_2	hydrogen peroxide
H_2S	hydrogen sulfide
IO	iodine oxide
MSA	methanesulfonic acid

MSH	methane thiol
N_2	nitrogen gas
NaOH	sodium hydroxide
ND	not detected
NO_3^-	nitrate
NSS-SO_4^{2-}	non-sea-salt sulfate
O_3	ozone
$OH^\cdot$	hydroxyl radical
OM	organic matter
rpm	revolutions per minute
S	sulfur
SO_2	sulfur dioxide
$SO_{(x)}$	various sulfur oxides
SO_4^{2-}	sulfate
Tg	teragram (10^{12} g)
Ve	volume of epilmnion
$\overline{X}$	mean
$\overline{Z}$	mean depth
Z_m	maximum depth
z	diffusive boundary layer thickness

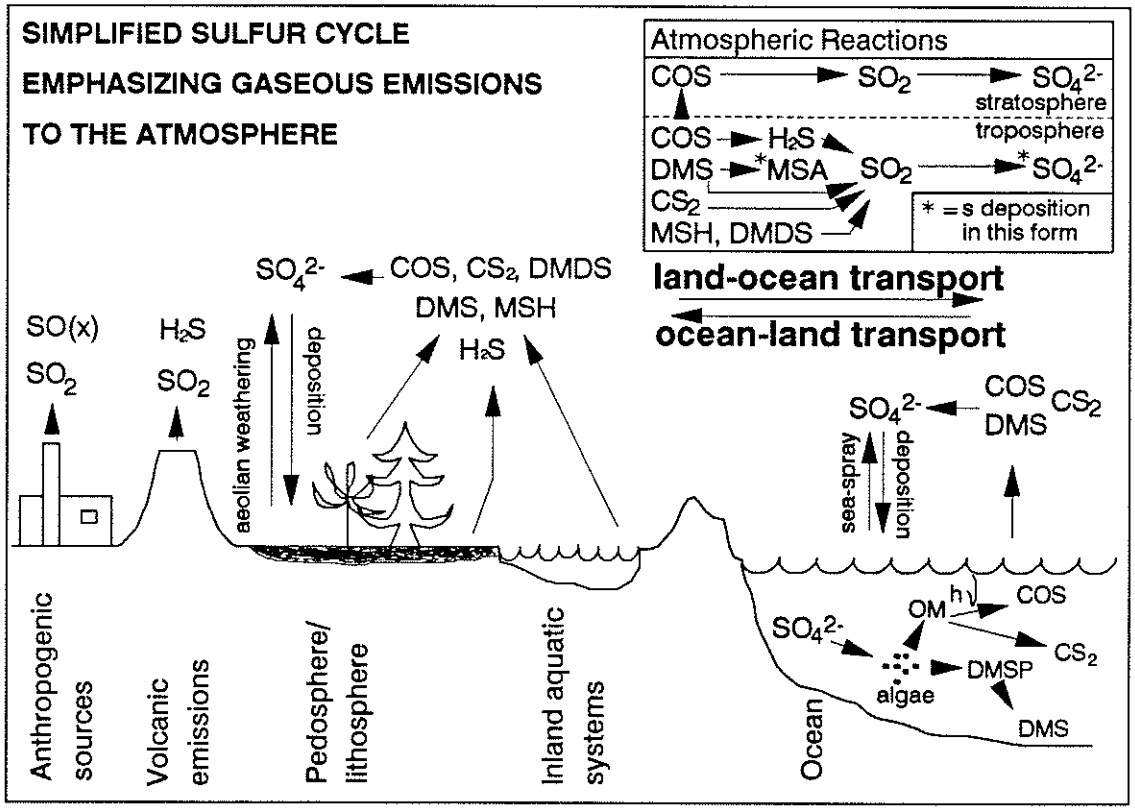
1. Literature Review

1.0. Introduction

The global sulfur cycle includes important reservoirs of sulfur as mineral deposits, dissolved oceanic sulfate, and organic compounds in living and dead organic matter. The atmosphere contains a very small pool of sulfur (estimated at 3.6 Tg S, Zehnder and Zinder 1980), which is only a fraction of the reserves in the lithosphere and hydrosphere (26.1×10^9 and 1.28×10^9 Tg S, respectively; Zehnder and Zinder 1980). Despite its small size, the atmospheric reservoir is important in the global sulfur cycle since it is a very dynamic pool with high rates of transfer and redistribution of species (Ryaboshapko 1983). Atmospheric forms of sulfur include gaseous molecules such as low molecular weight organic compounds, aerosols, and solutes in cloud droplets (Charlson et al. 1987).

Both natural and anthropogenic processes contribute to the atmospheric sulfur pool (Fig. 1.1). Anthropogenic emissions, such as the burning of fossil fuels, are dominated by gaseous sulfur dioxide (SO_2), and a variety of sulfur oxides often referred to as $SO_{(x)}$. The principal natural sources of atmospheric sulfur include aeolian weathering of sulfates, release of sea-salt sulfate from the oceans, and gaseous emissions from volcanoes and biological activity (Fig. 1.1). Natural gaseous emissions are composed of a wide range of species including hydrogen sulfide (H_2S)

Figure 1.1. Simplified sulfur cycle emphasizing atmospheric sulfur species.


SIMPLIFIED SULFUR CYCLE
EMPHASIZING GASEOUS EMISSIONS
TO THE ATMOSPHERE
Atmospheric Reactions
COS → SO2 → SO4 2-
stratosphere
troposphere
COS → H2S
DMS → *MSA
SO2 → *SO4 2-
CS2 →
MSH, DMDS →
* = s deposition in this form
land-ocean transport
ocean-land transport
SO4 2- ← COS, CS2, DMDS
DMS, MSH
H2S
SO(x)
SO2
H2S
SO2
aeolian weathering
deposition
SO4 2- ← COS CS2
DMS
sea-spray
deposition
OM hν COS
SO4 2-
CS2
DMSP
algae
DMS
Anthropogenic sources
Volcanic emissions
Pedosphere/ lithosphere
Inland aquatic systems
Ocean

and SO_2, and organic molecules, including dimethyl sulfide (DMS), methanethiol (MSH), and dimethyl disulfide (DMDS).

1.1. Global and climatic significance of sulfur emissions

1.1.0. Magnitude and climatic significance

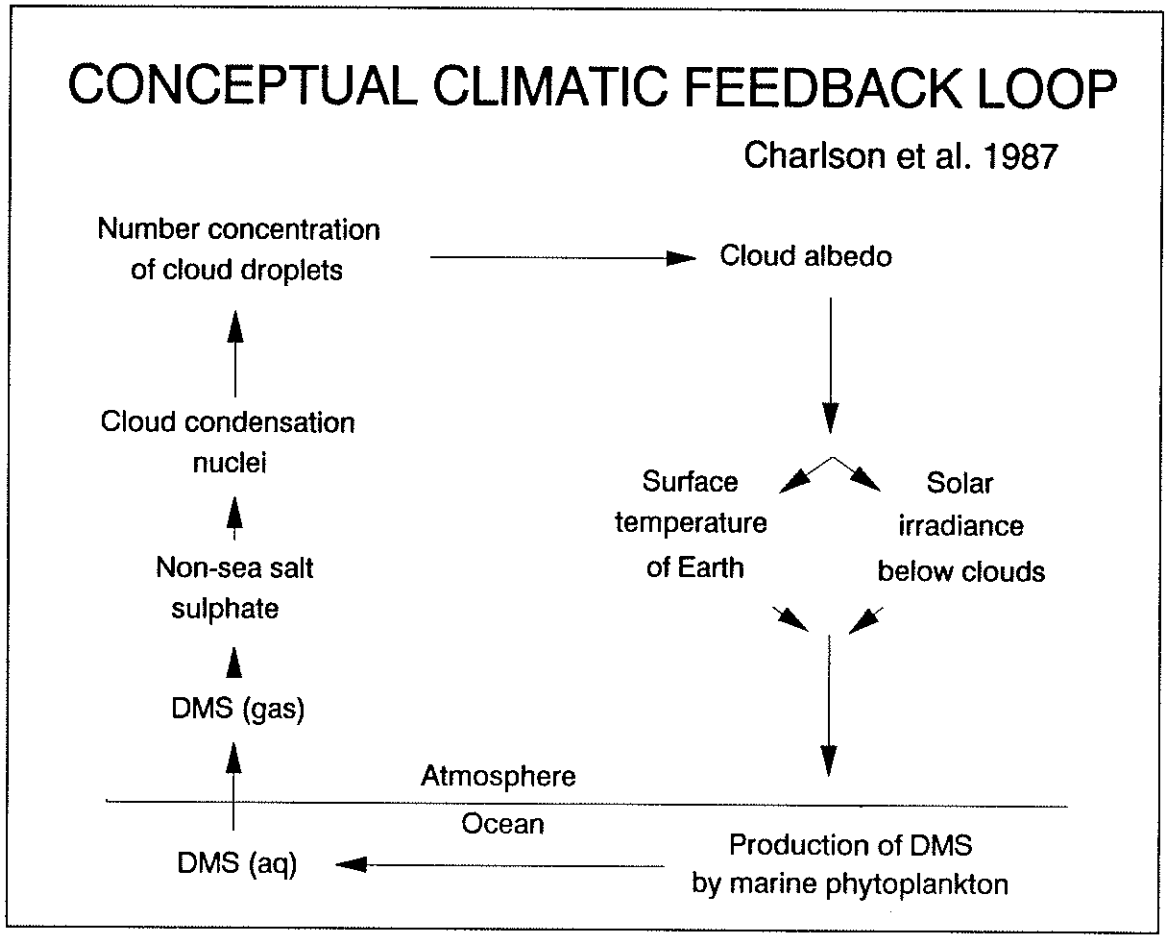
The production of volatile sulfur received particular interest in the late 1960's and 1970's when attempts were made to construct global models of sulfur cycling. Contrary to current theories of the time, atmospheric analyses indicated patterns of sulfur distribution inconsistent with an exclusively anthropogenic origin (Ericksson 1963). These early budgets identified the need for a natural source of precursors for non-sea-salt sulfate ($NSS\text{-}SO_4^{2-}$) in the atmosphere over the oceans. The magnitude of $NSS\text{-}SO_4^{2-}$ flux required by these early budgets was substantial, 35-270 Tg S yr^{-1} (Granat et al. 1976, Ericksson 1963). It was presumed that the volatile sulfur precursor was H_2S (Conway 1942, Junge 1963, Kellogg 1972, Ericksson 1963) until Lovelock et al. (1972) found an organic species, DMS, to be ubiquitous in ocean surface waters at nanogram levels. The aqueous concentrations indicated that DMS was super-saturated with respect to the overlying air, and that there would be a net flux to the atmosphere. This finding focussed considerable attention on the production of DMS and other organic

volatile species in marine environments.

Oceanic DMS emissions are currently estimated to contribute approximately 19-54 Tg S yr^{-1} to the atmosphere (Andreae 1990). The magnitude of this flux is approximately 25-50% of anthropogenic sulfur emissions, and is sufficient to account for methane sulfonic acid (MSA) and NSS-SO_4^{2-} in the marine atmosphere (Andreae 1990). Atmospheric concentrations of DMS typically range from 0.2-400 ng S m^{-3} (Andreae 1985, Andreae and Raemdonck 1983, Barnard et. al. 1982, Nguyen et. al. 1983, Andreae and Andreae 1988).

Beyond the significance to the global sulfur cycle, the atmospheric chemistry of DMS and other organic species can be important in climate regulation. Tropospheric oxidation of reduced atmospheric sulfides such as DMS and MSH is initiated by hydroxyl radicals ($OH^{\cdot}$) and to a lesser extent by nitrate radicals ($NO_3^{\cdot}$) (see below; Tyndall and Ravishankara 1989). Sulfate (SO_4^{2-}), one of the final oxidation products, acts as a nucleus for water condensation and therefore influences cloud formation and albedo, affecting both heat absorption and attenuation of incoming solar radiation (Fig. 1.2; Charlson et al. 1987, Andreae 1990). Furthermore, the oxidation of reduced sulfur compounds to species like SO_4^{2-}, SO_2, and MSA (Plane 1989) contributes to the natural acidity of precipitation (Lovelock et al. 1972, Nriagu et al. 1987, Charlson et al. 1987).

Figure 1.2. Conceptual climatic feedback loop (adapted from Charlson et al. 1987) showing how DMS emissions may affect cloud formation.


CONCEPTUAL CLIMATIC FEEDBACK LOOP
Charlson et al. 1987
Number concentration of cloud droplets
Cloud albedo
Cloud condensation nuclei
Surface temperature of Earth
Solar irradiance below clouds
Non-sea salt sulphate
DMS (gas)
Atmosphere
Ocean
DMS (aq)
Production of DMS by marine phytoplankton

Carbonyl sulfide (COS) is also found in ocean surface water at concentrations usually greater than equilibrium with the overlying atmosphere, approximately 0.03-1.0 nM (Rasmussen et al. 1982, Ferek and Andreae 1984, Andreae 1990). It is more stable in the troposphere than the other sulfur gases such as DMS and is therefore the only sulfur species to enter the stratosphere (Fig. 1.1), with the exception of SO_2 from volcanic emisssions (Andreae 1990). During volcanically quiescent periods, COS oxidation in the stratosphere is thought to maintain the stratospheric SO_4^{2-} aerosol layer (Crutzen 1976, Inn et al. 1979), which affects incoming solar radiation and is involved in processes such as ozone depletion (Hofmann 1990). It has even been suggested that changes in the SO_4^{2-} aerosol layer may have a greater impact on climate than perturbations in atmospheric CO_2 concentrations (Shaw 1983). The identification of the role of these volatile sulfur species in global sulfur cycling and climate regulation has led to renewed interest in potential sources and sinks of volatile sulfur.

1.1.1. Atmospheric and aqueous transformations

Atmospheric transformations of biogenic volatile sulfur are largely oxidation reactions, and involve a conversion from gaseous to aerosol or solute forms (Figs. 1.1, 1.2; Charlson et. al. 1985). In general, production from

biogenic sources transfers sulfur to the atmosphere in a reduced (-2) oxidation state (e.g. DMS, DMDS). Subsequent chemical reactions oxidize the sulfur to the (+4), and then to the (+6) oxidation level. One exception to this general pattern is the hypothesized reactions of COS to form H_2S (Fig. 1.1; Elliott et. al. 1987). Reported atmospheric concentrations of DMS, MSH, and COS range from 0.2-400 ng S m^{-3}, <0.96-48 ng S m^{-3}, and 580-1370 ng S m^{-3}, respectively (Andreae et. al. 1985, Andreae and Raemdonck 1983, Barnard et. al. 1982, Nguyen et. al. 1983, Belviso et. al. 1987, Berresheim 1987, Luczewski et. al. 1985). The principal products of the oxidation reactions, MSA and SO_4^{2-}, are then removed from the atmosphere by wet and dry deposition (Fig. 1.1; Charlson et. al. 1985).

Atmospheric reactions are largely mediated by $OH^{\cdot}$, oxygen (O_2), and $NO_{(x)}$ (Plane 1989, Hatakeyama 1989). With DMS and MSH, the oxidation is thought to occur largely through formation of methylthiyl radicals ($CH_3S^{\cdot}$; Tyndall and Ravishankara 1989), and can be accelerated by the presence of halogen oxides, particularly iodine oxide (IO; Barnes et. al. 1989). Atmospheric chemical residence times estimated for DMS range from 8-36 hours (Barnes et. al. 1989, Van Valin et. al. 1987).

Values for Henry's law constants (Adewuyi 1989, Tsuj et. al. 1990) indicate appreciable solubility of organic VSCs in water. Like the atmospheric reactions described

above, the solution chemistry of organic VSCs is dominated by oxidation reactions. Environmental oxidants such as hydrogen peroxide (H_2O_2), O_2, $OH^{\cdot}$, ozone (O_3), and chlorine (Cl_2), in addition to processes such as metal catalysis and photo-oxidation, contribute to liquid phase conversions (Adewuyi 1989). Because the thiolate anion is readily oxidized, species such as MSH and H_2S can undergo rapid conversion especially in alkaline medium. However, microbial decomposition of species like DMS is expected to be a more important sink (Kiene and Bates 1990).

1.2. Some significant natural sources of volatile sulfur

1.2.0. Microbial formation

The volatilization of sulfur during the microbial decomposition of organic matter has been recognized for more than 100 years. Volatile sulfur species and their specific precursors underwent initial investigations in the early part of this century. Tanner (1917, 1918) described the production of H_2S from sulfur-containing organic matter such as peptone and cystine by bacterial and fungal cultures. This was the first indication that simple organisms like yeasts were capable of splitting carbon-sulfur linkages. A succession of studies were conducted on sulfur transformations by micro-organisms, particularly fungi, in

the ensuing decades (reviewed by Bremner and Steele 1978).

Research into the biological methylation of sulfur led to important advances in understanding microbial sulfur metabolism. The interest in methylation arose from the fatal effects of "Gosio Gas" or trimethylarsine (Challenger 1951) produced by the fungal methylation of arsenic contained in wallpaper pigments. The ability of micro-organisms, particularly moulds, to carry out methylation reactions was therefore a subject of considerable interest. Initial experiments were conducted on selenium and tellurium (Rosenheim 1902), before being extended to sulfur in the 1930's. Challenger and Rawlings (1937) and Blackburn and Challenger (1938) studied the cleavage and methylation of aliphatic disulfides by *Penicillium brevicaule*. Birkinshaw, Findlay, and Webb (1942) first demonstrated methylation of an inorganic sulfur species, SO_4^{2-}, to MSH by *Schizophyllum commune* Fr. Investigations of the underlying mechanism for this reaction led to the discovery of the fission of alkyl-sulfur-carbon links by the fungus (Challenger and Charlton 1947), and was the first discovery of such a biochemical reaction in micro-organisms. This type of fission and methylation activity was found to extend to diallyl disulfide (Challenger and Greenwood 1949) and appeared to be a general action on simple aliphatic disulfides. Volatile sulfur products, DMS and MSH, were detected as products of these reactions, and study of mechanisms underlying this

fission led to an early understanding of the production of organic volatile sulfur species by micro-organisms (Stahl et al. 1949, Challenger 1951). However, as late as 1989, the enzymology of the reactions had not been fully elucidated (Taylor and Kiene 1989).

Extensive investigations into the environmental production of these organic volatile species began initially in the context of soil ecology. De Barjac (1952) and Greenwood and Lees (1956) detected mercaptan-like odours from soil treated with methionine. Frederick et al. (1957) identified MSH and DMDS from soils amended with methionine. This breakdown of methionine yielding volatile sulfur species was later determined to be a general ability of bacteria, actinomycetes, and fungi (Segal and Starkey 1969, Freney 1967).

There is significantly less knowledge about the production of COS and carbon disulfide (CS_2). COS was found be be evolved from pesticides in soil (Moje et al. 1964, Somers et al. 1967), and during anaerobic decomposition of manures (Elliott and Travis 1973). Banwart and Bremner (1975, 1976a,b) extended this knowledge by examining specific sulfur-containing precursors in their amended soil studies (Bremner and Steele 1978, Banwart and Bremner 1975, 1976 a,b). The production of CS_2 from sulfur-containing amino acids in soils (Banwart and Bremner 1975) was the first indication this species could be derived from

microbial activity.

In the last ten years, a considerable amount of effort has been focussed on biological mechanisms of volatile sulfur production in the environment (see Saltzman and Cooper, eds. 1989). A large range of sulfur-containing precursors and their volatile products have been identified (Bremner and Steele 1978, Kadota and Ishida 1972). In addition to degradation reactions, recent work (Drotar et al. 1987) has examined the methylation of H_2S to MSH and DMS by a wide range of organisms. Due to the emphasis on marine DMS, the production of this species during the breakdown of dimethyl sulfoniopropionate (DMSP) is probably the most studied of all the transformations (see section on aquatic studies).

1.2.1. Chemical production

Abiotic chemical processes also contribute to organic volatile sulfur production in the environment. Species such as COS and DMDS can be produced from the oxidation of organic compounds, and in the ocean, COS is largely derived from photo-oxidation processes (Andreae 1990). The mechanism for these reactions remains obscure, but is thought to be mediated by $OH^{\cdot}$. CS_2 is one volatile species which has been identified as a precursor of COS (Turco et al. 1980). DMDS also can arise from oxidation of another

volatile organic species, MSH. This reaction is an auto-oxidation that occurs in the presence of O_2 and trace metal ions (Adewuyi 1989).

It has recently been suggested (Sorenson 1988) that MSH may form from an abiotic chemical reaction between H_2S and CH_4 in sediments, given the low Eh and chemical conditions that occur in this environment. This hypothesis, however, has not yet been proven. It is known that H_2S can become incorporated into organic matter via addition across unsaturated bonds (Vairavamurthy and Mopper 1989). This mechanism has been shown to produce thiols in sediments, and may contribute to the formation of MSH.

1.2.2. Release from vascular plants

One of the least studied aspects of organic volatile sulfur formation is direct release from higher plants. Laboratory studies have generally focussed on inorganic sulfur emissions like H_2S (Hallgren and Fredriksson 1982, Joshi and Hollis 1976, Winner et al. 1981, Schmidt 1986). The emission of CS_2 (Haines et al. 1989), MSH, and DMS (Schmidt 1986) has not been studied to any extent. Formation of these volatile species has been linked to defense mechanisms against nematodes, insects, and fungi (Haines et al. 1989, Zehnder and Zinder 1980, Lewis and Papavizas 1970), sulfur metabolism during excess sulfur

availability (Schmidt 1986), and osmoregulation in plants such as the marsh grasses *Spartina alterniflora* and *S. patens* (Dacey et al. 1987, Morrison and Hines 1990).

1.3. Aquatic studies

1.3.0. Marine environments

As discussed, the early global models of sulfur cycling contained an important release of H_2S from aquatic systems, particularly the oceans. This H_2S was thought to originate during organic matter decomposition in the shallow shelf areas of the ocean or in the anaerobic water and soil of tidal areas (Junge 1960, Conway 1943, Granat et al. 1976). Dissimilatory SO_4^{2-} reduction was later considered to contribute to the aquatic production of H_2S, although few studies had addressed the relative contribution of the two sources (Gunkel and Oppenheimer 1963, Denser 1970). The emphasis on oceanic H_2S as a significant source of atmospheric sulfur came under increasing criticism in the middle 1970's (Kellogg et. al. 1975). This criticism arose primarily because no H_2S was detected in ocean surface waters, and because H_2S was expected to rapidly oxidize in surface waters (Kellogg et. al. 1975). The discovery of DMS ubiquitous in ocean surface waters at nanogram concentrations (Lovelock et al. 1972) provided a viable

alternative (Fig. 1.1).

Phytoplankton were identified as the principal source of this DMS based on (i) the wide distribution of a DMS precursor (DMSP) in algae (Challenger 1951, Ackman et. al. 1966, Cantoni and Anderson 1956, White 1982) and (ii) correlative studies examining DMS and Chl *a* distributions in the oceans (Andreae and Raemdonck 1983, Nguyen 1978). DMSP had been studied for some time (Challenger 1951; Ackman et al. 1966, Tocher et al. 1966) and the initial detection of DMS in two marine algae, *Polysiphonia fastigiata* and *P. nigrescens*, was made as early as 1935 (Haas 1935). Other S-methyl sulfonium compounds such as S-methyl methionine (Iida et al. 1985, Schiff 1962, White 1982) and phosphatidyl sulfocholine (Anderson et al. 1976) may contribute to DMS release from algae but are expected to play a very minor role as DMS precursors. The relationship between DMS and Chl *a* has retained a statistical significance in more recent studies (Andreae 1990), but is complicated by significant differences in DMS output by different algal species (Keller et. al. 1989, Andreae 1990).

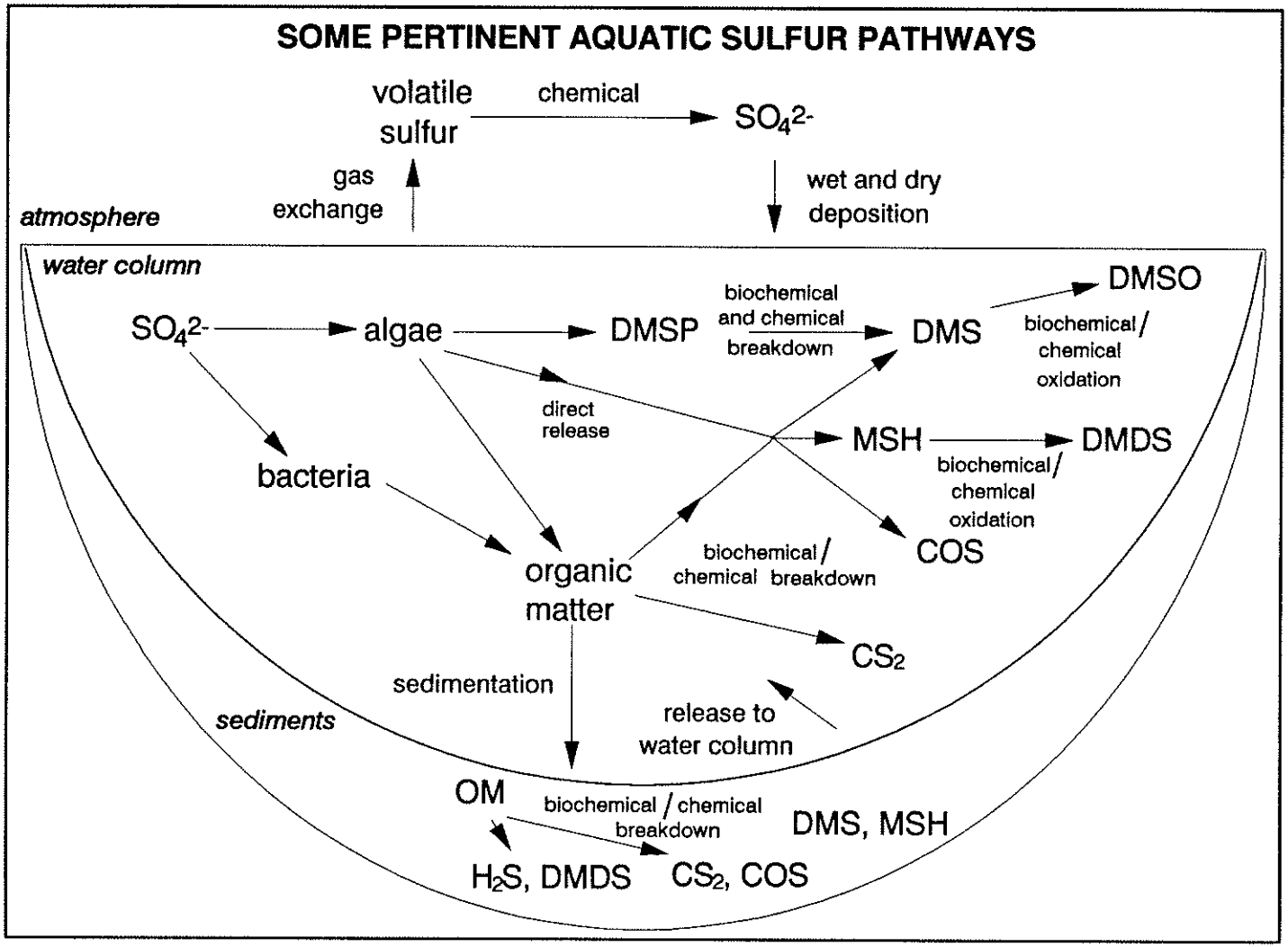
The initial measurements of DMS by Lovelock et. al. (1972) indicated DMS concentrations of 0.19 $\pm$ 0.44 nM in ocean surface waters. Subsequent studies, however, have often reported DMS concentrations of 1-2 orders of magnitude greater than the initial measurements (Andreae and Raemdonck 1983, Gibson et. al. 1988, Cooper and Matrai 1989). Mean

concentrations of oceanic DMS vary about 2-fold from 1.8 nM (Bates et. al. 1987) to 4.9 nM (Andreae 1990), depending on the region studied.

The production of DMS from algal DMSP is dependent on a variety of decomposition mechanisms. One of these processes, chemical breakdown due to $OH^{\cdot}$ (Dacey and Blough 1987), does not occur at a sufficiently high rate to account for observed DMS concentrations. Enzymatic processes, therefore, are likely more important. Microbial decomposition, for example, is considered to contribute significantly to the conversion of DMSP to DMS (Kiene 1990) in seawater (Fig. 1.3). Furthermore, high rates of sulfur volatilization have been observed from freshwaters during microbial decomposition of organic matter (Jenkins et al. 1967, Juttner 1981). It is now known that in addition to microbial decomposition, breakdown of DMSP during zooplankton grazing on algal cells can be a significant source of DMS (Dacey and Wakeham 1986).

CS_2 and COS are two other organic VSCs frequently detected in ocean surface waters (Figs. 1.1, 1.3; Lovelock 1974, Andreae 1990, Rasmussen et. al. 1982, Ferek and Andreae 1983, 1984, Turner and Liss 1985). CS_2 was first observed by Lovelock (1974) at a concentration of 0.014 nM. More recent determinations verify this initial value reporting a mean oceanic concentration of approximately 0.016-0.033 nM (Andreae 1990). This CS_2 is likely produced

Figure 1.3. Simplified scheme of how organic volatile sulfur compounds can be produced from sulfate in aquatic environments.


SOME PERTINENT AQUATIC SULFUR PATHWAYS
volatile sulfur
chemical
SO_4^{2-}
gas exchange
wet and dry deposition
atmosphere
water column
SO_4^{2-}
algae
DMSP
biochemical and chemical breakdown
DMS
DMSO
biochemical / chemical oxidation
direct release
MSH
DMDS
biochemical / chemical oxidation
bacteria
COS
organic matter
biochemical / chemical breakdown
CS_2
sedimentation
release to water column
sediments
OM
biochemical / chemical breakdown
DMS, MSH
H_2S, DMDS
CS_2, COS

from organic matter breakdown (Andreae 1990). COS is one other organic species that has been detected at concentrations in ocean surface waters of 0.03-1.0 nM (Rasmussen et. al. 1982, Ferek and Andreae 1983, 1984, Turner and Liss 1985). COS is believed to form from photo-oxidation of sulfur-containing organic matter, largely due to UV-B radiation and the presence of humic and fulvic acids (Andreae 1990, Zepp and Andreae 1989).

1.3.1. Freshwater environments

Fewer studies of inland lakes, both freshwater and salt water, are reported compared to the marine research. The evidence that oceanic DMS was derived from an osmoregulatory compound (DMSP) suggested freshwater systems would have very much lower concentrations of DMS (Turner and Liss 1985). However, early investigations of freshwaters (Bechard and Rayburn 1979) indicated that very high (up to 70,000 ng S $litre^{-1}$) concentrations of DMS could be found in the freshwaters of lakes and ponds. Challenger et al. (1957) reported large releases of DMS during alkali additions to the freshwater algae *Oedogorium* sp. and *Ulothrix* sp., suggesting the presence of DMSP. However, a more complex system exists in lakes due to the potential role of both sedimentary and water column production and destruction, and the greater diversity of volatile species (Wajon et al.

1985, Juttner et al. 1986, Hofbauer and Juttner 1988, Juttner 1983, Henatsch and Juttner 1990). The spectrum of species found in lakes included MSH, CS_2, DMDS, dimethyl trisulfide, diisopropyl disulfide, and diisopropyl trisulfide. Several of these studies have identified phytoplankton as the source of these species (Juttner et. al. 1986, Hofbauer and Juttner 1988, Juttner 1983, Bechard and Rayburn 1979), whereas others have identified sedimentary decomposition as the origin (Zinder and Brock 1978, Henatsch and Juttner 1988).

As described earlier, Bechard and Rayburn (1979), who made some of the initial measurements of DMS, MSH, and DMDS in freshwater systems, found species such as DMS produced largely during decomposition of algal cultures. Zinder et al. (1977) studied decomposition processes in blue-green algal mats and found significant production of MSH. However, microbial decomposition was not responsible for all of this production as Rasmussen (1974) and Bechard and Rayburn (1979) reported release of DMS, MSH, and DMDS by axenic cultures of freshwater algae (Fig. 1.3). In addition to algal material, microbial decomposition of exogenous organic matter such as methoxylated aromatic monomers (lignin components) have also been shown to contribute to freshwater concentrations of DMS and MSH (Finster et al. 1990). Until the initiation of this project, however, no systematic characterization of a wide range of interior

lakes had been undertaken, nor had there been a comprehensive study of sites of production of the various volatile species.

1.4. Objectives of this study

This study was designed to place lakes in the context of the global atmospheric sulfur cycle, and determine the significance of volatile sulfur species in lake sulfur cycling. At the time this work was initiated, almost no data were available on organic volatile sulfur in lakes. One of the principal objectives, therefore, was to identify and quantify species in a wide range of lakes and wetland areas. This work has studied in detail over 20 lakes and wetlands, which exhibit large differences in water chemistry and topographical and geographical situation including vegetation and climate (Table 1.1). The results have been significant in gaining an understanding of the spectrum of species and concentrations that are typical of different inland aquatic systems.

In addition to this descriptive approach, underlying mechanistic and process work was conducted leading to an increased understanding of (i) the importance of organic volatile sulfur formation in freshwater lake sulfur cycling (ii) rates of formation and destruction in the water column and sediments of lakes (iii) the contribution inland aquatic

Table 1.1. Systems studied.

Region	Lake/playa/wetland	Chemical characterization
Experimental Lakes Area, northwestern Ontario	303	freshwater Canadian Shield lakes
	114	
	302 South	
	302 North	
	226 South	
	239	
	NE bog on 239	
	304	
	661	
	225	
	221	
	470	
Northwestern Ontario Lake Size Series	Green	freshwater Canadian Shield lakes
	Linge	
	Sydney	
	Orange	
	Musclow	
	Trout	
Hudson Bay Lowlands	Kinosheo	freshwater wetland
	Interior Fen	
	Coastal Fen	
Salt Lakes, Southern Saskatchewan*	Humboldt	hyposaline
	Patience	hypersaline
	Waldsea	mesosaline
	Big Quill	hypersaline
	Little Manitou	hypersaline
	Chaplin East	hypersaline
	Chaplin West	hypersaline

* Classification of salt systems from Hammer 1986.

Briefly: hyposaline, 3-20 g litre^{-1}; mesosaline, 20-50 g litre^{-1}; hypersaline, >50 g litre^{-1}.

systems make to atmospheric sulfur, and (iv) the relationship between sulfate concentration, salt concentration, and organic volatile sulfur concentrations in hypersaline environments. This work is presented in four sections. Two chapters describe in detail the organic volatile sulfur characteristics of freshwater and sulfate-dominated salt lakes. The next two chapters concentrate on process studies describing the sites of MSH and DMS production and loss in a hypersaline and freshwater lake and the formation of organic volatile sulfur by short-term sulfate reduction.

1.5. References

Ackman, R. G., C. S. Tocher, and J. McLachlan. 1966. Occurrence of dimethyl-ß-propiothetin in marine phytoplankton. J. Fish. Res. Bd. Can. 23: 357-364.

Adewuyi, Y. G. 1989. Oxidation of biogenic sulfur compounds in aqueous media, p. 529-559. In E. S. Saltzman and W. J. Cooper [eds.], Biogenic Sulfur in the Environment. ACS 393.

Anderson, R., M. Kates, and B. E. Volcani. 1976. Sulphonium analogue of lecithin in diatoms. Nature 263: 51-53.

Andreae, M. O. 1990. Ocean-atmosphere interactions in the global biogeochemical sulfur cycle. Mar. Chem. 30: 1-29.

Andreae, M. O., and T. W. Andreae. 1988. The cycle of biogenic sulfur compounds over the Amazon basin. 1. Dry season. J. Geophys. Res. 93: 1487-1497.

Andreae, M. O., R. J. Ferek, F. Bermond, K. P. Byrd, R. T. Engstrom, S. Hardin, P. D. Houmere, F. LeMarrec, and H. Raemdonck. 1985. Dimethyl sulfide in the marine atmosphere. J. Geophys. Res. 900: 12,891-12,900.

Andreae, M. O., and H. Raemdonck. 1983. Dimethyl sulfide in the surface ocean and the marine atmosphere: a global view. Science 221: 744-747.

Banwart, W. L., and J. M. Bremner. 1976a. Volatilization

of sulfur from unamended and sulfate-treated soils. Soil. Biol. Biochem. 8: 19-22.

Banwart, W. L., and J. M. Bremner. 1976b. Evolution of volatile sulfur compounds from soils treated with sulfur-containing organic materials. Soil Biol. Biochem. 8: 439-443.

Banwart, W. L., and J. M. Bremner. 1975. Formation of volatile sulfur compounds by microbial decomposition of sulfur-containing amino acids in soils. Soil Biol. Biochem. 7: 359-364.

de Barjac, H. 1952. Contribution a l'etude due metabolisme des acides amines soufres, et specialement de la methionine dans le sol. Ann. Inst. Pasteur. 82: 623-628.

Barnes, I., V. Bastian, K. H. Becker, and D. Martin. 1989. Fourier transform IR studies of the reactions of dimethyl sulfoxide with OH, NO_3, and Cl radicals, p. 476-488. In Barnard, W. R., M. O. Andreae, W. E.

Watkins, H. Bingemer, W.-W. Georgii. 1982. The flux of dimethylsulfide from the oceans to the atmosphere. J. Geophys. Res. 87: 8787-8793.

Bates, T. S., J. D. Cline, R. H. Gammon, and S. R. Kelly-Hansen. 1987. Regional and seasonal variations in the flux of oceanic dimethylsulfide to the atmosphere. J. Geophys. Res. 92: 2930-2938.

Bechard, M. J., and W. R. Rayburn. 1979. Volatile organic

sulfides from freshwater algae. J. Phycol. 15: 379-383.

Belviso, S., N. Mihalopoulos, and B. A. Nguyen. 1987. The supersaturation of carbonyl sulfide (OCS) in rain waters. Atmos. Environ. 21: 1363-1367.

Berresheim, H. 1987. Biogenic sulfur emissions from the sub-Antarctic and Antarctic oceans. J. Geophys. Res. 92: 13,245-13,262.

Birkinshaw, J. H., W. P. K. Findlay, and R. A. Webb. 1942. Biochemistry of the wood-rotting fungi. 3. The production of methyl mercaptan by *Schizophyllum commune* Fr. Biochem J. 36: 526-529.

Blackburn, S., and F. Challenger. 1938. The formation of organo-metalloidal and similar compounds by micro-organisms. Part VI. Further studies on the fission of the disulphide link. J. Chem. Soc.: 1872-1878.

Bremner, J. M., and C. G. Steele. 1978. Role of micro-organisms in the atmospheric sulfur cycle, p. 155-201. In M. Alexander [Ed.], Adv. Microbiol. Ecol. Plenum.

Cantoni, G. L., and D. G. Anderson. 1956. Enzymatic cleavage of dimethylpropiothetin by *Polysiphonia Lanosa*. J. Biol. Chem. 222: 171-177.

Challenger, F. 1951. Biological methylation. Adv. Enzymol. XII. Nord, F. F., ed.

Challenger, F., R. Bywood, P. Thomas, and B. J. Hayward. 1957. Studies on biological methylation. XVII. The

natural occurrence and chemical reactions of some thetins. Arch. Biochem. Biophys. 69: 514-523.

Challenger, F., and P. T. Charlton. 1947. Studies on biological methylation. Part X. The fission of the mono- and di-sulphide links by moulds. J. Chem. Soc.: 424-429.

Challenger, F., and D. Greenwood. 1949. Sulphur compounds of the genus *Allium*: detection of *n*-propylthiol in the onion. The fission and methylation of diallyl disulphide in cultures of *Scopulariopsis brevicaulis*. Biochem. J. 44: 87-91.

Challenger, F., and A. A. Rawlings. 1937. The formation of organo-metalloidal and similar compounds by micro-organisms. Part V. Methylated alkyl sulphides. The fission of the disulphide link. J. Chem. Soc.: 868-875.

Charlson, R. J., W. L. Chameides, and D. Kley. 1985. The transformations of sulfur and nitrogen in the remote atmosphere background paper, p. 67-80. In J. N. Galloway et. al. [Eds.], The Biogeochemical Cycling of Sulfur and Nitrogen in the Remote Atmosphere. D. Reidel.

Charlson, R. J., J. E. Lovelock, M. O. Andreae, and S. G. Warren. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo, and climate. Nature 326: 655-661.

Conway, E. J. 1942. Mean geochemical data in relation to oceanic evolution. Proc. Roy. Irish Acad. 48: 119-159.

Cooper, W. J., and P. A. Matrai. 1989. Distribution of dimethyl sulfide in the oceans, p. 140-151. In E. S. Saltzman and W. J. Cooper [Eds.], Biogenic sulfur in the Environment. ACS 393.

Crutzen, P. J. 1976. The possible importance of COS for the sulfate layer of the stratosphere. Geophys. Res. Lett. 3: 73-76.

Dacey, J. W. H., and N. V. Blough. 1987. Hydroxide decomposition of dimethylsulfoniopropionate to form dimethyl sulfide. Geophys. Res. Lett. 14: 1246-1249.

Dacey, J. W. H., G. M. King, and S. G. Wakeham. 1987. Factors controlling emission of dimethylsulphide form salt marshes. Nature 330: 643-645.

Dacey, J. W. H., and S. G. Wakeham. 1986. Oceanic dimethylsulfide: production during zooplankton grazing on phytoplankton. Science 233: 1314-1316.

Denser, W. G. 1970. Carbon-13 in Black Sea waters and implications for the origin of hydrogen sulfide. Science 168: 1575-1577.

Drotar, A., G. A. Burton, Jr., J. E. Tavernier, and R. Fall. 1987. Widespread occurrence of bacterial thiol methyltransferases and the biogenic emission of methylated sulfur gases. Appl. Environ. Microbiol.

53: 1626-1631.

Elliott, S., E. Lu, and F. S. Rowland. 1987. Carbonyl sulfide hydrolysis as a source of hydrogen sulfide in open ocean seawater. Geophys. Res. Lett. 14: 131-134.

Elliott, L. F., and T. A. Travis. 1973. Detection of carbonyl sulfide and other gases emanating from beef cattle manure. Soil Sci. Soc. Am. Proc. 37: 700-702.

Ericksson, E. 1963. The yearly circulation of sulfur in nature. J. Geophys. Res. 68: 4001-4008.

Ferek, R. J., and M. O. Andreae. 1984. Photochemical production of carbonyl sulphide in marine surface waters. Nature 307: 148-150.

Finster, K., G. M. King, and F. Bak. 1990. Formation of methylmercaptan and dimethylsulfide from methoxylated aromatic compounds in anoxic marine and freshwater sediments. FEMS Microbiol. Ecol. 74: 295-302.

Frederick, L. R., Starkey, R. L., Segal, W. 1957. Decomposability of some organic sulfur compoiunds in soil. Soil Sci. Soc. Am. Proc. 21: 287-292.

Freney, J. R. 1967. Sulfur-containing organics, p. 229-259. In A. D. McLaren and G. H. Peterson, [Eds.]. Soil Biochemistry, Vol. 1. Marcel Dekker. New York.

Gibson, J. A. E., R. C. Garrick, H. R. Burton, A. R. McTaggart. 1988. Dimethylsulfide concentrations in the ocean close to the Antarctic continent. Geomicrobiol. J. 6: 179-184.

Granat, L., H. Rodhe, and R. O. Hallberg. 1976. The global sulphur cycle, p. 89-134. In B. H. Svensson and R. Soderlund [Eds.], Nitrogen, Phosphorus and Sulphur-Global Cycles. SCOPE 7. Ecol. Bull. 22.

Greenwood, D. J., and H. Lees. 1956. Studies on the decomposition of amino acids in soils. 1. A preliminary survey of techniques. Plant Soil 7: 253-268.

Gunkel, W., and C. H. Oppenheimer. 1963. Experiments regarding the sulfide formation in sediments of the Texas Gulf Coast, p. 674-684. In C. H. Oppenheimer [Ed.], Symposium on Marine Microbiology. Springfield.

Haas, P. 1935. The liberation of methyl sulphide by seaweed. Biochem. J. 29: 1297-1299.

Haines, B., M. Black, and C. Bayer. 1989. Sulfur emissions from roots of the rain forest *Stryphnodendron excelsum*, p. 58-69. In E. S. Saltzman and W. J. Cooper [Eds.], Biogenic Sulfur in the Environment. ACS 393.

Hallgren, J.-E., and S.-A. Fredriksson. 1982. Emission of hydrogen sulfide from sulfur dioxide-fumigated pine trees. Plant Physiol. 70: 456-459.

Hammer, U. T. 1986. The saline lake concept, p. 5-15. In U. T. Hammer, Saline lake ecosystems of the world. Dr. W. Junk.

Hatakeyama, S. 1989. Mechanisms for the reaction of CH_3S with NO_2, p. 459-463. In E. S. Saltzman and W. J. Cooper [Eds.], Biogenic Sulfur in the Environment. ACS

393.

Henatsch, J. J., and F. Juttner. 1990. Occurrence and distribution of methanethiol and other volatile organic sulphur compounds in a stratified lake with anoxic hypolimnion. Arch. Hydrobiol. 119: 315-323.

Hofbauer, B., and F. Juttner. 1988. Occurrence of isopropylthio compounds in the aquatic ecosystem (Lake Neusiedl, Austria) as a chemical marker for *Microcystis flos-aquae*. FEMS Microbiol. Ecol. 53: 113-122.

Hofmann, D. J. 1990. Increase in the stratospheric background sulfuric acid aerosol mass in the past 10 years. Science 248: 996-1000.

Inn, E. C. V., I. F. Vedder, B. J. Tyson, and D. O'Hara. 1979. COS in the stratosphere. Geophys. Res. Lett. 6: 191-193.

Iida, H., K. Nakanura, and T. Tokunaga. 1985. Dimethyl sulfide and dimethyl-ß-propiothetin in sea algae. Bull. Jap. Soc. Sci. Fish. 51: 1145-1150.

Jenkins, D., L. L. Medsker, and J. F. Thomas. 1967. Odourous compounds in natural waters. Some sulfur compounds associated with blue-green algae. Environ. Sci. Technol. 1: 731-735.

Joshi, M. M., and J. P. Hollis. 1977. Interaction of *Beggiatoa* and rice plant: detoxification of hydrogen sulfide in the rice rhizosphere. Science 195: 179-180.

Junge, C. E. 1963. Sulfur in the atmosphere. J. Geophys. Res. 68: 3975-3976.

Junge, C. E. 1960. Sulfur in the atmosphere. J. Geophys. Res. 65: 227-237.

Juttner, F. 1983. Volatile odorous excretion products of algae and their occurrence in the natural aquatic environment. Wat. Sci. Tech. 15: 247-257.

Juttner, F. 1981. Biologically active compounds released during algal blooms. Verh. Internat. Verein. Limnol. 21: 227-230.

Juttner, F., B. Hoflacher, and K. Wurster. 1986. Seasonal analysis of volatile organic biogenic substances (VOBS) in freshwater phytoplankton populations dominated by *Dinobryon*, *Microcystis*, and *Aphanizomenon*. J. Phycol. 22: 169-175.

Kadota, H., and Y. Ishida. 1972. Production of volatile sulfur compounds 1591 by microorganisms. Ann. Rev. Microbiol. 26: 127-138.

Kellogg, W. W., R. D. Cadle, E. R. Allen, A. L. Lazrus, and E. A. Martell. 1972. The sulfur cycle. Science 175: 587-596.

Kiene, R. P. Dimethyl sulfide production from dimethylsulfoniopropionate in coastal seawater samples and bacterial cultures. Appl. Environ. Microbiol. 56: 3292-3297.

Kiene, R. P., and T. S. Bates. 1990. Biological removal of

dimethyl sulphide from sea water. Nature 345: 702-705.

Kluczewski, S. M., K. A. Brown, and J. N. B. Bell. 1985. Deposition of carbonyl sulphide to soils. Atmos. Environ. 19: 1295-1299.

Lewis, J. A. and G. C. Papavizas. 1970. Evolution of volatile sulfur-containing compounds from decomposition of crucifers in soils. Soil Biol. Biochem. 2: 239-246.

Lovelock, J. E., R. J. Maggs, and R. A. Rasmussen. 1972. Atmospheric dimethyl sulphide and the natural sulphur cycle. Nature 237: 452-453.

Lovelock, J. E. 1974. CS_2 and the natural sulphur cycle. Nature 248: 625-626.

Moje, W., D. E. Munnecke, and L. T. Richardson. 1964. Carbonyl sulphide, a volatile fungitoxicant from nabam in soil. Nature 202: 831-832.

Morrison, M. C., and M. E. Hines. 1990. The variability of biogenic sulfur flux from a temperate salt marsh on short time and space scales. Atmos. Environ. 24A: 1771-1779.

Nguyen, B.C., B. Bonsang, and A. Gaudry. 1983. The role of the ocean in the global atmospheric sulfur cycle. J. Geophys. Res. 88: 10903-10914.

Nguyen, B.C., A. Gaudry, B. Bonsang, and G. Lambert. 1978. Reevaluation of the role of dimethyl sulphide in the

sulphur budget. Nature 275: 637-639.

Nriagu, J. O., D. A. Holdway, and R. D. Coker. 1987. Biogenic sulfur and the acidity of rainfall in remote areas of Canada. Science 237: 1189-1192.

Plane, J. M. C. 1989. Gas-phase atmospheric oxidation of biogenic sulfur compounds, p. 404-423. In E. S. Saltzman and W. J. Cooper [Eds.], Biogenic Sulfur in the Environment. ACS 393.

Rasmussen, R. A. 1974. Emission of biogenic hydrogen sulfide. Tellus 26: 254-260.

Rasmussen, R. A., M. A. K. Khalil, and S. D. Hoyt. 1982. The oceanic source of carbonyl sulfide (OCS). Atmos. Environ. 16: 1591-1594.

Rosenheim, O. 1902. The decomposition of selenium and tellurium by moulds and its influence on the biological test for arsenic. Proc. Chem. Soc. P. 138.

Ryaboshapko, A. G. 1983. The atmospheric sulphur cycle, p. 203-296. In M. V. Ivanov and J. R. Freney [Eds.], The Global Biogeochemical Sulphur Cycle. SCOPE 19.

Saltzman, E. S., and D. J. Cooper. 1989. Dimethylsulfide and hydrogen sulfide in marine air, p. 330-351. In E. S. Saltzman and D. J. Cooper [Eds.], Biogenic sulfur in the Environment. ACS 393.

Sandalls, F. J., and S. A. Penkett. 1977. Measurements of carbonyl sulphide and carbon disulphide in the atmosphere. Atmos. Environ. 11: 197-199.

Saltzman, E. S., and W. J. Cooper [Eds.]. 1989. Biogenic sulfur in the environment. ACS 393.

Schiff, J. A. 1962. Sulfur, p. 239-246. In R. A. Lewin [Ed.], Physiology and Biochemistry of Algae. Academic Press.

Schmidt, A. 1986. V. Regulation of sulfur metabolism in plants. Prog. Bot. 48: 133-150.

Segal, W., and R. L. Starkey. 1969. Microbial decomposition of methionine and identity of the resulting products. J. Bact. 98: 908-913.

Shaw, G. E. 1983. Bio-controlled thermostatis involving the sulfur cycle. Climatic Change 5: 297-303.

Somers, E., D. V. Richmond, J. A. Pickard. 1967. Carbonyl sulphide from the decomposition of captan. Nature 215: 214.

Sorensen, J. 1988. Dimethylsulfide and methane thiol in sediment porewater of a Danish estuary. Biogeochem. 6: 201-210.

Stahl, W. H., B. McQue, G. R. Mandels, and R. G. H. Siu. 1949. Studies on the microbiological degradation of wool. I. Sulfur metabolism. Arch. Biochem. 20: 422-432.

Tanner, F. W. 1917. Studies on the bacterial metabolism of sulfur. I. Formation of hydrogen sulfide from certain sulfur compounds under aerobic conditions. J. Bact. 2: 585-593.

Tanner, F. W. 1918. Studies on the bacterial metabolism of sulfur. II. Formation of hydrogen sulfide from certain sulfur compounds by yeast-like fungi. J. Am. Chem. Soc. 40: 663-669.

Taylor, B. F., and R. B. Kiene. 1989. Microbial metabolism of dimethylsulfide, p. 202-221. In E. S. Saltzman and W. J. Cooper [Eds.], Biogenic sulfur in the environment. ACS 393.

Tocher, C. S., R. G. Ackman, and J. McLachlan. 1966. The identification of dimethyl-ß-propiothetin in the algae *Syracosphaera carterae* and *Ulva Lactuca*. C. J. Biochem. 44: 519-522.

Tsuji, M., T. Nakano, and T. Okuno. 1990. Desorption of odor substances from water bodies to the atmosphere. Atmos. Environ. 24A: 2019-2021.

Turco, R. P., R. C. Whitten, O. B. Toon, J. B. Pollack, and P. Hamill. 1980. OCS, stratospheric aerosols, and climate. Nature 283: 283-286.

Turner, S. M., and P. S. Liss. 1985. Measurements of various sulphur gases in a coastal marine environment. J. Atmos. Chem. 2: 223-232.

Tyndall, G. S., and A. R. Ravishankara. 1989. Atmospheric reactions of CH_3S radicals, p. 450-458. In E. S. Saltzman and W. J. Cooper [Eds.], Biogenic Sulfur in the Environment. ACS 393.

Vairavamurthy, A., and K. Mopper. 1989. Mechanistic

studies of organosulfur (thiol) formation in coastal marine sediments, p. 231-242. In E. S. Saltzman and W. J. Cooper [Eds.], Biogenic sulfur in the environment. ACS 393.

Van Valin, C. C., H. Berresheim, M. O. Andreae, and M. Luria. 1987. Dimethyl sulfide over the western Atlantic ocean. Geophys. Res. Lett. 14: 715-718.

Wajon, J. E., R. Alexander, and R. I. Kagi. 1985. Dimethyl trisulphide and objectionable odours in potable water. Chemosphere 14: 85-89.

White, R. H. 1982. Analysis of dimethyl sulfonium compounds in marine algae. J. Mar. Res. 40: 529-536.

Winner, W. E., C. L. Smith, G. W. Koch, H. A. Mooney, J. D. Bewley, and H. R. Krouse. 1981. Rates of emission of H_2S from plants and patterns of stable sulphur isotope fractionation. Nature 289: 672-673.

Zehnder, A. J. B., and S. H. Zinder. 1980. The sulfur cycle, p. 105-145. In O. Hutzinger et. al. [Eds.], Environmental Chemistry. Vol. I. Part. A. The natural environment and the biogeochemical cycles. Springer-Verlag.

Zepp, R. G., and M. O. Andreae. 1989. Factors affecting the photochemical formation of carbonyl sulfide in seawater. EOS, Trans. Am. Geophys. Union 70: 1023.

Zinder, S. H., W. N. Doemel, and T. D. Brock. 1977. Production of volatile sulfur compounds during the

decomposition of algal mats. Appl. Environ. Microbiol. 34: 859-860.

2. Organic volatile sulfur in Canadian Shield lakes and its loss to the atmosphere

2.0. Acknowledgements

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2.1. Abstract

Identities, concentrations, and fluxes of volatile sulfur compounds (VSCs) were determined in eleven lakes in northwestern Ontario, Canada. Carbonyl sulfide (COS: up to 1.1 nM) and dimethyl sulfide (DMS: up to 11 nM) were present in surface-waters during most of the ice-free season. Depth profiles showed accumulations below the mixed layer of methanethiol (MSH), DMS, and dimethyl disulfide (DMDS). There was no effect of low pH or increased [SO_4^{2-}] (from 2.4 to 12.3 mg litre^{-1}) on the concentrations and identities of surface-water VSCs. Accumulation of DMS below the mixed layer was 9 times higher in an acidified system, however, compared to an unacidified reference lake.

Estimates of flux from two stratified lakes indicated that volatilization was not an important sulfur loss mechanism compared to others such as sedimentary SO_4^{2-} reduction.

Concentrations of MSH, DMS, and DMDS in shallow, Lakes 114 and 303 were often 5-30 times higher than any other lakes studied, and the flux from Lake 114 was about 0.96-1.6 times the estimated oceanic DMS flux, per unit of area. On a regional basis, in areas where SO_4^{2-} in precipitation is low, VSC export to the atmosphere from shallow lakes and bog pools may be significant compared to sulfur inputs through precipitation.

2.2. Introduction

The recognition that biogenic sulfur gases are important in the cycling of sulfur and in global climate regulation has prompted considerable interest in their production and fate. Volatile sulfur compounds (VSCs) typically identified in environmental studies include hydrogen sulfide (H_2S), dimethyl sulfide (DMS), methanethiol (MSH), carbonyl sulfide (COS), carbon disulfide (CS_2), and dimethyl disulfide (DMDS). All these compounds can be produced biologically although at least two (DMDS and COS) can form from abiotic reactions (e.g. Bremner and Steele 1978; Kadota and Ishida 1972).

Much of the research on VSCs has focussed on their production and flux from the oceans and coastal marine environments (e.g. Andreae and Barnard 1984). Lakes have received almost no attention. In this study I have identified and quantified VSCs in the water column and sediments of Canadian Shield lakes. Rates of VSC flux to the atmosphere, the importance of this loss to lake SO_4^{2-} budgets, and sites of VSC production in lakes were also studied.

2.3. Materials and methods

2.3.0. Site description. Two sets of lakes were monitored from May to October 1988 for the presence of VSCs. The first set consisted of several small (< 55 ha) lakes (226 South, 302 South, 114, 239, and 303) at the Experimental Lakes Area (ELA) in northwestern Ontario (Brunskill and Schindler 1971). Two of these lakes (Lake 302 South and Lake 114) have received experimental additions of sulfuric acid (Table 2.1). The second set of lakes was located in a geologically homogeneous area of the Canadian Shield near Red Lake, Ontario (50°N, 94°W). This set comprises larger lakes ranging in surface area from 88 ha (Green Lake) to 34,700 ha (Trout Lake) (Table 2.1). Samples were taken from surface water at the site of maximal depth in all lakes. In Trout Lake, a second site was in the center of a large, unstratified bay (z_{max} = 10 m). In Lakes 226 South and 302 South, depth profiles were obtained.

2.3.1. Sample collection. Surface samples were collected at a depth of 0.2 m by hand in silanized glass bottles. Samples from other depths were taken using a peristaltic pump and were overfilled three times before stoppering. After collection, all samples were immediately placed in the dark on ice. Analyses were conducted within 24 h of sampling; tests showed little alteration in sample integrity

Table 2.1. Morphometric parameters of the studied lakes and treatment information pertinent to 1988.

Lake	A_o (10^4 m^2)	$\bar{Z}$ (m)	Z_m (m)	$A_c:V_c$* (m^{-1})	Treatment
		ELA lakes			
226S	7.8	6.3	11.6	0.09	--
302S	10.9	5.1	10.6	0.10	H_2SO_4+
114	12.1	1.7	5.0	0.59	H_2SO_4∓
239	56.1	10.5	30.4	0.07	--
303	9.9	1.5	2.5	0.66	--
		Red Lake area lakes			
Green	88	7.7	18	0.08	--
Orange	169	14.4	28	0.05	--
Linge	706	8.4	22	0.11	--
Musclow	2219	19.3	43	0.03	--
Sydney	5750	20.0	71	0.05	--
Trout:deep	34700	13.7	47	0.07	--
shallow	--	--	10	--	

* ELA data based on Fee 1979

\+ Rudd et al. 1990 (L302S is currently acidified)

∓ Schindler and Turner 1982 (L114 was acidified from 1979-1987)

over this period (data not shown). Because of the high solubility of DMS, dip sampling of water compares well with other sampling methods (Andreae and Raemdonck 1983). COS is the least soluble, but solubility data for this compound also indicate that it should not be affected by dip sampling (Wilhelm et al. 1977).

Pore-water was obtained in two ways. In one method, sediment was collected with an Ekman corer. The surface 6 cm were transferred to silanized glass reagent bottles without headspace. Subsamples were centrifuged and the supernatant decanted and analyzed. The second method used a pore-water equilibration sampler (Hesslein 1976) with Nuclepore (2-μm) membrane, equilibrated in the sediment for 1 wk. Water from cells (4 ml each) 0-20 cm below the sediment surface was pooled for analysis.

2.3.2. Extraction of volatile sulfur compounds. VSCs were extracted and trapped cryogenically. The extraction apparatus consisted of a boiling flask, cold finger (water trap), and U-trap. To monitor sample extraction efficiency, an internal standard (DES in glycol, Holdway and Nriagu 1987) was added. Glassware was silanized with 10% dimethyldichlorosilane (Sigma Chemical Company) (Deprez et al. 1986).

In order to minimize manipulation, water samples were not filtered. There was little alteration in DMS

concentration when filtered samples were compared to unfiltered samples (data not shown), and MSH and DMDS showed no consistent change in concentration. This result suggests that the extraction procedure itself does not produce artificially DMS by disrupting dimethyl sulfoniopropionate (DMSP)-containing algal cells, a concern when analyzing for this gas in seawater.

To extract sulfur gases, a 250-ml water sample (analyzed in duplicate) was heated to approximately 65°C and sparged with UHP nitrogen (60 ml min^{-1}) for 50 min. Volatile sulfur compounds were trapped in a U-shaped tube that was filled with silanized glass wool and immersed in liquid nitrogen. Following extraction, the U-trap was evacuated, sealed, and heated to approximately 50°C. To inject the contents onto the GC column, the trap was fitted into a Carle GC sampling valve using luer connections.

2.3.3. Detection and quantification of volatile sulfur species. Sulfur gases were analyzed with a Varian 3700 gas chromatograph (GC) equipped with a dual-flame, photometric detector (FPD) at 200°C, with a Spectra-Physics model 4290 integrator. Optimal flow conditions were: H_2 (UHP), 140 ml min^{-1}; air No. 1 (zero zero), 80 ml min^{-1}; air No. 2 (zero zero), 170 ml min^{-1}; He (UHP) carrier, 40 ml min^{-1}.

A 2 m X 0.64 cm o.d., Teflon-coated aluminum column packed with 20% SE-30 on Chromsorb P AW/DMCS 60/80 mesh

(Analabs) was used with temperature programming: 35°C (1 min hold), 25°C min^{-1} to 105°C (4 min hold). These conditions provided adequate separation of H_2S, COS, MSH, DMS, DES, and DMDS, except at high H_2S concentrations when the COS peak was obscured (e.g. hypolimnetic samples in late summer).

Sulfur compounds were identified by comparing retention times to those of known sulfur standards. Confirmation was obtained by GC-mass spectrometry (see below). DMS and CS_2 had retention times of 4.6 and 4.8 min, respectively, but no CS_2 was detected with the FPD or during mass spectrometry.

Because the thiol moiety is oxidized readily, it is possible that the presence of DMDS in environmental samples resulted from the oxidation of MSH during extraction. In some environmental samples, however, e.g. Lake 114 pore-water (Table 2.2) and hypolimnetic Lake 226 samples (Table 2.3), MSH was detected in the absence of DMDS. This result suggests that MSH oxidation was limited.

H_2S was not detected by this purge-and-trap method in the epilimnetic waters of the lakes studied. Accurate measurement at the high levels found in the lake hypolimnion was not possible at the GC conditions used for the other volatile sulfur compounds. Therefore, H_2S values are not reported.

2.3.4. GC-MS analysis. To confirm the identity of the

Table 2.2. Organic VSC levels in pore-waters of Lake 114.

Date	Method	Species	Concentration(nM) Surface	Concentration(nM) Pore-water	Pore-water: Surface Water Ratio
26 Jul	centrifuged sediment	COS	0.65	Not resolved*	--
		MSH	3.7	53	14
		DMS	6.2	11	1.8
		DMDS	2.8	Not detected	--
3 Aug	*in situ* pore-water equilibration	COS	0.49	Not resolved	--
		MSH	14	120	8.9
		DMS	11	38	3.6
		DMDS	2.0	Not detected	--

* The high methane and H_2S levels found in the pore-water masked the detection of any COS present due to their similar retention times.

Table 2.3. Accumulation of organic VSCs below the mixed layer.

Lake	Compound	Accumulation rate (mmol m^{-2} d^{-1})	Hypolimnetic conditions* pH	Hypolimnetic conditions* $[SO_4^{2-}]$ (mg $litre^{-1}$)
302S	MSH	0.98	5.46-6.33	0.74-9.84
	DMS	0.57		
	DMDS	0.19		
226S	MSH	0.81	6.17-6.35	0.44-1.8
	DMS	0.066		

* The given range represents the lowest and highest values determined at a depth of 10 m from 10 May 1988 to 30 Aug 1988 for Lake 302 South, and from 30 May 1988 to 19 Sept 1988 for Lake 226 South (ELA, chemical data).

sulfur peaks, GC-mass spectrometry was conducted periodically. The column was a 10 m X 0.32 mm fused silica PoraPLOT Q capillary column (Chrompack Canada). The temperature program was: 40°C (1 min hold), 20°C min^{-1} to 220°C, then 1°C min^{-1} to 240°C (1 min hold). Water samples were extracted as described above.

GC-MS analyses, performed on the ELA lake samples at three different times, have confirmed the presence of H_2S, COS, MSH, DMS, and the internal standard, DES. No volatile sulfur species were detected during the GC-MS analyses that had not previously been identified by retention-time comparisons with sulfur standards using the FPD.

2.3.5. Calibration. Standard curves (Tangerman 1986) were determined each day of analysis in order to quantify the sulfur peaks extracted. Sulfur standards used routinely were COS (96+%), MSH (99.5+%), DMS (99+%), DMDS (99+%), and DES (98%) (all from Aldrich Chemical Company, Inc.).

2.3.6. Determination of extraction efficiencies. Extraction efficiency of each compound was determined to estimate recovery from water samples. Liquid sulfur standards were prepared by dissolution in anoxic ethylene glycol (Andreae and Barnard 1983) and dilution in distilled H_2O to concentrations similar to lakewater. Recoveries were as follows: COS, 95.0 $\pm$ 18.8%; MSH, 66.6 $\pm$ 7.4%; DMS, 96.7 $\pm$

5.1%; DMDS, 98.7 ± 6.9% (mean ± 1 S.D., n > 5 for each determination).

2.3.7. Preparation of the internal standard. The DES internal standard was prepared in anoxic ethylene glycol (Andreae and Barnard 1983, Holdway and Nriagu 1987) (99+%, spectrophotometric grade, Aldrich Chemical Company, Inc.) using silanized, 8-ml, glass, screw-capped vials fitted with Teflon-faced silicone septa. A primary standard of 300 ng ml^{-1} was prepared gravimetrically. A working standard in a second vial was made by further dilution to a final concentration of 4 ng S ml^{-1}; 25 ml of the working standard was added to environmental samples in order to determine extraction efficiency. Internal standard recovery was 92.4 ± 6.7% (mean ± S.D., n = 35).

2.3.8. Measurement of windspeed. Windspeed was measured on Lake 302 South using an anemometer (Belfort Instrument Company) equipped with a model DP101 One Channel Time of Event Recorder (Omnidata). The anemometer was placed near the lake's center; distance from the anemometer cups to the lake surface was 1 m. Windspeed was recorded from July to October. Prior to July, overlake wind speed was estimated using overland wind speed at a nearby meteorological site (K. Beaty pers. comm.), and the relationship between overlake and overland windspeeds developed from measurements

made when both sites were operating.

2.3.9. Estimation of mass transfer coefficient. The relationship between diffusive boundary-layer thickness and windspeed determined by Broecker et al. (1980) uses a wind velocity at a height of 10 m. The power-law model given in Eq. 1 (Panofsky and Dutton 1984) was used to convert the 1-m windspeed measurements to the estimated windspeed at a height of 10 m:

$$V_2/V_1 = (z_2/z_1)^p \qquad (1)$$

where: V_1 = mean windspeed at height z_1

V_2 = mean windspeed at height z_2

z_1 = height above the lake surface

z_2 = height above the lake surface

p = power law exponent

The value of p (0.24) was estimated from the relationship between power-law exponents and lake surface area (A. Solinske, University of Winnipeg, unpublished data). Diffusive boundary-layer thickness was estimated using the relationship of Broecker et al. (1980); mass transfer coefficients were then determined using the calculated molecular diffusivity of each species. The molecular diffusivity (at an annual mean temperature of 15°C) of each

compound was calculated by the method of Wilke and Chang (1955), updated by Hayduck and Laudie (1974). The estimated error of these diffusivities is approximately 10%.

The mean mass transfer coefficient on each day of analysis was used to estimate the flux of volatile sulfur species found that day in lake surface waters. On dates when the overlake wind speed was estimated from overland wind data, a mean daily wind speed was used to calculate the mass transfer coefficient for that date. The same mass transfer coefficients were used for estimating sulfur fluxes from Lakes 302 South, 226 South, 239, and 114. The diffusive boundary-layer thicknesses calculated in this study agreed well with those determined by Emerson et al. (1973) on another lake at the ELA.

2.3.10. Estimation of sulfur flux to the atmosphere. Estimates were made of sulfur loss to the atmosphere using the stagnant-film model of gas exchange (Lewis and Whitman 1924). Flux was calculated according to the equation:

$$F = k(C-C_o) \qquad (2)$$

where: F = gas exchange per unit area

k = mass transfer coefficient

C = gas concentration in the fluid phase

C_o = atmospheric concentration of the gas

The mass transfer coefficient was calculated as described above, and C_o was assumed to be negligible, based on estimates of atmospheric DMS concentrations over the ocean (Andreae et al. 1985; Barnard et al. 1982). COS has an atmospheric concentration of approximately 512 parts per trillion by volume (pptv; Torres et al. 1980) but this constitutes only 3-8% of the mean aqueous COS concentrations in the ELA lakes. This amount is within the error of the calculations, and was therefore not included in the equation. Fluxes on each day were averaged to generate the mean flux (Table 2.4). Each lake in the ELA area experiences essentially the same overlake wind. Therefore, differences in sulfur fluxes among lakes were dependent on differences in sulfur species concentrations. For this reason concentration data were analyzed in a Tukey multi-comparison test ($p < 0.05$) to determine differences in lake sulfur fluxes. A test of homogeneity of coefficients of polynomial equations (Milliken 1989) was used to test for differences in DMS temporal patterns ($p < 0.05$).

2.3.11. Calculation of accumulation rates below the mixed layer. Accumulation rates were calculated by determining the total mass of organic volatile sulfur below the mixed layer at two different times, and dividing the difference by the sediment surface area, and the elapsed time. The mass of each species was determined by multiplying the

Table 2.4. Estimates of sulfur flux to the atmosphere and its significance in lake sulfate budgets.

Lake	Species	Sulfur flux* (nmol S m^{-2} d^{-1}) Range	Mean	Sulfur lost per year via volatilization (mol yr^{-1})	%S+
302S	COS	108-540	250	6.5	0.066
	DMS	49-1,230	730	9	0.19
	DMDS	155-1,190	170	4.3	0.043
	MSH	--	--	--	--
	Total		1,150	29	0.30
Loss at fall overturn‡ (species below mixed layer)				7.5	0.07
239	COS	ND-330	170	23	0.22
	DMS	54-1,200	600	82	0.79
	DMDS	ND-410	34	4.7	0.04
	MSH	--	--	--	--
	Total		800	110	1.0
226S	COS	71-930	230	4.3	--
	DMS	106-2,370	820	16	--
	DMDS	ND-430	100	1.9	--
	MSH	ND-220	17	0.32	--
	Total		1,170	23	--
114	COS	85-1,400	440	13	0.52
	DMS	320-16,000	4,000	120	4.7
	DMDS	ND-7,500	1,900	54	2.2
	MSH	ND-25,000	6,200	190	7.4
	Total		12,500	380	15

* Assuming a negligible atmospheric concentration, and an ice-free period of 8 months.

+ $S=SO_4^{2-}$ lost within the lake as defined by the equation: I-O-Δm=S where I=input, O=outflow, and Δm=delta mass

L302S: S=9,810 moles yr^{-1} (Rudd et al. 1990)

L239: S=20.9 Keq (annual mean for 1981-1983; Schindler

(*Table 2.4, continued*)

et al. 1986)

L114: S=2450 moles (pre-acidification value from 1978; Schindler and Turner 1982)

∓ Loss at overturn assumes that the volatile species below the mixed layer were lost to the atmosphere, and chemical oxidations and conversions during mixing were negligible. Thus, it represents a maximal loss.

concentration in each depth interval by the volume of water in that interval and summing the values.

2.4. Results

2.4.0. Sulfur species and concentrations in surface waters. Five volatile sulfur compounds were identified: H_2S, COS, MSH, DMS, and DMDS (Table 2.5). The epilimnia of most lakes contained detectable concentrations of only COS (lake means: 0.09-0.61 nM, Table 2.5) and DMS (lake means: 0.48-1.6 nM, Table 2.5). H_2S, MSH, and DMDS were found generally only below the mixed layer (Figs. 2.1 and 2.2), although low levels (< 0.31 nM) of DMDS were occasionally detectable in the surface waters of Lakes 239, 226 South, and 302 South (Fig. 2.3A and B). An exception to this general pattern was found in a shallow, holomictic lake (Lake 114), where MSH and DMDS were easily detectable (up to 32 nM and 3.0 nM, respectively) at the lake surface, with COS and DMS also present (up to 1.1 and 11 nM, Fig. 2.3C, Table 2.5). Another shallow lake, Lake 303, also had elevated levels of MSH (Table 2.5).

With a few exceptions, in particular Lake 114 (Fig. 2.3C), DMS was the most abundant species (Figs. 2.3 A,B and 2.4; Table 2.5). Concentrations ranged from approximately 0.31 to 2.8 nM in most lakes, but Lake 114 commonly exhibited higher levels (up to 11 nM, Fig. 2.3C). Both the deep and shallow stations on Trout Lake, the largest lake, also had high DMS concentrations on at least one sampling date (3.6 nM and 5.1 nM for the deep and shallow stations,

Table 2.5. Time-weighted mean surface water VSC levels.

Lake		Volatile Sulfur Concentration (nM) COS	DMS	DMDS	MSH
ELA lakes					
302S	$\bar{X}$	0.36(0.11)	1.3(0.60)	0.091(0.090)	ND
	R	0.23-0.94	0.32-2.7	ND-0.31	ND
226S	$\bar{X}$	0.31(0.16)	1.3(0.5)	0.065(0.083)	0.018(0.060)
	R	ND-0.91	0.71-2.7	ND-0.28	ND-0.45
239	$\bar{X}$	0.26(0.12)	1.1(0.4)	0.020(0.050)	ND
	R	ND-0.53	0.36-2.6	ND-0.27	ND
114	$\bar{X}$	0.61(0.13)	6.6(2.9)	1.4(0.7)	8.6(5.8)
	R	0.37-1.1	0.75-11	ND-3.0	ND-32
303*	$\bar{X}$	0.38(0.15)	1.2(0.4)	0.043(0.043)	1.1(0.4)
	R	0.23-0.91	0.33-2.0	ND-0.170	ND-2.8
239 NE Bog	$\bar{X}$	NR	3.9(2.5)	0.097(0.059)	13(6)
	R	NR	0.65-11	ND-0.25	ND-38
Red Lake area lakes					
Green	$\bar{X}$	0.26(0.09)	0.95(0.37)	ND	ND
	R	ND-0.51	0.24-2.2	ND	ND
Orange	$\bar{X}$	0.12(0.16)	0.84(0.37)	ND	ND
	R	ND-0.69	0.26-2.3	ND	ND
Linge	$\bar{X}$	0.18(0.13)	0.65(0.20)	ND	ND
	R	ND-0.55	0.36-1.8	ND	ND
Musclow	$\bar{X}$	0.13(0.11)	0.48(0.19)	ND	ND
	R	ND-0.31	ND-0.94	ND	ND
Sydney	$\bar{X}$	0.16(0.08)	0.74(0.19)	ND	ND
	R	ND-0.26	0.42-1.3	ND	ND
Trout Deep	$\bar{X}$	0.19(0.10)	1.3(0.59)	ND	ND
	R	ND-0.51	0.28-3.6	ND	ND
Trout Shallow	$\bar{X}$	0.091(0.10)	1.6(1.1)	ND	ND
	R	ND-0.26	0.28-5.1	ND	ND

($\bar{X}$ = mean value from May to October given in nM, standard deviation in parentheses; R = range; ND = not detectable,

(*Table 2.5, continued*)

detection limit approx. 1 ng S; NR = not resolved due to high H_2S and CH_4 concns.)

* 303 values based on four measurements from August to October

Figure 2.1 Depth profiles of Lake 302 South determined on two separate dates. Sulfur species are as follows: (A) COS; (B) MSH; (C) DMS; (D) DMDS. The profiles were taken on two dates: 15 June 1988 (————), and 24 August 1988 (·····). The bottom of the mixed layer for each date is indicated by a horizontal line: 15 June 1988 (————), and 24 August 1988 (·····).

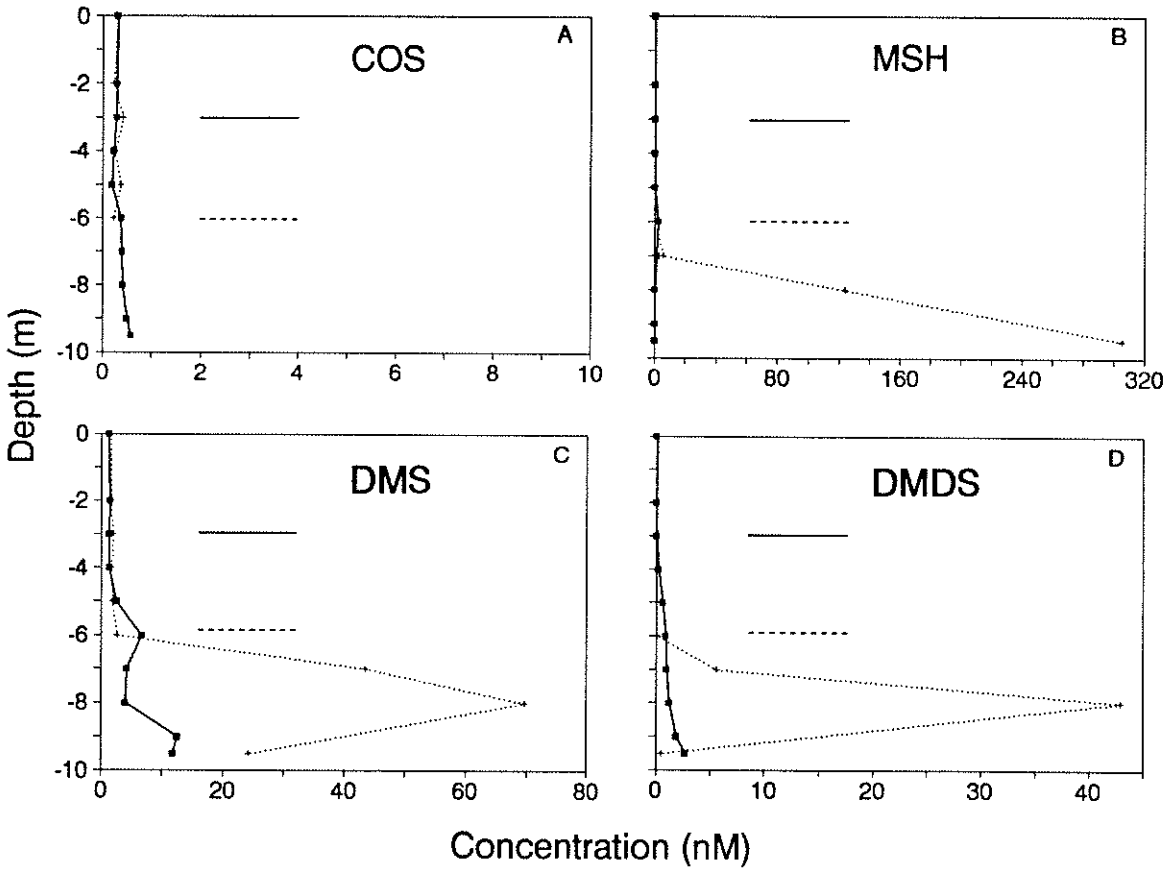

COS
A
MSH
B
DMS
C
DMDS
D
Depth (m)
Concentration (nM)
0
-2
-4
-6
-8
-10
0
2
4
6
8
10
0
80
160
240
320
0
20
40
60
80
0
10
20
30
40

Figure 2.2. Depth profiles of Lake 226 South determined on two separate dates. Sulfur species are as follows: (A) COS; (B) MSH; (C) DMS. The profiles were taken on two dates: 7 July 1988 (————), and 7 September 1988 (·····). The bottom of the mixed layer for each date is indicated by a horizontal line: 7 July 1988 (————), and 7 September 1988 (·····).

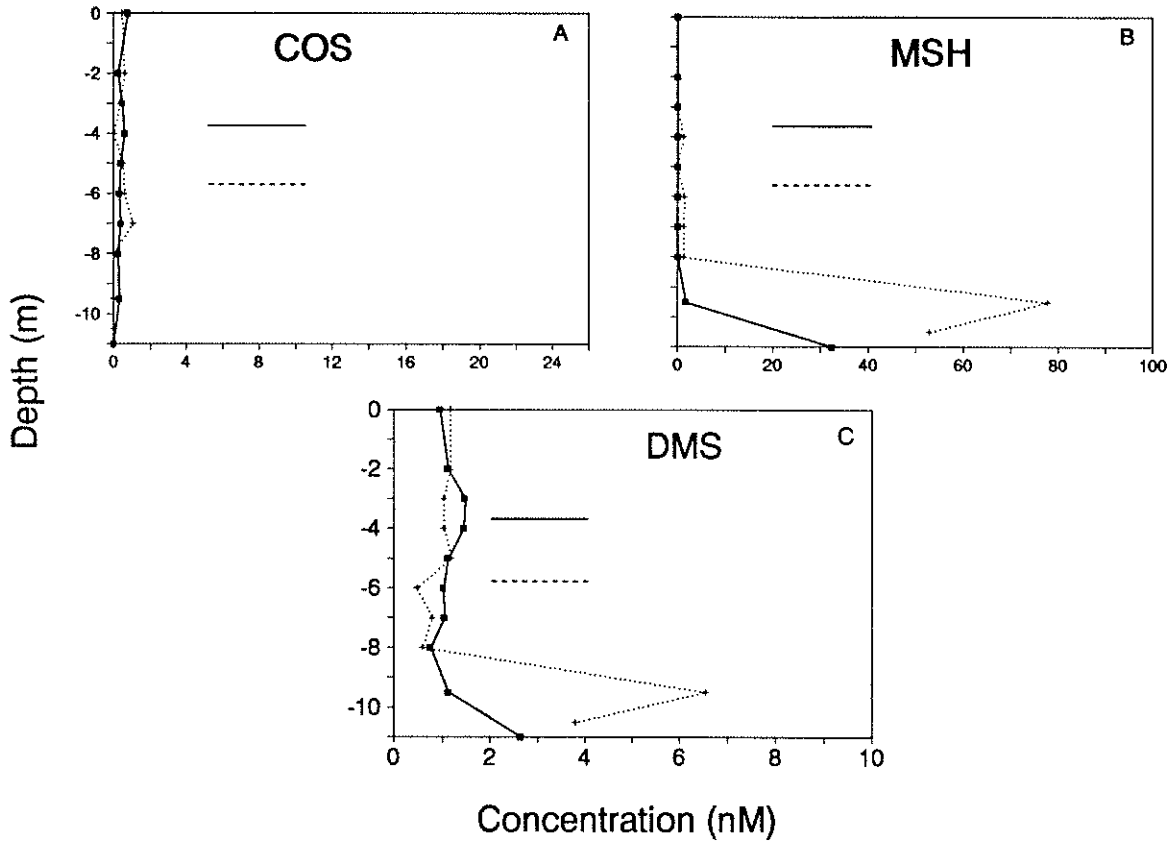

COS
A
MSH
B
DMS
C
Depth (m)
Concentration (nM)
0
-2
-4
-6
-8
-10
0
4
8
12
16
20
24
0
20
40
60
80
100
0
2
4
6
8
10

Figure 2.3. Surface VSC concentrations in four ELA lakes. (A) Lakes 302 South and 226 South. Bold lines represent Lake 302 South, thinner lines represent Lake 226 South (B) Lake 239 (C) Lake 114. Species differentiation for all graphs is described in the legend.

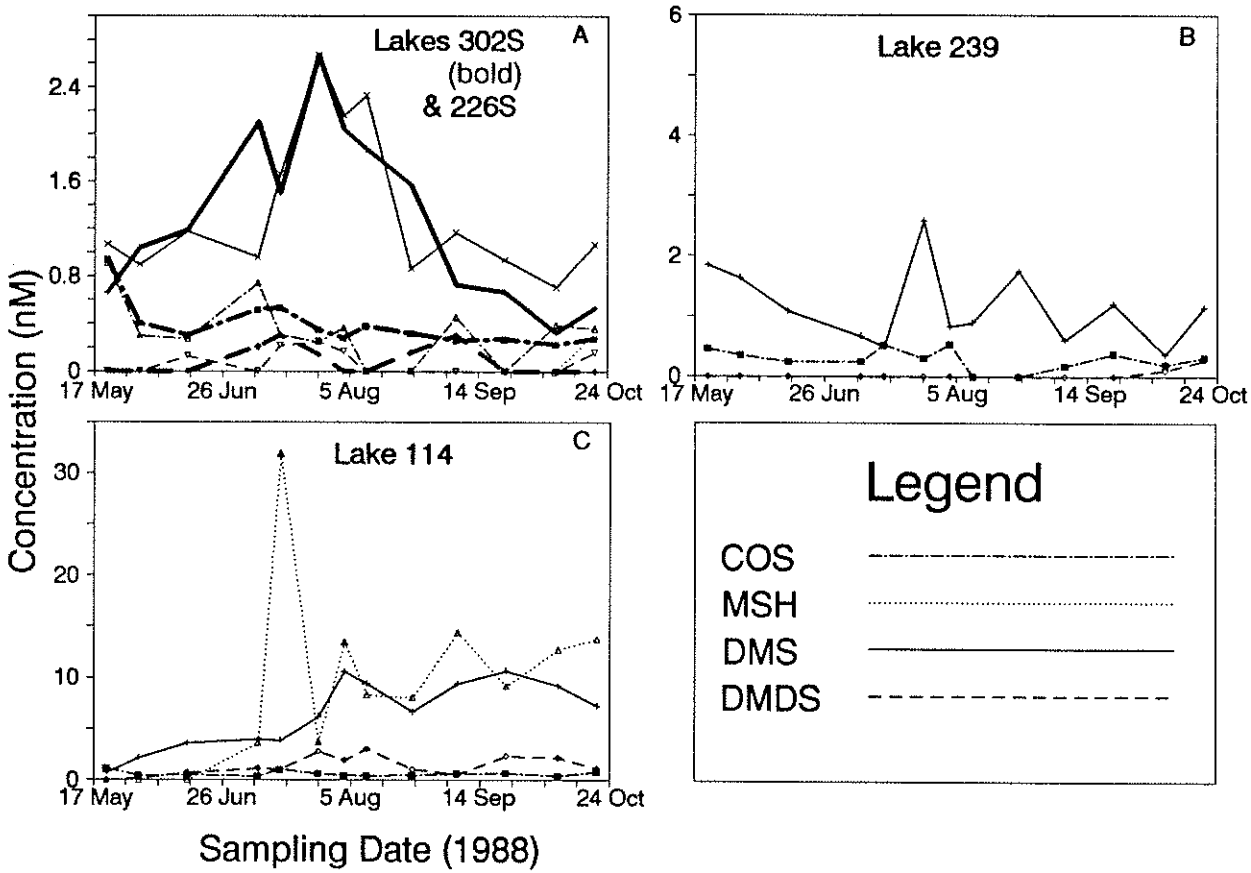
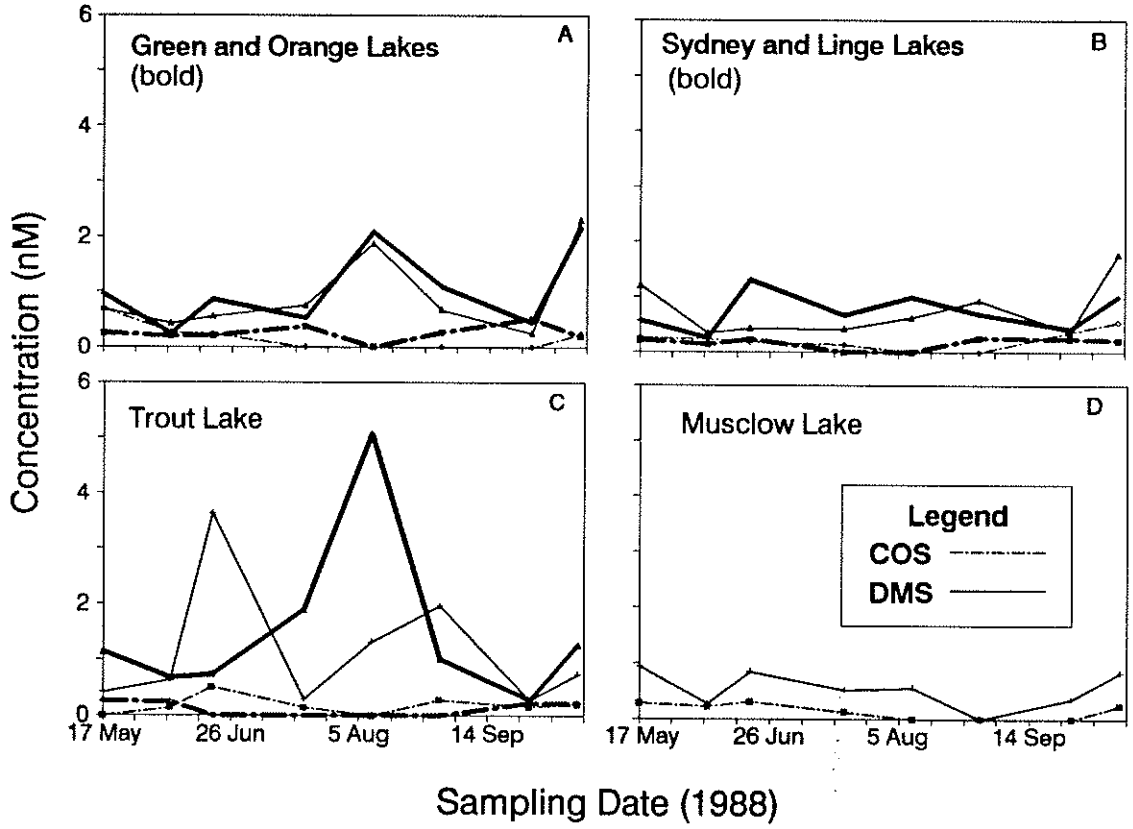

Lakes 302S
(bold)
& 226S
A
Lake 239
B
Lake 114
C
Concentration (nM)
Sampling Date (1988)
17 May
26 Jun
5 Aug
14 Sep
24 Oct
0
0.8
1.6
2.4
2
4
6
10
20
30
Legend
COS
MSH
DMS
DMDS

Figure 2.4. Surface VSC concentrations in six Red Lake area lakes. (A) Green Lake (bold) and Orange Lake. (B) Sydney Lake (bold) and Linge Lake. (C) Trout Lake, shallow (bold) and deep stations. (D) Musclow Lake. Species differentiation for all graphs is described in the legend in panel (D).


Green and Orange Lakes
(bold)
A
Sydney and Linge Lakes
(bold)
B
Trout Lake
C
Musclow Lake
D
Legend
COS
DMS
Concentration (nM)
0
2
4
6
17 May
26 Jun
5 Aug
14 Sep
Sampling Date (1988)

respectively; Fig. 2.4C, Table 2.5). COS, the other species detected routinely in surface waters, was usually at lower concentrations than DMS. ELA lakes tended to have higher COS and DMS concentrations than the Red Lake area lakes, which are larger (Figs. 2.3 and 2.4, Table 2.5).

DMDS and MSH, which were consistently found in Lake 114, were usually not detectable in the surface waters of the other lakes, except for Lake 303, which is also shallow and unstratified (Figs. 2.3 and 2.4, Table 2.5). In Lake 114, MSH concentrations were often higher than DMS, reaching up to 32 nM. DMDS and MSH were not detected at any time in the epilimnia of lakes in the Red Lake district (Table 2.5) and the former was only occasionally detectable in Lakes 226 South, 302 South, and 239, and at levels not exceeding 0.31 nM (Fig. 2.3, Table 2.5). MSH was found in the epilimnion of Lake 226 South only in late October (Fig. 2.3A).

Surface waters of acidified Lake 302 South contained concentrations of DMS, COS, and DMDS very similar to the unacidified reference lake, 226 South (Fig. 2.3A, Tables 2.4 and 2.6). Therefore, neither lower pH nor elevated SO_4^{2-} concentrations (from 2.4-12.3 mg litre^{-1}) had an obvious effect on VSC levels. Accumulation rates of DMS and DMDS below the mixed layer were greater, however, in the acidified lake (see below).

The very high mean concentrations of DMS and DMDS found in the surface waters of shallow Lake 114 (Table 2.5, Fig.

Table 2.6. Comparison of epilimnetic SO_4^{2-} concentrations and pHs in Lakes 302 South and 226 South (1988).

		pH		$[SO_4^{2-}]$ (mg litre^{-1})	
Lake	Dates	Range	Mean	Range	Mean
226S	30 May to 24 Oct	6.68-7.10	6.9	2.30-2.53	2.43
302S	10 May to 26 Oct	4.59-5.25	4.7	10.20-14.20	12.29

2.3C) were 5-70 times greater than the deeper lakes. Mean DMS and DMDS concentrations were also 2-14 times higher than found in the bog pool sampled (Table 2.5). MSH concentrations were similar in Lake 114 and the bog pool (Table 2.5); this species was usually undetectable in the surface water of the deeper lakes. In order to determine if the concentrations in Lake 114 were representative of unstratified, shallow lakes, analyses (August-October 1988) were done on another shallow ELA lake, Lake 303 (Table 2.1). During this period, DMS and COS levels in Lake 303 were not significantly different in the deeper, stratified lakes (Table 2.5), but MSH, which probably has a significant sediment origin, was very much higher in Lake 303 than in the deeper stratified lakes. The following year (1989), both DMS and MSH concentrations in Lakes 114 and 303 were high [Lake 114: concentrations up to 10.9 nM (DMS), 4.2 nM (MSH), and 6.3 nM (DMDS); Lake 303: concentrations up to 9.1 nM (DMS), 5.5 nM (MSH), and 4.2 nM (DMDS)].

Some seasonal patterns for VSC concentrations in surface water were discernible. For example, some lakes showed a peak in DMS concentration approximately midway through the summer (e.g. Lakes 239, 226 South, 302 South, 114, Green Lake, Orange Lake, and Trout Lake, shallow station; Figs. 2.3 and 2.4A,C). In other lakes, however, DMS concentrations fluctuated or remained relatively constant (e.g. Sydney Lake, Linge Lake, Musclow Lake, and

Trout Lake, deep station; Figs. 2.3C and 2.4B,C,D). COS had a midsummer minimum in most lakes (8 of the 11 studied; Figs. 2.3A,B and 2.4).

A test of homogeneity of coefficients of polynomial equations (Milliken 1989) was applied to the data to test for statistically significant differences ($p < 0.05$) in seasonal patterns of the ELA lakes. Quadratic equations of the form:

$$\log y = \beta_o + \beta_1(\log x) + \beta_2(\log x)^2 \qquad (3)$$

were fitted to DMS concentration (as y) and day number (as x) for Lakes 302 South, 226 South, 114, and 239 (data shown in Fig. 2.3). Significant fits were found for Lakes 114, 302 South, and 226 South. The analysis of covariance suggested by Milliken (1989) was used to test whether the coefficients β_o, β_1, and β_2 were significantly different for these three lakes. This analysis of temporal patterns suggested that the DMS concentrations in Lakes 302 South, 226 South, and 114 followed the same pattern, with Lakes 302 South and 226 South described by a common equation. A significantly larger β_o term was determined for Lake 114. The COS and DMDS data could not be fitted to smooth curves, preventing a similar set of analyses on these compounds.

2.4.1. VSC accumulation below the mixed layer in stratified

lakes. In the two lakes where measurements below the epilimnia were made (Lakes 302 South, acidified, and 226 South, reference), the deeper strata were found to contain significantly higher concentrations of MSH, DMS, and DMDS during summer stratification (Figs. 2.1 and 2.2). MSH accumulated at the highest rate in both lakes (0.98 mmol MSH m^{-2} d^{-1} in Lake 302 South and 0.81 mmol MSH m^{-2} d^{-1} in Lake 226 South, Table 2.3). These rates were similar despite the lower pH of Lake 302 South and elevated sulfate concentrations resulting from experimental acidification (Rudd et al. 1990; Table 2.3). Accumulation rates of DMS and DMDS, however, were very different in the two lakes. The DMS accumulation in Lake 302 South (0.57 mmol DMS m^{-2} d^{-1}, Table 2.3) was about 9 times higher than the DMS rate in Lake 226 South (0.066 mmol DMS m^{-2} d^{-1}, Table 2.3). No DMDS could be detected above the sediments in Lake 226 South, whereas an accumulation rate of 0.19 nmol DMDS m^{-2} d^{-1} was calculated for Lake 302 South. Following fall overturn in Lake 302 South, the only species detectable throughout the entire water column were COS and DMS, which were uniform in concentration.

2.4.2. Pore-water. In Lake 114, pore-water had MSH concentrations 8.9-14 times higher than the surface waters. DMS was also higher in pore-water by factors of 1.8 and 3.6 (Table 2.2). No DMDS was detectable in these analyses. Any

COS that might have been present was obscured by high concentrations of H_2S and CH_4.

2.4.3. Estimates of VSC flux to the atmosphere and its significance in the sulfur budgets of freshwater lakes. Estimates were made of sulfur losses to the atmosphere in four lakes (Table 2.4). The stratified lakes were not significantly different from each other ($p < 0.05$) in mean fluxes of COS, DMS, DMDS, or MSH. The total fluxes from these lakes ranged from 804-1,170 nmol S m^{-2} d^{-1}. The sulfur flux from unstratified Lake 114 was significantly greater ($p < 0.05$) by an order of magnitude (12,500 nmol m^{-2} d^{-1}, Table 2.4). This disparity was due principally to consistently higher concentrations of DMS, MSH, and DMDS.

2.4.4. Relationship to sulfate budgets. The significance of sulfur volatilization in the SO_4^{2-} budgets of lakes was estimated (Table 2.4). The total flux could account for only 0.3% and 1.0% of SO_4^{2-} lost via SO_4^{2-} reduction in Lakes 302 South and 239, respectively. Further, the loss of MSH, DMS, and DMDS from the deeper strata to the atmosphere at fall overturn represented only 0.07% of the SO_4^{2-} lost in Lake 302 South (Table 2.4). In Lake 114, however, total sulfur flux accounted for almost 15% of the "lost" SO_4^{2-}. Therefore, sulfur volatilization was an important term in the SO_4^{2-} budget of Lake 114.

2.5. Discussion

2.5.0. Concentrations and sources. In this study, DMS concentrations (lake means: 0.31 to 6.6 nM, Tables 2.5 and 2.7) were comparable to levels found in Hamilton Harbour, Lake Ontario (Table 2.7; Holdway and Nriagu 1987), but about 10-fold greater than concentrations in Lake Mendota surface waters (Table 2.7; Zinder and Brock 1978a). Two Antarctic Lakes, Burton Lake and Organic Lake (Deprez et al. 1986), contain DMS at concentrations higher than most lakes included in this study (Table 2.7). DMS concentrations determined for other environments, such as oceanic surface waters, salt marshes and wetlands, are in some cases higher and in some cases lower than in the lakes of our study (Table 2.7).

The main precursor of DMS in marine systems is dimethyl sulfoniopropionate (DMSP), a compound considered to play an important role in algal osmoregulation (e.g. Vairavamurthy et al. 1985). Attempts have therefore been made to correlate DMS concentrations with salinity, but salinity alone is not a good predictor (Iverson et al. 1989). This lack of fit is underscored by data from the freshwater lakes at the ELA, which have DMS concentrations similar to the mean open-ocean value (2.6 nM, Table 2.7), but which differ in salinity from the ocean by 4 orders of magnitude. The ratio of DMS:Chl *a* in the lakes [0.2-1 mmol DMS (mg Chl *a*)$^{-1}$]

Table 2.7. Concentrations of VSCs determined in a variety of environments. (ND-not detectable)

Species	Conc'n (nM)	Environment	Reference
DMS	2.63	Ocean-surface waters	Andreae and Barnard 1984
	0.031-34.3	Atlantic ocean	Turner et al. 1988
	5.77	wetlands(Canada)	Nriagu et al. 1987
	1,130	eutrophic f/w pond	Bechard and Rayburn 1979
	5-10	salt pond, epilimnion	Wakeham et al. 1987
	4.8-22.5	Burton L. (Antarctic) (under ice)	Deprez et al. 1986
	3.2	Organic L. (Antarctic) (surface)	Deprez et al. 1986
	11.3	Schleinsee-hypo. (max. value)	Henatsch and Juttner 1988
	0.63-1.15	Hamilton Harbour, L. Ontario (surface)	Holdway and Nriagu 1987
	0.10	Desjardins Canal (single date)	Caron and Kramer 1989
	0.016-0.161	L. Mendota (surface)	Zinder and Brock 1978a
	0.32-11	ELA lakes-surface	this study
	ND-5.1	Red Lakes-surface	this study
COS	0.23-0.32	Burton Lake-hypo.	Deprez et al. 1986
	"trace"	Schleinsee-hypo.	Henatsch and Juttner 1988
	0.79	Desjardins Canal (single date)	Caron and Kramer 1989
	0.10-0.37	Delaware Bay (surface)	Ferek and Andreae 1984
	0.02-0.06	Pacific Ocean (surface)	Ferek and Andreae 1983
	ND-1.13	ELA Lakes-surface	this study
	ND-0.69	Red Lakes-surface	this study
MSH	42-63	L. Schleinsee-hypo.	Henatsch and Juttner 1988
	ND	stratified lakes (surface)	this study
	ND-32	unstratified lakes (surface)	this study
	0.76	Desjardins Canal (single date)	Caron and Kramer 1989

was much smaller, however, than in the ocean (from about 4 up to 220, Iverson et al. 1989), and consistent with ratios observed along estuarine salinity gradients up to 25-30 $^{\circ}/_{\infty}$ (Iverson et al. 1989). Thus, it is important to note that low salinity does not mean that DMS will be low. Also, freshwater algae do release DMS with the addition of hydroxide (Challenger et al. 1957 and S. Richards, unpubl. data), although it is not clear if this release indicates the presence of DMSP or of another dimethyl sulfonium compound.

Despite the similarity in surface-water DMS concentrations in stratified lakes and the open ocean, the thinner diffusive boundary-layer thickness in the ocean results in higher fluxes of DMS to the atmosphere than estimated for our stratified lakes (Table 2.4). Total flux of sulfur from unstratified Lake 114 was approximately 0.96-1.6 times the estimated oceanic DMS flux rate, however, per unit of area (7,900-13,000 nmol m^{-2} d^{-1}, Barnard et al. 1982), and is comparable to the mean sulfur flux from a freshwater pond on Cedar Island, NC (7,100 nmol m^{-2} d^{-1}, Lamb et al. 1987).

Previously, volatile species other than DMS were virtually unstudied in lakes. We also routinely found COS in surface waters, at roughly constant levels and with mean epilimnetic values of approximately 0.09-0.61 nM (Table 2.5). In other studies (Deprez et al. 1986; Henatsch and

Juttner 1988), COS has been detected only in the hypolimnion. The reported hypolimnetic levels of COS in Lake Burton (Deprez et al. 1986; Table 2.7), however, are comparable to our surface-water concentrations; I could not quantify COS in the deeper strata of our lakes due to interference from H_2S and CH_4. In eutrophic Desjardins Canal, COS concentrations of approximately 0.79 nM have been found (Caron and Kramer 1989), which agrees well with the range found in our study (Table 2.5). In addition, oceanic studies have found COS at concentrations comparable to the epilmnia in our study (Table 2.7).

MSH was not usually found in the epilimnia of stratified lakes but was generally confined to the thermocline and hypolimnion where levels over 300 nM were found (Fig. 2.1B). Henatsch and Juttner (1988) also found MSH restricted to the hypolimnion in Schleinsee, with maximal concentrations of approximately 41.6-62 nM (about 5 times lower than maximal levels found in Lake 302 South, Fig. 2.1B). CS_2 has been found in lake systems previously (Deprez et al. 1986; Henatsch and Juttner 1988) but was not detected in this study.

The two potential sites of volatile sulfur production in freshwater systems are the sediments and the water column. I have evidence for important contributions by both sources. A significant sediment source was suggested by the following: late summer concentrations of MSH, DMS, and DMDS

below the mixed layer significantly greater than concentrations in the epilimnia (Figs. 2.1 and 2.2); mean surface water concentrations of MSH, DMS, and DMDS in unstratified, shallow Lake 114 higher than in any stratified lake (Table 2.5); and, pore-water analyses in Lake 114 indicating concentrations of MSH and DMS approximately 2-14 times higher than in overlying water (Table 2.2). MSH was detected only in water with close or recent sediment contact such as the surface waters of Lakes 114 and 303 (Fig. 2.3C, Table 2.5), water below the mixed layer (Figs. 2.1 and 2.2), and Lake 226 South surface waters after fall overturn (Fig. 2.3A). The production of volatile sulfur species by microbial decomposition in the sediments, then, had an important effect on both the concentration and speciation of the VSC's detected. Pore-water of the organic-rich, flocculent sediment from Lakes 114 and 303 contained concentrations of MSH and DMS up to 7 times greater than the pore-water of epilimnetic, sandy sediments in Lakes 239, 240 and 302 North (data not shown). Other studies have also found significant volatile sulfur concentrations in anoxic marine and lake waters and sediments (e.g. Henatsch and Juttner 1988). My data do contrast, however, with the findings of Zinder and Brock (1978 a, b) and Wakeham et al. (1987). In the latter study, sediments in a coastal salt pond were not a net source of DMS. The difference may be due to disparity in microbial populations, since Wakeham et

al. (1987) found anaerobic phototrophic bacteria capable of consuming DMS in the hypolimnion of the salt pond. Zinder and Brock (1978 a, b) did not find any VSCs other than H_2S associated with the sediments of Lake Mendota and suggested that sediments acted as a sink for DMS. My results demonstrate that this function is not universal for lake sediments.

Although sediment production apparently contributed to surface-water VSC concentrations in shallow lakes, there was also good evidence for a water-column source. In all the stratified lakes, regardless of size (7.8-34,700 ha; Table 2.5), there was close similarity in mean surface-water DMS and COS concentrations. This result would not be expected unless the dominant site of production was the water column, with similar production rates per unit of volume. Except for Lakes 114 and 303, all of these lakes had Ae:Ve ratios of 0.03-0.11 m^{-1} (Table 2.1). In addition, DMS concentrations found in Lake Ontario were similar (Table 2.7), and its Ae:Ve ratio is even smaller (6.63×10^{-5} m^{-1}, based on data from M. Nielson, CCIW, and US Environ. Prot. Agency/Environ. Can. 1987). Lakes 114 and 303 have Ae:Ve ratios of 0.59 and 0.66, respectively (Table 2.1). Therefore, in lakes with Ae:Ve ratios below a value between 0.11-0.59, water-column production may be most important in determining surface DMS concentration.

Formation of DMS in the water column may be due to the

breakdown of DMSP (e.g. Iverson et al. 1989), but the presence of this osmolyte in freshwater algae has not been studied. Other possible sources in the water column are the breakdown of sulfur-containing organic matter due to zooplankton grazing (Dacey and Wakeham 1986), microbial decomposition (Kadota and Ishida 1972; Bremner and Steele 1978) or abiotic chemical reactions. COS can be produced microbially or may originate from the chemical oxidation of sulfur-containing organic matter (Ferek and Andreae 1984; Turco et al. 1980; Belviso et al. 1987). In seawater, COS production is unrelated to the activity of living organisms (Andreae 1990).

2.5.1. Seasonal patterns. As described, there was no correlation between the mean epilimnetic COS and DMS concentrations and lake size (Tables 2.1 and 2.5). Time series demonstrated a tendency for the smaller lakes (< 200 ha) each to have a midsummer maximum in DMS concentration (Figs. 2.3 and 2.4A), which corresponded to a midsummer peak in microbial respiration in both the water column and in the sediments (unpublished data). Where no seasonal peak was observed (Figs. 2.4B,D), perhaps microbial utilization or gas exchange had increased in addition to production, or no peak in microbial production occurred. COS levels remained relatively constant in each lake throughout the study but had mid-summer minima in 8 of the 11 lakes. This pattern

was unexpected because biological activity is highest at that time and COS is most likely produced by photooxidation of dissolved organic matter (Ferek and Andreae 1984) or the oxidation of reduced sulfur molecules such as CS_2 and mercaptans (Turco et al. 1980; Belviso et al. 1987).

2.5.2. Effect of pH and sulfate concentration. An experimentally acidified lake (302 South) was compared to an unacidified reference lake (226 South) to determine if there was an effect on surface VSC concentrations by either acidification or an increase in SO_4^{2-} to levels found in acidified lakes (Table 2.6). The lakes were paired because of their similar bathymetries (Table 2.1). The surface waters of both the acidified and unacidified lakes had remarkably similar concentrations of epilimnetic COS and DMS over time (Fig. 2.3A), suggesting that acidification had not affected epilimnetic concentrations of these two VSC's. Vairavamurthy et al. (1985) similarly found that for *Hymenomonas carterae*, DMS production was independent of environmental SO_4^{2-} concentration, except at growth-limiting levels.

The rates of DMS and DMDS accumulation below the mixed layer were markedly higher in acidified Lake 302 South (Table 2.3), although the contrast between lake types must be drawn cautiously since it is based on just two systems. The higher accumulation rates in Lake 302 South were

unexpected, however, because DMS production in sediments was expected to originate from decaying organic matter such as sedimenting algal cells, and there has been no increase in primary production or sedimentation (Rudd et al. 1990) that would stimulate decomposition. Furthermore, since surface-water DMS concentrations were similar in Lakes 226 South and 302 South (Table 2.5, Fig. 2.3A), it is unlikely the higher accumulation rate resulted from the decomposition of algae with increased DMSP concentrations. There has, however, been an increase in dissimilatory SO_4^{2-} reduction rates (Rudd et al. 1990) leading to increased hypolimnetic H_2S production in Lake 302 South. This enhancement could lead to a greater production of DMS biologically from methylation of H_2S to MSH and then to DMS (Drotar et al. 1987) or abiotically via an interaction between CH_4 and H_2S (Sorenson 1988). There are not enough data, however, to delineate a relationship between H_2S and the organic sulfur species. Others (Wakeham et al. 1987) have found that H_2S is not an important precursor in the formation of DMS.

In acidified systems, one might expect a greater flux of COS to the atmosphere due to reduced hydrolysis of this compound (Belviso et al. 1987). Lakes 302 South and 226 South had comparable concentrations of this species throughout the study (Fig. 2.3A, Table 2.5), however, and therefore the estimated fluxes were not significantly different (Table 2.4).

2.5.3. Relationship to sulfate budgets. SO_4^{2-} is removed in these lakes by both algal uptake and SO_4^{2-} reduction (Rudd et al. 1990). A possible fate of this sulfur is volatilization from decomposition of algal sulfur or from reaction of H_2S with organic matter. This loss route accounted for only a very small portion of the SO_4^{2-} budget, however, even including losses at fall overturn from the thermocline and hypolimnion (Table 2.4). Because volatilization of COS, MSH, DMS, and DMDS in these stratified lakes was not an important loss route of reduced sulfur, it would not be an important source of alkalinity in acidified lakes. In Lake 114, however, the entire mixed layer is in contact with sediment and all four organic species were elevated. Sulfur volatilization was therefore an important term in the SO_4^{2-} budget of Lake 114 (Table 2.4). Sediment contact thus may be an important factor in determining the percentage SO_4^{2-} lost by volatilization.

One route of volatile sulfur loss not studied was the ebullition from sediments. Therefore diffusive fluxes (Table 2.4) may underestimate total fluxes.

2.5.4. Contribution to the atmosphere. Volatile sulfur release from both water and land surfaces can be oxidized in the atmosphere and re-deposited in forms such as SO_4^{2-} (Charlson et al. 1987). The total annual wet deposition of SO_4^{2-} in the ELA area is 5-10 mmol m^{-2} yr^{-1} (Barrie and Hales

1984). The estimated flux of sulfur from deep ELA lakes (Table 2.4) therefore represented 2-6% of this direct SO_4^{2-} deposition on the lake surface, and shallow Lake 114 returned as much as 30-60%, per unit of area. These values agree well with estimates of the percent contribution of DMS from wetlands to SO_4^{2-} in precipitation (3-18%, Barrie et al. submitted; up to 30%, Nriagu et al. 1987). Andreae and Andreae (1988) found a comparable return to the atmosphere of precipitated SO_4^{2-} in the Amazon Basin (35%). Interestingly, the range in lacustrine sulfur emissions (800-12,500 nmol m^{-2} d^{-1}, Table 2.4) is similar to the range of total volatile sulfur emissions from mid-continent soils in the United States (200-9,800 nmol m^{-2} d^{-1}, Lamb et al. 1987). Sulfur volatilization from soils and lakes in remote areas may therefore return 2-60% of the sulfur in wet SO_4^{2-} deposition, depending on the proportion of soil and lake types.

Volatile species such as COS and DMS play an important role in cloud formation and climate (Bates et al. 1987; Charlson et al. 1987; Turco et al. 1980). To construct models accurately predicting cloud formation and climate change, it is necessary to know natural fluxes of volatile sulfur species from various aquatic and terrestrial ecosystems. Based on our data, we estimate the total organic volatile sulfur flux from Canadian freshwater lakes to be 5-76 X 10^6 kg S yr^{-1}. In particular, if the data from

Lakes 114 and 303 (Tables 2.4 and 2.5) characterize other shallow lakes, there could be a regionally important flux of VSCs in areas where such lakes are abundant, as in the Hudson Bay Lowlands, the largest wetland in North America. Furthermore, the construction of large, shallow reservoirs may increase VSC inputs to the atmosphere. Already the surface area of artificial reservoirs built in Canada during the 1970's is equivalent to the surface area of Lake Ontario (R. Hecky, pers. comm.), and this source is likely to increase in the future as hydroelectric development progresses.

2.6. References

Andreae, M. O. 1990. Ocean-atmosphere interactions in the global biogeochemical sulfur cycle. Mar. Chem. 30: 1-29.

Andreae, M. O., and T. W. Andreae. 1988. The cycle of biogenic sulfur compounds over the Amazon Basin 1. Dry season. J. Geophys. Res. 93: 1487-1497.

Andreae, M. O., and W. R. Barnard. 1983 Determination of trace quantities of dimethylsulfide in aqueous solutions. Anal. Chem. 55: 608-612.

Andreae, M. O., and W. R. Barnard. 1984. The marine chemistry of DMS. Mar. Chem. 14: 267-279.

Andreae, M. O., R. J. Ferek, F. Bermond, K. P. Byrd, R. T. Engstrom, S. Hardin, P. D. Houmere, F. LeMarrec, and H. Raemdonck. 1985. Dimethyl sulfide in the marine atmosphere. J. Geophys. Res. 90(D7): 12891-12900.

Barnard, W. R., M. O. Andreae, W. E. Watkins, H. Bingemer, and H.-W. Georgii. 1982. The flux of dimethylsulfide from the oceans to the atmosphere. J. Geophys. Res. 87: 8787-8793.

Barrie, L. A., and J. M. Hales. 1984. The spatial distributions of precipitation acidity and major ion wet deposition in North America during 1980. Tellus 36: 333-355.

Bates, T. S., R. J. Charlson, and R. H. Gammon. 1987.

Evidence for the climatic role of marine biogenic sulphur. Nature 329: 319-321.

Bechard, M. J., and W. R. Rayburn. 1979. Volatile organic sulfides from freshwater algae. J. Phycol. 15: 379-383.

Bremner, J. M., and C. G. Steele. 1978. Role of microorganisms in the atmospheric sulfur cycle, p. 155-201. In M. Alexander [Ed.], Advances in Microbial Ecology, V. 2. Plenum.

Broecker, W. S., T.-H. Peng, G. Mathieu, R. Hesslein, and T. Torgersen. 1980. Gas exchange rate measurements in natural systems. Radiocarbon 22: 676-683.

Brunskill, G. J., and D. W. Schindler. 1971. Geography and bathymetry of selected lake basins, Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Can. 28: 139-155.

Caron, F., and J. R. Kramer. 1989. Gas chromatographic determination of volatile sulfides at trace levels in natural freshwaters. Anal. Chem. 61: 114-118.

Challenger, F., R. Bywood, P. Thomas, and B. J. Hayward. 1957. Studies on biological methylation. XVII. The natural occurrence and chemical reactions of some thetins. Arch. Biochem. Biophys. 69: 514-523.

Charlson, R. J., J. E. Lovelock, M. O. Andreae, and S. G. Warren. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature 326: 655-661.

Dacey, J. W. H., and Stuart G. Wakeham. 1986. Oceanic dimethylsulfide: Production during zooplankton grazing on phytoplankton. Science 233: 1314-1316.

Deprez, P. P., P. D. Franzmann, and H. R. Burton. 1986. Determination of reduced sulfur gases in Antarctic lakes and seawater by gas chromatography after solid adsorbent preconcentration. J. Chromatogr. 362: 9-21.

Drotar, A. M., G. A. Burton, Jr., J. E. Tavernier, and R. Fall. 1987. Widespread occurrence of bacterial thiol methyltransferases and the biogenic emission of methylated sulfur gases. Appl. Environ. Microbiol. 53: 1626-1631.

Emerson, S., W. Broecker, and D. W. Schindler. 1973. Gas-exchange rates in a small lake as determined by the radon method. J. Fish. Res. Bd. Can. 30: 1475-1484.

Fee, E. J. 1979. A relation between lake morphometry and primary productivity and its use in interpreting whole-lake eutrophication experiments. Limnol. Oceanogr. 24: 401-416.

Ferek, R. J., and M. O. Andreae. 1983. The supersaturation of carbonyl sulfide in surface waters of the Pacific Ocean offPeru. Geophys. Res. Lett. 10: 393-396.

Ferek, R. J., and M. O. Andreae. 1984. Photochemical production of carbonyl sulphide in marine surface waters. Nature 307: 148-150.

Hayduck, W., and H. Laudie. 1974. Prediction of diffusion

coefficients for nonelectrolytes in dilute aqueous solutions. A. I. Ch. E. J. 20: 611-615.

Henatsch, J. J., and F. Juttner. 1988. Capillary gas chromatographic analysis of low-boiling organic sulphur compounds in anoxic lake-water by cryoadsorption. J. Chromatogr. 445: 97-105.

Hesslein, R. H. 1976. An in situ sampler for close interval pore water studies. Limnol. Oceanogr. 21: 912-914.

Holdway, D. A., and J. O. Nriagu. 1987. A purge and trap gas chromatographic method for dimethyl sulfide in freshwater. Intern. J. Environ. Anal. Chem. 32: 177-186.

Iverson, R. L., F. L. Nearhoof, and M. O. Andreae. 1989. Production of dimethylsulfonium propionate and dimethylsulfide by phytoplankton in estuarine and coastal waters. Limnol. Oceanogr. 34: 53-67.

Kadota, H., and Y. Ishida. 1972. Production of volatile sulfur compounds 1591 by micro-organisms. Annu. Rev. Microbiol. 26: 127-138.

Lamb, B., H. Westberg. G. Allwine, L. Bamesberger, and A. Guenther. 1987. Measurement of biogenic sulfur emissions from soils and vegetation: Application of dynamic enclosure methods with Natusch filter and GC/FPD analysis. J. Atmos. Chem. 5: 469-491.

Lewis, W. K., and W. C. Whitman. 1924. Principles of gas

adsorption. Ind. Eng. Chem. 17: 1215-1220.

Milliken, G. A. 1989. Analysis of covariance: multiple covariats, p. 51-60. In Proc. 14th Annu. SAS Users Group Int.

Nriagu, J. O., D. A. Holdway, and R. D. Coker. 1987. Biogenic sulfur and the acidity of rainfall in remote areas of Canada. Science 232: 844-847.

Panofsky, H. A., and J. A. Dutton. 1984. The power law for the wind profile, p. 130-131. In Atmospheric Turbulence. Models and methods for engineering applications. Wiley.

Rudd, J. W. M., C. A. Kelly, D. W. Schindler, and M. Turner. 1990. A comparison of the acidification efficiencies of nitric and sulfuric acids by two whole-lake addition experiments. Limnol. Oceanogr. 35: 663-679.

Schindler, D. W., and M. A. Turner. 1982. Biological, chemical and physical responses of lakes to experimental acidification. Water Air Soil Pollut. 18: 259-271.

Schindler, D. W., M. A. Turner, M. P. Stainton, and G. A. Linsey. 1986. Natural sources of acid neutralizing capacity in low alkalinity lakes of the Precambrian Shield. Science 232: 844-847.

Sorensen, J. 1988. Dimethylsulfide and methane thiol in sediment porewater of a Danish estuary. Biogeochemistry. 6: 201-210.

Tangerman, A. 1986. Determination of volatile sulphur compounds in air at the parts per trillion level by tenax trapping and gas chromatography. J. Chromatogr. 366: 205-216.

Torres, A. L., P. J. Maroulis, A. B. Goldberg, and A. R. Bandy. 1980. Atmospheric OCS measurements on project Gametag. J. Geophys. Res. 85: 7357-7360.

Turco, R. P., R. C. Whitten, O. B. Toon, J. B. Pollack, and P. Hamill. 1980. OCS, stratospheric aerosols and climate. Nature 283: 283-286.

United States Environmental Protection Agency and Environment Canada. 1987. The Great Lakes: an environmental atlas and resource book. 1987.

Vairavamurthy, A., M. O. Andreae, and R. L. Iverson. 1985. Biosynthesis of dimethylsulfide and dimethylpropiothetin by *Hymenomonas carterae* in relation to sulfur source and salinity variations. Limnol. Oceanogr. 30: 59-70.

Wakeham, S. G., B. L. Howes, J. W. H. Dacey, R. P. Schwarzenbach, and J. Zeyer. 1987. Biogeochemistry of dimethylsulfide in a seasonally stratified coastal salt pond. Geochim. Cosmochim. Acta 51: 1675-1684.

Wilhelm, E., R. Battino, and R. J. Wilcock. 1977. Low-pressure solubility of gases in liquid water. Chem. Rev. 77:219-261.

Wilke, C. R., and P. Chang. 1955. Correlation of diffusion

coefficients in dilute solutions. A. I. Ch. E. J. 1: 264-270.

Zinder, S. H., and T. D. Brock. 1978a. Production of methane and carbon dioxide from methane thiol and dimethyl sulphide by anaerobic lake sediments. Nature 273: 226-228.

Zinder, S. H., and T. D. Brock. 1978b. Methane, carbon dioxide, and hydrogen sulfide production from the terminal methiol group of methionine by anaerobic lake sediments. Appl. Environ. Microbiol. 35: 344-352.

3. Organic volatile sulfur concentrations in lakes which range in sulfate and dissolved salt concentration over five orders of magnitude

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3.1. Abstract

The identities and concentrations of organic volatile sulfur compounds (VSCs) were determined in seven salt lakes in southern Saskatchewan, Canada, and in freshwater ponds of the Hudson Bay Lowlands (HBL). The lakes and ponds studied covered a range of SO_4^{2-} (0.0002-64 g (SO_4^{2-}) litre^{-1}) and salt (0.003-370 g salt litre^{-1}) concentration over five orders of magnitude. Lakes with >20 g (SO_4^{2-}) litre^{-1} had concentrations of carbonyl sulfide (COS), methane thiol (MSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and carbon disulfide (CS_2) that were several orders of magnitude higher than concentrations measured previously in lakes and in the oceans. DMS was the dominant species, reaching the highest yet recorded concentration of 3,000 nM in one lake. In the HBL ponds, even though waters were chemically very dilute, organic VSC concentrations were similar to those measured previously in less dilute freshwater lakes.

There was no correlation between [DMS] and dissolved salt concentration. However, there was a correlation between SO_4^{2-} concentration and (i) DMS, (ii) MSH and (iii) total VSC concentration in the salt lakes. When taking all lakes and ponds together, DMS concentrations were similar in systems covering a range of SO_4^{2-} concentration over five orders of magnitude [0.0002-20 g (SO_4^{2-}) litre^{-1}], but above

this concentration range, large increases in DMS concentrations were observed.

The mean flux of total organic sulfur to the atmosphere from the salt lakes ranged from 2.5-400 μmol m^{-2} d^{-1}. In at least four lakes, more sulfur was lost to the atmosphere than was deposited onto the lake surface as SO_4^{2-}.

3.2. Introduction

Biogenic sulfur gases are produced both chemically and biochemically in a variety of environments. Species such as dimethyl sulfide (DMS) and carbonyl sulfide (COS) are of particular significance due to their roles in climate modification (Hofmann 1990, Charlson et al. 1987) and global sulfur cycling (Aneja and Cooper 1989). Much attention has therefore been placed on understanding factors affecting DMS production in the oceans, and that of its principal marine precursor, dimethyl sulfoniopropionate (DMSP). Attempts to link factors such as salinity and Chl *a* to DMS and DMSP have indicated complex relationships in which phytoplankton speciation and cell disruption by zooplankton grazing are significant factors (Keller et al. 1989, Dacey and Wakeham 1986).

Most efforts have been directed at studying DMS in marine settings (for a review, see Andreae 1990). There are few data for freshwater systems (low dissolved salt and SO_4^{2-} concentration) or hypersaline environments. In this study I have extended the chemical spectrum of aquatic systems investigated by studying athalassic salt lakes in the interior prairie region of North America and chemically dilute wetland ponds in the Hudson Bay Lowlands (HBL; Table 3.1). This study has thus covered a five order of magnitude range of SO_4^{2-} concentration (mean values: 0.0002-64 g (SO_4^{2-})

Table 3.1. Geographic and morphometric summary of the studied systems. (Salt lakes data from Hammer and Haynes 1978)

System	West Longitude	North Latitude	A_0 (ha)	Z_m (m)	$\bar{Z}$ (m)
Prairie Salt Lakes					
Humboldt	105°06′	52°09′	1720	8.0	4.8
Patience	106°20′	52°07′	970	2.0	---
Waldsea	105°12′	52°17′	460	14.3	8.1
B Quill	104°22′	51°55′	30740	2.6	1.5
L Manitou	105°30′	51°48′	1330	5.2	3.6
Chaplin E	106°37′	50°26′	1410	< 1	---
Chaplin W	106°42′	50°26′	1940	< 1	---
Northern Ontario wetland					
Hudson Bay Lowlands	approx. 81°	approx. 51°	0.05-20	0.1-1	0.1-1

Table 3.2. Chemical summary of the studied systems.

(Chemical ranges for May to October 1990)

Lake	$[SO_4^{2-}]$ (g $litre^{-1}$)	Dissolved salt* (g $litre^{-1}$)	Ionic Strength (M)	Dominant Anion
Prairie salt lakes				
Humboldt	1.7-2.0	2.5-3.3	0.05-0.07	SO_4^{2-}
Patience	2.0-7.2	137.5-368.3	5.57-5.80	Cl^- +
Waldsea	14.7-18.	24.8-42.1	0.63-0.90	SO_4^{2-}
B Quill	45.1-67.6	66.4-89.9	1.81-1.97	SO_4^{2-}
L Manitou	47.7-65.2	90.5-114.4	2.21-2.64	SO_4^{2-}
Chaplin E	58.0-121.8	76.4-175.5	1.61-3.77	SO_4^{2-}
Chaplin W	54.6-98.5	80.4-158.8	1.34-3.21	SO_4^{2-}
Northern Ontario wetland				
HBL ∓ Kin	0.0002-0.0009	0.0035		HCO_3^-
IFen	0.00002	0.0254		HCO_3^-
CFen	0.00006	0.0142		HCO_3^-
Comparative systems				
Sea-water §	2.8	34.9	0.65	Cl^-
Freshwater		< 0.5		HCO_3^-
ELA mean ‖	0.003	0.008		HCO_3^-

* Dissolved salt concentration for the salt lakes based on total weight of Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Mn^{2+}, Cl-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NO_2^-, NO_3^-, NH_4^+

\+ Patience Lake has become Cl^- dominated artificially from potash mine tailings (Hammer and Parker 1984)

∓ HBL, Hudson Bay lowlands. Kin = Kinosheo, I = Interior, C = Coastal. Dissolved salt concentration based on total weight of the major ions: Na^+, K^+, Mg^{2+},

(*Table 3.2, continued*)

Ca^{2+}, Cl^-, and SO_4^{2-}.

§ Seawater [SO_4^{2-}] and salt concentration: Walton Smith 1974; Ionic strength: Stumm and Morgan 1970

‖ ELA, Experimental Lakes Area (Armstrong and Schindler 1971)

litre^{-1}, Table 3.2) and dissolved salt concentration (0.003-370 g salt litre^{-1}, Table 3.2), and extends measurements of organic volatile sulfur compounds (VSCs) to previously unstudied hypersaline (> 40 g salt litre^{-1}) environments, rich in SO_4^{2-} and Cl^- salts.

The extremely wide chemical range of these non-marine systems has allowed relationships between the concentrations of dissolved salt, SO_4^{2-}, and volatile sulfur to be examined. Because SO_4^{2-} is a source of sulfur for volatile sulfur production, variations in its concentration may in turn influence organic VSC concentrations. Furthermore, the concentration of dissolved salt may influence at least one species, DMS, since its marine precursor (DMSP) is thought to act in algal osmoregulation. Therefore, both SO_4^{2-} concentration and dissolved salt concentration may influence organic VSC concentrations (Vairavamurthy et al. 1985, Reed 1983, Dickson et. al. 1980). Except at growth-limiting concentrations (< 0.07 g litre^{-1}) of SO_4^{2-}, salinity has been identified as the more important parameter. *In situ* data agree with these culture studies (Richards et. al. 1991, Iverson et. al. 1989). However, the maximum salinity in these investigations was approximately 70 $^{o}/_{oo}$, and the maximum SO_4^{2-} concentration approximately 3 g litre^{-1}. In the present study, concentrations of dissolved salt and SO_4^{2-} up to 370 g salt litre^{-1} and 120 g (SO_4^{2-}) litre^{-1}, respectively, were studied.

3.3. Materials and Methods

3.3.0. Study site. The five salt lakes and two playas (lakes in very shallow depressions which may temporarily evaporate to dryness) included in this study are located in southern Saskatchewan, Canada, approximately 50-52°N, and 104-107°W (Table 3.1). Five lakes, Patience, Big Quill, Waldsea, Humboldt, and Little Manitou, are part of the Saskatchewan Plains physiographic division, whereas Chaplin Playa is in the Alberta High Plains (Hammer and Haynes 1978). Extensive physical and chemical characterization of these lakes has been reported earlier (e.g. Hammer and Haynes 1978 and Hammer 1978), and only a brief summary is given here (Table 3.2). It should be noted, however, that although the seven lakes studied encompass a large range of ion concentrations, all are SO_4^{2-} dominated except for Patience Lake (Cl^- dominated). Most lakes experienced large seasonal fluctuations in water chemistry throughout the study (2-3 fold variations in SO_4^{2-} and dissolved salt concentration, Table 3.2). These concentration changes are caused by the dilution effects of freshwater (e.g. snowmelt and precipitation), and the concentrating effect of evaporation during the summer.

Samples were also obtained from thirteen wetland ponds in the Hudson Bay Lowlands (HBL) in northern Ontario, Canada (Table 3.1). Ponds were sampled at three sites in the

Northern Wetlands Study: Kinosheo, an open bog area with acidic ponds, and two fen sites (interior and coastal) with neutral to alkaline ponds (Jeglum and Cowell 1982, Pala and Boissonneau 1982).

3.3.1. Sampling method. Water samples were taken by hand approximately 50 cm below the surface, except in shallow playas and HBL ponds (Chaplin, East and West basins) where the accessible water was often less than 10 cm in depth. In these systems, water samples were taken just under the air-water interface, with as little disturbance to the sediments as possible. Chloramphenicol and tetracycline (125 and 75 mg $liter^{-1}$, respectively; Kiene and Bates 1990) were added immediately to eliminate microbial activity which might affect sample integrity. Samples were immediately placed on ice in the dark until analysis (within 3 days). Lakes were sampled approximately every 3-4 weeks from ice-out (early May) until the end of September, 1990. For HBL samples, wetland ponds within each zone were numbered, and selected pools were sampled betweeen 1 and 5 times from June to October, 1990.

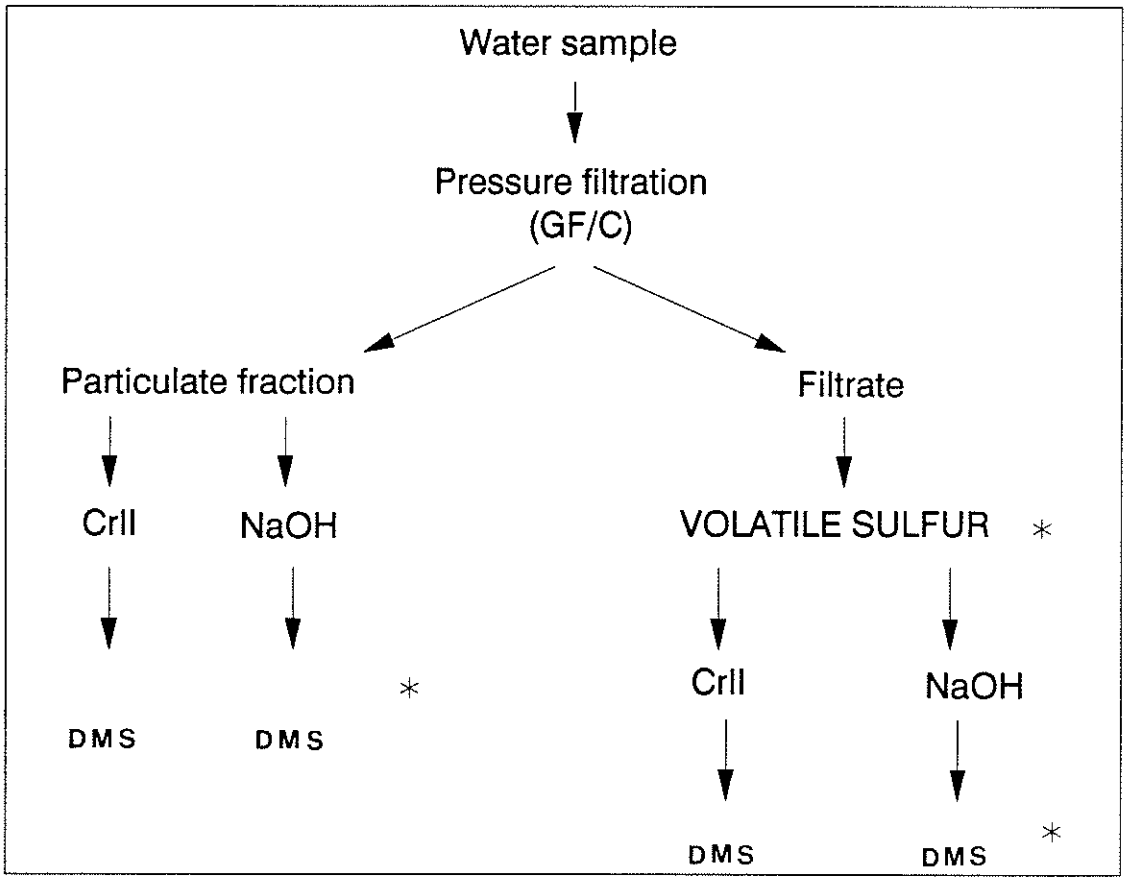
3.3.2. Volatile sulfur analyses. Organic volatile sulfur concentrations were determined by gas chromatography (Richards et al. 1991). Briefly, a purge-and-trap technique was used to pre-concentrate the volatile sulfur compounds in

a U-trap immersed in liquid nitrogen. A gas chromatograph (Varian 3700) equipped with a flame photometric detector (GC-FPD) enabled quantitation and identification of the different sulfur gases. The temperature programme was as follows: 30°C (1 minute hold), 10°C min^{-1} to 105°C (9 minute hold). Gaseous sulfur compounds were identified by retention time comparisons to sulfur standards (Aldrich).

The sample analysis scheme for salt lakes (Fig. 3.1) included a filtration step. Filtration is not important for chemically dilute freshwater samples (Richards et al. 1991), but is usually performed prior to DMS analyses in marine samples due to the potential disruption of DMSP-containing algal cells. Unfiltered water from some lakes (e.g. Big Quill) consistently gave higher DMS concentrations than filtered samples. A filtration step was therefore included in the analysis of all salt lakes. Because HBL samples were freshwater and were not expected to contain DMSP, they were analyzed without filtration.

Following volatile sulfur analysis, filtered water was subjected to (a) Chromium II [Cr (II)] reduction for determination of aqueous dimethyl sulfoxide (DMSO) concentrations (Andreae 1980a), and (b) sodium hydroxide (NaOH) hydrolysis for DMSP analyses (Keller et al. 1989). The volatile sulfur species resulting from these treatments were trapped and analyzed as described above. Particulate material collected on the filters was also treated with

Figure 3.1. Analysis scheme used for salt lake samples. The chromium reduction step was used to release any MSH bound to metal ions. H_2S released by this treatment was not quantified.


Water sample
Pressure filtration
(GF/C)
Particulate fraction
Filtrate
CrII
NaOH
VOLATILE SULFUR
*
CrII
NaOH
*
DMS
DMS
DMS
DMS
*

Cr(II) and NaOH, and the volatile sulfur products analyzed in the same manner. Cr(II) was used for DMSO analyses despite the low yield (42%, Andreae 1980a) in preference to sodium borohydride, which can lead to DMS release from DMSP (Andreae 1980 a, b). HBL samples were not tested for the presence of DMSP or DMSO.

3.3.3. Estimation of sulfur flux to the atmosphere.
Sulfur flux was calculated using the stagnant film model of gas exchange (Lewis and Whitman 1924). This model is based on the following equation:

$$F = k(C_{aq} - C_{atmos})$$

where: F = flux to the atmosphere

k = mass transfer coefficient

C_{aq} = aqueous concentration of gas

C_{atmos} = atmospheric concentration of gas

Mass transfer coefficients were obtained from calculated molecular diffusivities and estimated boundary layer thicknesses. Molecular diffusivities at 20°C for each species were calculated by the method of Wilke and Chang (1955), updated by Hayduck and Laudie (1974) and using viscosities appropriate for the chemistry of each lake. Boundary layer thicknesses were estimated from wind speed

measurements (AES Canada) at the closest major centre (Saskatoon: Humboldt, Big Quill, Waldsea, Little Manitou, and Patience Lakes; Moose Jaw: Chaplin East and West Playas). Wind speed measurements were used to estimate diffusive boundary layer thickness using the data of Wanninkhof et al. (1986). Since a salinity of up to 75 $^{o}/_{oo}$ (NaCl dominated) does not affect the relationship between wind speed and boundary layer thickness (Wanninkhof 1986), any effect of salinity on boundary layer thickness was not included in the calculations. Because DMS occurred at extremely high concentrations in several systems (up to 3 μM), fluxes for this species were corrected for atmospheric DMS concentrations using Henry's law constants for reduced sulfur compounds in seawater (Adewuyi 1989). Fluxes were calculated for each sampling date, and averaged to generate a mean flux for the period May to September.

3.3.4. Total sulfur content of algae. Benthic or suspended algal clumps were collected, washed with distilled water, and analyzed for total sulfur content using the methods of Tabatabai and Bremner (1970) and Amaral et al. (1989).

3.3.5. Pore-water concentrations. Sediments were collected using an Ekman dredge, and stored anaerobically on ice in vessels with no headspace. Sediment pore-water was obtained

by centrifuging sediment at 3,000 rpm for approximately 20 min under anoxic conditions. An aliquot of the pore-water was analyzed as described above.

3.3.6. Radiotracer analyses. The formation of organic VSCs from hydrogen sulfide (H_2S) was examined by analyzing the volatile radiolabelled sulfur species produced from $^{35}SO_4^{2-}$. $Na_2{}^{35}SO_4$ (specific activity: 5.4 X 10^6 dpm μmol^{-1} S) was added to surface water of undisturbed sediment cores obtained from Chaplin West playa, and these were incubated for about 70 hrs at *in situ* temperatures. Sediment pore-water, obtained by centrifugation, was analyzed for ^{35}S-organic VSCs as described elsewhere (Amaral et al., in prep.). Briefly, a splitter connected to the end of the GC column before the FPD detector allowed column effluent to be trapped in saturated $HgCl_2$. This was then analyzed in a scintillation counter for ^{35}S-activity associated with the various volatile sulfur species.

3.3.7. Chemical analyses. Ion (Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Mn^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NO_2^-, NO_3^-, NH_4^+) concentrations were determined as described elsewhere (Stainton et. al. 1977). The sum of these ions was used to determine the dissolved salt concentration (in g $litre^{-1}$) referred to in the text.

Oxygen concentrations were determined using the Winkler

method. Although the Miller method is more accurate when high carbonate concentrations are present (Walker et. al. 1970), significant underestimates (> 10 %) of oxygen occur with the Winkler method only above 50 meq (HCO_3^- + CO_3^{2-}) $litre^{-1}$. This is approximately twice the dissolved inorganic carbon (DIC) concentrations in the salt lakes studied here.

3.4. Results

3.4.0. Species and concentrations in surface waters. Five organic volatile sulfur compounds (VSCs) were detected in the surface waters of the lakes studied: COS, MSH, DMS, CS_2, and DMDS. Each saline lake or playa contained all five species at some point in the open water season (Table 3.3). DMS occurred at the highest concentrations in Chaplin West, up to 3050 nM S (Aug. 15, Chaplin West; Table 3.3, Fig. 3.2Cii). Time-weighted mean surface water concentrations of the individual species, COS, MSH, DMS, CS_2, and DMDS, differed by up to three orders of magnitude among lakes (Table 3.3).

Mean total VSC concentrations in the east and west basins of Chaplin playa were 4-10 times greater than the next highest system, Big Quill Lake, and 70-180 times greater than the mean total concentrations in Humboldt and Patience Lakes. The latter two lakes had the lowest mean total VSC concentrations, at 8.64 and 8.96 nM, respectively.

HBL samples also contained the same five organic VSCs, but most species were only transiently detectable, depending on the site studied (Table 3.3). Although the Kinosheo region contained concentrations of COS, MSH, DMS, CS_2, and DMDS similar to Humboldt Lake (mean concentrations: nd-4.4 nM), the coastal and interior fens generally had concentrations of organic VSCs about 50% lower (mean

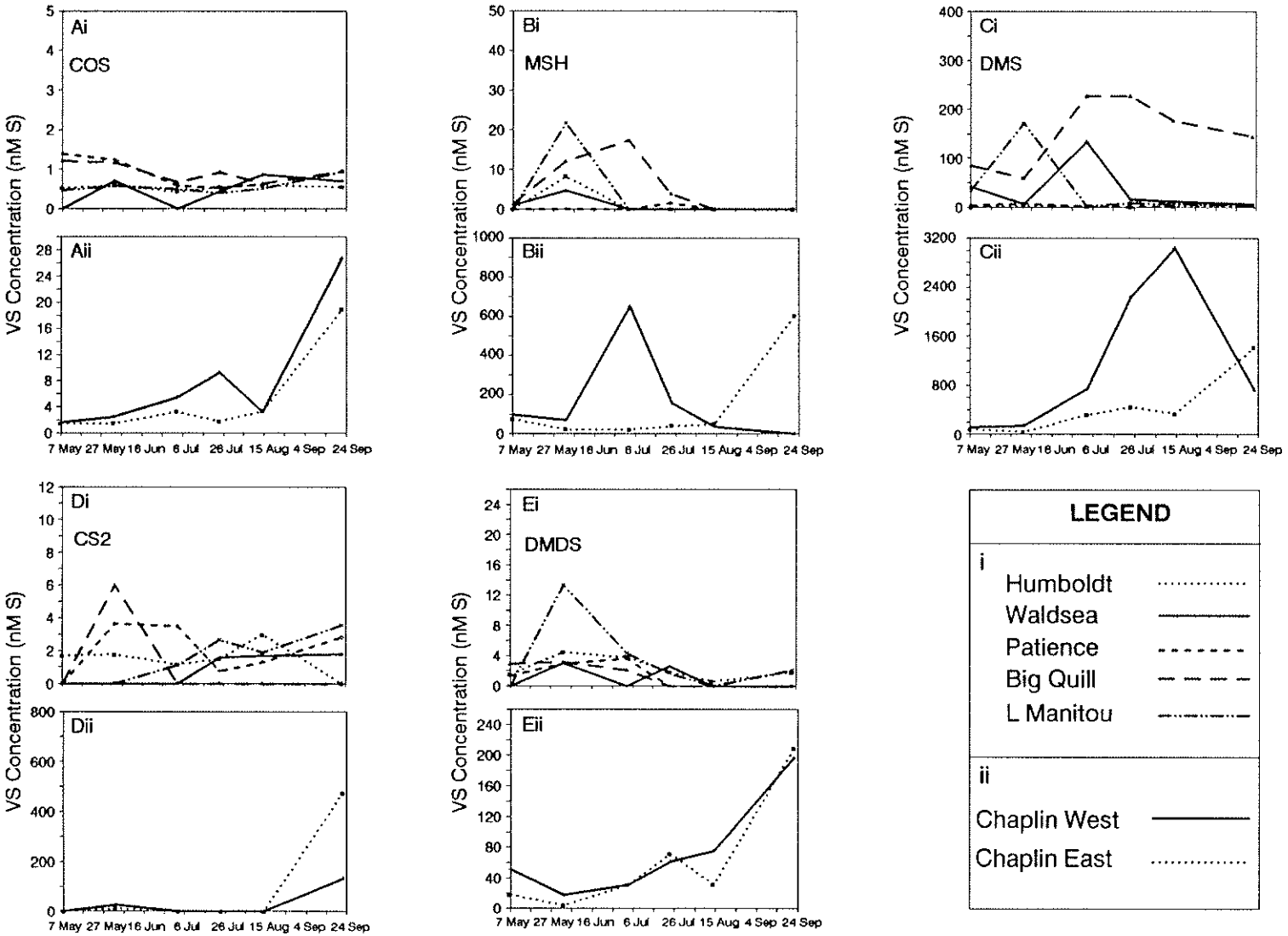
Table 3.3. Time-weighted mean surface water concentrations. Salt systems are listed in order of increasing $[SO_4^{2-}]$ ($\bar{X}$ = time-weighted mean; R = range; ND = not detected).

System		Volatile sulfur concentration (nM)				
		COS	MSH	DMS	CS_2	DMDS
Prairie Salt Lakes						
Humboldt	$\bar{X}$	0.55	1.7	2.3	1.6	2.5
	R	0.44-0.60	ND-8.3	0.94-3.9	ND-3.0	0.67-4.5
Patience	$\bar{X}$	0.857	0.28	3.9	2.3	1.6
	R	0.53-1.4	ND-1.5	1.7-8.3	0.75-3.6	ND-3.6
Waldsea	$\bar{X}$	0.50	1.1	36.6	0.85	1.0
	R	ND-0.86	ND-4.7	6.2-133.9	ND-1.8	ND-3.0
Big Quill	$\bar{X}$	0.90	6.6	157	1.2	1.3
	R	0.64-1.2	1.4-18	60-228	ND-6.0	ND-3.2
Little Manitou	$\bar{X}$	0.57	4.6	43	1.5	4.1
	R	0.40-0.94	ND-22	3.2-170	ND-3.6	ND-13
Chaplin East	$\bar{X}$	4.7	120	423	69	56
	R	1.5-19	23-600	53-1430	ND-480	5.0-210
Chaplin West	$\bar{X}$	7.6	180	1290	24	68
	R	1.7-27	ND-650	110-3050	ND-130	18-200
Hudson Bay lowlands, northern Ontario*						
Kinosheo (7)	$\bar{X}$	0.72-2.2	ND-1.0	0.39-4.4	ND-0.83	ND-0.97
	R	0.37-2.4	ND-2.4	0.37-7.8	ND-2.7	ND-1.8
Coastal Fen (3)	$\bar{X}$	0.57-1.1	ND	0.35-1.8	ND	ND
	R	ND-1.6	ND	ND-2.8	ND	ND
Interior Fen (3)	$\bar{X}$	0.45-0.57	ND	0.48-0.90	ND-1.1	ND
	R	0.26-0.68	ND	ND-1.0	ND-1.4	ND

* number of ponds sampled are given in parentheses following the region name; range in means are for all ponds sampled

Figure 3.2. Organic volatile sulfur concentrations in the salt lakes. Each sulfur compound is presented separately, with the upper panel designated (i) containing data for Humboldt, Waldsea, Patience, Big Quill, and Little Manitou Lakes. The lower panel designated (ii) contains data for Chaplin West and Chaplin East.

(A) COS (B) MSH (C) DMS (D) CS_2 (E) DMDS


Ai
COS
Aii
Bi
MSH
Bii
Ci
DMS
Cii
Di
CS2
Dii
Ei
DMDS
Eii
VS Concentration (nM S)
7 May 27 May 16 Jun 6 Jul 26 Jul 15 Aug 4 Sep 24 Sep
LEGEND
i
Humboldt
Waldsea
Patience
Big Quill
L Manitou
ii
Chaplin West
Chaplin East

concentrations: nd-1.8 nM; Table 3.3). Concentrations of MSH, DMS, CS_2, and DMDS in all wetland ponds were orders of magnitude lower than found in salt lakes with [SO_4^{2-}] greater than 20 g (SO_4^{2-}) $litre^{-1}$.

3.4.1. Temporal patterns. In each salt lake, there was a clear seasonal peak in the concentration of DMS. For five of the seven systems this occurred in early June (Little Manitou and Humboldt, Fig. 3.2Ci), or early July (Waldsea, Patience, and Big Quill, Fig. 3.2Ci). The west and east basins of Chaplin playa had peaks in late August and September, respectively (Fig. 3.2Cii).

Other species such as MSH and DMDS had clear maxima in all salt lakes (Fig. 3.2B,E). The highest concentration of MSH measured was 650 nM (Chaplin West, Table 3.3, Fig. 3.2Bii). Peaks in MSH and DMDS coincided except for one lake, Chaplin West (Fig. 3.2 Bii,Eii). Concentrations of MSH and DMDS were always lower than DMS except for single points in Humboldt and Patience Lakes (Fig. 3.2 Bi, Ei).

The concentration of COS varied the least, with only a 10-fold difference in mean concentration between the salt lakes (Fig. 3.2A, Table 3.3). A clear peak in COS concentration was observed in Chaplin Playa only, after substantial evaporation had occurred in September (Fig. 3.2Aii). COS concentrations remained relatively constant at 0.5-1.0 nM in five of the seven lakes (Fig. 3.2Ai). CS_2

also had no seasonal peak in five systems (Humboldt, Waldsea, Patience, Big Quill, and Little Manitou Lakes; Fig. 3.2Di). However, in Chaplin playa, a late season maxima of CS_2 was observed, coinciding with the peak in COS concentration (Figs. 3.2Aii, Dii).

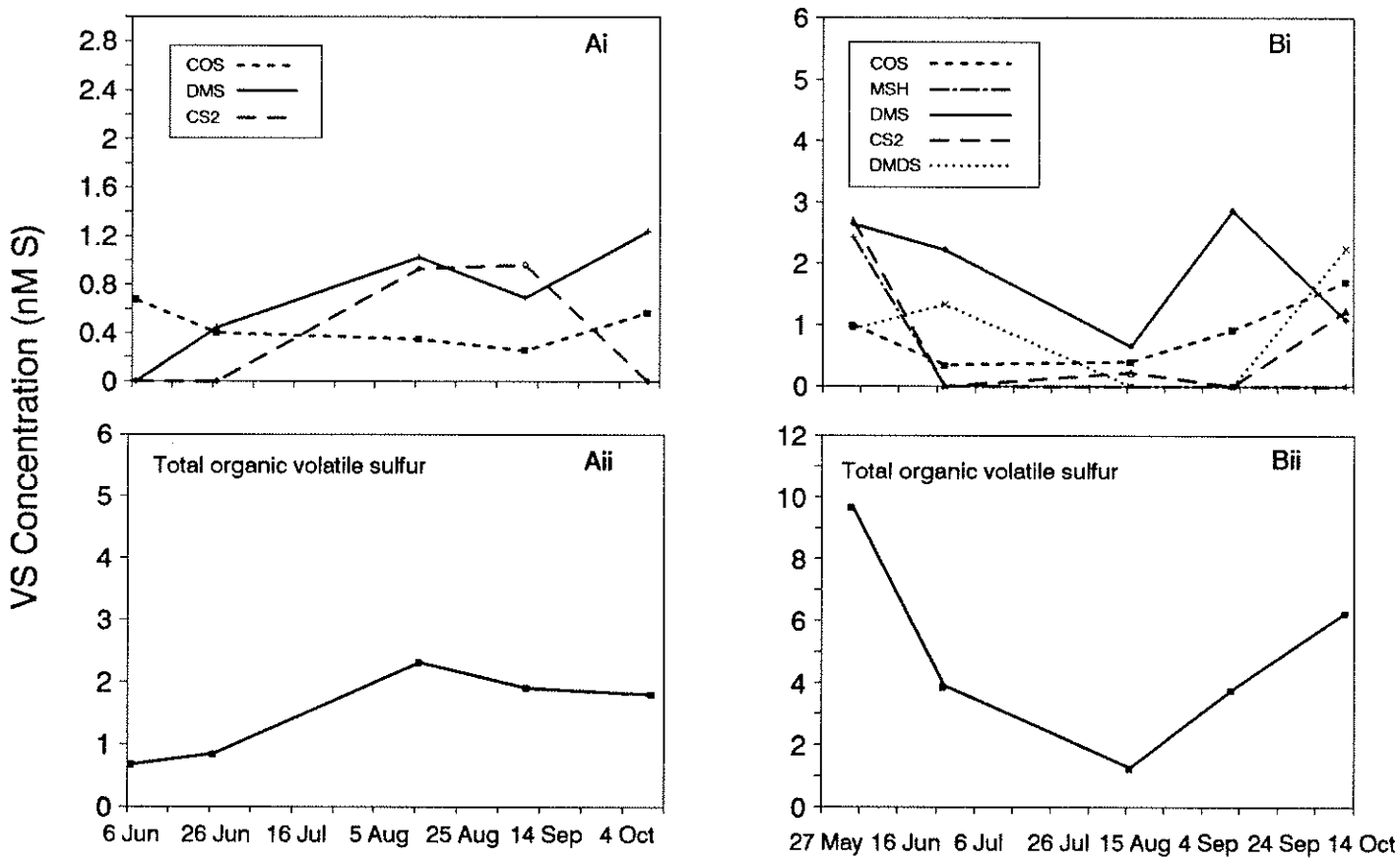
Two freshwater HBL ponds (Interior Fen, Pond 22 and Kinosheo, Pond 10) were sampled frequently enough to analyze temporal patterns. While the concentration of COS in Pond 22 (Fig. 3.3Ai) remained relatively constant, the concentrations of DMS and CS_2 reached maxima in late summer and fall, respectivley. Concentrations in Pond 10 were higher (Table 3.3, Fig. 3.3B), and showed greater variability throughout the season. With the exception of DMS which peaked in September, COS, MSH, CS_2, and DMDS (Fig. 3.3Ai,Bi) were present at the highest concentrations in the spring and fall. Seasonal variations in the total concentration of all organic VSCs indicated a slight increase in the late summer and fall in Pond 22 (Fig. 3.3Aii), and spring and fall maxima in Pond 10 (Fig. 3.3Bii).

3.4.2. Correlation between sulfate and organic VSCs. Within the salt lake data set, there was a significant correlation between mean SO_4^{2-} concentration and (i) mean DMS concentration (correlation to $\log_{10}$ [DMS], $r = 0.93$; $0.005<P<0.01$), (ii) mean MSH concentration (correlation to

Figure 3.3. Organic volatile sulfur concentrations in two ponds in the Northern Wetland Study. The upper panel designated (i) contains data for individual species. The lower panel designated (ii) shows data for the sum of individual species.

(A) Interior Fen, Pond 22

(B) Kinosheo, Pond 10


VS Concentration (nM S)
Ai
COS
DMS
CS2
2.8
2.4
2
1.6
1.2
0.8
0.4
0
Bi
COS
MSH
DMS
CS2
DMDS
6
5
4
3
2
1
0
Total organic volatile sulfur
Aii
6
5
4
3
2
1
0
6 Jun
26 Jun
16 Jul
5 Aug
25 Aug
14 Sep
4 Oct
Total organic volatile sulfur
Bii
12
10
8
6
4
2
0
27 May
16 Jun
6 Jul
26 Jul
15 Aug
4 Sep
24 Sep
14 Oct

$\log_{10}$ [MSH], r = 0.90, 0.02<P<0.05), and (iii) mean total organic VSC concentration (correlation to $\log_{10}$ [total organic VSC], r = 0.93, 0.005<P<0.01; Fig. 3.4). No correlations with SO_4^{2-} concentration were found for COS, CS_2, and DMDS. Significantly, there was no correlation between dissolved salt concentration and (i) mean total organic VSC concentration (r = -0.12), or (ii) mean DMS concentration (r = -0.12).

3.4.3. Estimates of flux to the atmosphere. Mean organic VSC atmospheric flux differed among the salt lakes by almost 200 times, from 2.5 μmol m^{-2} d^{-1} (Patience Lake, Table 3.4), to 400 μmol m^{-2} d^{-1} (Chaplin West, Table 3.4). The significantly higher fluxes from the east and west basins of Chaplin playa were principally due to the very high concentrations of MSH and DMS.

3.4.4. DMSP, DMSO, Chl *a*, and the sulfur content of algae. In the salt lakes, aqueous DMSO concentrations ranged up to 180 nM. However, only in Humboldt, Patience, and Little Manitou Lakes was DMSO a comparatively significant pool of sulfur, often 2-3 times greater than DMS concentrations (Table 3.5). In four systems (Big Quill, Chaplin West, Chaplin East, and Waldsea), DMSO concentrations were usually less than 1/10 DMS concentrations. DMSO correlated to DMS in Chaplin East playa only (r = 0.82; 0.05<P<0.10).

Figure 3.4. Correlation between mean sulfate concentration and mean volatile sulfur concentration. The mean volatile sulfur concentration was plotted on the y-axis as a $\log_{10}$ value. Mean values are time-weighted averages for all measurements made in 1990.

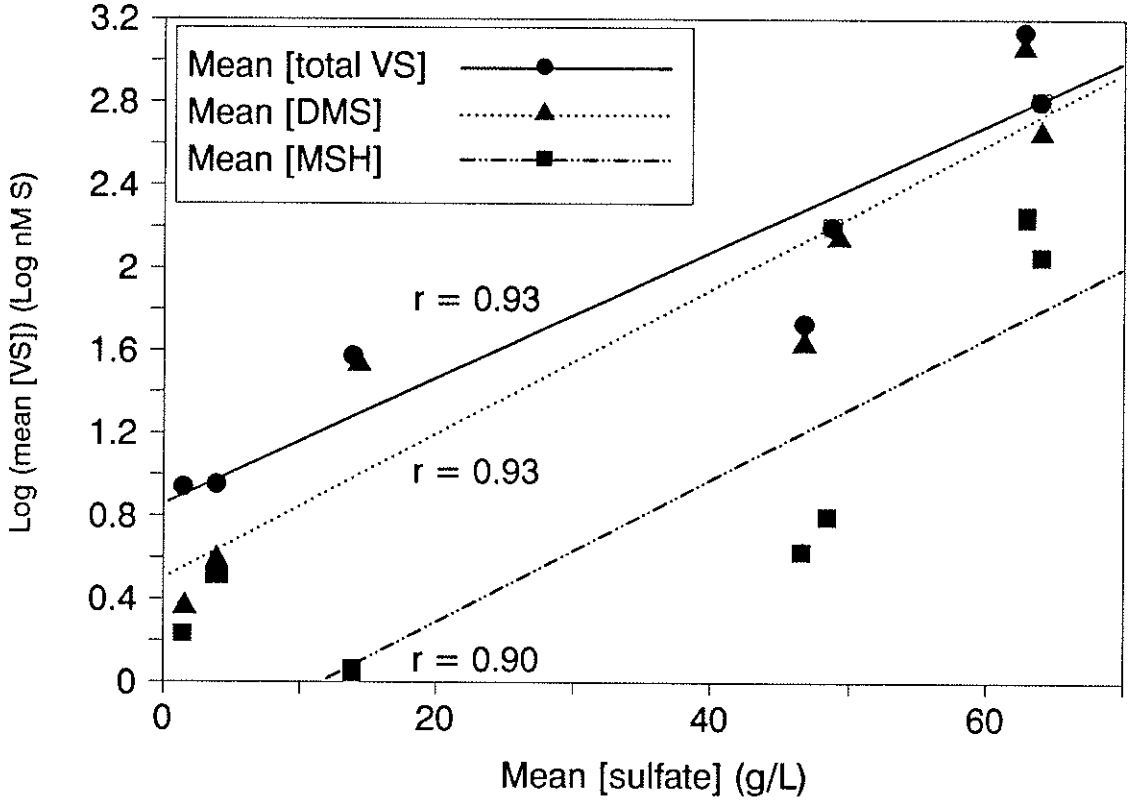

Mean [total VS]
Mean [DMS]
Mean [MSH]
r = 0.93
r = 0.93
r = 0.90
Log (mean [VS]) (Log nM S)
Mean [sulfate] (g/L)
0
0.4
0.8
1.2
1.6
2
2.4
2.8
3.2
0
20
40
60

Table 3.4. Estimates of sulfur flux to the atmosphere for the period May to September 1990.

Lake	Species	Flux (μmol S m^{-2} d^{-1}) Range	Mean	Total
Humboldt	COS	0.25-0.7	0.4	
	MSH	ND-7	1.2	
	DMS	0.4-3.1	1.5	
	CS_2	ND-1.8	1.1	
	DMDS	0.25-6	2.2	
				6
Patience	COS	0.11-0.5	0.22	
	MSH	ND-0.4	0.07	
	DMS	0.3-1.8	0.8	
	CS_2	0.20-1.2	0.7	
	DMDS	ND-1.0	0.4	
				2.5
Waldsea	COS	ND-0.7	0.24	
	MSH	ND-4.0	0.8	
	DMS	2.1-160	40	
	CS_2	ND-0.72	0.35	
	DMDS	ND-2.7	0.7	
				35
Big Quill	COS	0.2-0.9	0.5	
	MSH	ND-9	3	
	DMS	45-80	55	
	CS_2	ND-5	0.8	
	DMDS	ND-3	1.0	
				60
Little Manitou	COS	0.2-0.6	0.4	
	MSH	ND-15	2.5	
	DMS	1.1-100	21	
	CS_2	ND-1.2	0.7	
	DMDS	ND-9	2.5	
				30
Chaplin East	COS	0.6-10	2.5	
	MSH	7-300	65	
	DMS	21-650	30	
	CS_2	ND-260	45	
	DMDS	2.5-12	30	
				200
Chaplin West	COS	1.1-15	4	
	MSH	ND-210	65	
	DMS	60-800	315	
	CS_2	ND-75	15	
	DMDS	9-105	35	
				400

Table 3.5. Chlorophyll *a*, $DMSP_T$, and DMSO. (R = range; $\bar{X}$ = mean; ND = not detected)

Lake		Chl *a** ($mg\ m^{-3}$)	DMS:Chl *a* ($X\ 10^3$) ($mmol\ mg^{-1}$)	$DMSP_T$+ (nM)	DMSO∓ (nM)
Humboldt	R	68-170	0.022	ND-11	ND-71
	$\bar{X}$	106		4	10
Patience	R	21-150	0.057	1.0-18	ND-62
	$\bar{X}$	68		10	11
Waldsea	R	0.77-1.9	30.5	2.3-65	0.86-93
	$\bar{X}$	1.2		50	17
B Quill	R	42-180	1.2	22-1,400	5.2-102
	$\bar{X}$	130		800	21
L Manit	R	2.3-8.8	7.8	0.96-24	0.43-14
	$\bar{X}$	5.5		20	6
Chap E	R	2.3-30	21.2	2.1-250	4.0-114
	$\bar{X}$	20		110	21
Chap W	R	9.5-39	64.5	25-550	8.1-180
	$\bar{X}$	20		340	36

* n = 3

\+ $DMSP_T$: Both particulate and aqueous DMSP; n = 5

∓ DMSO: Values were corrected for a Cr(II) reduction yield of 42% (Andreae 1980a); n = 5

Mean DMSP concentrations were 2-5 fold higher than the mean DMS concentrations in four systems (Humboldt, Patience, Waldsea and Big Quill Lakes, Tables 3.3, 3.5). Again, Chaplin East playa was the only system with a correlation between the two species ($r = 0.8$; $0.05<P<0.10$). The highest total DMSP ($DMSP_T$; aqueous and particulate fractions) concentrations were detected in Big Quill Lake (up to 1400 nM, Table 3.5), a system which also had high Chl *a* values (up to 180 mg m^{-3}, Table 3.5). Plankton identification was performed on one sample from each lake in order to correlate DMSP production and algal speciation (Table 3.6).

Mean Chl *a* concentrations in most systems (Humboldt, Patience, Big Quill, Chaplin East, Chaplin West) ranged from 20-130 mg m^{-3}, and only Waldsea and Little Manitou had means less than 10 mg m^{-3} (Table 3.5). Mean DMS concentration: mean Chl *a* ratios ranged from 2.2×10^{-5} to 6.5×10^{-2} mg m^{-3} (Table 3.5).

Suspended algal clumps obtained from Big Quill and Little Manitou Lakes contained 2.0% and 1.4% S g^{-1} dry weight (Table 3.7). This is at the upper range of values determined elsewhere for freshwater algae (Table 3.7). Separate analyses of inorganic and organic sulfur were not done, but other studies have found sulfur in viable algae in predominantly organic forms (Amaral et al., in prep.).

3.4.5. Volatile sulfur production from radiolabelled

Table 3.6. Plankton identification. The order of listing is not significant.

Lake*	Date	Plankton identification
Humboldt	24 July	*Stephanodiscus niagarae* *Aphanizomenon flos aquae* *Chroomonos acuta* *Pseudoanabaena sp.* *Pediastrum boryanium*
Patience	25 July	*Dunaliella sp.*
Waldsea	24 July	*Chaetocera sp.* *Peridinium cf. polonium* *Chrysochromulina parva* *Flenodinium gymnodinium* *Echinocoleum sp.* *Rhodomonos minuta* *Oocystis sp.* *Strobilidium* (protozoa) *Heliozoan* *Nitzschia closterium* (diatom) *Amphidium sp.* (rotifers eating oocystis)
Big Quill	24 July	*Oocystis* cf. *solitaria* *Glenodinium* cf. *edax* *Carteria sp.* *Nitzschia closterium* *Mesodinium* cf. *pulix* (protozoa) *Askenasia sp.* (protozoa) *Chaetocera sp.*
Chaplin E	24 July	*Euglena sp.* noviculoid diatom in mucilage (zooplankton feces and detritus)
Chaplin W	24 July	mostly detritus noviculoid diatoms and euglinoids

* Sample from Little Manitou Lake was not preserved adequately for identification

Table 3.7. Sulfur content of viable algae.

Algal source	%S/g dry wt.	Estimated S content as DMSP (%) *
Big Quill	2.0	2.3-5.0%
Little Manitou	1.4	0.5-1.3%
Lake 302 S +	0.17-0.86 mean: 0.55	Not Done
"avg." algae ∓	0.6	Not Reported
freshwater lakes in SE US	0.15-1.58 §	Not Reported

* DMSP % estimated from Chl *a* and DMSP concentrations, and using a ratio of carbon:Chl *a* of 100:1, by weight (Hecky and Kilham 1988)

\+ freshwater lake at the Experimental Lakes Area, Ontario, Canada; algal data (J. Amaral, pers. comm.)

∓ F. P. Healey 1973

§ Goldman et al. 1972

sulfate. $H_2{}^{35}S$ was the only detectable free volatile sulfur species produced from $^{35}SO_4^{2-}$ in Chaplin West sediment cores. No ^{35}S activity was associated with any of the other volatile sulfur peaks.

3.5. Discussion

3.5.0. Comparison to other systems. This work spans a natural range of aqueous SO_4^{2-} and Cl^- concentrations, from 0.0002 to 120 g (SO_4^{2-}) $litre^{-1}$ (Table 3.2), and 0.0001 to 272 g (Cl^-) $litre^{-1}$ (data not shown). The low extreme was represented by HBL samples, which have concentrations of SO_4^{2-} and dissolved salt 1,000-10,000 times lower than the ocean, and the upper extreme was represented by hypersaline Chaplin playa and Patience Lake.

Surface water samples from Chaplin playa had concentrations of organic VSCs (e.g. MSH, DMS) two to three orders of magnitude greater than other marine and freshwater systems (Table 3.3; Richards et al. 1991). Chaplin playa had SO_4^{2-} concentrations approximately 20-40 times greater than those in the ocean, and its dissolved salt concentration (and ionic strength) were 2-6 times greater than the ocean (Table 3.2). DMS concentrations as high as 3,050 nM were detected in this lake, and are the highest yet reported in a natural aqueous system. Interestingly, DMS concentrations in Patience Lake were almost three orders of magnitude lower than DMS concentrations in Chaplin playa (Patience Lake, mean DMS concentration: 3.9 nM, Table 3.3). The dissolved salt concentration in Patience Lake was comparable to, or higher than, Chaplin playa (0.8-4.8 times Chaplin Playa), but it contained much lower concentrations

of SO_4^{2-} [2.0-7.2 g (SO_4^{2-}) $litre^{-1}$, Table 3.2].

Five lakes in this study (Waldsea, Little Manitou and Big Quill Lakes, Chaplin East and West) had mean surface DMS concentrations 5.5-3,700 times greater than the fresh water values of northwestern Ontario lakes (Table 3.3; Richards et al. 1991). Six of the salt systems (Waldsea, Little Manitou, Patience, Big Quill, Chaplin East and West) had mean DMS concentrations 1.5-490 times the mean surface water oceanic DMS concentration (Table 3.3; oceanic mean: 2.6 nM, Andreae and Barnard 1984).

Two Antarctic saline lakes, Burton and Organic Lakes (Deprez et al. 1986, Franzman et al. 1987), have surface water DMS concentrations less than 20 nM, with maximum concentrations of 1600 nM (Organic Lake) in the monimolimnion just above the oxic-anoxic interface. This monimolimnetic concentration in Organic Lake was previously the highest recorded DMS concentration. Organic Lake and Chaplin playa differ about 2-fold in salt concentration (approx. 200 g salt $litre^{-1}$, and 80-180 g salt $litre^{-1}$, respectively), and contain substantially different ion ratios (Table 3.2; Franzmann et al. 1987). There is some evidence suggesting H_2S reacts with organic matter to produce precursors of organic VSCs (see below). This mechanism of formation could explain the extremely high concentrations of DMS (> 2,000 nM, Table 3.3) that were detected in surface waters of Chaplin playa, even with

exchange to the atmosphere. Because SO_4^{2-} reduction does not occur in Organic Lake, and H_2S was not detected (Franzmann et al. 1987), formation via H_2S would probably not occur in this lake.

COS was present in 5 salt lakes (Humboldt, Patience, Waldsea, Big Quill and Little Manitou Lakes) at concentrations comparable to freshwater Canadian Shield lakes at ELA (Table 3.3; Richards et al. 1991), and about 2 times Burton Lake in the Antarctic (Deprez et al. 1986). However, Chaplin playa (East and West basins) had mean COS concentrations 5-15 times higher than the other five salt systems in this study. Interestingly, MSH was detectable in the surface waters of all the salt lakes in this study regardless of lake depth, whereas it was detected only once in the epilimnia of stratified freshwater lakes (Richards et al. 1991), and was usually not detectable in HBL samples (Table 3.3). Mean concentrations of DMDS were 0.7-3400 times mean values for stratified and unstratified freshwater lakes at the ELA.

While high SO_4^{2-} lakes had dramatically increased concentrations of VSCs, lakes with extremely low SO_4^{2-} concentrations had VSCs similar to many intermediate SO_4^{2-} waters. Ponds at the Kinosheo site on the HBL [0.0002-0.0009 g (SO_4^{2-}) litre^{-1}] were similar to two shallow, unstratified lakes (Lakes 303 and 114) at the ELA [0.003 g (SO_4^{2-}) litre^{-1}; Richards et. al. 1991) and to hyposaline

Humboldt Lake [1.7-2.0 g (SO_4^{2-}) $litre^{-1}$]. However, in the coastal and interior fens, MSH, DMS, CS_2, and DMDS were present at about 2-fold lower concentrations than in Kinosheo (Table 3.3), and were similar to the surface waters of stratified lakes at the ELA and in the Red Lake area (Richards et al. 1991). Thus, for a range of SO_4^{2-} concentrations from 0.002 to 2 g (SO_4^{2-}) $litre^{-1}$, and a dissolved salt concentrations from 0.003 to 3 g salt $litre^{-1}$, the concentrations of organic VSCs fall within a fairly narrow range.

3.5.1. DMS:Chl *a* ratios. Mean [DMS]: mean Chl *a* ratios were between 3-6 orders of magnitude less than have been reported for the ocean (Table 3.5; mean oceanic values: 15.05 and 24.00 mmol mg^{-1}, Iverson et al. 1989). Therefore, either (i) DMS was more effectively removed in these salt lakes through microbial decomposition and chemical oxidations, or (ii) oceanic phytoplankton species have a greater relative output of DMS than phytoplankton species found in these salt lakes. However, even if there is a lower relative output by phytoplankton in the salt lakes, the standing crop of algae in the salt systems was at least 1-2 orders of magnitude greater than in the ocean (Table 3.5, Iverson et al. 1989). Furthermore, the sulfur content of viable algae from Big Quill and Little Manitou was relatively high (Table 3.7). These two factors together

could explain DMS concentrations being significantly greater than the ocean (Table 3.3), despite an apparently lower production per unit of algal biomass. In addition, there may be a significant contribution from sediment production.

3.5.2. Significance of flux to the atmosphere. The mean total organic VSC flux from these salt lakes (2.5-400 μmol m^{-2} d^{-1}, Table 3.4) was up to 500 times the total mean sulfur flux from freshwater lakes (Richards et al. 1991), and 1/5 to 50 times the DMS flux from the ocean, per unit area (7.9-13 μmol m^{-2} d^{-1}, Barnard et al. 1982; 9 μmol m^{-2} d^{-1}, Andreae and Raemdonck 1983). Interestingly, the range of flux from salt lakes (nd to 800 μmol m^{-2} d^{-1}, Table 3.4) is very similar to the range found for salt marshes (nd to 1250 μmol m^{-2} d^{-1}, summarized in Morrison and Hines 1990) where *Spartina alterniflora* stands release the greatest amount of DMS.

Annual wet SO_4^{2-} deposition in southern Saskatchewan is approximately 10-20 mmol m^{-2} yr^{-1} (Barrie and Hales 1984), and therefore the salt systems volatilized 2-700% of the SO_4^{2-} in wet precipitation, per unit area. Of course, the greatest source of SO_4^{2-} to these systems is not precipitation but ground water and melt-water runoff (Hammer et al. 1975). Systems with SO_4^{2-} concentration greater than approximately 20 g (SO_4^{2-}) $litre^{-1}$ emitted more sulfur to the atmosphere than was supplied to the lake surface as SO_4^{2-}. Lakes with

SO_4^{2-} concentration greater than approximately 20 g (SO_4^{2-}) $litre^{-1}$, therefore, would act as "sulfur pumps" to the atmosphere. At least two lakes (Big Quill and Little Manitou) and two playas (Chaplin East and West) contributed more sulfur to the atmosphere than was deposited on their surface. The Saskatchewan salt lakes in a total land area of 2.9×10^5 km^2 (estimated from data in Hammer at al. 1975) were estimated to release as much as 4×10^5 kg S annually.

3.5.3. Possible origins of organic VSCs. Mechanisms of organic VSC formation were not studied. However, it is likely that the breakdown of sulfur-containing organic matter (Kadota and Ishida 1972, Bremner and Steele 1978) and reactions of H_2S (Amaral et al., in prep.) contributed to organic VSC concentrations in the salt lakes.

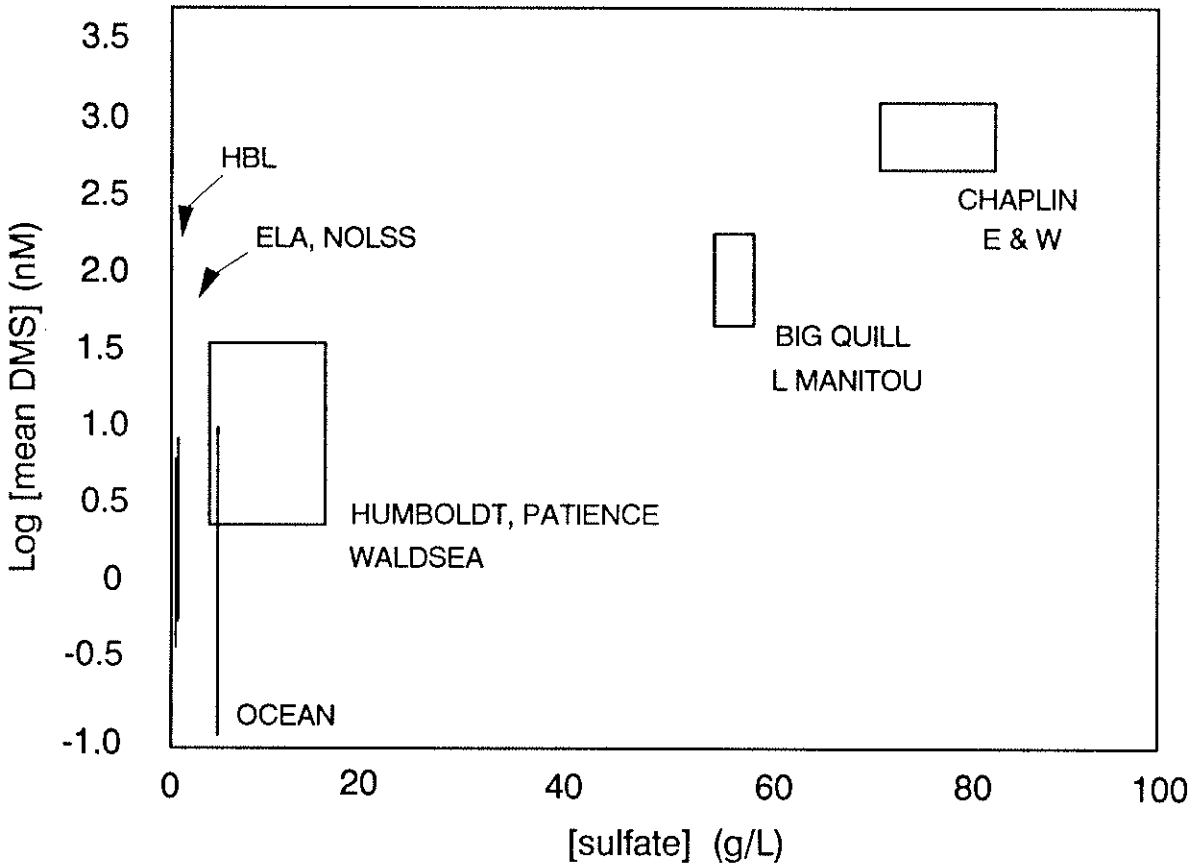
In several systems, both algal biomass and algal sulfur content were high (chl *a* up to 180 mg m^{-3}, Table 3.5; algal sulfur content up to 2% S g^{-1} dry weight, Table 3.7). Breakdown of this algal-derived organic matter likely contributed to organic VSC formation via known pathways such as microbial decomposition and zooplankton grazing (Kadota and Ishida 1972, Bremner and Steele 1978, Wakeham and Dacey 1978). DMSP was detected in all lakes and therefore algae also contributed to DMS production in the salt lakes (Table 3.5).

With the exception of Waldsea Lake (Table 3.2), salt systems with SO_4^{2-} concentrations up to 20 g (SO_4^{2-}) $litre^{-1}$ (Humboldt, Patience, and Waldsea Lakes, Table 3.2) contained DMS concentrations similar to relatively dilute systems such as the ocean and freshwater lakes (Fig. 3.5; Richards et al. 1991). However, above approximately 20 g (SO_4^{2-}) $litre^{-1}$, large increases in the concentration of DMS and MSH were found (Fig. 3.5). These results do not conflict with previous studies which have not found an effect of SO_4^{2-} concentration on DMS concentrations; maximum SO_4^{2-} concentrations in those studies were usually less than 3 g (SO_4^{2-}) $litre^{-1}$ (Vairavamurthy et al. 1985, Dickson et al. 1980, Reed 1983).

The correlation to SO_4^{2-} concentration suggested a link to dissimilatory SO_4^{2-} reduction, because the assimilatory pathway is independent of SO_4^{2-} concentration. These observations, therefore, suggest the product of dissimilatory SO_4^{2-} reduction, H_2S, influenced organic VSC concentrations. In support of this idea, the highest organic VSC concentrations (Chaplin playa, Table 3.3) occurred in the presence of 3-10 mM [H_2S] (data not shown).

The relationship between organic VSC and H_2S may be direct or indirect. Direct formation from H_2S could occur via sulfide incorporation into sedimentary organic matter (Luther et al. 1986, Amaral et al., in prep), and subsequent breakdown of the organic matter releasing low molecular

Figure 3.5. Effect of sulfate concentration on DMS concentration. The range in mean DMS concentration for each system is plotted against the mean sulfate concentration. Salt lakes were grouped together according to similarity in sulfate concentration (Table 3.2), and therefore are represented by boxes, not vertical lines. The oceanic range is based on data from Matrai and Cooper (1989).


3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
-1.0
Log [mean DMS] (nM)
HBL
ELA, NOLSS
HUMBOLDT, PATIENCE
WALDSEA
OCEAN
BIG QUILL
L MANITOU
CHAPLIN
E & W
0
20
40
60
80
100
[sulfate] (g/L)

weight sulfur-containing compounds. In addition, biological methylation of H_2S can occur to produce organic volatile compounds (Drotar et al. 1987).

H_2S could also indirectly affect organic VSC concentrations by lowering Eh, and subsequently decreasing oxidation reactions which are a sink for reduced volatile compounds (Adewuyi 1989). In support of this, there was an inverse correlation ($r = -0.83$, $0.02<P<0.05$) between SO_4^{2-} concentration and the ratio of mean [DMSO]:mean [DMS]. Decreased oxygen solubility in salt solutions could also have contributed to reducing oxidation rates.

These data are the first to demonstrate a relationship between [SO_4^{2-}] and organic VSCs at SO_4^{2-} concentrations that are not growth-limiting. The question of whether this is a direct dependence on H_2S due to a novel mechanism of formation, or is an indirect effect of increased chemical stability, will be an interesting one to answer.

3.6. References

Adewuyi, Y. G. 1989. Oxidation of biogenic sulfur compounds in aqueous media, p. 527-559. In E. Saltzmann and W. Cooper [Eds.], Biogenic sulfur in the environment. ACS 393.

Amaral, J. A., R. H. Hesslein, J. W. M. Rudd, and D. Fox. 1989. Loss of total sulfur and changes in sulfur isotopic ratios due to drying of lacustrine sediments. Limnol. Oceanogr. 34:1351-1358.

Andreae, M. O. 1990. Ocean-atmosphere interactions in the global biogeochemical sulfur cycle. Mar. Chem. 30: 1-29.

Andreae, M. O. 1986. The ocean as a source of atmospheric sulfur compounds, p. 331-362. In Buat-Menard [Ed.], The role of air-sea exchange in geochemical cycling. D. Reidel.

Andreae, M. O. 1980a. Determination of trace quantities of dimethylsulfoxide in aqueous solutions. Anal. Chem. 52: 150-153.

Andreae, M. O. 1980b. Dimethylsulfoxide in marine and freshwaters. Limnol. Oceanogr. 25(6): 1054-1063.

Andreae, M. O. and W. R. Barnard. 1984. The marine chemistry of DMS. Mar. Chem. 14: 267-279.

Andreae, M. O. and H. Raemdonck. 1983. Dimethyl sulfide in the surface ocean and the marine atmosphere: a

global view. Science 221: 744-747.

Aneja, V. P., and W. J. Cooper. 1989. Biogenic sulfur emissions. A review. p. 2-13. In E. S. Saltzman and W. J. Cooper [Eds.], Biogenic sulfur in the environment. ACS 393.

Armstrong, F. A. J., and D. W. Schindler. 1971. Preliminary chemical characterization of waters in the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Canada. 28: 171-187.

Barnard, W. R., M. O. Andreae, W. E. Watkins, H. Bingemer, and H.-W. Georgii. 1982. The flux of dimethylsulfide from the oceans to the atmosphere. J. Geophys. Res. 87(C11): 8787-8793.

Barrie, L. A., and J. M. Hales. 1984. The spatial distributions of precipitation acidity and major ion wet deposition in North America during 1980. Tellus 36: 333-355.

Bremner, J. M. and C. G. Steele. 1978. Role of micro-organisms in the atmospheric sulfur cycle, p. 155-201. In M. Alexander [Ed.], Advances in microbial ecology. Vol. 2. Plenum.

Brimblecombe, P. and D. Shooter. 1986. Photo-oxidation of dimethylsulphide in aqueous solution. Mar. Chem. 19: 343-353.

Charlson, R. J., J. E. Lovelock, M. O. Andreae, and S. G. Warren. 1987. Oceanic phytoplnakton, atmospheric

sulphur, cloud albedo and climate. Nature 326: 655-661.

Cooper, W. J., and P. A. Matrai. 1989. Distribution of dimethyl sulfide in the oceans, p. 140-151. In E. S. Saltzman and W. J. Cooper [Eds.], Biogenic sulfur in the Environment. ACS 393.

Dacey, J. W. H., and S. G. Wakeham. 1986. Ocean dimethylsulfide: production during zooplankton grazing on phytoplankton. Science 233: 1314-1316.

Deprez, P. P., P. D. Franzmann, and H. R. Burton. 1986. Determination of reduced sulfur gases in Antarctic lakes and seawater by gas chromatography after solid adsorbent preconcentration. J. Chromatogr. 362: 9-21.

Dickson, D. M., R. G. Wyn Jones, and J. Davenport. 1980. Steady state osmotic adaptation in *Ulva lactuca*. Planta 150: 158-165.

Drotar, A., G. A. Burton, Jr., J. E. Tavernier, and R. Fall. 1987. Widespread occurrence of bacterial thiol methyltransferases and the biogenic emission of methylated sulfur gases. Appl. Environ. Microbiol. 53: 1626-1631.

Franzmann, P. D., P. P. Deprey, H. R. Burton, and J. van den Hoff. 1987. Limnology of Organic Lake, Antarctica, a meromictic lake that contains high concentrations of dimethyl sulfide. Aust. J. Mar. Freshw. Res. 38: 409-17.

Hammer, U. T. 1978. The saline lakes of Saskatchewan III. Chemical characterization. Int. Revue ges. Hydrobiol. 63: 311-335.

Hammer, U. T., R. C. Haynes, J. M. Heseltine, and S. M. Swanson. 1975. The saline lakes of Saskatchewan. Verh. Internat. Verein. Limnol. 19: 589-598.

Hammer, U. T., and R. C. Haynes. 1978. The saline lakes of Saskatchewan II. Locale, hydrography and other physical aspects. Int. Revue ges. Hydrobiol. 63: 179-203.

Hammer, U. T. and Parker, R. C. 1984. Limnology of a perturbed highly saline Canadian lake. Arch. Hydrobiol. 102: 31-42.

Hayduck, W., and H. Laudie. 1974. Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions. A. I. Ch. E. J. 20: 611-615.

Healey, F. P. 1973. Inorganic nutrient uptake and deficiency in algae. CRC Crit. Rev. Microbiol. 3(1): 69-113.

Hecky, R. E., and P. Kilham. 1988. Nutrient limitation of phytoplankton in freshwater and marine environments: A review of recent evidence on the effects of enrichment. Limnol. Oceanogr. 33: 796-822.

Hofmann, D. J. 1990. Increase in the stratospheric background sulfuric acid aerosol mass in the past 10 years. Science 248: 996-1000.

Iverson, R. L., F. L. Nearhoof, and M. O. Andreae. 1989.

Production of dimethylsulfonium propionate and dimethylsulfide phytoplankton in estuarine and coastal waters. Limnol. Oceanogr. 34: 53-67.

Jeglum, J. K., and D. W. Cowell. 1982. Wetland ecosystems near Kinoje lakes, southern interior Hudson Bay lowland. Naturaliste can. 109: 621-635.

Keller, M. D., W. K. Bellows, and R. R. L. Guillard. 1989. Dimethyl sulfide production in marine phytoplankton, p. 167-182. In E. Saltzmann and W. Cooper [Eds.], Biogenic Sulfur in the Environment. ACS 393.

Kiene, R. P., and T. S. Bates. 1990. Biological removal of dimethyl sulphide from sea water. Nature 345: 702-705.

Lewis, W. K., and W. C. Whitman. 1924. Principles of gas adsorption. Ind. Eng. Chem. 17: 1215-1220.

Luther, G. W., T. M. Church, J. R. Scudlark, and M. Cosman. 1986. Inorganic and organic sulfur cycling in salt-marsh pore waters. Science 232: 746-749.

Morrison and Hines. 1990. The variability of biogenic sulfur flux from a temperate salt marsh on short time and space scales. Atmos. Environ. 24A: 1771-1779.

Pala, S., and A. Boissonneau. 1982. Wetland classification maps for the Hudson Bay lowland. Naturaliste can. 109: 653-659.

Reed, R. H. 1983. The osmotic responses of *Polysiphonia Lanosa* (L.) Tandy from marine and estuarine sites:

Evidence for incomplete recovery of turgor. J. Exp. Mar. Biol. Ecol. 68: 169-193.

Richards, S. R., C. A. Kelly, and J. W. M. Rudd. 1991. Organic volatile sulfur in lakes of the Canadian Shield and its loss to the atmosphere. Limnol. Oceanogr. 36: 468-482.

Saltzmann, E. S., and W. J. Cooper [Eds]. 1989. Biogenic sulfur in the environment. ACS 393.

Sherwood, J. E., F. Stagnitti, M. J. Kokkinn, and W. D. Williams. 1991. Dissolved oxygen concentrations in hypersaline waters. Limnol. Oceanogr. 36: 235-250.

Stainton, M. P., M. J. Capel, and F. A. J. Armstrong. 1977. The chemical analysis of freshwater, 2nd ed. Can. Fish. Mar. Serv. Misc. Spec. Publ. 25.

Stumm, W., and J. J. Morgan. 1970. Aquatic chemistry. An introduction emphasizing chemical equilibria in natural waters. Wiley-Interscience.

Tabatabai, M. A., and J. M. Bremner. 1970. An alkaline oxidation method for the determination of total sulfur in soils. Soil Sci. Am. Proc. 34: 62-65.

Turner, S. M., G. Malin, and P. S. Liss. 1989. Dimethyl sulfide and (dimethylsulfonio)propionate in European coastal and shelf waters, p. 183-200. In E. S. Saltzman and W. J. Cooper [Eds.], Biogenic Sulfur in the Environment. ACS 393.

Vairavamurthy, A., M. O. Andreae, and R. L. Iverson. 1985.

Biosynthesis of dimethylsulfide and dimethylpropiothetin by *Hymenomonas carterae* in relation to sulfur source and salinity variations. Limnol. Oceanogr. 30: 59-70.

Walker, K. F., W. D. Williams, and U. T. Hammer. 1970. The Miller method for oxygen determination applied to saline lakes. Limnol. Oceanogr. 15: 814-815.

Walton Smith, F. G. (Ed.). Handbook of Marine Science. 1971. Vol. 1 (CRC Press: Ohio).

Wanninkof, R. H. 1986. Gas exchange across the air-water interface determined with man made and natural tracers. PhD thesis. Columbia University.

Wilke, C. R., and P. Chang. 1955. Correlation of diffusion coefficients in dilute solutions. A. I. Ch. E. J. 1: 264-270.

4. Sources and sinks of organic volatile sulfur compounds in lakes.

4.0. Acknowledgements

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4.1. Abstract

Rates and sites of organic volatile sulfur production in lakes and loss to the atmosphere were studied in a salt lake in southern Saskatchewan, and a dilute freshwater lake at the Experimental Lakes Area (ELA) in northwestern Ontario, Canada. These lakes differed in salt concentration by 5 orders of magnitude.

In the dilute freshwater lake (Lake 114), water column DMS production in the light accounted for 90% of whole-lake DMS production. Sediment release was a comparatively minor DMS source (approximately 10%). In a hypersaline lake (Patience Lake), however, sediments were the principal net source (100% of measured lake production). The greatest loss mechanism in both lakes was as flux to the atmosphere (Lake 114, 800 nmol m^{-2} d^{-1}; Patience Lake, 430 nmol m^{-2} d^{-1}).

The principal source of MSH in the freshwater lake was sediment production (1080 nmol m^{-2} d^{-1}). Seventy percent of this MSH was destroyed in the water column (-770 nmol m^{-2} d^{-1}, calculated value), and flux to the atmosphere accounted for the remainder (310 nmol m^{-2} d^{-1}).

In this and other freshwater lakes, sediment pore-water concentrations of both DMS and MSH were correlated to sediment type, with the greatest concentrations (up to 190 nM) in flocculent, organic-rich sediment.

4.2. Introduction

Organic volatile sulfur compounds (VSCs) are present in the entire spectrum of aquatic systems, from oceans to freshwater Canadian Shield lakes to hypersaline lakes (Andreae 1990, Richards et al. 1991, Richards et al., in prep.). Previous work suggests that in lakes both the water column and sediments are the site of organic VSC production, including species like dimethyl sulfide (DMS), methanethiol (MSH), and dimethyl disulfide (DMDS; Richards et al. 1991). However, the relative magnitude of production of VSCs at these sites has not been established.

Water column production of DMS in lakes was initially suggested by the occurrence of similar surface water DMS concentrations in lakes with widely differing epilimnetic sediment surface area (Ae) to epilimnion volume (Ve) ratios (Ae:Ve; Richards et al. 1991).

An additional sediment source in lakes was also suggested by the occurrence of higher surface water MSH, DMS, and DMDS concentrations in unstratified, shallow lakes when compared to stratified lakes (Richards et al. 1991). Furthermore, sediment pore-waters contain DMS and MSH concentrations up to 14 times greater than overlying water, and hypolimnetic accumulations of DMS, MSH, and DMDS occur during stratification (Henatsch and Juttner 1990, Richards et al. 1991). These data suggest sediments are important in

VSC production in addition to the water column.

In this study I measured the relative importance of the sites of production and loss of DMS and MSH in a shallow, freshwater lake. Because DMS is linked to osmoregulation in algae, DMS production and loss in a shallow, hypersaline lake was also examined.

4.3. Materials and Methods

4.3.0. Sample collection and site description. Lakes 114, 239, 240, 302 North and South, 661, 225, 303, and 304 are all freshwater lakes in the Experimental Lakes Area (ELA) in the Canadian Shield area of northwestern Ontario, Canada (Brunskill and Schindler 1971). Patience Lake is a NaCl-dominated lake in southern Saskatchewan, Canada, in the Great Plains physiographic division (Hammer and Haynes 1978). Samples from freshwater lakes were collected from July to September 1989, and from Patience Lake in July 1990. Surface water samples were obtained by hand in silanized glass bottles and then immediately placed on ice in the dark. Samples from lakes at the ELA were analyzed for organic VSCs within two hours of collection, and always within 24 hours. Because Patience Lake was further from the site of analysis, tetracycline and chloramphenicol (75 and 125 mg $litre^{-1}$; Kiene and Bates 1990) were added immediately to samples from this lake to prevent microbial activity and alteration of sample integrity. Samples from this lake were analyzed within 3 days. Budgets were constructed for Lake 114 and Patience Lake, two shallow lakes differing in ion concentration by five orders of magnitude (Table 4.1).

4.3.1. Organic volatile sulfur analysis. The method for analyzing lake water has been described in detail (Richards

Table 4.1. Morphometric and chemical data for Lake 114 and Patience Lake.

Lake*	A_o (10^4 m^2)	Volume (10^8 L)	$\bar{Z}$ (m)	Conductivity (mmho/cm)	Dominant Anion
114	12.1	2.07	1.7	0.019 +	HCO_3^-
Patience	563	56.3	1.0	280	Cl^-

* Lake 114 data from Brunskill and Schindler 1971
Patience Lake data from Hammer 1986

\+ mean conductivity in ELA lakes (Armstrong and Schindler 1971)

et al. 1991). Briefly, a purge-and-trap method was used to cryogenically pre-concentrate organic VSCs in a glass U-trap immersed in liquid N_2. The contents of the U-trap were injected onto a GC column containing 20% SE-30 on Chromsorb P (60/80 mesh). Sulfur species were detected using a dual-flame photometric detector (FPD). Retention time comparisons to sulfur standards (Aldrich) were used to identify the sulfur peaks. GC-mass spectrometry was used previously to confirm retention time identifications (Richards et al. 1991). GC-standardization was accomplished using volumetric dilution of sulfur standards (Tangerman 1986).

4.3.2. Sediment release. Sediment release of organic VSCs in Lake 114 was monitored by placing plexiglass sediment chambers over the sediment surface. The chambers measured 0.5 m X 0.5 m X 0.1 m, with a horizontal skirt around the open bottom that sealed the box to the sediment. A battery-driven magnetic stirrer (1 rpm) was used to prevent stratification within the chamber. Light and dark differences were determined by using both clear and opaque chambers. The VSC concentrations were monitored by sampling the contents of the chambers at specific time intervals. In some experiments, oxygen was also measured. Progressively decreasing oxygen concentrations indicated that chambers were positioned correctly on the sediment surface, without

leakage. Sampling was stopped after sufficient data points were obtained.

In Patience Lake, sedimentary release was measured by incubating sediment cores in natural daylight and in the dark at *in situ* temperatures, ± 2°C. At specific times, overlying water in successive cores was removed for analysis. MSH concentrations were too low for detection with the small sample volumes obtained from sediment cores. Therefore this species was not budgeted in Patience Lake.

4.3.3. Water column processes. In both Lake 114 and Patience Lake, bottle incubations were used to monitor water column changes. In Lake 114, both clear and opaque silanized glass bottles were placed at a depth of 1 m in the water column, and analyzed for VSCs at different time points.

In Patience Lake, clear and opaque bottles were placed in an open, uncovered incubator, and maintained at *in situ* temperatures, ± 2 °C. At pre-determined times, antibiotics were added to one "light" and one "dark" bottle (see "Sample Collection"). Bottles were then removed from the incubator and placed on ice in the dark until analysis.

4.3.4. Pore-water collection. Pore-water was obtained by centrifuging sediment at 3,000 rpm for 20 minutes. Potential losses of volatile species were minimized by

capping the centrifuge tubes, and using small vessels to avoid a large headspace. N_2 was used to flush centrifuge tubes prior to use in order to ensure anaerobic conditions. Mixed sediment was obtained by collecting the top 0-6 cm of sediment from Ekman grab samples. In order to obtain concentration profiles, cores were taken by hand. These cores were sliced into 2 cm sections, and centrifuged to obtain the pore-water. Concentrations were measured in the same way as described above for lake water.

4.3.5. Flux calculations. Flux to the atmosphere was calculated using the stagnant boundary layer model of Lewis and Whitman (1924). For Lake 114, windspeed was measured by anemometer and recorded using an Omnidata datapod. Because of the close proximity of Patience Lake to Saskatoon, windspeed data for Saskatoon was obtained from AES Canada and used for modelling Patience Lake. The relationship of Wanninkhof et al. (1986) between wind speed and gas exchange was used to determine boundary layer thicknesses. Flux was calculated from the mean daily boundary layer thickness and the measured concentration on that date. Molecular diffusivities were calculated as described earlier (Richards et al. 1991) using the relationship of Hayduck and Laudie (1974). Molecular diffusivities were calculated separately for Lake 114 and Patience Lake to account for differences in both temperature and salt concentration of the two systems.

4.4. Results

4.4.0. Surface water concentrations. A similar spectrum of organic VSCs were detected in the surface waters of both Lake 114 and Patience Lake, including COS, DMS, MSH, and DMDS (Fig. 4.1). CS_2 was detected in Patience Lake only. Time-weighted mean concentrations of DMS and MSH in Lake 114 (6.6 and 8.6 nM, respectively, Fig. 4.1) were 1.7 and 30 times greater than concentrations in Patience Lake (3.9 and 0.28 nM, respectively, Fig. 4.1). COS (mean concentrations, Lake 114: 0.61 nM; Patience Lake: 0.86 nM) and DMDS (mean concentrations, Lake 114: 1.4 nM: Patience Lake: 1.6 nM) were present at very similar concentrations in the two lakes (Fig. 4.1).

4.4.1. Sediment release rates. In both Lake 114 and Patience Lake sediment release of DMS was observed (Table 4.2). In Lake 114, sediment release was always greater under dark conditions (dark: 8.6 and 12.5 nmol m^{-2} hr^{-1}, light: 0 and 3.1 nmol m^{-2} hr^{-1}; Table 4.2). In Patience Lake, dark release exceeded light release on one of two sampling dates (4 July, 1990; Table 4.2). Mean release rates were up to one order of magnitude greater in Patience Lake than Lake 114 (Table 4.2).

In Lake 114, MSH release was also measured, and its accumulation rate was approximately 2-20 times higher than

Figure 4.1. Organic VSC surface water concentrations.

(A) Patience Lake, 1990

(B) Lake 114, 1988

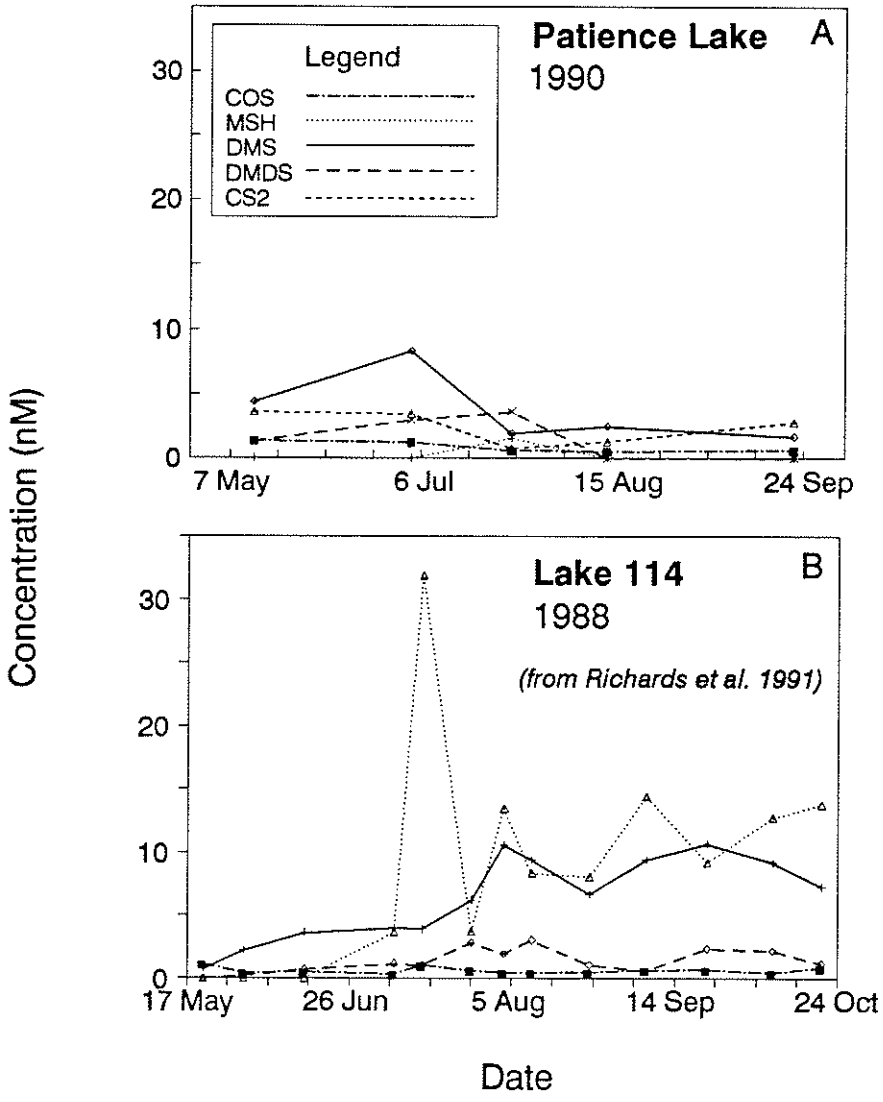

Legend
COS
MSH
DMS
DMDS
CS2
Patience Lake
1990
A
30
20
10
0
7 May
6 Jul
15 Aug
24 Sep
Lake 114
1988
B
(from Richards et al. 1991)
30
20
10
0
17 May
26 Jun
5 Aug
14 Sep
24 Oct
Concentration (nM)
Date

Table 4.2. Lake 114 and Patience Lake: Dissolved O_2, DMS, and MSH concentrations with time in sediment chambers and cores, and sediment release rates calculated from these measurements.

Date	Time (hours)	[O_2] (mg/L) Dk	[O_2] (mg/L) Lt	DMS (nmol) Dk	DMS (nmol) Lt	MSH (nmol) Dk	MSH (nmol) Lt
LAKE 114							
7-8	0	Not Done		60	65	(20)*	(20)
Sept.	3.25			70	70	Not Detected	
1989	8			90	90	Not Detected	
	21.3			130	60	395	82.5
	26.2			117.5	57.5	445	140
	31.4			175	67.5	635	127.5
Rate (nmol m^{-2} hr^{-1}) +				**8.6**	**0.0**	**74**	**17**
18-21	0	4.6	4.6	57.5	57.5	Not Detected	
Sept.	21	4.5	4.3	75	100		
1989	31.4	1.7	3.4	125	87.5		
	45.5	0.9	3.2	112.5	95		
	51.5	Not Done		150	Not Done		
	74.5	0.4	1.4	NDone	NDone		
	79.2	0.3	Not Done	250	Not Done		
Rate (nmol m^{-2} hr^{-1}) +				**12.5**	**3.1**	**0.0**	**0.0**
PATIENCE LAKE							
4	0 ∓	Not Done		0.65	0.65	Not Detected	
July	11.5			1.1	0.8		
1990	34			2.3	1.3		
	81.5			20.7			
Rate (nmol m^{-2} hr^{-1}) §				**130**	**10**	**0.0**	**0.0**
24	0 ∓	Not Done		0.87	0.76	Not Detected	
July	27.3			2.0	3.5		
1990	47.5			3.6	3.3		
Rate (nmol m^{-2} hr^{-1}) §				**30**	**30**	**0.0**	**0.0**

(Table 4.2, continued)

* MSH was not detected in samples until 21.3 hours. This was probably because of the relatively small sample volumes (50 ml) used, and the initially low concentration. Therefore, the surface water concentration (20 nmol) at the start of the experiment was used as the concentration at time = 0.

+ Sediment release rates from sediment chambers calculated using a surface area of 2500 cm^2

∓ Sediment release rates from cores calculated using core surface area of 19.63 cm^2

§ The sulfur mass at time = 0 was taken from the surface water concentration in the lake at the time cores were obtained.

that of DMS (Table 4.2). As observed for DMS, the sediment release of MSH was greater (approximately 4-5 times) in the dark than the light (74 nmol m^{-2} hr^{-1} and 16.6 nmol m^{-2} hr^{-1}, respectively; Table 4.2). The quantity of MSH in the small sample volumes obtained from Patience cores were below detection limits. Therefore, sources and sinks for MSH are not reported for Patience Lake.

4.4.2. Pore-water concentrations of organic VSCs. In both Lake 114 and Patience Lake, concentrations of DMS and MSH in sediment pore-waters were 2-160 times greater than concentrations in the overlying water (Table 4.3). The direction of the concentration gradient supported the measured accumulation of MSH and DMS above the sediments in sediment chambers and cores (Table 4.2). In eight other lakes, sediment pore-water concentrations of DMS and MSH were greater than the overlying water (Table 4.3; S. Richards, unpubl. data).

Pore-water MSH concentrations were almost always greater than pore-water DMS concentrations (Table 4.3), and in Lake 114 the rate of MSH accumulation above the sediments was 2-20 times greater than DMS accumulation on Sept. 7-8 (Table 4.2). However, MSH concentrations in the overlying water, with one exception, were lower than DMS concentrations. These data suggested water column MSH consumption was proportionately greater than water column

Table 4.3. Comparison of epilimnetic sediment (0-6 cm) and surface water DMS and MSH concentrations.

Lake	Sediment type	Date	VSC Conc'n (nM) Porewater DMS	Porewater MSH	Surface DMS	Surface MSH	Ratio P.W.: Surf. DMS	Ratio P.W.: Surf. MSH
114*	floccy organic	26Jul88	11	53	6.2	3.7	1.8	14
		3Aug88	38	120	11	14	8.9	3.6
Pat.	salt & OM	24Jul90	60	250+	2.0	1.5	30	>160
239≠	sandy	9Aug89	4.6	ND	1.1	ND	4.6	--
240	sandy	11Aug89	4.4	27				
225	floccy organic	8Aug89	15	159	1.3	ND	12	>3000§
661	floccy organic	11Jul89	6.9	16	0.69	ND	10	>270§
239≠	muddy	25Jul89	7.5	17	1.1	ND	6.8	>280§

* Richards et al. 1991

\+ MSH pore-water value from 4-6 cm slice.

≠ Time-weighted mean surface water concentration for 1988 (Richards et al. 1991)

§ Ratio is based on an approximate detection limit of 0.06 nmoles

DMS consumption.

A correlation between sediment pore-water concentrations and sediment type was observed. Organic-rich, flocculent sediments contained pore-water with mean DMS and MSH concentrations of 29 and 9.6 nM, respectively (n = 10; data not shown). Pore-water from sandy, low porosity sediments contained less than one-third these concentrations (n = 6; DMS: 5.1 nM, MSH: 3.2 nM; data not shown). This suggested an important variation in organic VSC production in ligh as compared to low porosity sediments.

4.4.3. Sediment profiles. Sediment profiles in Lakes 114 and 303 were determined on 3 dates in each lake (Figs. 4.2, 4.3). Two species were detected, DMS and MSH. DMS concentrations were sometimes uniform with depth, but tended to be relatively higher (60 nM) at the lower depths (4-6 cm) in late September (Figs. 4.2A, 4.3A).

MSH concentrations were much more dynamic, although the seasonal trend was similar to DMS (Figs. 4.2B, 4.3B). In general, pore-water profiles showed a progressive decrease in concentration in the top layers. By September the highest concentrations of MSH were in the lower layers (4-6 cm).

4.4.4. Water column incubations. In Lake 114, net water column production of DMS in bottle incubations was almost

Figure 4.2. Lake 114 sediment profile

(A) DMS

(B) MSH

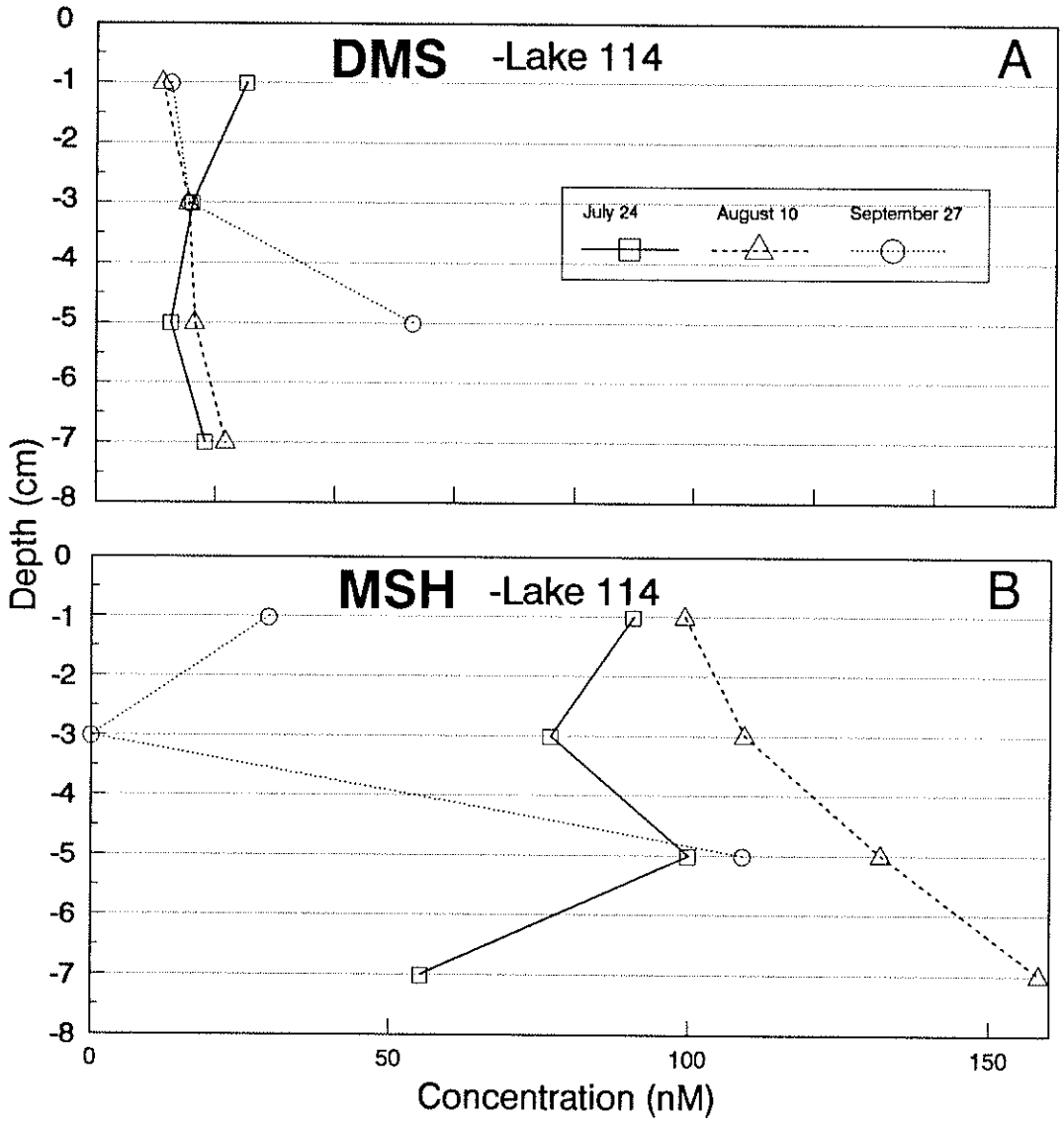
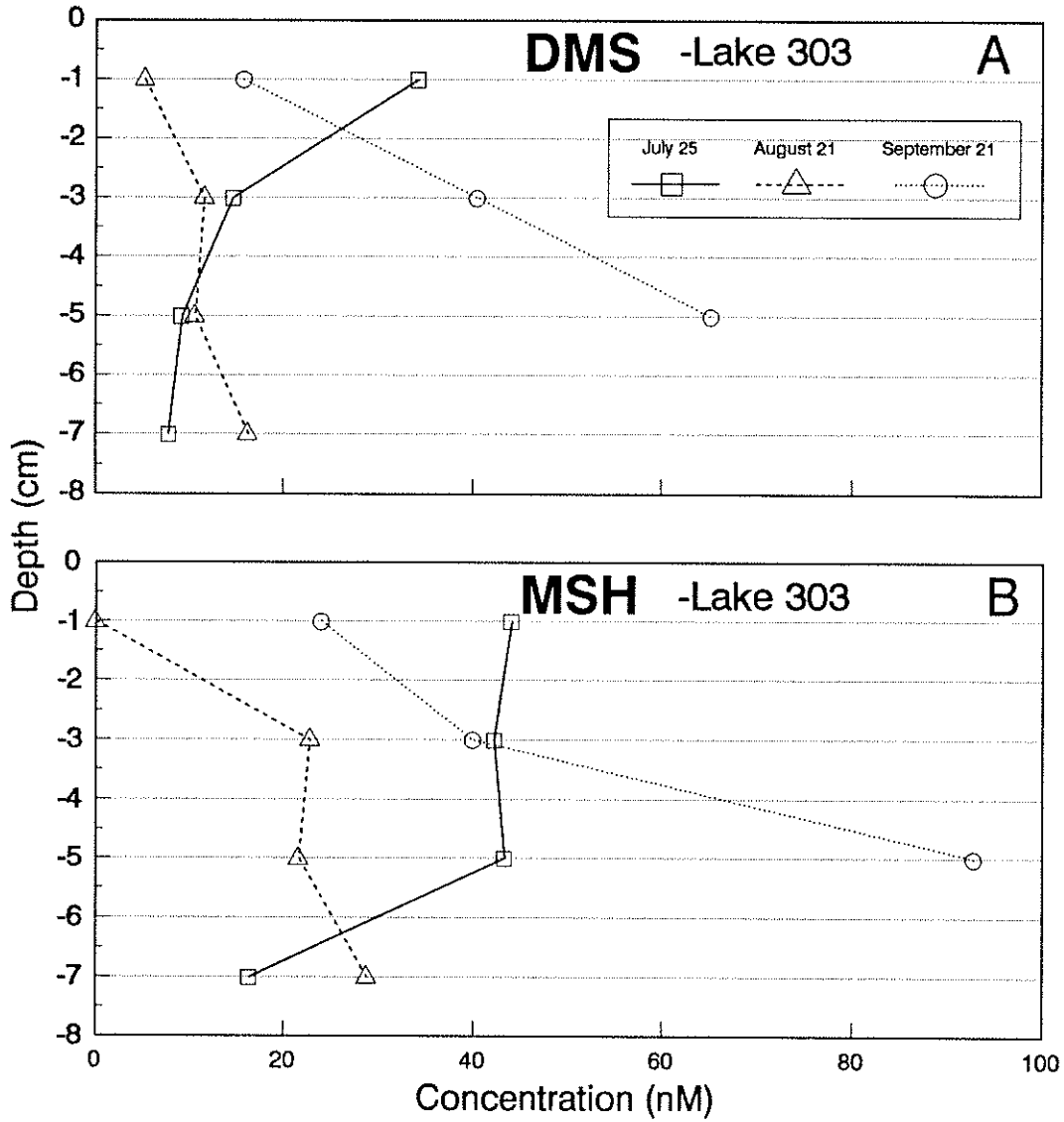

DMS -Lake 114
A
July 24
August 10
September 27
MSH -Lake 114
B
Depth (cm)
0
-1
-2
-3
-4
-5
-6
-7
-8
0
50
100
150
Concentration (nM)

Figure 4.3. Lake 303 sediment profile

(A) DMS

(B) MSH


DMS -Lake 303
A
July 25
August 21
September 21
MSH -Lake 303
B
Depth (cm)
0
-1
-2
-3
-4
-5
-6
-7
-8
0
20
40
60
80
100
Concentration (nM)

three times greater in the light (0.08 nmol litre^{-1} hr^{-1} or 136 nmol m^{-2} hr^{-1}, Table 4.4) than in the dark (0.03 nmol litre^{-1} hr^{-1} or 51 nmol m^{-2} hr^{-1}, Table 4.4). In Patience Lake, however, no detectable change in DMS concentration occurred in the water samples under either light or dark conditions (Table 4.4).

In Lake 114, the water column was a site of net destruction for MSH (-25 nmol m^{-2} hr^{-1}, calculated value). MSH was not detectable (<0.06 nM) in bottle incubations from Patience Lake, although it was in the surface water determination (time = 0). This again suggested net destruction occurred in the water column.

4.4.5. Diel patterns. Diel monitoring of surface water concentrations was done on Lakes 302 South and 114 at the ELA (Fig. 4.4). On three of four dates, peaks in the concentrations of DMS and MSH occurred during the afternoon. The amplitude of these cycles varied from 0.5-4 nM, depending on the species and date, which represented usually about a 10% change in concentration over a 24 h period. In one study (26 July, Fig. 4.4C), the cycle in DMDS concentration (also measured) appeared to lag behind the peak in DMS and MSH. This was possibly an indication of DMDS production from MSH oxidation in the water column.

Table 4.4. Lake 114 and Patience Lake: DMS concentrations with time in bottle incubations and rates of change.

Lake	Date	Time (hr)	Light * [DMS](nM)	Dark * [DMS](nM)
114	12 Sep 1989	0	2.7	2.7
		6.5	3.0	3.6
		10.5	3.6	3.6
		23.5	4.4	3.7
Rate (nmol l^{-1} hr^{-1})			**0.08**	**0.03**
(nmol m^{-2} hr^{-1}) +			**136**	**51**
Patience	4 July 1990	0 ∓	1.96	1.96
		11.5	2.0	1.7
		34	1.7	2.1
Rate (nmol l^{-1} hr^{-1})			**No detectable trend**	
(nmol m^{-2} hr^{-1}) +			**No detectable trend**	
Patience	24 July 1990	0 ∓	2.5	2.5
		27.3	1.8	3.0
		47.5	2.0	2.1
Rate (nmol l^{-1} hr^{-1})			**No detectable trend**	
(nmol m^{-2} hr^{-1}) +			**No detectable trend**	

* Concentrations in Lake 114 are means of triplicates samples; concentrations in Patience Lake are from single determinations

\+ Areal rate calculated using mean depths given in Table 1: Lake 114, 1.7 m; Patience Lake, 1 m.

∓ Concentration at time = 0 taken from the surface water concentration determined on that date.

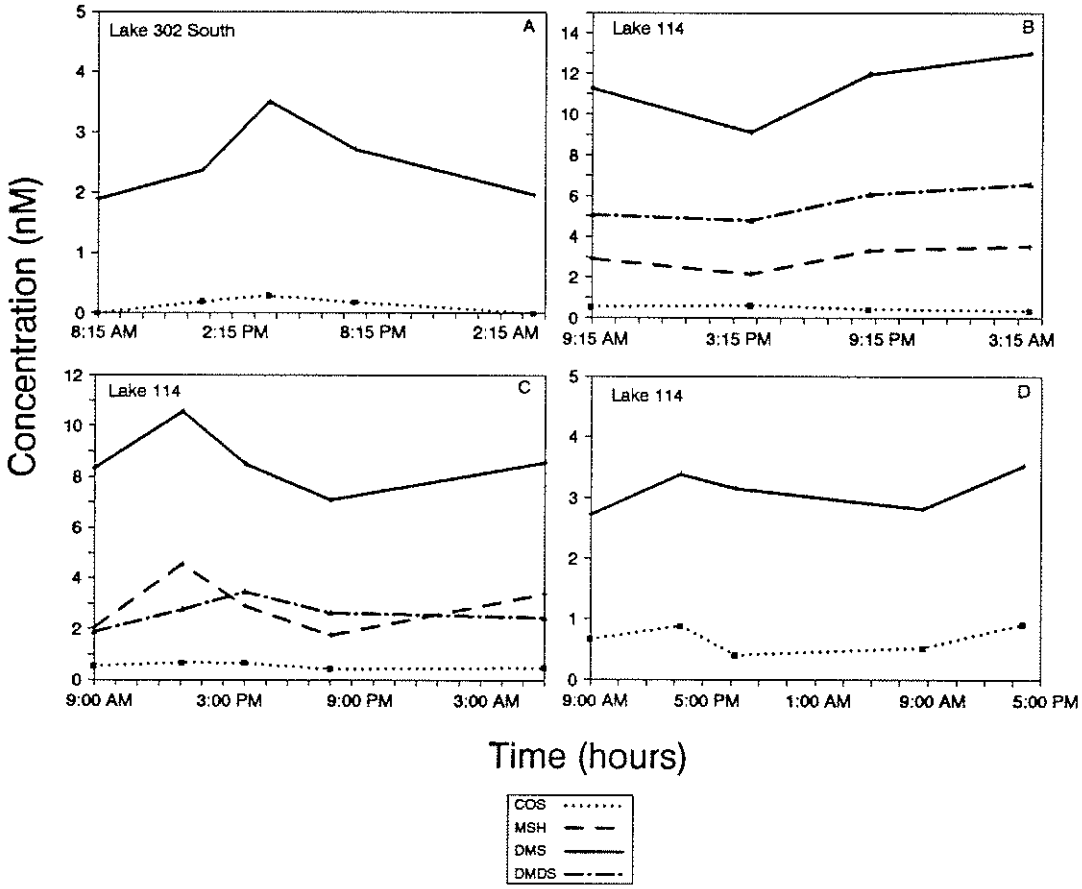
Figure 4.4. Diel studies in freshwater lakes.

(A) 302 South, 26 July 1989

(B) 114, 17 July 1989

(C) 114, 26 July 1989

(D) 114, 12 September 1989


Lake 302 South
A
Lake 114
B
Lake 114
C
Lake 114
D
Concentration (nM)
Time (hours)
8:15 AM
2:15 PM
8:15 PM
2:15 AM
9:15 AM
3:15 PM
9:15 PM
3:15 AM
9:00 AM
3:00 PM
9:00 PM
3:00 AM
9:00 AM
5:00 PM
1:00 AM
9:00 AM
5:00 PM
COS
MSH
DMS
DMDS

4.4.6. Atmospheric flux estimates. Flux of DMS to the atmosphere was comparable in both Lake 114 and Patience Lake (33 and 18 nmol S m^{-2} d^{-1}, Table 4.5). MSH flux to the atmosphere from Lake 114 was approximately one-half the DMS flux (13 nmol S m^{-2} d^{-1}, Table 4.5).

4.4.7. Lake budgets for DMS and MSH. Data from Tables 4.2, 4.4, and 4.5 were used to calculate a daily rate of change for each site in both lakes (Table 4.6). The number of light and dark hours in a 24 hour period were taken into account in the budget calculations. In Lake 114, the major source of DMS was the water column (2210 nmol S m^{-2} d^{-1}; Table 4.6, Fig. 4.5A). Sedimentary production (130 nmol S m^{-2} d^{-1}) accounted for only about 6% of the total lake production. The major sink for DMS was loss to the atmosphere (800 nmol S m^{-2} d^{-1}).

Unlike DMS, MSH appeared to be derived principally from the sediments (net lake production: 1080 nmol S m^{-2} d^{-1}; Table 4.6, Fig. 4.5B). Because the flux to the atmosphere (310 nmol m^{-2} d^{-1}, Table 4.6) was so much smaller, significant decomposition must have occurred in the water column (-770 nmol S m^{-2} d^{-1}, calculated value).

In Patience Lake, the only net source of DMS was from the sediments (720-1320 nmol S m^{-2} d^{-1}, Table 4.6, Fig. 4.6). No net production or destruction was measured in the water column. The flux to the atmosphere (430 nmol S m^{-2} d^{-1}, Table

Table 4.5. Lake 114 and Patience Lake: Gas exchange.

Date	Cpd.	Windspeed at 1 m* ($m\ s^{-1}$)	z^+ (um)	Molecular Diffusivity‡ ($10^5\ cm^2\ s^{-1}$)	Air/Water Flux§ ($nmol\ m^{-2}\ hr^{-1}$)
LAKE 114					
12 Sep 89	DMS	1.00	298.2	1.0	33
12 Sep 89	MSH	1.00	298.2	1.1	13
PATIENCE LAKE					
4 Jul 89	DMS	2.08	226.3	0.6	18
24 Jul 89	DMS	1.92	237.0	0.6	18

* Windspeed is a 24 hour mean

\+ z = diffusive boundary layer thickness

‡ Calculated from equation given in Hayduck and Laudie (1974), using η (viscosity) = 1.64 cp. for Patience Lake

§ Atmospheric concentration assumed to be negligible

Table 4.6. Budgets for Lake 114 and Patience Lake: Whole lake changes (units in nmol m^{-2} d^{-1}).

Lake*	Cpd.	Water* Lt.	Water* Dk	Sediments* Lt	Sediments* Dk	Atmos. Loss	Balance of Sources/Sinks+ +	Balance of Sources/Sinks+ -
114	DMS	1600	610	1.6	130	800	2340	800
	MSH	(-770)		200	880	310	1080	1080
Pat.	DMS	No change		150	1170	430	1320	430
	DMS	No change		450	270	430	720	430

* 24 hour rates calculated using data in Tables 2 and 5, and light regimes as follows: Lake 114, 12 hr light/12 hr dark; Patience Lake, 15 hr light/9 hr dark

\+ "Balance of sources and sinks" is a comparison of the total production and loss in a 1 m^2 column of water, over a 24-hour period

Figure 4.5. Lake 114: Budgets of DMS and MSH sources and sinks. Numbers shown are for the whole lake change in a 24-hour period. They have been corrected for the light regime at that time.

(A) DMS (B) MSH

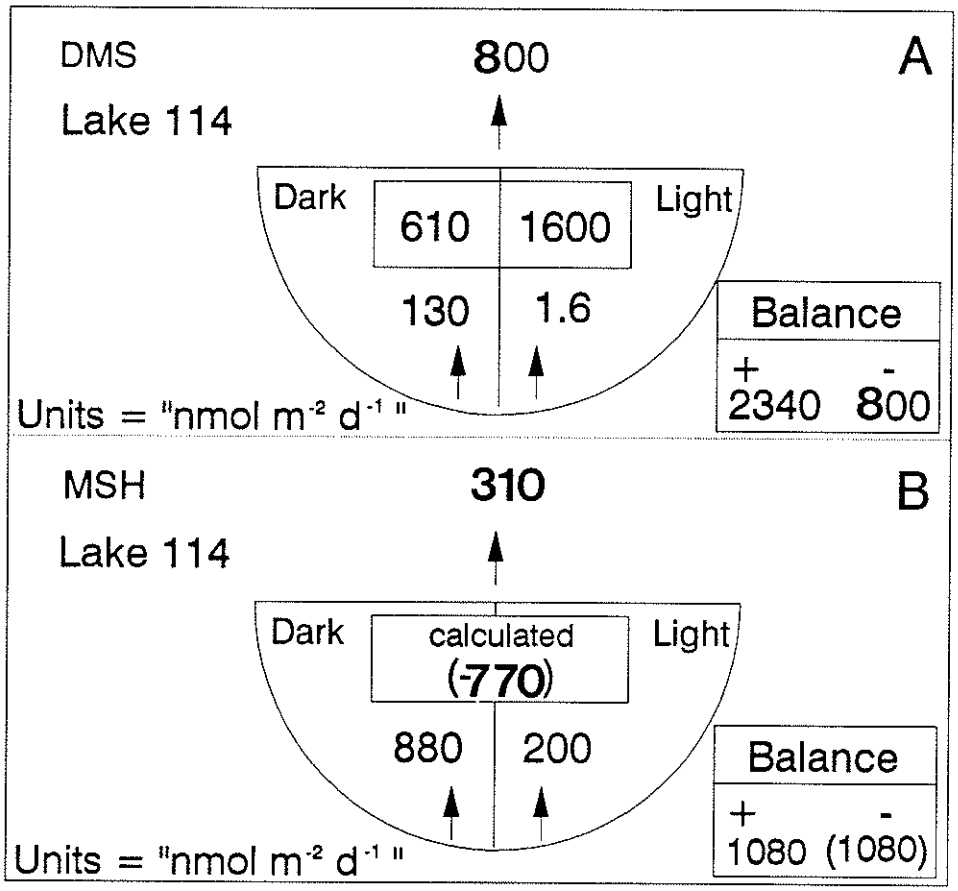
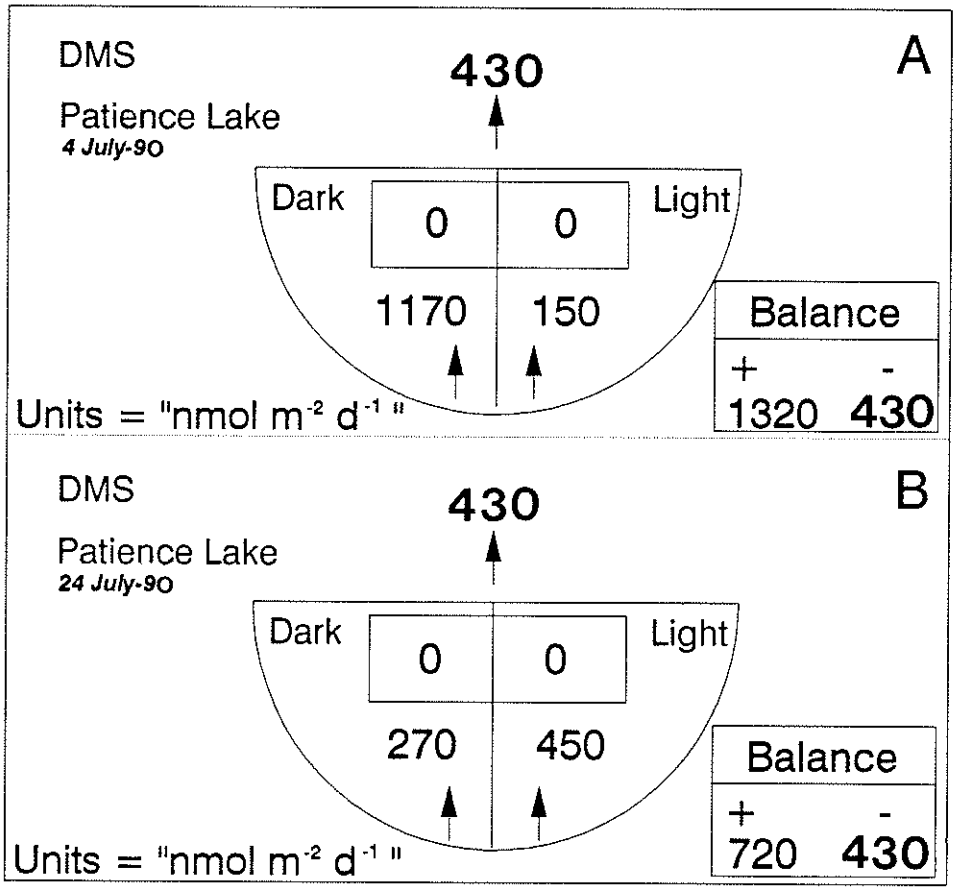

DMS
Lake 114
800
A
Dark
610
1600
Light
130
1.6
Balance
+
2340
-
800
Units = "nmol m-2 d-1 "
MSH
Lake 114
310
B
Dark
calculated
(-770)
Light
880
200
Balance
+
1080
-
(1080)
Units = "nmol m-2 d-1 "

Figure 4.6. Patience Lake: Budgets of DMS sources and sinks. Numbers shown are for the whole lake change in a 24-hour period. They have been corrected for the light regime at that time.

(A) 4 July 1990 (B) 24 July 1990


DMS
Patience Lake
4 July-90
430
A
Dark
Light
0
0
1170
150
Balance
+
-
1320
430
Units = "nmol m-2 d-1 "
DMS
Patience Lake
24 July-90
430
B
Dark
Light
0
0
270
450
Balance
+
-
720
430
Units = "nmol m-2 d-1 "

4.6) was less than the sediment flux.

A MSH budget for Patience Lake was not possible because MSH was often undetectable in the small sample volumes used from core incubations.

4.5. Discussion

The principal objective of this study was to determine the major sources and sinks of DMS and MSH in lakes. Marine studies of DMS production and loss have appropriately emphasized water column processes in studies of DMS cycling in the oceans (Andreae 1990). In lakes, however, sediments often contribute importantly to substance cycling and therefore it is important to determine the relative importance of the water column, sediments, and atmosphere as sources and sinks in lakes. Identification of these sites is a necessary step in the understanding of the cycling of DMS and MSH in lakes, and in the designing of future studies of these processes.

4.5.1. Water column DMS production. Freshwater Lake 114 and hypersaline Patience Lake had very different patterns of DMS production. In Lake 114, DMS originated largely in the water column, whereas in Patience Lake the sediments were the most important site of production (Table 4.6). The dominance of water column production in Lake 114 was not entirely unexpected, since previous work had found similar epilimnetic DMS concentrations in freshwater lakes with widely differing ratios of epilimnetic sediment surface area to epilimnion volume (Ae:Ve; Richards et al. 1991). In Lake 114, water column production could have been due to (i)

freshwater algae, which have been shown to produce both DMSP (M. Keller, pers. comm., Challenger et al. 1957, S. Richards, unpubl. data) and DMS (Caron 1990, Bechard and Rayburn 1979), or (ii) microbial decomposition of sulfur-containing organic matter (Finster et al. 1990, Bremner and Steele 1978). The fact that light affected DMS production in this lake (Tables 4.2, 4.4, Fig. 4.4) and the lack of any measureable light or dark DMS production in the water column of Patience Lake, suggested predominantly an algal role.

In contrast to the results from Lake 114, the water column was not a site of net DMS production in Patience Lake on two separate dates (Table 4.4). These results were surprising because Patience Lake is hypersaline, and it was expected that the breakdown of algal DMSP (thought to function in osmoregulation, Cooper and Matrai 1989) would be an important precursor of DMS. Algal biomass in Patience Lake was approximately 1.5-25 times greater than Lake 114 (L. 114, unpubl. data; Patience Lake, Richards et al., in prep.). However, in marine studies, algal mass, indicated by measurements of chl a, has not been a particularly good predictor of ocean DMS and DMSP concentrations (Keller et al. 1989, Turner et al. 1989). Because only certain phytoplankton produce these compounds, algal speciation has been identified as a major factor in determining DMS production (Turner et al. 1989, Cooper and Matrai 1989, Keller et al. 1989). In Patience Lake, the phytoplankton

population was overwhelmingly dominated by *Dunaliella salina* (Richards et al., in prep., Hammer and Parker 1984). This alga uses glycerol as a solute for osmoregulation (Hammer and Parker 1984). DMSP, therefore, is likely not an important precursor of DMS in Patience Lake, even though this lake contains 100,000 times more dissolved salt than Lake 114 (Table 4.1), which has a mixed algal flora (Schindler and Holmgren 1971). The lower mean DMS concentrations in Patience Lake (Richards et al. 1991) demonstrated that waters of higher salinity do not necessarily contain higher DMS concentrations from DMSP breakdown. This supports previous observations comparing DMS concentrations in freshwater lakes and the ocean (Caron 1990, Richards et al. 1991).

The sediments were the most important site of DMS production in Patience Lake (Table 4.6). Measured sediment-to-water column fluxes were 2-10 times greater than Lake 114, and pore-water concentrations were 2-5 times greater (Table 4.3). It is hypothesized that these higher pore-water concentrations and sediment fluxes were linked to higher rates of dissimilatory sulfate reduction in sediments of Patience Lake. Sulfate reduction rates are directly related to sulfate concentrations in the surface water of lakes (Kelly and Rudd 1984) and Patience Lake had sulfate concentrations (mean concentration, 1990, 2.8 g $litre^{-1}$; Richards et al., in prep.) 3 orders of magnitude greater

than Lake 114 (2.5 mg litre^{-1}). Higher concentrations of H_2S from dissimilatory sulfate reduction could affect DMS concentrations either by (i) direct formation of DMS from H_2S via biological methylation (Drotar et al. 1987) or (ii) increased stabilization of DMS at high sulfide concentrations. Benthic algae were not expected to contribute significantly to sediment production of DMS since *Dunaliella salina* (algal species in Patience Lake) likely does not produce either DMSP or DMS (see above).

4.5.2. Sediment production of MSH. Unlike DMS, which was produced in the water column of Lake 114, MSH was destroyed in the water column (Table 4.6, Fig. 4.5). Although the MSH flux from the sediments was approximately 10-20 times greater than the DMS flux (sediment chambers, Table 4.2), the MSH released by the sediments likely reacted chemically in the water column to produce a non-volatile sulfur species. This would result in large pore-water:surface water ratios, as observed (Table 4.3). MSH contains a thiol moiety, which readily oxidizes (Adewuyi 1989) and this likely explains the comparatively low MSH concentrations in the water column.

4.5.3. Significance of light in DMS and MSH production. A role for light in both DMS and MSH fluxes was apparent in a number of different measurements: water column incubations

in Lake 114 (Table 4.4), sediment incubations (Table 4.2), and changes in *in situ* concentrations over a 24 hour cycle in the lakes (Fig. 4.4). In the water column, light had a positive influence on DMS production in Lake 114 (Table 4.4, Fig. 4.4). The diel pattern of water column DMS production (Fig. 4.4) supported an algal source for DMS, suggesting a link between diel changes in algal metabolism and DMS production. The mechanism for the light/dark effect is unknown. Also, the effect is not consistent. For example, a similar positive effect on surface DMS concentration under light conditions was observed in the Sargasso Sea (Andreae and Barnard 1984), but Turner et al. (1989) found higher DMS concentrations in the dark for a bloom of *Phaeocystis pouchetti*.

In contrast to the water column, light usually had a negative effect on DMS and MSH accumulation above the sediments (Table 4.2). This decreased accumulation in the light may have been due to (i) utilization of DMS and MSH as electron donors by photoautotrophic microorganisms (Zeyer 1987, Visscher et al. 1991) or (ii) oxidation of DMS and MSH due to oxygen production by benthic algae. Oxidation of reduced sulfur species in sediments (e.g. iron sulfides and organic sulfur compounds) has been shown to occur due to oxygen production by benthic algal mats (Amaral et al., in prep.).

4.5.4. DMS and MSH budgets. For DMS, flux to the atmosphere was a major loss route, while calculated water column destruction was more significant than atmospheric flux for MSH (Lake 114, Table 4.6). The calculated DMS flux for Lake 114 (Table 4.5) was lower than the mean flux reported previously (Richards et al. 1991), probably because this flux was measured in middle to late September, and concentrations of DMS were decreasing.

The greatest source of error in the lake budgets was likely associated with the flux estimates. Molecular diffusivities for DMS and MSH (Table 4.5) were calculated (see Methods), not measured, and the relationship between windspeed and flux requires further refinement. Error associated with these calculations may be the reason that the budgets did not balance (Table 4.6).

However, the lake budgets demonstrated both the sediments and water column can be important sources of both DMS and MSH (Table 4.6). Both sites should therefore be considered potential MSH and DMS sources in future lake studies. Furthermore, production rate differences in the light and dark indicated both measurements are required to draw an accurate picture of MSH and DMS production and loss.

4.6 References

Adewuyi, Y. G. 1989. Oxidation of biogenic sulfur compounds in aqueous media, p. 527-559. In E. S. Saltzmann and W. J. Cooper [Eds.], Biogenic sulfur in the environment. ACS 393.

Amaral, J. A., M. Turner, C. A. Kelly, J. W. M. Rudd, and R. Flett. In prep. The influence of benthic algal development on sulfur cycling in lakes acidified below pH 5.

Andreae, M. O. 1990. Ocean-atmosphere interactions in the global biogeochemical sulfur cycle. Mar. Chem. 30: 1-29.

Armstrong, F. A. J. and D. W. Schindler. 1971. Preliminary chemical characterization of waters in the Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Canada. 28: 171-187.

Andreae, M. O., and W. R. Barnard. 1984. The marine chemistry of dimethylsulfide. Mar. Chem. 14: 267-279.

Bechard, M. J., and W. R. Rayburn. 1979. Volatile organic sulfides from freshwater algae. J. Phycol. 15: 379-383.

Bremner, J. M., and C. G. Steele. 1978. Role of micro-organisms in the atmospheric sulfur cycle, p. 155-201. In M. Alexander [Ed.], Adv. Microbiol. Ecol. Vol. 2. Plenum.

Brunskill, G. J. and D. W. Schindler. 1971. Geography and bathymetry of selected lake basins, Experimental Lakes Area, northwestern Ontario. J. Fish. Res. Bd. Can. 28: 139-155.

Caron, F. 1990. Production of volatile sulfides from freshwater algae and implications to the environment. PhD. thesis. McMaster University.

Challenger, F., R. Bywood, P. Thomas, and B. J. Hayward. 1957. Studies on biological methylation. XVII. The natural occurrence and chemical reactions of some thetins. Arch. Biochem. Biophys. 69: 514-523.

Cooper, W. J., and P. A. Matrai. 1989. Distribution of dimethyl sulfide in the oceans. A review. p. 140-151. In E. S. Saltzmann and W. J. Cooper [Eds.], Biogenic sulfur in the environment. ACS 393.

van Diggelen, J., J. Rozema, D. M. J. Dickson, and R. Broekman. 1986. ß-3-dimthylsulphoniopropionate, proline, and quaternary ammonium compounds in *Spartina Anglica* in relation to sodium chloride, nitrogen, and sulphur. New Phytol. 103: 573-586.

Finster, K., G. M. King, and F. Bak. 1990. Formation of methyl mercaptan and dimethylsulfide from methoxylated aromatic compounds in anoxic marine and freshwater sediments. FEMS Microbiol. Ecol. 74: 295-302.

Hammer, U. T. 1986. Saline lake ecosystems of the world. Monographiae Biologicae. 59. H. J. Dumont, Ed. Dr. W.

Junk.

Hammer, U. T., and R. C. Haynes. 1978. The saline lakes of Saskatchewan II. Locale, hydrography, and other physical aspects. Int. Revue ges. Hydrobiol. 63: 179-203.

Hammer, U. T. and R. D. Parker. 1984. Limnology of a perturbed highly saline Canadian lake. Arch. Hydrobiol. 102: 31-42.

Hayduck, W., and H. Laudie. 1974. Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions. A. I. Ch. E. J. 20: 611-615.

Henatsch, J. J., and F. Juttner. 1990. Occurrence and distribution of methane thiol and other volatile organic sulphur compounds in a stratified lake with anoxic hypolimnion. Arch. Hydrobiol. 119: 315-323.

Keller, M., W. K. Bellows, and R. R. L. Guillard. 1989. Dimethyl sulfide production in marine phytoplankton. p. 167-182. In E. S. Saltzmann and W. Cooper [Eds.], Biogenic sulfur in the environment. ACS 393.

Kelly, C. A., and J. W. M. Rudd. 1984. Epilimnetic sulfate reduction and its relationship to lake acidification. Biogeochemistry 1: 63-77.

Kiene, R. P., and T. S. Bates. 1990. Biological removal of dimethyl sulphide from sea water. Nature 345: 702-705.

Lewis, W. K., and W. C. Whitman. 1924. Principles of gas adsorption. Ind. Eng. Chem. 17: 1215-1220.

Richards, S. R., C. A. Kelly, and J. W. M. Rudd. 1991. Organic volatile sulfur in lakes of the Canadian Shield, and its loss to the atmosphere. Limnol. Oceanogr. 36: 468-482.

--------, ----------, ----------. In prep. Organic volatile sulfur in systems ranging in sulfate and dissolved salt concentration over five orders of magnitude.

Schindler, D. W., and S. K. Holmgren. 1971. Primary production and phytoplankton in the Experimental Lakes Area, northwestern Ontario, and other low-carbonate waters, and a liquid scintillation method for determining ^{14}C activity in photosynthesis. J. Fish. Res. Bd. Canada 28: 189-201.

Tangerman, A. 1986. Determination of volatile sulphur compounds in air at the parts per trillion level by tenax trapping and gas chromatography. J. Chromat. 366: 205-216.

Turner, S. M., G. Malin, and P. S. Liss. 1989. Dimethyl sulfide and (dimethylsulfonio)propionate in European coastal and shelf waters, p. 183-200. In E. S. Saltzmann and W. J. Cooper [Eds.], Biogenic sulfur in the environment. ACS 393.

Visscher, P. T., P. Quist, and H. van Gemerden. 1991. Methylated sulfur compounds in microbial mats: in situ concentrations and metabolism by a colorless sulfur

bacterium. Appl. Environ. Microbiol. 57: 1758-1763.

Wanninkhof, R., J. R. Ledwell, and W. S. Broecker. 1985. Gas exchange-wind speed relation measured with sulfur hexafluoride on a lake. Science 227: 1224-1226.

Zeyer, J., P. Eicher, S. G. Wakeham, and R. P. Schwarzenbach. 1987. Oxidation of DMS to DMSO by phototrophic purple bacteria. Appl. Environ. Microbiol. 53: 2026-2032.

5. The production of volatilizable organic sulfur from short-term sulfate reduction in sediments

5.0. Acknowledgements

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5.1. Abstract

The formation of organic volatile sulfur compounds (VSCs) from sulfate (SO_4^{2-}) was studied by incubating freshwater lake sediments with ^{35}S-sulfate ($^{35}SO_4^{2-}$). Although free organic $V^{35}SCs$ were not detected in the pore-water, ^{35}S-methane thiol ($M^{35}SH$), ^{35}S-dimethyl sulfide ($DM^{35}S$), and ^{35}S-dimethyl disulfide ($DMD^{35}S$) were extracted using pyrophosphate (PPi) buffer. Acidic chromic chloride (Cr II) released primarily $M^{35}SH$ from the solid matrix. It is hypothesized that the extracted organic VSCs were released from a potential precursor pool produced from the reaction of hydrogen sulfide (H_2S) with sedimentary organic matter. These H_2S-derived sulfur compounds were estimated to account for at least 5% of *in situ* pools. The results suggested increased loading of an inorganic sulfur species (SO_4^{2-}) could stimulate sedimentary organic VSC production by increasing the precursor pool size.

5.2. Introduction

The most environmentally significant pathway leading from sulfate (SO_4^{2-}) to organic volatile sulfur compounds (VSCs) is thought to be initiated by the assimilatory reduction of SO_4^{2-} to form organic sulfur species. During chemical and biochemical breakdown of these organic species, volatile sulfur compounds are released (Bremner and Steele 1978, Andreae 1990). This mechanism underlies the production of dimethyl sulfide (DMS) from algal dimethyl sulfoniopropionate (DMSP) in the water column (Andreae 1990, Richards et al. 1991), as well as much sedimentary production of DMS, methanethiol (MSH), carbon disulfide (CS_2), and dimethyl disulfide (DMDS) (Kiene 1987, Kelly and Baker 1990, Richards et al. 1991, Richards et al., in prep.). In this pathway, the rate of organic sulfur production is not dependent on $[SO_4^{2-}]$, since most organisms are not SO_4^{2-}-limited. Furthermore, the breakdown of organic matter can be influenced by factors such as the microbial population present, composition of the organic material, and available electron acceptors (Oremland and Pokin 1982, Kelly et. al. 1988, Wetzel 1983).

Another pathway leading to organic VSC production begins with dissimilatory SO_4^{2-} reduction by microbes. In this pathway, the H_2S produced from SO_4^{2-} reduction is biotically or possibly abiotically methylated (Drotar et al.

1987, Sorenson 1988). Because dissimilatory SO_4^{2-} reduction is dependent on $[SO_4^{2-}]$ in most freshwater sediments (Cook and Schindler 1983, Kelly and Rudd 1984), this pathway of organic VSC formation would also likely correlate to $[SO_4^{2-}]$.

Another possible mechanism linking H_2S to organic VSC production is via incorporation into sedimentary organic matter, with subsequent breakdown and release of volatile species. There is extensive evidence that H_2S reacts with organic matter in sediments and pore-water to form non-volatile organic sulfur compounds (Rudd et al. 1986, Vairavamurthy and Mopper 1987, Vairavamurthy and Mopper 1989, Mango 1983), but its importance in the production of the volatile species listed above is not known. In this study, radiolabelled SO_4^{2-} ($^{35}SO_4^{2-}$) was used to determine whether organic VSCs are produced from short-term SO_4^{2-} reduction in sediments. Breakdown of ^{35}S-methionine to organic V^{35}SCs was also studied.

5.3. Materials and Methods

5.3.0. Sampling site and methods. Epilimnetic sediment was obtained from Lakes 303 and 239 at the Experimental Lakes Area (ELA) in northwestern Ontario, Canada (Schindler and Brunskill 1971). Sediment was collected using an Ekman dredge. The top 0-4 cm was pooled and stored in erlenmeyer flasks without headspace to ensure anaerobic conditions. Lake 303 sediment is a flocculent, organic-rich sediment with a high porosity (> 0.95). Sediment from Lake 239 is muddy in consistency, with a porosity of about 0.85-0.9.

5.3.1. Radiotracer incubations and volatile sulfur analyses. $^{35}SO_4^{2-}$ (9.6 X 10^8 dpm ml^{-1}) and unlabelled SO_4^{2-} (52 μmol) were added to 100 ml of sediment slurry (specific activity: 5.4 X 10^6 dpm μmol^{-1} S). These additions were made by micro-pipettor under a continuous stream of N_2 to ensure anaerobic conditions. Incubations were conducted in the dark at 20°C and sediment aliquots were removed at pre-determined time intervals. Pore-water was obtained by centrifugation and then analysed for unlabelled and $V^{35}SCs$ by a purge-and-trap method (Richards et al. 1991). Column effluent from a Varian 3700 gas chromatograph was split in most cases between a flame photometric detector (FPD) and a proportional counter (PC) in a 1:2 ratio, respectively. Data obtained from the proportional counter are presented as

radiochromatogram scans. In other cases, VSCs in the column effluent were trapped in vials containing saturated $HgCl_2$ and the volatile $V^{35}SCs$ quantified by scintillation counting (LKB Rackbeta). For scintillation counting, the total radioactivity of each peak was determined by summing the radioactivity in vials corresponding to that peak.

5.3.2. Sediment extractions and chromium reduction. Pyrophosphate (PPi) buffer (pH = 8) was used to solubilize sedimentary organic matter (Kononova 1961, Strickland and Fitzgerald 1985), while acidic chromous chloride (CrII) was used to release VSCs bound via metal-sulfur and sulfur-sulfur bonds (Zhabina and Volkov 1978). However, organic carbon-sulfur linkages would not be affected by this treatment (e.g. Cutter and Oatts 1987, Canfield et. al. 1986).

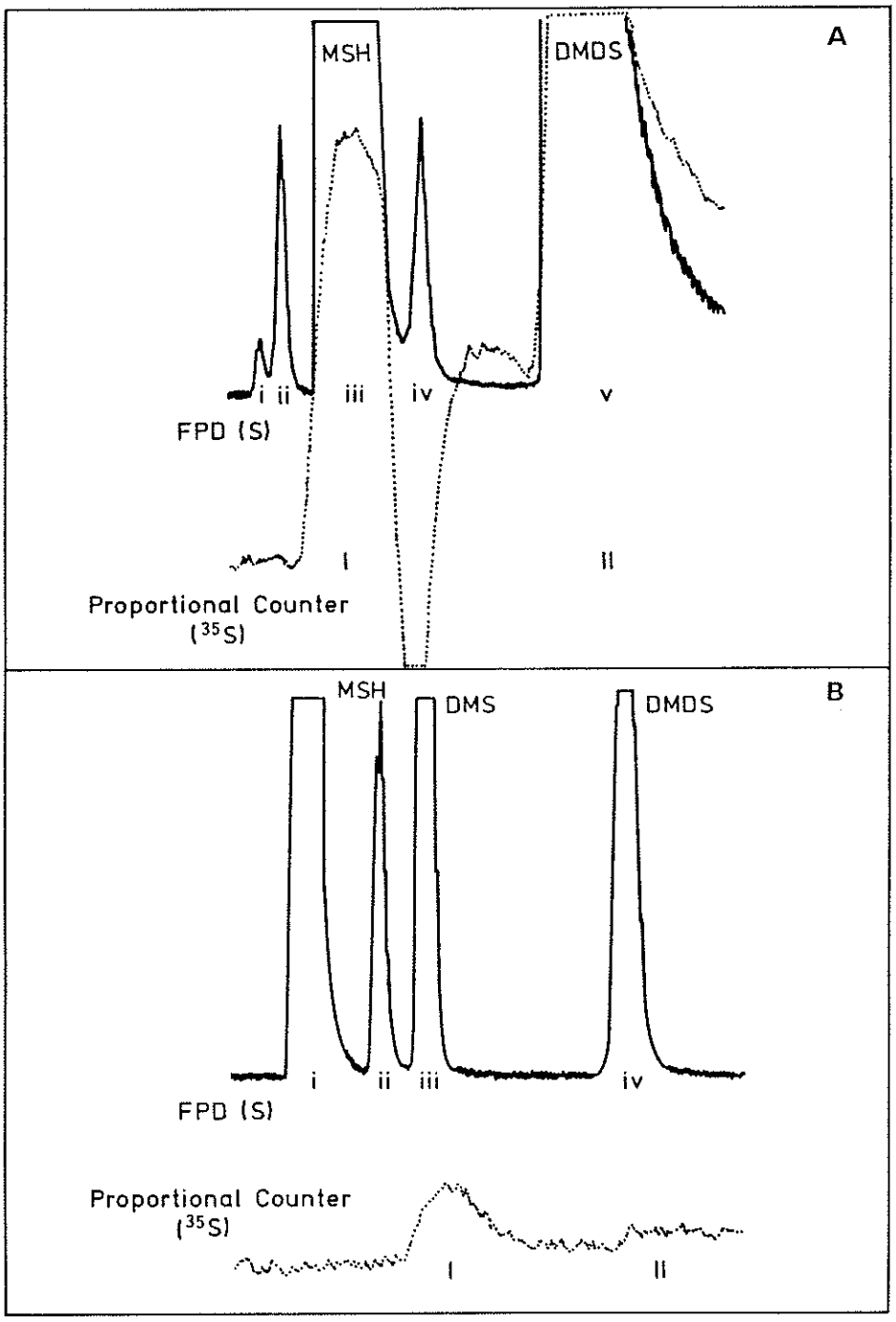
5.4. Results

5.4.0. Methods check. In order to determine whether the methods were adequate to detect formation of $V^{35}SCs$, initial incubations were conducted with ^{35}S-methionine to ensure formation of VSCs by decomposition processes. ^{35}S-Methionine additions resulted in easily detectable concentrations of soluble $M^{35}SH$, $DMD^{35}S$, and $DM^{35}S$ (Fig. 5.1). $^{35}SO_4^{2-}$ additions produced $H_2{}^{35}S$ (data not shown). These results were expected and indicated that the methods were adequate to detect ^{35}S-labelled volatile products.

The quenching observed between PC peaks I and II (Fig. 5.1A) was due to an unidentified compound. Quenching of a PC can occur by molecules that readily capture electrons, such as halogenated molecules, nitro compounds, and polycyclic hydrocarbons (Nuclear Chicago 1966). The baseline elevation following the inverse peak (prior to PC II; Fig. 5.1A) likely occurred due to moderate contamination of the counting chamber with ^{35}S, following the $M^{35}SH$ peak. Sulfur is known to have counter poisoning effects (Nuclear Chicago 1966).

5.4.1. "Free" and extractable ^{35}S-labelled organic VSCs. When sediment was incubated with $^{35}SO_4^{2-}$, $H_2{}^{35}S$ was produced (data not shown), but organic $V^{35}SCs$ were not detected in the pore-water. Therefore, the sediment was extracted with

Figure 5.1. Gas chromatogram and radiochromatogram scans of Lake 303 sediment pore-water. Sediments were amended with ^{35}S-methionine and incubated at room temperature for (A) 46 hours and (B) 147 hours.


A
MSH
DMDS
i ii
iii
iv
v
FPD (S)
I
II
Proportional Counter
(^{35}S)
B
MSH
DMS
DMDS
i
ii
iii
iv
FPD (S)
Proportional Counter
(^{35}S)
I
II

buffer and acidic CrII to determine if these treatments would release volatile species from the solid sediment matrix.

PPi buffer (pH = 8) extracts of sediment from Lake 239 released up to 0.25% and 0.12% of the ^{35}S-label as $M^{35}SH$ and $DM^{35}S$, respectively (Table 5.1). Lake 303 sediments released four species, $M^{35}SH$, $DM^{35}S$ (shown in a radiochromatogram scan, Fig. 5.2), $DMD^{35}S$, and one unidentified ^{35}S-peak. Again, $M^{35}SH$ was released in the greatest quantity, comprising up to 0.25% of the $^{35}SO_4^{2-}$ added (Table 5.1). These peaks were identified by retention time comparisons to sulfur standards (MSH, trapped for 4-5 min; DMS, trapped for 5.5-6.8 min; DMDS, trapped for 9.3-10.8 min; Table 5.1). $M^{35}SH$ was present at the highest concentration, and had a similar temporal pattern in the two sediments (Table 5.1). It maintained a relatively constant concentration from 14-37 h, then increased 5-6 times by 9 d (Table 5.1). $DMD^{35}S$ in the Lake 303 sediment extract followed the same general pattern as the $M^{35}SH$, increasing 3.5 times by 9 days (Table 5.1). This $DMD^{35}S$ was likely the product of $M^{35}SH$ oxidation (Adewuyi 1989). Unlike $M^{35}SH$, extractable $DM^{35}S$ levels were transient over the incubation period, peaking at 14-37 h, then declining to low concentrations by 9 d (Table 5.1). PPi (pH = 6.5) extractions did not release any organic VSCs, even when the pH of the extracted material was increased with base (data not shown).

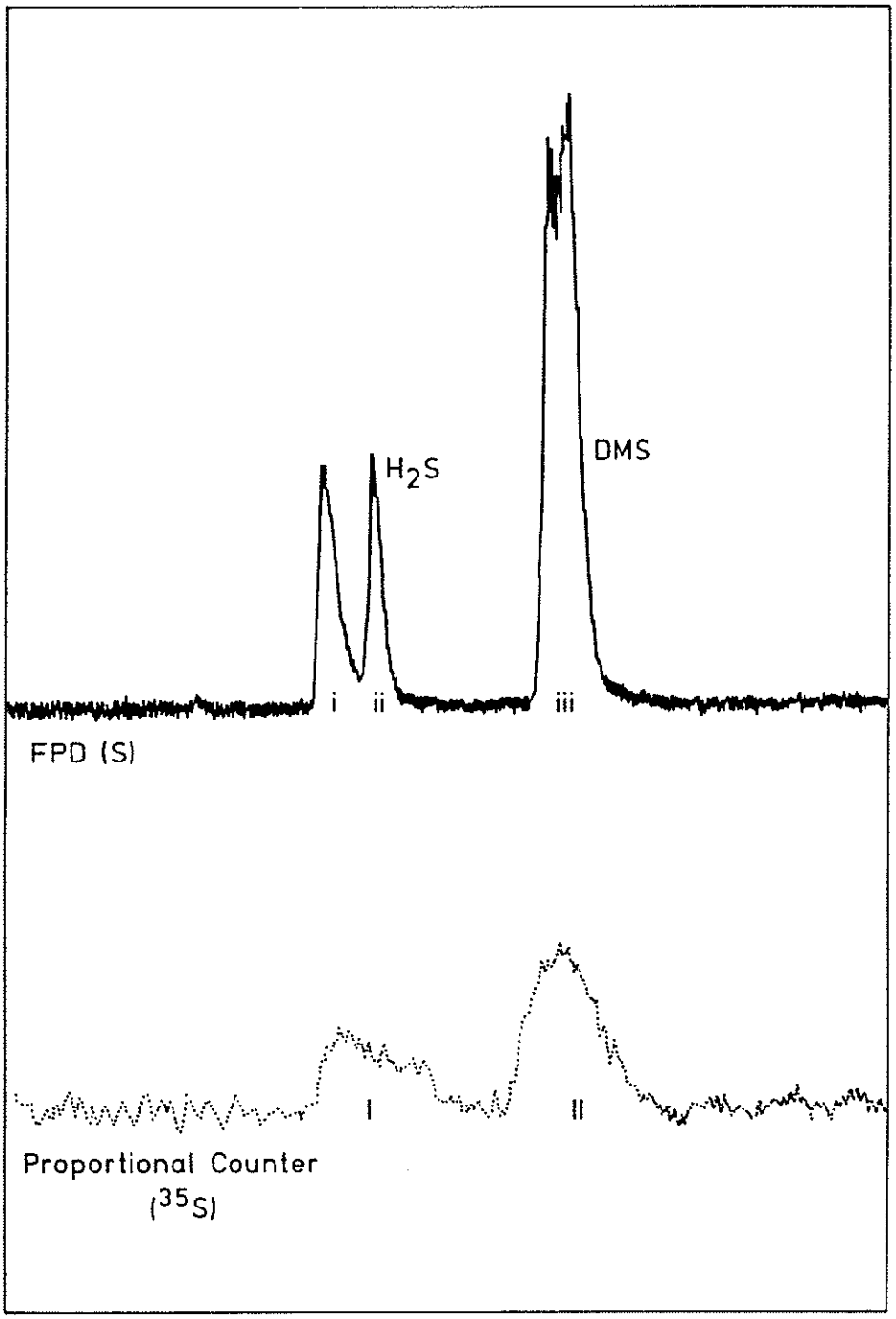
Table 5.1. ^{35}S-labelled organic VSCs released from PPi (pH = 8 extraction and CrII reduction. (ND = not detected)

Time	$M^{35}SH$ dpm/ml	%S*	$DM^{35}S$ dpm/ml	%S	$DMD^{35}S$ dpm/ml	%S	^{35}S-"X" + dpm/ml	%S	^{35}S-TOTAL dpm/ml	%S
Lake 239: PPi (pH=8)										
14h	690	0.04	208	0.01	ND	--	ND	--	898	0.05
37h	700	0.04	1916	0.12	ND	--	ND	--	2616	0.16
9d	3951	0.25	39	0.002	ND	--	ND	--	3990	0.25
Lake 239: CrII										
14h	249	0.02	ND	--	ND	--	ND	--	249	0.02
37h	223	0.01	ND	--	ND	--	ND	--	223	0.01
Lake 303: PPi (pH=8)										
14h	605	0.04	1272	0.08	604	0.04	1132	0.07	3613	0.23
37h	796	0.05	616	0.04	21	0.001	20	0.001	1453	0.09
9d	3858	0.25	752	0.05	2129	0.14	583	0.04	7322	0.48

* %S = % of added ^{35}S

\+ "X" = unidentified peak

Figure 5.2. Gas chromatogram and radiochromatogram of a pyrophosphate buffer (pH = 8) extract of Lake 303 sediment. Sediments were amended with $^{35}SO_4^{2-}$.


H_2S
DMS
i
ii
iii
FPD (S)
I
II
Proportional Counter
(^{35}S)

CrII reduction yielded exclusively $M^{35}SH$. This pool did not change in concentration from 14-37 hours (Table 5.1), and was approximately 6-30% of the total PPi (pH = 8) extractable organic $V^{35}SCs$.

It is expected that the majority of the $^{35}SO_4^{2-}$, not accounted for in the above fractions, was also reduced and incorporated into other organic and inorganic fractions in the sediments (J. Amaral, pers. comm.). This proportion of the radiolabel was not followed in the present study.

5.5. Discussion

5.5.0. Structure. The release of organic VSCs by PPi (pH = 8) and CrII suggested a sedimentary pool of organic sulfur that could easily release organic VSCs. NaOH is used routinely to analyze for DMSP by hydrolyzing it to acrylic acid and DMS. Significantly, this same breakdown of DMSP to yield DMS and acrylic acid occurs naturally in the environment. The analyses in this study, PPi (pH = 8) extractions, were milder than DMSP analyses. It is expected, therefore, that breakdown of the "precursor" species, like DMSP, would also occur in the environment.

Although the chemical structures of the precursors were not elucidated, the conditions under which the volatile species were released suggested the presence of certain types of sulfur bonds. Significantly, the release of organic $V^{35}SCs$ from the solid sediment matrix was base-dependent. This was shown by extracting sediments with PPi (pH = 6.5). Following these acidic extractions, the solid sediment was separated from the extracted, solubilized material. Significantly, no organic $V^{35}SCs$ were detected in the extract, even when the pH of the material was increased with NaOH (data not shown). Therefore, the release of organic $V^{35}SCs$ from the solid sediment matrix was base (OH^-)-dependent.

At high pH levels, sulfonium-carbon bonds can be

cleaved (e.g. DMS release from DMSP; Keller et al. 1989) and sulfur-sulfur bridges reduced (Cardone 1972). Under certain conditions, carbon-carbon bonds may also be reduced (see below). Therefore, the volatile species released under basic conditions could have been linked to the sediment matrix as sulfonium groups or via disulfide or carbon-carbon bonds.

The release of $M^{35}SH$ with CrII (Table 5.1) suggested the presence of a CH_3-^{35}S- group linked to the solid matrix via a metal-sulfur bond or possibly a disulfide linkage (Zhabina and Volkov 1978). Mopper and Taylor (1986) found thiols in coastal marine sediments were bound principally via disulfide linkages, not S-metal bonds. The presence of CH_3-^{35}S-metal or CH_3-^{35}S-S- bonds may indicate that free $CH_3{}^{35}SH$ produced reacted quickly in the sediment matrix with other thiol groups and metals (e.g. Fe).

5.5.1. Source. It is probable that $H_2{}^{35}S$ from dissimilatory $^{35}SO_4^{2-}$ reduction reacted in the sediments with organic matter to produce the sulfur pool from which the $V^{35}SCs$ were extracted. Assimilatory $^{35}SO_4^{2-}$ reduction was not thought to contribute significantly to the "precursor pool". This conclusion was based on (a) the relatively short incubation period (as little as 14 hr, Table 5.1), and (b) the increase in "precursor pool" size resulting from the SO_4^{2-} addition (see below). As discussed, assimilatory SO_4^{2-} reduction is

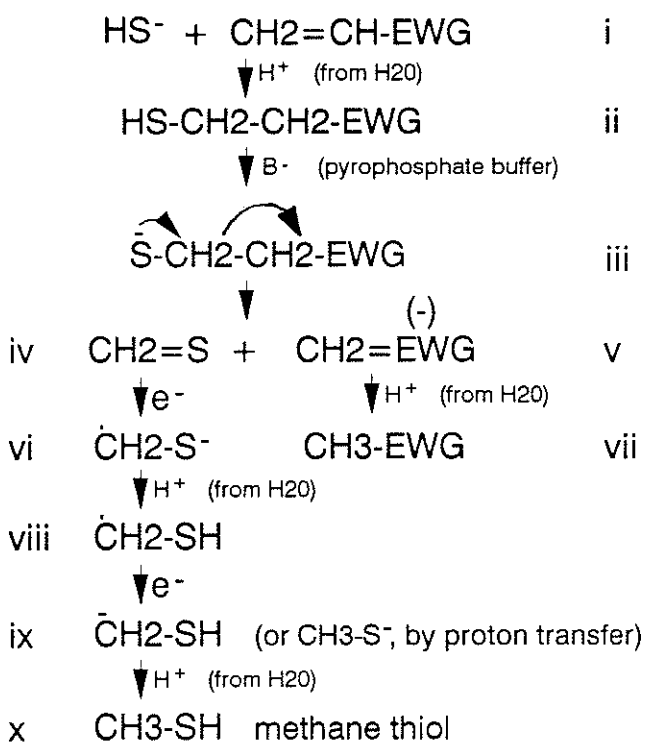
not SO_4^{2-}-limited if there is sufficient carbon available (Cook and Schindler 1983, Kelly and Rudd 1984).

The mechanism by which these "precursors" form was not studied, although the incorporation of H_2S into organic matter is well known (Rudd et al. 1986, Vairavamurthy and Mopper 1987, 1989, Mango 1983). A possible mechanism for the production of organic VSCs via H_2S (Fig. 5.3) involves the well-established addition of HS^- across a -C=C- double bond adjacent to an electron withdrawing group (EWG) such as $-CO_2H$ or -C=O (Vairavamurthy and Mopper 1987) and at other reactive sites (Luther et. al. 1986). Deprotonation of the -SH group and fission as shown (iii, Fig. 5.3) would lead to thioformaldehyde (iv, Fig. 5.3). Under sedimentary reducing conditions, this species could lead to MSH, as shown (x, Fig. 5.3). This mechanism is analogous to a reverse "aldol" condensation. Theoretically, the resulting MSH could react further with sedimentary organic matter and participate in a comparable series of reactions to yield DMS.

5.5.2. Importance of this pathway to the production of sedimentary organic VSCs. The organic $V^{35}SCs$ in this study were released under basic (pH = 8) conditions. As discussed, base hydrolysis is used routinely to analyse for marine DMSP, a precursor compound which breaks down naturally in aquatic environments to form DMS (Andreae 1990, Keller et. al. 1989). Therefore, it is expected that the

Figure 5.3. Hypothesized mechanism for the formation of an organic volatile sulfur compound (methanethiol) from H_2S incorporation into sediment organic matter. "EWG" refers to "electron withdrawing group".

Possible mechanism for organic VSC production from hydrogen sulfide



organic VSCs released with dilute base (pH = 8) in this study would likely be released *in situ* by chemical or microbial processes. The potential importance of this pathway in the production of sedimentary organic VSCs was estimated by calculating the incorporation of SO_4^{2-}-sulfur after 9 d into the most important precursor pool, PPi (pH = 8) extractable MSH.

Unamended Lake 239 sediments (no SO_4^{2-} added) contained 1400 nM PPi extractable MSH. Using the specific activity of the $^{35}SO_4^{2-}$, this fraction increased by 700 nM, or 50%, following SO_4^{2-} addition. Since pore-water [SO_4^{2-}] was increased 10-fold by the addition, the *in situ* contribution of SO_4^{2-} reduction to extractable MSH was estimated to be 5% of the extractable MSH pool (i.e. one tenth of the observed increase). Of course, part of the endogenous VSC precursor pool may have originated at least partially from assimilatory pathways.

In radiotracer studies, the possibility of isotope exchange must be addressed. Research to date suggests that the important isotope exchange reactions for sedimentary sulfur occur largely between inorganic species such as elemental sulfur (S°), bisulfide ion (HS^-), and ferrous sulfide (FeS) (Fossing and Jorgenson 1990 a,b). Stable sulfur linkages such as the C-S bonds in CS_2 are not subject to isotope exchange (Cooley et. al. 1939). Furthermore, incubations of $^{35}S^\circ$, H_2S, and cysteine have failed to yield

^{35}S-cysteine in 28 hours (J. Amaral, pers. comm.). In the present study, therefore, it is not expected that the ^{35}S-labelled species arose from isotope exchange processes.

5.5.3. Evidence from other studies. The data from this study show that short-term dissimilatory SO_4^{2-} reduction may have a measurable effect on the production of extractable, and possibly free VSCs, in lake sediments. Evidence for an effect on free VSCs was found in field studies, described below. It is interesting, however, that DMS was the dominant organic VSC in all *in situ* studies, whereas in our experiments, base-extractable MSH dominated. In a whole-lake sulfuric acid addition experiment (Richards et al. 1991) DMS accumulation below the mixed layer was 9 times higher in artificially acidified (H_2SO_4) Lake 302 South, when compared to a reference basin. This greater accumulation could not be attributed to increased decomposition of organic matter, since primary production had not increased. Furthermore, in a study of salt lakes (Richards et al., in prep.) there was a positive correlation ($r = 0.93$) between $[SO_4^{2-}]$ and mean (i) total organic VSC concentrations (ii) [DMS], and (iii) [MSH], with semi-$\log_{10}$ plots showing linearity. Finally, a study of organic volatile sulfur production during mushroom cultivation found a 4-fold increase in DMS production with SO_4^{2-} addition (Derikx et al. 1991). These studies provide support for the results of the

laboratory experiments. The production of organic VSC precursors by H_2S reaction with the solid matrix could be an important link between SO_4^{2-} and the formation of sedimentary organic volatile sulfur.

5.6. References

Adewuyi, Y. G. 1989. Oxidation of biogenic sulfur compounds in aqueous media. Kinetics and environmental implications, p. 527-559. In E. S. Saltzmann and W. J. Cooper [Eds.], Biogenic sulfur in the environment. ACS 393.

Bremner, J. M., and C. G. Steele. 1978. Role of microorganisms in the atmospheric sulfur cycle, p. 155-201. In M. Alexander [Ed.], Advances in microbial ecology. Vol. 2.

Canfield, D. E., R. Raiswell, J. T. Westrich, C. M. Reaves, and R. A. Berner. 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. Chem. Geol. 54: 149-155.

Cardone, M. J. 1972. Di- and polysulfides. In The analytical chemistry of sulfur and its compounds II. Karchmer, J. H. Vol. 29 Chemical Analysis. Wiley.

Cook, R. B., and D. W. Schindler. 1983. The biogeochemistry of sulfur in an experimentally acidified lake. Ecol. Bull. 35: 115-127.

Cutter, G. A., and T. J. Oatts. 1987. Determination of dissolved sulfide and sedimentary sulfur speciation using gas chromatography-photoionization detection. Anal. Chem. 59: 717-721.

Derikx, P. J. L., F. H. M. Simons, H. J. M Op den Camp, C. van der Drift, L. J. L. D. Van Griensven, and G. D.

Vogels. 1991. Evolution of volatile sulfur compounds during laboratory-scale incubations and indoor preparation of compost used as a substrate in mushroom cultivation. Appl. Environ. Microbiol. 57: 563-567.

Drotar, A., G. A. Burton, Jr., J. E. Tavernier, and R. Fall. 1987. Widespread occurrence of bacterial thiol methyltransferases and the biogenic emission of methylated sulfur gases. Appl. Environ. Microbiol. 53: 1626-1631.

Keller, M. D., W. K. Bellows, and R. R. L. Guillard. 1989. Dimethyl sulfide production in marine phytoplankton, p. 167-182. In E. S. Saltzman and W. J. Cooper [Eds.], Biogenic sulfur in the environment. ACS 393.

Kelly, C. A., and J. W. M. Rudd, D. W. Schindler. 1988. Carbon and electron flow via methanogenesis, SO_4^{2-}, NO_3^-, Fe^{3+}, and Mn^{4+} reduction in the anoxic hypolimnia of three lakes. Arch. Hydrobiol. Beih. 31: 333-344.

Kelly, C. A., and J. W. M. Rudd. 1984. Epilimnetic sulfate reduction and its relationship to lake acidification. Biogeochemistry 1: 63-77.

Kelly, D. P., and S. C. Baker. 1990. The organosulphur cycle: aerobic and anaerobic processes leading to turnover of C_1-sulphur compounds. FEMS Microbiol. Rev. 87: 241-246.

Kiene, R. P., and P. T. Visscher. 1987. Production and fate of methylated sulfur compounds from methionine and

dimethylsulfoniopropionate anoxic salt marsh sediments. Appl. Environ. Microbiol. 53: 2426-2434.

Kononova, M. M. 1961. Present-day ideas on the composition of soil humus and the nature of humic substances, p. 45-100. In M. M. Kononova [Ed.], Soil Organic Matter. Pergamon Press. New York.

Luther, G. W. 1987. Pyrite oxidation and reduction: molecular orbital theory considerations. Geochim. Cosmochim. Acta. 51: 3193-3199.

Luther, G. W. T. M. Church, J. R. Scudlark, and M. Cosman. 1986. Inorganic and organic sulfur cycling in salt-marsh pore waters. Science 232: 746-749.

Mango, F. D. 1983. The diagensis of carbohydrates by hydrogen sulfide. Geochim. Cosmochim. Acta 47: 1433-1441.

Mopper, K. and B. F. Taylor. 1986. Thiols in coastal marine sediments, p. 324-339. In M. L. Sohn [Ed.], Organic Marine Geochemistry. ACS 305.

Nuclear Chicago. 1966. Instruction manual. Model 4998 gas radiochromatography counting system (Effective Serial #59). Nuclear Chicago Corporation.

Oremland, R. S., and Polcin, S. 1982. Methanogenesis and sulfate reduction: competitive and noncompetitive substrates in estuarine sediments. Appl. Environ. Microbiol. 44: 1270-1276.

Richards, S. R., C. A. Kelly, and J. W. M. Rudd. 1991.

Organic volatile sulfur in lakes of the Canadian Shield and its loss to the atmosphere. Limnol. Oceanogr. 36: 468-482.

--------, ---------, ------------. In prep. Organic volatile sulfur in systems ranging in sulfate and dissolved salt concentration over five orders of magnitude.

Rudd, J. W. M., C. A. Kelly, and A. Furutani. 1986. The role of sulfate reduction in long term accumulation of organic and inorganic sulfur in lake sediments. Limnol. Oceanogr. 31: 1279-1289.

Sorenson, J. 1988. Dimethylsulfide and methane thiol in sediment porewater of a Danish estuary. Biogeochem. 6: 201-210.

Strickland, T. C., and J. W. Fitzgerald. 1985. Incorporation of sulphate-sulphur into organic matter extracts of litter and soil: involvement of ATP sulphurylase. Soil Biol. Biochem. 17: 779-784.

Vairavamurthy, A., and K. Mopper. 1987. Geochemical formation of organosulphur compounds (thiols) by addition of H_2S to sedimentary organic matter. Nature 329: 623-625.

Vairavamurthy, A., and K. Mopper. 1989. Mechanistic studies of organosulfur (thiol) formation in coastal marine sediments, p. 231-242. In E.S. Saltzman and W. J. Cooper [Eds.], Biogenic Sulfur in the Environment.

ACS 393.

Wetzel, R. G. 1983. Sediments and microflora, p. 591-614. In R. G. Wetzel, Limnology. 2nd edition.

Zhabina, N. N., and I. I. Volkov. 1978. A method of determination of various sulfur compounds in sea sediments and rocks, p. 735-746. In W. E. Krumbein [Ed.], Environmental biogeochemistry and geomicrobiology. Vol. 3. Methods, metals and assessment. Ann Arbor Science.

6. Summary

6.0. Identification, concentration, and fluxes.

Organic volatile sulfur in the study lakes occurred as five species: COS, MSH, DMS, CS_2, and DMDS. These compounds were present in ponds on the Hudson Bay Lowlands, Canadian Shield lakes in northwestern Ontario, and salt lakes and playas in southern Saskatchewan. There were, however, significant concentration differences between these systems. The surface waters of stratified freshwater lakes usually contained mean DMS and COS concentrations of 0.8-1.2 nM and 0.2-0.5 nM, respectively. Shallow lakes and bogs were generally much higher in mean concentration: DMS: up to 6.6 nM; MSH: up to 13 nM; DMDS: up to 1.4 nM. The highest values in this study, however, were found in Saskatchewan salt lakes. These systems contained mean DMS concentrations up to 1,300 nM. These differences illustrated two important parameters affecting surface water concentrations, depth and $[SO_4^{2-}]$.

In freshwater lakes, surface water concentrations were strongly influenced by depth, with shallow, unstratified systems (Lake 239 NE bog, Lakes 303 and 114) containing DMS and DMDS concentrations 5-70 times greater than stratified lakes in the same geographic area. Mean flux to the atmosphere from a shallow lake (12,500 nmol m^{-2} d^{-1}) was

approximately 10 times greater than from the stratified lakes, and this loss represented as much as 15% of the SO_4^{2-} budget.

A second parameter affecting organic volatile sulfur concentrations was $[SO_4^{2-}]$. This effect was observed in (a) surface waters when $[SO_4^{2-}]$ exceeded approximately 20 g (SO_4^{2-}) $litre^{-1}$, and (b) in the hypolimnion of a lake receiving H_2SO_4 additions. Likely the correlation to $[SO_4^{2-}]$ demonstrates a link to H_2S production (see below). In the salt systems containing up to 100 g (SO_4^{2-}) $litre^{-1}$, H_2S was present in millimolar concentrations (3-10 mM), and DMS concentrations up to 3 μM were found. Mean sulfur fluxes from these high SO_4^{2-} systems were as high as 400,000 nmol m^{-2} d^{-1}, 32 times more than the highest mean freshwater flux observed.

6.1. Rates and sites of formation

Both sedimentary and water column production contributed to DMS and MSH formation in lakes. A water column source for DMS was initially suggested by the observation that similar surface water DMS concentrations occurred in lakes with very different water column volume to sediment surface area (Ae:Ve) ratios. The significance of sedimentary production was indicated by hypolimnetic

accumulations in stratified lakes, and the comparatively high concentrations of most species in the surface waters of shallow lakes and bogs. These initial observations were extended by examining sources and sinks for MSH and DMS.

Sedimentary release was the most significant net source of MSH, and this species was largely destroyed in the water column. For DMS, however, processes in both the sediments and the water column were net sources. In freshwater Lake 114, water column production in the light was the most important site. However, in hypersaline Patience Lake, sediments were the most significant site of DMS production. Mechanisms contributing to production and destruction were not studied, but diel patterns in DMS and MSH concentrations suggested direct release by freshwater algae occurred. Organic matter decomposition likely contributed to both sedimentary and water column production, as well.

Radiotracer experiments indicated precursors of organic volatile species may form from an abiotic addition of H_2S to pre-existing organic matter. These potential precursors are hypothesized to breakdown and form organic VSCs, although "free" VSCs were not detected. Formation via H_2S would explain the higher DMS accumulation rate in the hypolimnion of acidified Lake 302 South, and the extremely high DMS concentrations in systems containing over 20 g (SO_4^{2-}) litre^{-}

[1]. Linking formation of volatile sulfur to the dissimilatory reduction pathway is consistent with the observed correlation to SO_4^{2-} at high SO_4^{2-} concentrations [> 20 g (SO_4^{2-}) $litre^{-1}$].

6.2. Organic VSCs in lakes and the ocean: some similiarities and differences

DMS and COS are the two principal organic VSCs in ocean surface waters. DMS forms from the breakdown of algal DMSP, and COS is thought to be produced during the photo-oxidation of organic matter. In the ocean, the water column is therefore the principal site of formation for both species. Because of the important role oceanic DMS has in global sulfur cycling and cloud formation, marine studies have focussed on DMS production and flux to the atmosphere. Production of DMS in the oceans is dependent on factors affecting algal DMSP formation and breakdown, and DMS:Chl *a* ratios (mmol mg^{-1}) reach as high as 56.8 in oceanic studies (Iverson et al. 1989).

In lakes, a greater spectrum of organic VSCs reach significant concentrations, although DMS and COS are present at concentrations comparable to those in the ocean. Unlike the ocean, sedimentary production is important in lakes, in

addition to water column processes. The relative importance of the two sites is affected by factors such as lake depth and time of year.

Algal DMSP was detected in both freshwater and salt lakes. DMSP has often been assigned a role in osmoregulation. However, particularly in freshwater systems, it may also function as a sulfur storage molecule and bacteriocidal agent. DMS:Chl *a* ratios are very much smaller in lake systems (<1 mmol mg^{-1}), both freshwater and saline.

The flux of volatile sulfur from the oceans is far more significant globally than sulfur emissions from lakes. However, inland aquatic systems can be regionally significant contributors to atmospheric sulfur in areas where shallow lakes and wetlands are abundant. Furthermore, the highest mean fluxes observed from hypersaline, SO_4^{2-}-dominated playas were almost two orders of magnitude higher than the highest mean freshwater emission rate. It is likely that anthropogenic activity will significantly impact the magnitude of these inland aquatic fluxes. For example, the formation of shallow aquatic systems from reservoir construction could increase volatile sulfur emissions from interior regions. Conversely, greenhouse warming may decrease prairie emissions if the water table is lowered

sufficiently to eliminate many existing hypersaline playas.

6.3. References

Iverson, R. L., F. L. Nearhoof, and M.O. Andreae. 1989. Production of dimethylsulfonium propionate and dimethyl sulfide by phytoplankton in estuarine and coastal waters. Limnol. Oceanogr. 34: 53-67.