DOE/OR/00033--T707

THE OCEANIC CYCLE AND GLOBAL ATMOSPHERIC
BUDGET OF CARBONYL SULFIDE

by

Peter S. Weiss

MASTER

A dissertation submitted in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy

University of Washington

1994

RECEIVED

JUN 12 1997

OSTI

Approved by _____
Chairperson of Supervisory Committee

Program Authorized
to Offer Degree _____

Date _____

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

21 DEC 95

In presenting this dissertation in partial fulfillment of the requirements for the Doctoral degree at the University of Washington, I agree that the Library shall make its copies freely available for inspection. I further agree that extensive copying of this dissertation is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for copying of reproduction of this dissertation may be referred to University Microfilms, 1490 Eisenhower Place, P.O. Box 975, Ann Arbor, MI 48106, to whom the author has granted "the right to reproduce and sell (a) copies of the manuscript in microform and/or (b) printed copies of the manuscript made from microform."

Signature _____

Date _____

The Government reserves for itself and others acting on its behalf a royalty free, nonexclusive, irrevocable, world-wide license for governmental purposes to publish, distribute, translate, duplicate, exhibit, and perform any such data copyrighted by the contractor.

University of Washington

Abstract

The Oceanic Cycle and Global Atmospheric Budget
of Carbonyl Sulfide

by Peter S. Weiss

Chairperson of the Supervisory Committee: Professor Richard H. Gammon
Department of Chemistry

A significant portion of stratospheric air chemistry is influenced by the existence of carbonyl sulfide (COS). This ubiquitous sulfur gas represents a major source of sulfur to the stratosphere where it is converted to sulfuric acid aerosol particles. Stratospheric aerosols are climatically important because they scatter incoming solar radiation back to space and are able to increase the catalytic destruction of ozone through gas phase reactions on particle surfaces. COS is primarily formed at the surface of the earth, in both marine and terrestrial environments, and is strongly linked to natural biological processes. However, many gaps in the understanding of the global COS cycle still exist, which has led to a global atmospheric budget that is out of balance by a factor of two or more, and a lack of understanding of how human activity has affected the cycling of this gas. The goal of this study was to focus on COS in the marine environment by investigating production/destruction mechanisms and recalculating the ocean-atmosphere flux.

Analytical work was carried out using the electron capture sulfur detector (ECD-S) for gas chromatography. This system was optimized for COS so that air and seawater-equilibrated air samples could be directly injected without preconcentration.

This research was carried out on two cruises aboard the NOAA ship *Surveyor* during long meridional transects between 55°N and 70°S along 140°W in the Pacific Ocean.

The major findings of these research activities are:

1. Photoproduction of COS is at a maximum between 313 and 336 nm in natural sunlit waters. Tropical water surface and column production rates are 68 pM/day and 360 nmol/m²/day, respectively. Antarctic surface and column production rates are 101 pM/day and 620 nmol/m²/day, respectively.

2. Wide regions of the open ocean were found to be undersaturated with respect to atmospheric equilibrium of COS. The global open ocean sea-air flux of COS was found to be -0.032 (-0.010 to -0.054) which represents a very weak sink of atmospheric COS.

3. Daily COS concentration losses in surface waters were used to determine seawater lifetimes, which agreed to hydrolysis lifetimes to within 15%.

4. Atmospheric COS mixing ratios displayed < 5% interhemispheric ratio. However, seasonal variation in the northern hemisphere may have been as high as 10%.

5. A simple steady-state model was developed to predict seasonal cycles of atmospheric COS.

TABLE OF CONTENTS

	Page	
List of Figures	xi	
List of Tables	xiii	
1. INTRODUCTION PART I: THE CLIMATIC IMPORTANCE		
OF CARBONYL SULFIDE IN THE ATMOSPHERE	1	
1.1 Introduction	1	
1.2 COS in the Stratosphere	5	
1.3 Stratospheric Aerosols and Climate	6	
1.3.1 The Earth's Radiation Balance	7	
1.3.2 The Catalytic Destruction of Ozone	7	
1.4 Atmospheric Distribution of COS	12	
1.5 The Global Atmospheric Budget of COS	14	
1.5.1 Sources	15	
1.5.2 Sinks	20	
1.6 Seasonal Trends in Atmospheric COS	22	
2. INTRODUCTION PART II: THE MARINE CYCLE OF COS		25
2.1 Introduction	25	
2.2 Photochemical Production	25	
2.3 Dark Production	27	
2.4 Dissolved Organic Material	29	
2.5 Penetration of Sunlight into Natural Waters	31	
2.6 Chemical Removal	31	
2.7 Air-Sea Exchange	33	
2.7.1 Models for the Exchange Coefficient	34	
2.7.2 Measurements of the Exchange Coefficient	36	

2.7.3 Dependence of K_w on Wind Speed	38
2.8 Purpose of this Work	40
3. ANALYTICAL METHODS	41
3.1 Introduction	41
3.2 Past Measurements with the ECD-S	42
3.3 Details of the Current ECD-S	43
3.3.1 The Electron Capture Detector	47
3.3.2 The Silver Catalyst	48
3.3.3 The Palladium Catalyst	52
3.3.4 Chromatographic Columns	55
3.3.5 Integration and Data Acquisition	60
3.3.6 Summary of Operating Parameters	60
3.4 Specific Problems Associated with the ECD-S	60
3.4.1 The Blank	62
3.4.2 The LEPs	63
3.4.3 Switch-Out Disturbance	64
3.4.4 Catalyst Performances	66
3.5 Sampling	67
3.5.1 Ambient Atmospheric Air	68
3.5.2 The Weiss Equilibrator	69
3.5.2.1 Equilibrator Response Time	69
3.5.2.2 Equilibrator Model	71
3.5.3 The Ferek Equilibrator	75
3.5.4 The Purge and Trap System	77

3.5.5 Sample Loops	81
3.6 Standards	81
3.6.1 High Concentration Tank Standard	81
3.6.2 Permeation Tubes	82
3.6.3 Ambient Level Tank Standard	86
3.7 Quantification and Instrument Performance	88
3.7.1 Quantification	88
3.7.2 Accuracy and Precision	91
 4. PHOTOPRODUCTION OF CARBONYL SULFIDE IN SOUTH PACIFIC OCEAN WATERS AS A FUNCTION OF IRRADIATION WAVELENGTH	 93
4.1 Abstract	93
4.2 Introduction	94
4.3 Experimental	95
4.4 Results and Discussion	98
 5. A REEVALUATION OF THE OPEN OCEAN SOURCE OF CARBONYL SULFIDE TO THE ATMOSPHERE	 105
5.1 Abstract	105
5.2 Introduction	106
5.3 Experimental	110
5.4 Results and Discussion	112
5.5 Conclusion	131

6. MODELING THE SEASONALITY OF ATMOSPHERIC COS	134
6.1 Introduction	134
6.2 The Model	134
6.3 Flux Scenarios	137
6.4 Model Results and Discussion	142
7. COS IN POLAR ICE CORES	148
7.1 Introduction	148
7.2 Climate Information from Ice Cores	148
7.3 COS as a Proxy for Stratospheric Sulfate and Trace Sulfur Gases	152
7.4 Analytical Methods	153
7.5 Results and Discussion	156
8. MISCELLANEOUS FINDINGS: COS INCUBATION EXPERIMENTS AND A REEVALUATION OF THE POLLUTION SOURCE OF COS	159
8.1 Introduction	159
8.2 COS Incubation Experiments	159
8.3 A Reevaluation Of The Pollution Source Of COS	162
9. CONCLUSION	166
9.1 Conclusions of This Study	166
9.2 Areas for Future Work	167
BIBLIOGRAPHY	170

APPENDIX: QUICKBASIC PROGRAM <u>SEASBURD.BAS</u>	183
--	-----

List of Figures

Number	Page
1.1 Global atmospheric cycle of COS	3
1.2 Annual variation of atmospheric COS since 1975	11
1.3 Comparison of seasonal cycles of COS and CO ₂	24
2.1 Schematic of marine cycle of COS in surface waters of the open ocean	26
2.2 Stagnant film gas exchange model	35
2.3 Concentration of radon gas as a function of depth	37
2.4 Measurements of gas transfer velocities and two different transfer velocity/wind speed relationships	39
3.1 Schematic of the ECD-S system	44
3.2 Schematic of the chromatographic and catalyst systems	46
3.3 Comparison of standards before and after silver catalyst conditioning	50
3.4 Comparison of standards with palladium catalyst at 40°C and 200°C	54
3.5 A typical chromatogram at 562 pptv	58
3.6 Effect of Pd catalyst temperature on COS and LEP peak heights	65
3.7 Schematic of the Weiss equilibrator	70
3.8 Equilibrator response time experiment	72
3.9 Schematic of the Ferek equilibrator	76
3.10 Schematic of the purge and trap in sample collection mode	78
3.11 Schematic of the purge and trap in sample injection mode	79
3.12 Calibration history of the Scott standard	83
3.13 Schematic of the permeation tube system	85
3.14 COS concentration trend in ambient level tank standard	87

3.15	Four calibration curves	90
4.1	Cruise 1 track of the Surveyor	96
4.2	Action spectra, solar irradiance, surface production rate spectra, and column production rate spectra	100
4.3	Photoproduction of OCS with 297 nm radiation	102
4.4	Action spectra from four locations and a comparison to previous work	103
5.1	Cruise 2 track of the Surveyor	113
5.2	Latitudinal dependence of COS saturation ratios in seawater	114
5.3	Diurnal cycles of dissolved COS concentrations	117
5.4	Regional and seasonal distribution of COS flux	126
5.5	Ambient atmospheric mixing ratios of COS in 5° averages	129
6.1	Seasonal and hemispheric fluxes of COS, scenario 1	139
6.2	Seasonal and hemispheric fluxes of COS, scenario 2	140
6.3	Seasonally distributed burdens and fluxes, scenario 1	143
6.4	Seasonally distributed burdens and fluxes, scenario 2	145
6.5	Model output of scenario 2 vs. atmospheric data	146
7.1	Ice core records from Vostok	149
7.2	Schematic of the formation of ice records	151
7.3	Schematic of the experimental setups for ice core analysis	155
8.1	Comparison of incubation experiments with hydrolysis decays	161

List of Tables

Number	Page
1.1 Comparison of the most important reduced sulfur gases	4
1.2 Global sources and sinks of COS	16
3.1 Comparison of column packing materials	57
3.2 Summary of operating parameters	61
3.3 Retention times of various compounds	64
3.4 Loss rate of permeation tubes	86
3.5 Factors contributing to measurement uncertainty	92
4.1 Photoproduction of OCS in sea water	99
5.1 Global sources and sinks of COS: previous and revised estimates	108
5.2 Comparison of measures decay times of COS concentration in seawater with hydrolysis lifetimes	118
5.3 Comparison of weiss equilibrator with bubbling equilibrator and purge and trap	120
5.4 Calculation of COS sea-air flux	125
5.5 Observed coastal ocean saturation ratios	128
5.6 Ambient atmospheric data from both cruises	130
6.1 Estimated fluxes of COS used for model input	138
6.2 The distribution of CS ₂ emissions (Tg)	141
8.1 Atmospheric mixing ratios of COS in "polluted environments"	164

ACKNOWLEDGEMENTS

This dissertation research could not have been performed successfully without the help and guidance of a number of people to whom I am very appreciative. I owe special thanks to my advisor Richard Gammon who continually encouraged and complimented me and treated me with a great deal of respect. I had the pleasure of taking his oceanography class at Friday Harbor, which inspired me to do research in geochemistry. I would also like to thank the other members of my committee, especially Bob Charlson, for being part of the initial inspiration for this project.

I owe tremendous thanks to my advisors at NOAA/PMEL, Jim Johnson and Tim Bates, who made it possible for me to participate on the ocean cruises and fostered my growth as a research scientist on a daily basis. Jim was continually helpful in the laboratory, always willing to give his expert assistance, and Tim acted as a mentor for my writing and bigger scientific questions. Other people at NOAA who were helpful include Trish Quinn, Cyndi Zenker, Karen Kreutzer, Cynthia Graff, Drew Hamilton, Dave Covert, Ryan Whitney, Paulette Murphy, Fred Menzia, and Jerry Davison.

Oliver Zafiriou and Steve Andrews were extremely helpful in the photoproduction studies during the second cruise, and also in writing our research paper together. The crew of the Surveyor made my 92 sea days an enjoyable experience (except for the equator crossing).

Very helpful people at the University of Washington include: Diane Hunn, Michelle Shulman, Susan Harder, Paul Quay, and Jim Murray.

The folks in Grenoble, France, including Patricia Martinerie, Dominique Raynaud, Jean-Marc Barnola, and Herve' Cabot also deserve my appreciation.

This research was performed under appointment to the U.S. Department of Energy, Graduate Fellowships for Global Change Program, administered by Oak Ridge Institute for Science and Education.

Finally, I would like to express my gratitude to the following friends and family for being my support and my livelihood during the past five years: my parents, my sister, Suzanne, Mike, Leah, Anthea, Cat, Chris, Julia, Lise, and Robin. Yahoo!!!

Chapter 1

Introduction Part I: The Climatic Importance of Carbonyl Sulfide in the Atmosphere

1.1 Introduction

For being invisible, the atmosphere has some amazing properties. Not only can it be compressed into a dense enough medium to hold up a Boeing 747, but it also contains some very important trace gas species that are believed to be crucial in the regulation of the earth's climate. Research on trace gases has expanded greatly in the past few decades, primarily a result of our greater awareness of their link to climate and the popular scientific and political issues like acid rain, global warming, ozone depletion, and marine ecology to name a few. There are literally thousands of different types of trace gases in the atmosphere, yet by volume they are all completely insignificant. N_2 , O_2 , and argon occupy about 99.966% of dry air, leaving about 0.034% for everything from aldehydes to zeolite dust. The gas of focus in this study, carbonyl sulfide (COS, OCS), has an average mixing ratio of 500 ppt, or put on the percent scale, 0.00000005% by volume. Ironically, this is the most concentrated and ubiquitous sulfur gas in the atmosphere.

COS is a biogenic gas, as are many of the trace gases in the atmosphere. If COS (or the precursor CS_2) were not continuously released from the world's biota then its concentration would fall to near zero (except for a small volcanic input) due to the favorable thermodynamics of the reactions with oxidizing radicals in the atmosphere. All reduced trace gases are also out of thermodynamic equilibrium and most have current-day background concentrations that appear to be controlled to a large degree by biological activity. This curious interrelationship between the biosphere and atmosphere has been examined in detail by Lovelock (1989) and others under the concept of the Gaia Hypothesis. This hypothesis postulates "that the physical and chemical condition of the surface of the Earth, of the atmosphere, and of the oceans has been and is actively made

fit and comfortable by the presence of life itself." COS appears to play a part in one or more climate-controlling feedback mechanisms and is thus interesting to study under the Gaian paradigm. The current state of understanding of the biogeochemical cycle of COS is depicted in Figure 1.1, with many of the details being discussed in later sections.

COS shares many commonalities with the other reduced sulfur gases (DMS, CS₂, and H₂S are the main ones), as their sources are distributed fairly uniformly across the globe and they are strongly linked to bacteriological processes in soils and swamps. COS is a partially oxidized sulfur gas so it is also produced by photooxidation of larger organo-sulfur molecules. Its main difference, however, is that it is rather inert in the atmosphere. Its gas-phase reaction with the OH radical (the major sink for most reduced gases) is quite slow (Table 1.1), and consequently this give COS a very slow turnover time in the atmosphere, on the order of 44 years by this process alone, compared to 1-20 days for the other sulfur gases mentioned.

Gases with turnover times of greater than one year are able to penetrate the strong inversion that separates the troposphere from the stratosphere. COS has an estimated lifetime of 1-10 years with respect to all its sinks and thus is the most significant non-volcanic source of sulfur to the stratosphere. COS becomes fully photo-oxidized to sulfuric acid once in the stratosphere, and in the presence of water vapor, forms an aerosol particle.

These aerosol particles have a strong climatic effect for a number of different reasons. First, they are roughly the same dimension as the wavelength of incoming visible solar radiation (0.1-0.5 μm diameter) and strongly interact with light by Mie scattering. A fraction of the scattered light is sent back to space producing a cooling effect at the earth's surface. Second, since stratospheric pressures are low and molecular collisions are less frequent, aerosol particles provide needed surfaces for many species to

Figure 1.1. Global atmospheric cycle of COS, modified from Gammon and Charlson (1993).

Table 1.1: Comparison of the Most Important Reduced Sulfur Gases

	COS	Dimethyl Sulfide	H ₂ S	CS ₂
Mixing ratio (pptv)	400 - 900	1 - 440	0 - 830	3 - 190
Rate coefficient at 298°K with OH radical ^a	$< 4 \times 10^{-14}$	$(9.1-45) \times 10^{-12}$	5×10^{-12}	$(0.43-2) \times 10^{-12}$
Lifetime in troposphere with respect to OH sink	44 years	0.6 days	4.4 days	12 days

^a(Units = cm³/molecule/s) For reactions with O₂ present, and assuming an OH density of 5×10⁵ molecules/cm³. Table adapted from Warneck (1988).

react, lowering activation barriers and increasing reaction rates. N₂O₅, for example, reacts on the surface of H₂SO₄ droplets and forms HNO₃, which ties up nitrogen that would otherwise be available to react with the chlorine species that destroy ozone.

With research in the area of ozone depletion and stratospheric chemistry rapidly expanding, a better understanding of the geochemistry of COS is also sought after. Thus, the main focus of this study was to try and fill some of the gaps and paint a more complete picture of COS in the atmosphere. This was hopefully accomplished by

numerous measurements of COS in the marine environment, a reevaluation of its global atmospheric budget, and an attempt to make measurements in ice core samples.

1.2 COS in the Stratosphere

Crutzen (1976) was the first to point out that during volcanically quiescent periods, COS is the dominant gaseous molecule in the stratosphere to form sulfate aerosol particles. SO_2 and H_2S had been proposed by Junge (1974) to be possible transporters of sulfur from the troposphere, but on the basis of their fast removal times, Crutzen (1976) discounted this possibility. COS was discovered in tropospheric air by Hanst et al. (1975), and was first measured in the stratosphere by Inn et al. (1979). Both Crutzen (1976) and Turco (1979) modeled the COS distribution as a function of height in the stratosphere, based on the photochemical reactions known to dissociate COS. They predicted that almost all the COS is converted to SO_2 between 20 and 25 km, which is just above the background layer of aerosol particles (~20 km) discovered by Junge et al. (1961). Subsequent measurements of COS mixing ratios by Inn et al. (1979) at 15 and 31 km and Engel and Schmidt (1994) between 21 and 30 km, generally agreed with the predicted COS vertical distribution. Servant's (1986) measurements of sulfate aerosol particles between 12 and 20 km verified that a source of SO_4^{2-} from the oxidation of COS was sufficient to explain the distribution of SO_4^{2-} in the stratosphere. Furthermore, it appeared that OH attack of COS is negligible and that photodissociation is the main removal pathway. Engel and Schmidt (1994) calculated that COS removal in the stratosphere accounts for between 0.047-0.11 Tg COS/yr, giving a turnover time with respect to this process of 69 ± 28 years. This lifetime is longer than the previously published lifetime of 28 years (Inn et al., 1981).

Recent results from a one-dimensional photochemical model (Chin and Davis, 1995) suggest that the COS flux to the stratosphere is as high as 0.64 Tg/yr, but that only 0.06 Tg/yr is removed in the stratosphere through photochemical reaction, with the remainder returning downward to the troposphere. This study also suggests that the currently accepted flux of COS to the stratosphere is not sufficient to explain the background aerosol levels in the Junge layer by a factor of 2-5. They question whether background aerosol levels have been overestimated due to inaccurately assigning the label "volcanic quiescence" to periods that do have significant volcanic inputs. They also point out that large uncertainties associated with knowing the residence time of stratospheric sulfur could have lead to inaccurate model determinations of the COS flux required to sustain the Junge layer. Finally, they cite the possibility of another sulfur source to the stratosphere, namely jet aircraft emissions as another discrepancy between theirs and earlier works.

1.3 Stratospheric Aerosols and Climate

The presence of dust in the stratosphere was suggested in the 1920's (Gruner and Kleinert, 1927) but it was not until much later that initial samples were collected by Junge et al. (1961) and found to composed of sub-micron sulfate. This pioneering work earned Junge the distinction of having this stable layer of haze between 10-25 km named after him. It was also realized that these airborne particles can influence weather and climate, atmospheric electricity and the trace composition of the atmosphere (Turco et al., 1982). Two important climatic effects of stratospheric aerosols will be discussed: the earth's radiation balance, and the catalytic destruction of ozone.

1.3.1 The Earth's Radiation Balance

The contribution of the optical depth of the stratosphere to the total optical depth of the atmosphere is quite small: about 1-5% depending on location and season (Kaufman, 1993; McCormick, 1986). Thus, small changes in the stratospheric aerosol number concentration are not expected to have a huge effect on the light scattering properties of the whole atmosphere. Turco et al. (1980) estimated that a 10-fold increase in COS would result in a 4-fold increase in stratospheric optical depth (from 0.005 to 0.019), comparable to the optical depth increase observed from a modest volcanic eruption (Fuego, Agung). They also predicted a global surface cooling by about 0.1°K from such an increase, which is on the threshold of climatic significance. Taubman and Kasting (1995) have recently insisted that the intentional release of COS to the atmosphere is not an environmentally acceptable remedy for global warming caused increases in CO₂. However, since present concentrations of COS and CS₂ (a COS precursor) are quite low, a small unintentional increase in the emission quantities by industrial activities could have a large effect on atmospheric concentrations, and hence climate.

1.3.2 The Catalytic Destruction of Ozone

Ozone in the stratosphere plays a unique and important role in the Earth's biological system by strongly absorbing harmful UV radiation. Ozone is produced continually in the upper stratosphere by the reactions:

and intercepts the biologically damaging UV-B radiation (280-320 nm) through the reaction:

With the products of 1.3, ozone is reformed via reaction 1.2. Ozone is also continually being destroyed through families of naturally and artificially occurring radicals that contain chlorine, nitrogen, hydrogen or oxygen atoms. Of particular concern are the chlorine radicals that are produced from destruction of the human-made chlorofluorocarbons (CFCs). CFCs are basically inert in the troposphere but are rapidly photo-dissociated under UV light (185-215 nm, Warneck, 1988) above 30 km in the stratosphere:

One Cl atom can destroy literally hundreds-of-thousands of ozone molecules through the catalytic sequence (Molina and Rowland, 1974):

In the 1970's concern over increasing emissions of CFCs led to numerous studies aimed at assessing their possible impact on the concentration of ozone in the stratosphere. The results of these studies indicated that at current CFC emission levels, globally averaged total column ozone concentrations would decrease by only 5-20% over the next 100 years (Solomon, 1988). This low estimate arose because it was thought that much of the inorganic chlorine in the stratosphere was tied up in reservoir species, HCl and ClONO₂, which are inert towards ozone. However, it was soon evident that these figures had been seriously underestimated when Farman et al. (1985) discovered that ozone over Antarctica had decreased by over 50% during the past decade, but only during the spring season. This phenomenon was totally unexplainable by the current gas-phase Cl/O₃ chemical reactions, and prompted speculations about other mechanisms. Subsequent

model studies (Solomon, 1986, McElroy, 1986) showed that in the lower levels of the stratosphere (10-20 km) where most of the ozone resides, the reservoir species, HCl and ClONO₂, can undergo a particular type of reaction that had not been considered before the results of Solomon (1986):

This reaction, which liberates molecular chlorine and easily photodissociates into two chlorine radicals, does not occur in the gas phase but rather on the surfaces of polar stratospheric clouds. PSCs come in two types: type II PSCs form at temperatures below about 187°K and are composed primarily of water ice and frozen HNO₃. Type I PSCs appear to be primarily composed of nitric acid trihydrate and are formed at temperatures less than 195°K. Type II PSCs (0.1-1 μm diameter) are usually about an order of magnitude smaller than type I (Granier and Brasseur, 1992). Both types are usually confined to the region above Antarctica because of the extreme cold temperature requirement, thus explaining why severe ozone depletion was first discovered over this part of the earth. However, more recent developments suggest that significant ozone depletion is occurring at warmer temperatures over the Arctic and mid-latitudes as well, causing even more concern about the health of the earth's radiation shield (Rodriguez et al., 1991). A new mechanism of global ozone depletion was proposed which involves the reactions:

These reactions occur on the surfaces of liquid sulfuric acid aerosol particles which are ubiquitous in the stratosphere (Tolbert et al., 1988; Rodriguez et al., 1988; Hofmann and Oltmans, 1992). As a result of these reactions, the reservoir species N₂O₅ and ClONO₂ are depleted, ClO and OH are liberated leading to the eventual destruction of ozone.

In light of reactions 1.7 and 1.8, Prather (1992) predicted that "catastrophic ozone losses" could occur after a major volcanic eruption. Indeed, the deepest, most extensive ozone "hole" ever recorded occurred in 1992 (Zurer, 1993) as a result of increased levels of ClO over Antarctica after the eruption of Mt. Pinatubo in 1991 (Solomon et al., 1993). Hofmann and Solomon (1989) also suggested that low ozone levels in 1983 were due to the violent eruption of El Chichon. On the other hand, Fahey et al. (1993) suggested that ozone loss over mid-latitude regions is not as sensitive to huge increases in stratospheric aerosol burden compared with ozone loss over Antarctica because reaction 1.7 is slowed appreciably at warmer stratospheric temperatures. Also, sulfur aerosol particles in the Junge layer provide less surface area available for heterogeneous reactions than PSCs (Granier and Brasseur, 1992).

Between each major volcanic eruption, the aerosol burden of the stratosphere is thought to decay back to non-zero level as a result of the constant upward flux of COS from the troposphere. Hofmann (1990) has suggested that the background aerosol level increased by $5 \pm 2\%$ during the period 1979-1989 over a northern mid-latitude site, and speculated the causes to be increases in COS flux and/or jet aircraft emissions. The size distribution of these particles has shifted to favor larger sizes, indicating that new material entering the stratosphere is being scavenged by pre-existing particles. While this increase in sulfate may have an unnoticeable effect on global temperature, the influence on stratospheric ozone could be more significant.

The atmospheric burden of COS has not been increasing significantly and thus must be ruled out as the cause for the increasing stratospheric sulfate burden. A compilation of all the atmospheric measurements since the 1970's was published by Mihalopolous et al. (1991) and shows no clear trend (Figure 1.2). Measurements by ground-based infrared spectroscopy between 1977 and 1991 show that the total-column

Figure 1.2. Annual variation of atmospheric COS since 1975. Key to numbers: 1. Sandalls and Penkett (1977); 2. Maroulis et al. (1977); 3. Torres et al (1980); 4) Hoyt (1982); 5) Rasmussen et al. (1982); 6. Johnson and Harrison (1986); 7. Carroll (1985); 8. Belviso (1986); 9. Ferek and Andreae (1984); 10. Johnson and Harrison (1986); 11. Bingemer et al. (1990); 12. Mihalopolous et al. (1989); 13. Johnson and Bates (1993); 14. Mihalopolous et al. (1991); 15. Staubes and Georgii (1993); 16. This Work.

abundance of COS has varied by a maximum of 0.2% per year, which is not statistically different than 0.0% (Rinsland et al., 1992). Bandy et al., 1992, compiled all their measurements made since 1977 in the Northern Hemisphere and observe no clear trend either. Prinn et al. (1995) have recently reported that OH radical atmospheric concentrations have remained constant ($\pm 0.2\%$) since 1978, thus implying that OH trends are not a factor in controlling long-term COS trends. Long-term constancy in COS necessitates a net balance between its global sources and sinks, which is not consistent with published field measurements. The budget currently lacks closure with the total sources exceeding the total sinks by about 50%. The atmospheric budget of COS will be discussed in greater detail in the following section.

1.4 Atmospheric Distribution of COS

Since COS was first measured in the troposphere in the 1970's (Hanst et al., 1975) and an average concentration of around 500 parts per trillion by volume (pptv) was revealed (Sandalls and Penkett, 1977), efforts were made to understand the spatial and temporal trends of this important gas. The first extensive data set of COS from a wide latitudinal range (57°S to 70°N) over the Pacific Ocean was published by Torres et al. (1980). They reported an average mixing ratio for COS of 512 ± 65 ppt with no significant latitudinal gradient. Very similar results were obtained by Rasmussen et al. (1982) and Johnson and Harrison (1986), both of whom found a very constant mixing ratio ($500 \text{ pptv} \pm 10\%$) with $<5\%$ latitudinal variation between the northern and southern hemispheres. Khalil and Rasmussen (1984) placed a lower limit on the atmospheric lifetime of COS at one year based on its nearly constant mixing ratio with height and its seemingly random temporal variability. They also put constraints on the location and magnitude of sources and sinks of COS, based on the lack of a large concentration

gradient between the two hemispheres. In particular, they suggested that pollution sources can account for not more than 25% of the total sources of COS both directly and indirectly (as CS_2). Thus, there was not much cause for concern that COS levels were increasing due to large increases in emissions associated with industrial emissions (as was the case for CO_2 and CH_4). However, Bingemer et al. (1990) found a large latitudinal gradient in the atmospheric mixing ratio over the Atlantic Ocean in the marine boundary layer. They reported an inter-hemispheric ratio (IHR) of 1.25 ($\text{IHR} = [\text{COS}]_{\text{north}} / [\text{COS}]_{\text{south}}$) which was significantly greater than any previous measurements over the Pacific. Back trajectory analysis of the air masses they sampled showed that its origins several days prior to the measurement were from industrial regions of Northern Europe. The fact that COS levels reached nearly 900 pptv in some air samples, and that these high values correlated reasonably well with elevated levels of methane and carbon monoxide, led Bingemer et al. (1990) to the conclusion that there could be a significant contribution of anthropogenic sources to the global COS budget. Johnson et al. (1993) also reported a high IHR of 1.15 from aircraft measurements over the Atlantic during the Chemical Instrumentation Test and Evaluation (CITE-3) project. In this study, three independent COS measurement techniques were employed and gave results that agreed to within measurement uncertainties, indicating that the anomalous trend observed by Bingemer et al. (1990) was probably real and not an instrumental artifact. Johnson et al. (1993) suggested that the large IHR they observed could result from a large seasonally dependent sink located predominantly on the continents of the northern hemisphere. There has been no attempt to explain, however, how COS, with a long tropospheric lifetime, could have such a different latitudinal gradient in the atmosphere over the Atlantic compared to the Pacific. For other trace gases with shorter

lifetimes, air over the Pacific is usually more representative of the unperturbed atmosphere because it is more isolated from industrial emissions on the continents.

Atmospheric measurements from this work, presented in Chapter 5, show a trend over the Pacific ($0.95 < \text{IHR} < 1.05$) which is in general agreement with previous studies in this region (Johnson and Harrison, 1986; Torres et al., 1980; Rasmussen et al., 1982). Our large numbers of measurements from a wide latitudinal range (70°S - 55°N) show a seasonal dependence on the IHR that had not previously been reported, and could indicate the relative magnitude and/or phase of the sources and sinks of COS between the two hemispheres.

There is very little information on the seasonal trends of COS mixing ratios in the atmosphere. Only one study (Mihalopolous et al., 1991) reports two continuous one-year time series of COS measurements from Amsterdam Island in the Indian Ocean (37°S) which shows less than 5% seasonal variation between the summer maximum and the winter minimum. Northern hemisphere seasonality appears to be higher, based on results from Rinsland et al. (1992). From total column burden measurements, they found a summer maximum roughly 5% higher than the winter minimum, suggesting that surface seasonality could be up to 10%. Bandy et al. (1992) report no detectable seasonality from a compilation of all their measurements spanning 15 years. In general, seasonally resolved measurements have been hindered by the fact that seasonal variations are on the order of the imprecision of the measurement, making it difficult to distinguish between real changes and instrumental noise.

1.5 The Global Atmospheric Budget of COS

Knowledge of the lifecycle of a gas is key to better understanding and interpreting its atmospheric distribution in time and space. Considerable research has been devoted to

identifying and calculating the magnitude of the sources and sinks of COS. In spite of this effort, there is still a large discrepancy between the sum of the sources and the sum of the sinks. Because the long term concentration trend of COS in the atmosphere has remained relatively constant, COS is expected to have a balanced atmospheric budget, yet only by assuming a large and currently unsubstantiated "missing sink", or assuming that some sources are seriously overestimated, can the budget be brought into balance. The most recently published tabulation of the global budget is presented in Table 1.2 (Chin and Davis, 1993). Previous budget estimates are also shown for comparison (Johnson, 1985; Khalil and Rasmussen, 1984; Goldan et al., 1988). The revised budget presented in this work can be found in Chapter 5. The following discussion (some of which can be found in Chapter 5) summarizes the current state of knowledge on each of the sources and sinks.

1.5.1 Sources

Carbon Disulfide

A significant source of COS is from the reaction of carbon disulfide (CS_2) with OH radical in the atmosphere:

These reactions proceed faster under cooler temperatures and in the presence of O_2 , which prevents the CS_2OH adduct from undergoing a reverse reaction. The rate constant for this reaction has been measured at about $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Barns et al., 1983; Jones et al., 1982; Wine et al., 1980; Hynes et al., 1988) giving CS_2 a tropospheric lifetime of about 12 days based on the assumption that atmospheric oxidation is the only significant sink process (Khalil and Rasmussen, 1984). The conversion efficiency (moles

Table 1.2: Global sources and sinks of COS: Published Budget Estimates

Sources	Chin and Davis (1992) Tg COS/yr	Goldan et al (1988) Tg COS/yr	Johnson (1985) Tg COS/yr	Khalil and Rasmussen (1984) Tg COS/yr
oceans	0.32(0.16-0.64)	0.2 - 0.8	0.25	0.60(0.3-0.9)
CS ₂ oxidation	0.34(0.17-0.61)	--	0.7	0.60(0-2)
soil and marsh	0.27(0.14-0.52)	0.07 - 0.2	0.5	0.42(0.2-0.6)
DMS oxidation ¹	0.17(0.10-0.28)	--	--	--
biomass burn	0.14(0.04-0.26)	0.1 - 0.5	0.2	0.20(0.1-0.5)
anthropogenic	0.05(0.03-0.07)	0.04 - 0.4	0.15	0.14(0.04-0.45)
volcano	0.02(0-0.09)	--	0.02	0.02(0.01-0.05)
total sources	1.31(0.65-2.47)	(0.5-2.0)	1.82	2 (≤ 5)
Sinks				
vegetation	0.43(0.16-0.91)	0.2 - 0.6	0.97	1.1(≤3.3)
stratosphere	--	0.10 - 0.16	0.15	0.1(≤0.2)
reaction w/ OH	0.13(0.02-0.80)	0.1	0.7	0.8(0.1-1.5)
photolysis	0.03(0.02-0.04)	--	--	--
reaction w/ O	0.02(0.01-0.03)	--	--	0.03
total sinks	0.58 (0.19-1.8)	(0.4-0.9)	0.60 (0.19-1.8)	2.03

¹DMS source not included in Chin and Davis, taken from Barnes et al. (1994).

of COS produced per mole of CS₂ consumed) is estimated to be about 0.81 ± 0.06 (Chin and Davis, 1993). Quantifying a global flux of CS₂, and thus the contribution to the COS budget, has been difficult because its average tropospheric concentration is only 10 ppt (Johnson et al., 1993; Kim and Andreae, 1987; Maroulis and Bandy, 1980). Andreae (1990) suggested that CS₂ is ubiquitous in the surface ocean and the oceans may represent an important source. CS₂ may also have large sources associated with power plants, chemical manufacturing and tire dust (Pos and Berresheim, 1993; Chin and Davis, 1993; Kim and Andreae, 1987; Khalil and Rasmussen, 1984). It has been suggested that the majority of COS coming from industrial sources, is actually emitted as CS₂ and thus represent an indirect source. Microbial processes in soils and swamps are also thought to be significant sources as well (Adams et al., 1981; Goldan et al., 1987; Lamb et al., 1987). Overall, the COS source from CS₂ conversion has been estimated by Chin and Davis (1993) to be 0.17-0.61 Tg COS/yr.

Dimethyl Sulfide

Recent work by Barnes et al. (1994) has suggested that DMS can be oxidized to form COS with a yield of $0.7 \pm 0.2\%$, accounting for a global source of COS of 0.10-0.28 Tg COS/yr. DMS is the most important organic sulfur compound emitted to the atmosphere because it is the primary source of non-seasalt sulfate aerosol particles through the reaction with OH radicals during the day and NO₃ radicals during the night. Reaction with OH proceeds by both addition and abstraction pathways, but it has been shown that the hydrogen abstraction channel accounts for 75% of the overall reaction at 300°K (Stickel et al., 1993):

The fate of CH_3SCH_2 radicals under atmospheric conditions is generally accepted to proceed by the following sequence of reactions (Stinkel et al., 1993; Wallington et al., 1993):

Crutzen (1983) suggested that in addition to thermal decomposition shown above, $\text{CH}_3\text{SCH}_2\text{O}$ (methyl thiolfomate) could also react with O_2 to form CH_3SCHO which then could react with OH to form H_2O , CH_3 , and COS . Barnes et al. (1987) attempted to measure the formation yield of COS by this mechanism, but found a reaction yield of only 0.01%, concluding that DMS oxidation was an insignificant source of COS . However, Barnes et al. (1994) subsequently discovered that the presence of NO_x (ppm levels) in the photo-reactors significantly affects the kinetics and measured product distributions. Barnes et al. (1994) observed COS formation only under NO_x -free conditions, which prevented the scavenging of CH_3S radicals by NO_2 , and allowed CH_3S to react with O_2 to eventually form COS . Clearly more detailed work needs to be done to determine the exact dependency of COS formation on NO_x concentration, because the presence of NO_x is ubiquitous in the atmosphere (average mixing ratio ~10 ppb in remote environment), and could prevent significant COS formation under ambient conditions.

Soils, Swamps and Marshes

These environments contain large amounts of anaerobic sulfate-reducing bacteria that synthesize various sulfur gases including OCS and CS_2 (Bates et al., 1992; Guenther et al., 1989; Goldan et al., 1987; Steudler and Peterson, 1984; Adams et al., 1981). However, the magnitude of the flux from these sources has been called into question

lately because past measurement techniques may have given artificially high results (Castro and Galloway, 1991). The technique involves placing an enclosure around the study area, flushing with sulfur-free air, and measuring the flux from the study area. Castro and Galloway (1991) showed that sulfur-producing organisms in soil respond to a sulfur-depleted environment by producing sulfur gases. When ambient air is used as the chamber flush gas, the soil organisms actually take up COS and CS₂. Work by de Mello and Hines (1994) showed that the direction of the COS flux was dependent on whether a static or dynamic enclosure had been used. Fried et al. (1992) showed that peat, soil, and moss do emit COS and CS₂ using the Castro and Galloway technique, but that the addition of growing plants causes uptake. It appears that the direction of the COS flux in soils depends on soil conditions such as temperature, soil moisture, and nitrogen content, in addition to the types of plants and organisms present. Chin and Davis (1993) suggest that the results of Goldan et al. (1987) and Lamb et al. (1987) are the most representative of the different soil and marsh environments found on the earth, as opposed to the results of Castro and Galloway (1991) which apply to only one soil type in one location. Chin and Davis (1993) therefore assign a range of 0.14-0.52 Tg COS/yr for the soil, marsh and swamp source.

The Oceans

A detailed discussion of the ocean source (and sink) of COS is presented in Chapters 2 and 5.

Other Sources

Biomass burning is a significant source of hundreds of different trace gases to the atmosphere including COS (0.05-0.3 Tg COS/yr) (Crutzen and Andreae, 1990).

Industrial emissions from coal-fired power plants and chemical industries may produce significant amounts of COS and even more CS₂ (0.03-0.06 Tg COS/yr), but there are few data. Fried et al. (1992) measured COS emissions from automobile exhaust and determined that automobiles are an insignificant source globally (0.005-0.02 Tg COS/yr). Automobile tire wear may constitute a small source (0.036-0.044 Tg COS/yr) globally (Pos and Berresheim, 1993). Volcanoes are a minor source of COS as well because of their sporadic and infrequent nature (0.006-0.09 Tg COS/yr) (Belviso et al., 1986).

1.5.2 Sinks of COS

Loss to the Stratosphere

The upward flux of COS to the stratosphere is the most important process climatically, yet it accounts for less than 10% of the proposed total tropospheric source flux, or 0.03-0.1 Tg COS/yr (Turco et al., 1980; Crutzen, 1976). In the stratosphere photochemical oxidation converts COS to sulfuric acid (H₂SO₄), which eventually forms aerosol particles.

Reactions in the Troposphere

Destruction by OH radicals was originally thought to be the major sink for COS in the troposphere analogous to that for most other reduced gases (Turco et al., 1980), based on reaction rates published by Kurylo (1978). The reaction was identified as:

with $\Delta H = -35$ kcal/mol, an exothermic reaction. However, these reactions were later found to be slow and of minor importance for COS (0.02-0.8 Tg COS / yr) (Wahner and

Ravishankara, 1987; Cheng and Lee, 1986). The lifetime for COS by this reaction alone is about 44 years (Warneck, 1988), comparable to the stratospheric photochemical sink.

The Plant Sink

Deposition of COS to land plants has been proposed to be a major sink (Fall et al., 1988) although it is difficult to quantify on a global basis. Goldan et al. (1988) described the mechanism as being analogous to photosynthetic CO₂ uptake by plants. COS enters the stomata of a leaf and undergoes hydrolysis to CO₂ and H₂S by the carbonic anhydrase enzyme. Brown and Bell (1986) found that in rye grass, the H₂S produced is either assimilated into amino acids, oxidized to sulfate, or emitted from the plant. These studies were all done under controlled laboratory conditions, and with only a few plant types.

Subsequent field measurements, however, showed that COS uptake is not as universal as was first proposed. Berresheim and Vulcan (1991) found no evidence for COS uptake from a pine forest, and actually observed significant COS emissions during the summer daylight hours when the trees were photosynthetically active. They suggested that COS uptake could be species specific. Fried et al. (1993) transported a Canadian bog to a rooftop in Boulder, Colorado and simulated ambient conditions inside an enclosure in order to measure COS. They found uptake in the bogs that had growing vascular plants present, although the uptake rates were much too small to account for the huge sink required to balance the budget. Mihalopolous et al. (1989) made the first observations of the plant sink in an unperturbed field situation. During an inland inversion event where gases are trapped close to the surface, they measured COS up to 750 m from a balloon and saw a pronounced deficit in COS near the surface. This deficit increased over time indicating that the plants at the surface were taking up COS faster

than it could be produced. Again, however, there was no indication that the plant sink was large enough to offset the magnitude of the sum of the proposed sources.

Atmospheric measurements by Johnson et al. (1993) showed a trend that was consistent with there being a large plant sink located in the northern regions of Canada, i.e. a decrease in atmospheric COS in air that had advected from northern Canada. However, field results from Fried et al (1993) and de Mello and Hines (1994) on temperate and boreal wetlands showed that northern wetlands are not a large sink for COS, and are likely insufficient to account for the atmospheric trend observed by Johnson et al. (1993).

1.6 Seasonal Trends in Atmospheric COS

Information on the sources and sinks of COS can be indirectly obtained from observations of the seasonal cycle of atmospheric COS concentrations. Because COS sources and sinks are largely controlled by biologically related processes, the seasonal nature of these processes should dictate the seasonal nature of the atmospheric signal. Such is the case for atmospheric CO₂: terrestrial vegetation is a major sink for CO₂, and one that is unevenly distributed across the earth, with the northern hemisphere containing 2/3rds of the land mass and thus a large portion of the photosynthesizing land plants that consume CO₂. Atmospheric CO₂ has a pronounced seasonal cycle in the northern hemisphere and a much smaller one in the southern hemisphere.

Atmospheric data from different seasons for COS are sparse, but what little data there are, indicate that the seasonal cycle for COS is less than 10% peak-to-peak amplitude variation. One data set is from total-column infrared measurements at Kitt

Peak, Arizona (32°N) and the Jungfraujoch, Switzerland (46°N) (by Rinsland et al. (1992), who found a COS maxima in the spring/summer. Some of their seasonal signal was attributed to changes in tropopause height, although by accounting for this correction, they still report a seasonality of 5% with a distinct spring/summer maximum. CO₂ at these latitudes has a distinct summer/fall minimum (Figure 1.3) (CMDL Report, 1993) which argues against a sink process for COS that is identical to CO₂, i.e. plant uptake. Bandy et al. (1992) report no significant seasonality (< 5%) in a compilation of all their data in the northern hemisphere since 1977 and organized by season. However, their data are not from continuous measurements and could be subject to systematic errors between field measurement projects. Mihalopolous et al. (1991) measured COS at Amsterdam Island in the Indian Ocean (38°S) from 1987-1990 and reported no significant seasonal trend either (<5%). However, this neither argues for or against the plant sink because if COS is analogous to CO₂, then no seasonal trend should be expected there simply because of the lack of land plants in that part of the world.

To better resolve this mystery about seasonal cycles, high precision measurements are needed, that are able to measure a 5-10% seasonal variation. This remains to be done. This goal was an early aim of this project and some preliminary work toward this goal is presented in Chapter 6, where I developed a simple model predicting the seasonal trend in atmospheric COS by assuming a balance between sources and sinks. The majority of research contained in this dissertation, however, is focused on the marine cycle of COS. Background information concerning the marine cycle of COS will be the subject of the following chapter.

Figure 1.3. Comparison of seasonal cycles of COS and CO_2 with least squares 4th-order polynomial fits. CO_2 data is from CMDL Report (1993) from Mauna Loa, 20°N 156°W , COS data is from Rinsland et al. (1992) 32°N 112°W . Note that the difference in maxima are out of phase by about 3 months.

Chapter 2

Introduction Part II: The Marine Cycle of COS

2.1 Introduction

This chapter discusses the details of COS production and loss in surface seawater, and attempts to review the latest research on its biogeochemistry. The oceans cover a large fraction of the earth's surface and a better knowledge of the cycling of COS within the oceans can lead to a better understanding of the atmospheric budget. The current understanding of the marine cycle of COS is presented in Figure 2.1.

2.2 Photochemical Production

COS is produced photochemically from biogenic organosulfur compounds in the marine euphotic zone, which has been demonstrated by a number of laboratory and field experiments (Ferek and Andreae, 1984; Zepp and Andreae, 1990, 1994; Uher and Andreae, 1994). Indirect evidence for photochemical production first came from Ferek and Andreae (1984) who found COS surface seawater concentrations to display a pronounced diurnal cycle, with a maximum occurring each day about 2-4 hours after the solar maximum at local noon. Such diurnal behavior was very analogous to earlier measurements of carbon monoxide, which was known to be produced by UV photolysis of dissolved organic carbon (DOC) (Conrad et al., 1982). Ferek and Andreae (1984) found that COS production was independent of salinity, photosynthetic activity, and microbial activity, indicating that COS formation resulted from photooxidation of non-living DOC, or the more general term, dissolved organic material (DOM). In the laboratory, Ferek and Andreae (1984) then found that COS was also produced by UV-irradiation of seawater and solutions of several biochemically relevant organosulfur compounds. Zepp and Andreae (1990) pointed out that the organosulfur compounds used by Ferek and Andreae (1984) (cysteine, methionine, glutathione, dimethyl-propiothetin)

Figure 2.1. Schematic of marine cycle of COS in surface waters of the open ocean. UV light enters surface ocean waters where it photolyzes DOM and forms COS, which can either undergo hydrolysis to form sulfide ions, mix to deeper waters, or vent out the mixed layer. Additionally, dark production mechanisms could form appreciable quantities of COS. Light penetration depth is based on average values for chlorophyll and DOM for open ocean, and data from the RITS cruises. Range of DOM values is from RITS cruises, and percentage of DOM that is dissolved organic sulfur (DOS) is from an estimate from Wolfe (1992). Average $[\text{COS}]_{\text{aq}}$ is from this work, and average $\text{S}^{=}$ is from Elliot et al. (1987).

do not directly absorb sunlight, but rather undergo photosensitized oxidation to form COS. Laboratory evidence for this mechanism was recently reported by Zepp and Andreae (1994) who observed over 10 times more COS produced by photolysis in a solution containing a mixture of cysteine and DOM compared to solutions of only cysteine or DOM separately.

Photosensitized oxidation appears to involve absorption of a UV photon by a chromophore located on a DOM or other inorganic molecule, and the subsequent formation of a solvated reactive chemical transient such as OH radical (Mopper and Zhou, 1990). Zepp and Andreae (1994) speculate that the transient then attacks the bivalent S atom or sulfhydryl H atom of an organic sulfur compound or sulfur containing portion of a DOM molecule.

2.3 Dark Production

There is some recent evidence that COS can be produced in seawater by means other than with photons. The strongest evidence for "dark" production of COS comes from Ulshofer et al. (1995) who found dark production rates that are 10-50% of photoproduction rates depending on whether open ocean or coastal areas are measured. These figures were generated by including a zeroth order dark production term into a model fit of diurnal decay behavior. Dark production was further substantiated by dark incubation experiments where only hydrolysis and dark production could occur. Ulshofer et al. (1995) found dark production rates that agreed with those observed based on field measurements and model fits.

The data presented here in Chapter 4 shows some evidence for dark production, in the control samples that were incubated with only room light for about 12 hours. A 50% concentration increase was observed, but no conclusions could be drawn because of lack of data.

The revised COS hydrolysis rate constants published by Radford-Knoery and Cutter (1994) may show evidence of dark production, even though this is not stated in their paper. Radford-Knoery and Cutter (1994) report hydrolysis rates that are 28-74% slower than the previous studies of Elliot et al. (1987, 1989). RKC used filtered seawater samples for hydrolysis rate determination, whereas Elliot et al. used artificial solutions, making dark production only possible in the RKC experiment. Furthermore, the range of 28-74% is consistent with the dark production estimates given by Ulshofer et al. (1995) and Weiss et al. (1995a).

Radford-Knoery and Cutter (1994) also observed elevated concentrations of COS at depths below the mixed layer where there is no light, and vertical mixing of COS from the surface is unlikely because of its short lifetime (hours) in seawater. This suggests in-situ production of COS. Their depth profiles show a steep COS gradient from the surface down to about 50 meters which is consistent with a photochemically produced gas, receiving its input light energy from the sea surface. Concentrations fall to near zero below 50 meters until 100 meters where the concentrations rise, unexplainably, although simultaneously with nitrate. They suggest that this correlation could indicate the recycling of organic matter in the water column. Further down the water column, a huge COS maxima (70-170 pmol/L) was observed at depths of about 550 meters. RKC suggest that this could be a result of advection along isopycnal surfaces of water that is rich in sedimentary particles from terrestrial run-off. They cite a previous work (Cutter and Radford-Knoery, 1993) which found very high COS concentrations in anoxic sediments from the Chesapeake Bay that they believe are associated with elevated levels of Al and Fe found in the same 550 meter open ocean water rich in COS.

There is a thermodynamic reason why COS levels could be extremely elevated in anoxic sediments, namely the presence of very high levels of sulfide, which is a by-

product of anaerobic bacteria. COS is known to undergo the following base-catalyzed hydrolysis reaction at the pH of seawater (8.1-8.3):

From Johnson (1985) the ΔG° of reaction 2.1 is -24.01 kcal/mol and the equilibrium constant (K) is 4×10^{17} at 25°C. Using these numbers and $[\text{HCO}_3^-]_{\text{aq}} = 2 \times 10^{-3}$ M, $[\text{COS}]_{\text{aq}} = 8 \times 10^{-12}$ M, and pH = 8.1, it can be calculated what concentration of HS^- in reaction 2.1 is required to favor production of COS. The limiting value of HS^- is found to be 2.5×10^{-3} M (Johnson, 1985), which is orders of magnitude higher than ambient sulfide concentrations in the open ocean (Radford-Knoery and Cutter, 1994). In coastal and estuarine sediments, however, concentrations of sulfides can easily reach millimolar levels (Thompson et al., 1991) thus causing some reversal of reaction 2.1 to form COS.

Other production mechanisms explaining the high concentrations of COS at 550 meters (RKC, 1994) and in sediment porewaters (RKC, 1993) have been suggested. COS may be produced directly in marine sediments, since Steudler and Peterson (1984) measured fluxes from salt marsh sediments. Another suggestion is COS formation from pyrite oxidation, which has been observed in saturated soils (Stedman et al., 1984). More research is clearly needed in this area.

2.4 Dissolved Organic Material

Dissolved organic carbon (DOC) in seawater represents one of the largest reservoirs of carbon of the earth (Mopper and Degens, 1979). The main fraction of this DOC is believed to be composed of old, biologically refractory material, including humic substances (Williams and Druffel, 1987). "Biologically refractory" refers to the condition of the DOC compounds that have already been processed by biological organisms and represent the smallest molecular units that are no longer metabolically useful. It appears that DOC in the deep ocean is very old (>6000 yrs) based on its ^{14}C content (Williams

and Druffel, 1987), which suggests that DOC turnover is quite slow. Pathways and rates responsible for this apparent slow turnover remain largely unknown, which has limited the understanding of a large part of the oceanic carbon cycle. However, several studies have recently observed a removal pathway whereby aquatic humic substances are photochemically degraded by sunlight, resulting in the formation of biologically labile and/or volatile compounds (Kieber et al., 1989; Keiber et al., 1990; Valentine and Zepp, 1993). In a particular experiment, Kieber et al. (1989) showed that the biological uptake of pyruvate ($\text{CH}_3\text{COCOO}^-$) was highly correlated to its photochemical production rate in seawater from a precursor compound that has a nominal molecular weight of 500. This indicated that photochemical degradation pathway is the rate-limiting step for the removal of a large fraction of oceanic DOC by living organisms (Mopper et al, 1991). In another study, Kieber et al. (1990) presented detailed action spectra on the formation of various carbonyl compounds from the photodegradation of DOC solutions from inland, coastal, and open ocean waters. They reported that the primary chromophores in the wavelength range 200-550 nm for natural waters are terrestrially-derived humic substances, which constitute the major fraction of naturally occurring DOM. Photoproduction of carbonyl compounds was highest in waters that had the highest concentrations of DOM (inland>coastal>open ocean). Humic substances in seawater are biological in origin, resulting from the washing of the continents by ground water and rivers draining into the ocean. The photoproduction of COS appears to fit into this category of formation of low molecular weight compounds from the photolysis of humic substances, since both photoproduction rates and dissolved COS concentrations are highest in coastal/shelf regions (Zepp and Andreae, 1990, 1994; Weiss et al., 1995a).

2.5 Penetration of Sunlight into Natural Waters

As sunlight penetrates down into fresh and marine waters, the great bulk of the radiation is absorbed by natural dissolved or particulate substances. In order to understand the formation of low molecular weight compounds such as COS, one must be able to quantitatively describe the spectral irradiance ($E(z,\lambda)$), which is a function of depth (z) and wavelength (λ). According to Baker and Smith (1982) UV light penetration in seawater can be parameterized as follows:

$$E(z, \lambda) = E(0^-, \lambda) e^{-K_T(\lambda)z} \quad (2.2)$$

where $E(0^-, \lambda)$ is the total downward solar irradiance just below the ocean surface, and K_T is the diffuse attenuation coefficient which can be written:

$$K_T(\lambda) = K_W(\lambda) + K_C(\lambda) + K_D(\lambda) \quad (2.3)$$

K_W is the clear water component, K_C is the chlorophyll component, and K_D is the dissolved organic material component. Thus, with a knowledge of chlorophyll and DOM distributions along with meteorological parameters such as total column ozone and cloud cover fraction (to determine $E(0^-, \lambda)$), a penetration profile with depth can be calculated from sunlight data at the top of the atmosphere. Other models of undersea light fields have been published by Zepp and Cline (1977), and Sikorski and Zika (1993).

2.6 Chemical Removal

COS is a molecule somewhat analogous to CO_2 , with a sulfur atom replacing one of the oxygens. Both molecules are sparingly soluble in seawater having Henry's law coefficients around 1.0 at 25°C. Both COS and CO_2 react with water to form thiocarbonates and carbonates, respectively. A main difference between COS and CO_2 is that reaction with water represents a major sink for COS because this reaction is not reversible, whereas $\text{CO}_{2(g)}$ can be released from carbonate ions by simply changing the pH.

Early research on the reaction of COS with water (hydrolysis) at neutral pHs by Thompson et al. (1935) led to the following proposed reaction:

Philip and Dautzenberg (1965) investigated hydrolysis in basic solutions and were able to detect the presence of an unstable monothiocarbonate (MTC) intermediate:

Elliot et al. (1987, 1989) made more precise measurements of rate constants for both reactions 2.4 and 2.5 between pHs 4-10 and verified the results from the earlier works. Rate constants were determined from first-order decay plots of COS concentration loss vs. time, with a least squares fit to the linearized expression:

$$\ln(C_t) = \ln(C_o) - k_{\text{hyd}}t \quad (2.7)$$

where C_t is the concentration of COS at time t , C_o is the initial concentration, and k_{hyd} is the hydrolysis rate constant, taken from the slope of the fit line. Temperature dependence of these reactions were determined using an Arrhenius Expression:

$$\ln(k_{\text{hyd}}) = \ln(A) - E_a/RT \quad (2.8)$$

where A is a constant, E_a is the activation energy, R is the ideal gas law constant, and T is temperature. E_a or A need not be known to evaluate temperature dependence, since a plot of $\ln(k_{\text{hyd}})$ vs. $1/T$ yields $-E_a/R$ as the slope and $\ln(A)$ as the intercept.

Elliot et al. (1987, 1989) found that COS hydrolysis in natural waters (ph 4-10) proceeds simultaneously along acidic (pH independent) and alkaline (pH dependent) reaction pathways, with a rate constant that is the sum of the rates along both pathways:

$$k_{\text{hyd}} = k_{\text{acidic}} + 10^{-\text{pOH}} \times k_{\text{alkaline}} \quad (2.9)$$

At the pH of seawater $k_{\text{alkaline}} > k_{\text{acidic}}$, which is analogous to CO_2 , indicating that rate control for hydrolysis of COS is via hydration by either OH^- or H_2O . However, k_{hyd} for

COS is several orders of magnitude slower than k_{hyd} for CO_2 , perhaps because HCO_3^- is much more stable than HSCO_2^- .

Elliot et al. (1989) measured and estimated lifetimes of each of the species in the COS/MTC/ SH^- system and verified that MTC was a fleeting intermediate between COS and sulfide ion. MTC has an estimated lifetime of 0.05 s (at 298°K) with respect to conversion to SH^- , and a lifetime of 10^4 s with respect to dehydration back to COS (alkaline pathway). Thus, this system can be thought of as nearly irreversible, with conversion to sulfide dominating dehydration in competition for MTC.

2.7 Air-Sea Exchange

COS can be lost from surface waters by venting of the mixed layer to the atmosphere, provided that the concentration of seawater COS is greater than the atmospheric concentration divided by H . A brief overview of the theory of air-sea exchange will be presented.

The basic equation governing air-sea exchange is:

$$F = K_w \Delta C \quad (2.10)$$

where ΔC is the concentration difference between a surface concentration in equilibrium with the atmosphere and a "bulk" seawater concentration driving the flux F , and K_w is the transfer velocity. The majority of research on air-sea exchange has focused on determining K_w for different gases and under different wind and sea-state conditions (Liss and Slater, 1974; Broecker et al., 1974; Deacon, 1977; Smethie et al., 1985; Liss and Merlivat, 1986; Wanninkhof, 1992). K_w is expressed in units of distance/time, and represents the velocity at which the gas is able to move between different media (liquid or air).

2.7.1 Models for the Exchange Coefficient

There have been three main models used to describe K_w : stagnant film, surface renewal, and boundary layer. The stagnant film model which is the simplest to visualize, assumes that the main resistance to gas transfer is molecular diffusion through a hypothetical stagnant layer of water adjacent to the interface (Bolin, 1960). It is shown pictorially in Figure 2.2. The air above the film is assumed to be well mixed, as is the water underneath the film. The speed with which a gas travels through the film is directly proportional to the molecular diffusivity (D) of the gas, which is proportional to molecular volume and temperature. The thickness of the film (z) is dependent on the degree of agitation of the sea surface by wind and wave motion. Thus, $K_w \approx D/z$. A higher wind speed will result in more surface agitation, a thinner film, and a more rapid exchange rate.

In the surface renewal model, the concept of a stagnant film is retained, but is periodically replaced by "slabs" of new fluid from the bulk below, and film replacement is the rate limiting step to gas transfer. Transfer velocities are predicted to vary with the square root of the molecular diffusivities in this model, as opposed to the film model which predicts a linear dependence of K_w on D . However, since rates of diffusion between most gases of oceanographic interest show only a range of about 1.5, the range in K_w using the two models will only be about 15%.

The main difference in the boundary layer model is that transfer velocities are proportional to the $-2/3$ power of the Schmidt number (Sc), which is defined as the ratio of the kinematic viscosity of seawater to the molecular diffusivity (ν/D) (Deacon, 1977). This model arises from theoretical and experimental information on the transfer of momentum, heat, and mass at surfaces. This relationship has been used to estimate K_w for COS from known K_w s of Rn (Andreae and Ferek, 1992).

Figure 2.2. Stagnant film gas exchange model. A thin film of stagnant water separates well mixed water from the overlying well mixed atmosphere. Gases are transferred through the stagnant layer by molecular diffusion only and the thickness of the film is given by the degree of agitation of the sea (i.e. wind speed). Gas in the water grades from its surface concentration to that which is in equilibrium with the atmospheric concentration.

Although the stagnant film model ($K_w \propto Sc^{-1}$) is the most mathematically simple and was shown to be accurate in describing the fluxes from a lake of gases with differing diffusivities (Torgerson, 1982), it is not typically used for most calculations of the exchange coefficient. Wanninkhof (1992) suggests that for a smooth liquid interface (wind speeds < 5 m/s) $K_w \propto Sc^{-2/3}$, while for an interface with waves, $K_w \propto Sc^{-1/2}$.

2.7.2 Measurements of the Exchange Coefficient

Exchange coefficients have been measured directly both in the laboratory using wind tunnels and wave tanks, and in the field, on lakes and the ocean. The earliest studies used depth profile measurements of radioactive tracers in the sea (^{222}Rn and ^{14}C) to determine the film thickness (z) and calculate K_w using the stagnant film model. The radon deficiency method was first suggested by Broecker (1965) and later tested by Broecker and Peng (1971) and Peng et al. (1974). This method allows the exchange coefficient in local areas to be measured by observing the loss of radon in the surface waters to the overlying air, which is practically devoid of Rn. ^{222}Rn is a radioactive gas with a half-life of 3.85 days and it is continually produced in seawater by its parent ^{226}Ra . A typical Rn profile is shown in Figure 2.3. Because the half-life of Rn is much shorter than the mixing time between the mixed layer and the water below it (thermocline), the decrease of Rn in the surface layer can be entirely attributed to gas evasion. The flux of Rn out the mixed layer can be written (Liss, 1982):

$$F = k_{\text{Rn}} (A_i - A_a) = \lambda \int_{-\infty}^0 (A_e - A_z) dz \quad (2.11)$$

where k_{Rn} is the required transfer velocity, A_i is the activity of ^{222}Rn (equal to the decay constant $\times$ concentration), A_a is the activity to be expected in the water that is in equilibrium with the overlying atmosphere (taken as zero since atmospheric $A_{^{222}\text{Rn}}$ is

Figure 2.3. (From Broecker and Peng (1982)) Concentration of radon gas as a function of depth at Atlantic Geosecs Station 57 (24°S 35°W). The concentration expected if no Rn were escaping is shown by the dashed line. The shaded area is the total amount of Rn lost to the atmosphere, and can give an estimate of transfer velocity. The dotted line represents the temperature profile and shows the depth extent of the mixed layer.

small and the solubility is low), A_e is the activity of ^{222}Rn expected in the water from the decay of ^{226}Ra , A_z is the measured activity of ^{222}Rn at some depth z , and λ is the decay constant of ^{222}Rn (0.18 day^{-1}). By solving this equality for each measured profile, as in Figure 2.3, values of the transfer velocity for Rn gas can be obtained. The mean k_{Rn} for all of the GEOSECS data is 11.9 cm/hr (Liss and Merlivat, 1986).

Carbon-14 in the form of $^{14}\text{CO}_2$ was first used as a tracer for gas exchange by Craig (1957). ^{14}C atoms are produced by cosmic rays from molecular nitrogen and are transferred into the ocean by gas exchange. Before nuclear testing, the influx of natural radiocarbon was balanced by its decay in the ocean, leading to a steady state concentration. With the use of the stagnant film model, an average value of z was calculated for the world's oceans of 40 microns, and $K_w\text{CO}_2 = 20 \text{ cm/hr}$. Gas exchange rates were also determined from data collected after nuclear testing increased the $^{14}\text{CO}_2$ influx rate to the oceans (Broecker and Peng, 1974).

2.7.3 Dependence of K_w on Wind Speed

Considerable research has focused on the dependence of the transfer velocity on wind speed (u). Early work by Kanwisher (1963) suggested that K_w is approximately proportional to the square of the wind velocity. Liss and Merlivat (1986) defined three wind speed regimes, which cause distinctly different sea-states, and sea-surface characteristics. The first is for $u < 3.6 \text{ m/s}$ and is characterized by a smooth surface. The second is for $3.6 < u < 13 \text{ m/s}$ and is called the rough surface regime, and the third is for $u > 13 \text{ m/s}$, named the breaking wave regime. Liss and Merlivat (1986) empirically derived 3 separate linear equations for the three wind speed regimes that represent a reasonable fit to $^{14}\text{CO}_2$ and Rn gas exchange rates determined under field and wind tunnel conditions (Figure 2.4). These equations are shown in Chapter 5 and are used to calculate an air-sea flux for COS. An expression for exchange coefficient from Wanninkhof (1992) are also

Figure 2.4. Oceanic measurements from different field experiments of the liquid phase gas transfer velocity as a function of wind speed measured at a height of 10 meters (Liss and Merlivat, 1986). The dotted line represents the transfer velocity - wind speed relationship from Wanninkhof (1992) and the solid line is the relationship from Liss and Merlivat (1986). All data have been converted to $Sc = 600$, corresponding to CO_2 at $20^\circ C$, and by assuming that $K_w \propto Sc^{-1/2}$.

used in Chapter 5 which state that K_w is proportional to u^2 , similarly to Kanwisher (1963). From Figure 2.4, it can be seen that the Liss and Merlivat (1986) expressions give K_w s that are consistently lower than the experimental data at higher wind speeds, whereas Wanninkhof (1992) perhaps overestimates K_w at low winds. Transfer velocities using the Wanninkhof (1992) relationship are always higher, by up to a factor of two, and have the advantage of a factor that is adjustable depending on whether short- or long-term wind speeds are used. Both the Liss and Merlivat (1986) and Wanninkhof (1992) relationships were used in Chapter 5, with a result presented that is an average value of the two. Presently, the uncertainty in the transfer velocity arising from the different expressions, is the major uncertainty in the calculation of the global flux of many trace gases to or from the sea.

2.8 Purpose of this Work

The main focus of this work was to understand the biogeochemistry of COS in seawater and estimate the role of the oceans in the global budget of COS. Both production and loss mechanisms of COS in seawater were investigated: photoproduction rates were determined in a variety of waters in the Pacific ocean, and diurnal concentration losses in the surface waters were compared to predicted hydrolysis lifetimes. The air-sea flux was reevaluated by measuring ΔC in a variety of ocean regions and seasons. A representative value for the open ocean was determined which is considerably lower than previous estimates, suggesting that the open ocean is insignificant in the global budget of COS. Work was carried out on two oceanographic cruises with NOAA in 1993-1994, with a prototypical instrument called the electron capture sulfur detector. The experimental aspects of this work are the focus of the next chapter.

Chapter 3

Analytical Methods

3.1 Introduction

The main goal of my analytical work has been the development of a gas chromatography (GC) system that collects continuous COS concentration data on oceanographic cruises. The instrument I have developed uses a conventional electron capture detector (ECD) in conjunction with a unique post-column reaction system to convert COS (and many other reduced sulfur species) into a fluorinated derivative (presumably SF_6), that is easily detectable with an ECD. Termed the ECD-S by Johnson and Lovelock (1988), this system takes advantage of the high selectivity of gas chromatography, and the high sensitivity and low cost of an ECD. Sulfur gas measurements have traditionally been made using a flame photometric detector (FPD) - equipped GC, but have had to rely on sample preconcentration in order to obtain the necessary sensitivity to detect COS at ambient atmospheric levels. FPD's are also subject to increased noise due to constant motion associated with a ship.

The development of the ECD-S was a result of the collaboration between Jim Johnson at NOAA/PMEL, who made extensive sulfur gas measurements using GC/FPD, and James Lovelock, the originator of the ECD. Their ultimate motivation was to be able to measure DMS quickly and precisely in and above the world's oceans in order to gain essential information on the theory that biogenic DMS is involved in a climate-controlling feedback mechanism (Charlson et al., 1987). Early work by Lovelock (Simmonds et al., 1976) showed that the ECD could be used to measure ambient levels of SF_6 (~1.5 pptv) by first passing air through a reduction catalyst to convert interfering molecular oxygen into water. Benner and Lamb (1985) later improved the design and decreased the response time making it more amenable to airborne tracer studies. The problem for Johnson and Lovelock was how to convert reduced sulfur gases like COS to

a fluoro-derivative with reasonable efficiency. Laboratory work by Johnson found that AgF_2 was an efficient fluorinating agent, in addition to it being in solid form and therefore relatively easy and safe to handle. Thus the first ECD-S was assembled in a relatively compact form, allowing for its subsequent mounting on ships and airplanes for in-situ analysis of COS, DMS, CS_2 and other sulfur gases.

3.2 Past Measurements with the ECD-S

The first laboratory-based ECD-S system gave exceptional results, measuring reduced sulfur down to the low femtomole level, 2 orders of magnitude lower than a conventional FPD (Johnson and Lovelock, 1988). Analysis times were only limited by the retention times of the latest eluting compounds, typically 10 minutes, making the system very useful for environmental analysis. Several disadvantages of the system, however, were also identified including the propensity for drifting fluorination efficiencies due to decaying fluorine concentrations in the catalyst, and the sensitivity to molecular oxygen, making it necessary to operate a switch-out valve downstream of the column. The system is also intolerant to H_2O , which deactivates the fluorinating catalyst.

The first field applications of the ECD-S were measurements of dissolved DMS in surface seawater (Johnson et al., 1987). DMS partial pressures in seawater ranged from 0.5-5 nanoatmospheres and injection of 2-5 mls of seawater-equilibrated air gave a response well above the detection limit, which was approximately 50-100 pptv. Atmospheric DMS was not measured with the ECD-S on this project because its average concentration is only 1-200 pptv in the remote marine boundary layer.

Automated sample preconcentration was later incorporated into an ECD-S system used aboard the NASA aircraft Electra during the CITE-3 intercomparison study (Johnson and Bates, 1993; Johnson et al., 1993). This allowed for an MDL of 2-5 ppt for DMS, COS, and CS_2 , making ambient air measurements of all these gases possible.

Relative to an FPD used on the same study, the ECD-S obtained the same sensitivity using a tenth of the sample size. The amount of air, however, that could be cryogenically preconcentrated and analyzed by the ECD-S was limited by the presence of water in the sample which would contaminate the fluorination catalyst, even though a water trap was located upstream of preconcentration. Presumably, ice-crystals were being swept downstream in the sample line, leading to the conclusion that removal all traces of water or oxygen from the carrier and sample streams is a crucial and challenging aspect of the ECD-S system. Nonetheless, the results of CITE-3 proved that the ECD-S could obtain the necessary sensitivity, accuracy and precision to make it comparable to, and sometimes more desirable than, other sulfur gas measurement techniques currently used (FPD, GC/MS). In particular, this system, which was optimized for DMS analysis, obtained a very tightly grouped data set of atmospheric COS in the tropics, with an estimated measurement precision of about 2%. These encouraging results were the main motivation for the subsequent analytical development that I performed. The original goal was to be able to make continuous measurement at the 1% precision level, in order to detect seasonal changes in atmospheric COS concentration. Although this goal was never realized, considerable improvements were made on the ECD-S, which make it a more reliable instrument.

3.3 Details of the Current ECD-S

Figure 3.1 is a schematic of the entire ECD-S including the sampling setup, used on both RITS cruises. Figure 3.2 shows just the chromatography and post-column reaction parts of the system. Following is a detailed description of each component of the system.

Figure 3.1
See figure caption on
next page

Figure 3.1. Continued Schematic of the ECD-S system used on oceanographic cruises for automated measurements of air and seawater COS. Following is a description of each numbered item. 1) An external air supply for the zero air generator. 2) The zero-air generator, manufactured by Aadco, or Peak Scientific. 3) Pressure Regulator, SS diaphragm, CGA 350 fitting. 4) High concentration COS standard, ~2000 psi. 5) Mass flow controller (Tylan) 0-10 mL/min. 6) Mass flow controller (Tylan) 0-5 L/min. 7) Air-Cadet (Cole-Parmer) diaphragm pump, pumping air from mast of ship. 8) Pressure gauge. 9) Back pressure regulator, used to pressurize the line to 5 psi. 10) Valco valve, hand operated, used for switching between two different dehydration loops. 11) Solenoid valve, controlled by the HP event control module, used to switch between ambient air and equilibrator samples. 12) Back pressure regulator, used to pressurize the standard stream. 13) Solenoid valve, used to switch between sample and standard runs. 14) Dewar filled with isopropyl alcohol held at ~-40°C with a Neslabs cryocool refrigerator, used to dehydrate the sample as it passes through the loop. 15) Digital flow meter used to measure flow through sample loop. Also used to measure N_2/F_2 flow through permeation cylinder when recharging. 16) Valco valve, computer controlled, used to switch out the oxygen peak. 17) Valco valve, computer controlled, used to inject the sample. 18) Silver catalyst. 19) Palladium catalyst. 20) Electron capture detector. 21) Chromatographic column. 22) Permeation source for ~200 ppm fluorine. 23) Gauge for measuring column head pressure. 24) Unused gauge. 25) Gauge for measuring hydrogen pressure upstream of the crimp. 26) Gauge for measuring the post-column back pressure. 27) Temperature controller for the silver catalyst. 28) Temperature controller for the column. 29) Temperature controller for the palladium catalyst. 30-32) Same pump-gauge-pressure regulator set-up as 7-9, used for sampling air from the equilibrator. 33) N_2 carrier gas. 34) Pressure regulator, SS diaphragm, CGA 580 fitting. 35) H_2 cylinder. 36) Pressure regulator, SS diaphragm, CGA 350 fitting. 37) 1% F_2 in N_2 cylinder. 38) Pressure regulator, (Air Products E11-T-C334A), 679M fitting. 39) HP 3393A Integrator. 40) PC computer for data transfer.

Figure 3.2. Schematic of the Chromatographic and Catalyst Systems. Following is a description of each numbered component. 1) Gauge for measuring post-column back pressure, primarily caused by the Pd catalyst. Component 26 in Figure 3.1. 2) Flow Controller, Veriflo SC440, for F_2 flow. 3) Gauge for measuring column head pressure, component 23 in Figure 3.1. 4) F_2 permeation source. N_2 flows through 30 meters of thin-walled Teflon tubing while F_2 permeates through the Teflon giving a lower concentration of F_2 in N_2 . 5) Same as (2), for make-up flow. 6) 6-port, 1/8", old-style Valco valve shown in the load position with a 5 mL sample loop. 7) Column heater block made of Aluminum and temperature controlled at 40-100° C. 8) 8-port, 1/16", old-style Valco valve shown in the inject position, used to switch-out oxygen. 9) Back pressure regulator used to match pressure shown on (1). 10) Silver catalyst in a temperature controlled block. 11) Palladium catalyst in a temperature controlled block.

3.3.1 The Electron Capture Detector

The ECD is a very commonly used detector for GC in the analysis of compounds with electro-negative atoms, especially halogens. Scientists in the 1950's and 1960's used the ECD extensively for the measurement of chlorinated pesticides and polychlorinated biphenyls in the environment, instigating a wave of concern for the deterioration of global ecosystems. Lovelock (1958) was an early developer of an ECD prototype, called the beta-ray argon detector, which measures an increase in ionization (and current) when traces of foreign gas are added to the carrier gas (argon) under conditions of constant beta-particle irradiation. This detector fell into disuse and was primarily replaced by the flame ionization detector which gave a much more linear response. However, Lovelock and Lipsky (1960) reported on a new ionization detector, the first ECD, which relied on the capture of free electrons by neutral molecules (M^0):

In the presence of an ionized gas, electronegative neutral entities (M^0) react to form negative ions with mobilities far less than that of electrons. Inside the ionization cell, a potential across two electrode is kept small enough so that only electrons are collected, while the current is monitored. Negative ions cause a decrease in the standing current because they are more likely to recombine with positive ions than they are to migrate to the positive electrode (David, 1974). This decrease in current amplified and registered as a chromatographic peak. Nickel 63 and tritium are commonly used as sources of beta particles, with nickel being more common due to its ability to withstand temperatures up to 400°C (O'Brien, 1977). Cell geometries vary, but most common is the coaxial cylindrical electrode design, where the ^{63}Ni foil forms the outer electrode (cathode) and a pulsed voltage is applied between the inner and outer electrodes to produce a current of migrating electrons. The ECD is capable of detecting 10^{-12} g of electron capturing species, and has become one the most sensitive detectors for gas chromatography.

The ECD used in this study is a VICI (ECD140BN) which has been designed such that its flow characteristics have been carefully controlled. Important considerations are that there are no trapped gas volumes to contaminate consecutively run samples, thorough mixing at the cell volume entrance, and a small overall cell volume to minimize detection time and peak broadening. The routine operating temperature of the detector was 275°C, with little observed dependence of detector performance on temperature. Argon with 5% methane was tested as a make-up gas, to maximize performance of the ECD, but no obvious benefit was observed compared to straight N₂.

At the onset of this study, a HP 5880 ECD was used, and observed to produce a comparable signal-to-noise ratio as the VICI. Advantages of the VICI include its very small physical dimensions (6.12" x 4.3" x 3.62"), and its analog output as opposed to the proprietary digital output of the HP 5880.

Start-up time for the VICI ECD appears to depend on how long it has sat with no gas flow. After periods of 3 months (the time that the equipment sat on the ship before its return to Seattle) with no flow, the ECD attained a stable baseline in less than 48 hours with just N₂ flow. When the detector was first used, it had not seen flow in more than a year, and conditioning with 5 mL/min of H₂ at 375°C for 24 hours was necessary to quiet substantial baseline noise.

3.3.2 The Silver Catalyst

The silver catalyst is shown as component 10 in Figure 3.2. A plug of silver wool (approx. 10 g) is located inside a stainless-steel 10 cm x 1/8" OD tube over which a steady stream of 200 ppm F₂ in N₂ flows (~30 ml/min). With a sample flow of about 30 ml/min, the total flow of gas over the silver wool is about 60 ml/min. It is assumed that when ample F₂ is maintained over the silver wool that AgF₂ is produced which is the actual fluorinating agent. AgF₂ has been commonly used to fluorinate hydrocarbons

industrially since the 1940's (Meshri, 1986). Producing AgF_2 in a similar fashion was first proposed by Lovelock (1973) and the fluorination in this system is based on the original concept.

Before the silver catalyst can be an effective fluorinating agent it needs to be conditioned, by passing 1% F_2 in N_2 over the silver at 200°C for several hours. Reasonably consistent fluorination efficiencies have been maintained for several month periods after conditioning, as long as the diluted (200 ppm) F_2 stream is continually swept through the tube. This requirement is evidence that AgF_2 is the fluorinating agent and that it is formed on the surfaces of the silver wool. The lifetime of the silver within the tube has not been established during the length of this study (more that two years) indicating that AgF_2 is reformed from the continual supply of F_2 , and fluorination is a catalytic process.

The conditioning of the silver with 1% F_2 in N_2 at high temperatures was used not only to start up the instrument, but periodically to improve the signal-to-noise ratio. Figure 3.3 shows the drastic effect of conditioning the Ag. In this case, the catalyst had lost all fluorination capability after the system was taken apart and put back together, and the system only showed a response to SF_6 when a mixture of SF_6 and COS was injected. After F_2 conditioning the integrator response to the two compounds was comparable. Unfortunately, however, the discovery of this conditioning process came between the two cruises and prior to this, the system would regain its sensitivity after a shut-down slowly over time, probably from the slow conversion of Ag to AgF_2 with 200 ppm F_2 in N_2 . Because of the discovery of this conditioning process, the results from the first cruise suffer from poor measurement precision, compared to the second cruise.

The operating temperature of the silver catalyst used in this work was set at approximately 10°C above the ambient lab temperature, usually 40°C . This is very different from the work of Johnson and Lovelock (1988) and Johnson and Bates (1993),

Before F₂ ConditioningAfter F₂ Conditioning

Figure 3.3. Injections of 0.25 mL of PM standard (~100 ppb SF₆ and 600 ppb COS) before and after conditioning of the silver catalyst with 1% F₂ in N₂ at 200°C for 2 hours. The peak heights of COS and SF₆ after conditioning were similar.

who found that optimal temperatures for the silver were around 250°C. In this work, cooler temperatures were used because of a significant advantage obtained in the signal to noise ratio. I found that operating the Ag at temperatures above 100°C produced considerable baseline noise, which more than offset any increase in fluorination efficiency that was thought to occur. The work of Johnson and Bates (1993) could tolerate increased baseline noise since they employed sample preconcentration to obtain the necessary sensitivity to measure COS at 500 ppt. Since this work analyzed whole air samples, ambient level peaks were lost in the noise when the Ag catalyst was run too hot. One possible reason for increased noise (and presumably, signal) when the Ag is warmer is greater fluorination of impurities in the carrier stream and hence more electron-capturable species being swept to the detector. Cooler temperatures were found to provide adequate conversion of COS to SF₆, without too much unwanted spiky noise.

A steady flow of approximately 200 ppm of F₂ in N₂ is maintained to the silver catalyst tube by a permeation cell, shown as component 4 in Figure 3.2. Described in detail in Johnson and Lovelock (1988), the cell is constructed from a nickel-coated-brass vessel fitted with a stainless-steel lid and sealed with a TFE O-ring. Approximately 30 meters of 0.066" OD 0.042" ID TFE tubing (Cole Parmer) through which N₂ flows at about 30 mL/min, are coiled inside the cell. The cell is filled to atmospheric pressure with 1% F₂ in N₂ from a high pressure cylinder (AirCo), and F₂ is able to permeate through the TFE tubing resulting in a steady source of low concentration F₂ exiting from the cell, which is directed towards the Ag catalyst. A concentration of 200 ppm was estimated by assuming that all of the initial F₂ in the vessel (30 mL STP) permeates out at a constant rate over a 5-day period (the amount of time to exhaust fluorination efficiency). For maximum stability of the instrument the F₂ cell is recharged with 1% F₂ / 99% N₂ every 2 days. A vessel containing a mixture of 75% charcoal and 25% K₂CO₃ is located at the exit of the cell to neutralize the F₂ that escapes during the recharging

process. The neutralization reactions are probably of the form (Encyclopedia of Chemical Technology, 1980):

Neutralization lasts for about one year before the odor of F_2 begins to leak out.

3.3.3 The Palladium Catalyst

Just downstream of the silver catalyst is a similar stainless-steel tube filled with Pd coated Alumina, component 11 in Figure 3.2. The primary function of this catalyst is to destroy excess F_2 leaving the silver catalyst, which would produce an unacceptably large signal in the ECD, and convert it to HF which produces only a minor baseline noise increase. The design of this catalyst comes from Lovelock's design on an SF_6 analyzer (Simmonds et al., 1976) in which Pd on asbestos fiber heated to 300°C in the presence of hydrogen was used to destroy interfering oxygen. Preparation of the Pd on Alumina, as described in Johnson and Lovelock (1988), involves dissolving 540 mg of $\text{Pd}(\text{NO}_3)_2$ hydrate (Aldrich) in 30 mL of distilled water and adding 7.0 g of GC grade 60/80 mesh alumina (Supelco). After evaporation, the $\text{Pd}(\text{NO}_3)_2$ coated alumina is packed into the steel tube dimensioned above, and heated to 350°C with 20 mL/min H_2 passed through the tube for 2 hours. This process conditions the Pd by reducing $\text{Pd}(\text{NO}_3)_2$ to Pd, NH_3 , and H_2O , and makes an effective reducing catalyst. The downstream end of the catalyst tube is fitted with a stainless steel frit to prevent any particles from being swept into the detector. Up to 20 psi of pressure drop can be created by flow restrictions from the Pd coated alumina, as indicated by a pressure gauge on the front of the main GC unit (component 26 in Figure 3.1). Over a period of about 6 months to a year, the alumina

becomes more dense and back pressure tends to rise. This presumably is caused by F_2 reacting with the alumina, forming $AlF_3(s)$, thus usually making the replacement of the Pd catalyst a semiannual event.

Hydrogen is supplied just upstream of the Pd at about 2-3 mL/min and continually reduces the Pd back to its elemental state, in addition to causing the reaction:

The low flow rate is controlled by a crimp in 1/16" stainless-steel tubing and pressure regulator located on the hydrogen cylinder. Without the flow of H_2 the signal on the detector goes down and the chromatograms become much noisier.

The temperature of the Pd catalyst was routinely set at 40°C, for maximum signal to noise ratio, a similar strategy as with the Ag catalyst. Johnson and Lovelock (1988) and Johnson and Bates (1993) both found that a hot (250°C) Pd catalyst was most effective in enhancing the reducing environment, based on the early work of Simmonds et al. (1976) and Benner and Lamb (1985). However, the goal of this work was to measure COS at 500 ppt with an SNR of at least 5, and thus the process of determining the operating temperature of the Pd was based simply on the practice of minimizing baseline noise while maximizing the COS peak. Extensive tests showed that the quantity R' , defined as:

$$R' = \frac{\text{Response [COS]}}{\text{Response [Impurities]}} \quad (3.7)$$

where *Response* is the relative response of the ECD-S to COS or other contaminant peaks, increases with temperature of the Pd catalyst, as was found by Johnson and Lovelock (1988). This means that compounds that are incompletely fluorinated are destroyed effectively in a hot Pd catalyst. However, the increase in baseline noise as the Pd temperature increases is quite detrimental in obtaining reliable chromatography. This effect is shown in Figure 3.4, where the baseline noise increases nearly 10-fold just by

Figure 3.4. Comparison of chromatograms with palladium catalyst at 40°C and 200°C. The amount of baseline noise when the catalyst is hot increased by an order of magnitude.

heating the Pd to 200°C. Thus, the conclusion was drawn that as long as other compounds did not co-elute or otherwise interfere with COS they would be ignored and the Pd was run cool to produce a relatively stable baseline. Positive results, however, were obtained with the Pd run hot (200-250°C) during work at LGGE in Grenoble, France. This points out that future studies need to be done on the Pd catalyst to determine the optimal operating conditions.

3.3.4 Chromatographic Columns

The purpose of the column is to separate two or more components in a complex mixture. Two factors characterize the usefulness of a column and its packing material for the task of separation: selectivity and efficiency. Selectivity increases as the amount of time between peaks that are registered by the detector increases. Ideally there should be no peak overlap, while minimizing the total analysis time. Efficiency is a measure of the number of separations that can be performed in a given column length. The term HETP or "height equivalent theoretical plates" is used to calculate efficiency:

$$HETP = \frac{L}{N} \quad (3.8)$$

where L is the length of the column and N is the theoretical plates, given by:

$$N = 16 \left(\frac{{}^tR_2}{W_2} \right)^2 \quad (3.9)$$

where W_2 is the peak width at the baseline for compound 2, and tR_2 is the retention time for column 2.

The specific factors affecting HETP have been characterized by the Van Deemter equation:

$$HETP = A + \frac{B}{\mu} + C\mu \quad (3.10)$$

where A, B, and C are constants, and μ is the average linear velocity of the carrier gas. The minimum in a plot of HETP vs. μ represents the maximum separation efficiency for the parameters of a particular column (i.e. carrier flow rate, particle mesh size, column length, packing material, etc.). A (for packed columns, which were used exclusively in this study) depends on the turbulence in the column, B depends on longitudinal molecular diffusion within the gas phase, and C is a result of mass transfer of the sample between the stationary phase and the carrier gas (Supina, 1974). In practice, however, minimizing HETP may not provide the optimal conditions for a particular analysis. For the analyses in this study, I chose to sacrifice some separation efficiency in order to address other chromatography concerns, which are outlined below. Optimal operating conditions were determined experimentally.

The process of selecting a column involved testing for specific criteria which would make it amenable to continuous COS analysis:

- 1) Does the column adequately separate COS from other sulfur gases that are likely to give a large response in the ECD-S, namely DMS?
- 2) Is there adequate separation between COS and O₂ in order to operate a switch-out valve with minor baseline disturbance?
- 3) Does the COS peak come out sharply and with minimal tailing?
- 4) Can the column be run isothermally?
- 5) Is there adequate separation of COS from other interfering compounds?

Often, a particular column would have a strong advantage for a particular criteria, while being unacceptable for another. Table 3.1 shows a list of all the different column packings tested ranked in order of preference.

The carrier gas used in all studies was N₂, usually ultra-high purity, although prepure grades were usually acceptable. Practically speaking, criteria 2, 3, and 5 were the primary considerations in testing these columns, since all these materials were advertised

Table 3.1. A Comparison of Various Column Packing Materials Used in this Study

Column Type	Manufacturer	Material	Advantages	Disadvantages
Carbopack 60/80 1.5% XE-60 1.0% H ₃ PO ₄	Supelco	Graphitized Carbon	<ul style="list-style-type: none"> • Sharp Peaks • Good Separation 	<ul style="list-style-type: none"> • Need > 9ft column • Sensitive to Water
Chromisil 310 60/80	Supelco	Silica Gel	<ul style="list-style-type: none"> • Sharp Peaks • Fair Separation 	<ul style="list-style-type: none"> • Max Temp. 100°C • Need > 10ft column
Porapack QS 80/100	Alltech	Porous Styrene- divinyl-benzene	<ul style="list-style-type: none"> • Strongly Retains COS • Short Column Lengths Possible 	<ul style="list-style-type: none"> • Poor Resolution Between COS and Impurities • Significant Column Bleed
HayesSep Q 80/100	Alltech	Porous Styrene- divinyl-benzene	<ul style="list-style-type: none"> • Strongly Retains COS • Short Column Lengths Possible 	<ul style="list-style-type: none"> • Poor Resolution Between COS and Impurities • Significant Column Bleed
Deactigel 60/80	Supelco	Silica Gel	<ul style="list-style-type: none"> • None 	<ul style="list-style-type: none"> • Not Usable for COS Analysis at < 1ppb Levels

as being able to separate various sulfur gases and are designed to run isothermally. Only packed columns (ID = 1/16") were tested in this study because of the constraint of needing to inject up to 5 mLs of whole air, which would not be acceptable in a megabore or capillary column, even though these types of columns are inherently more efficient.

Figure 3.5 shows a typical chromatogram obtained with the Carbopack XE-60 1/16" ID x 9' length, which is the column used on the second cruise. This chromatogram represents optimum chromatography obtained during this study. Key features of this chromatogram have been identified by numbers. Feature 1 is a small disturbance caused by injection of the contents of the sample loop onto the column. The head pressure of the column was usually about 40 psi, and the 5 mL sample loop was at 1 atmosphere, causing

SEP 24, 1993 13:38

RT	HEIGHT	TYPE	WIDTH	HEIGHT%
1.595	4121	BP	.108	.93901
2.488	7946	BV	.127	1.81057
2.648	35418	VV	.178	8.07833
2.897	94214	VP	.154	21.46755
4.242	113251	VV	.375	25.88760
5.906	9211	VV	.204	2.09881
7.920	174696	PP	.303	39.80614

Figure 3.5. A typical chromatogram obtained during laboratory analysis of a standard at 562 ppt. The numbered features are described in the text.

a brief decrease in head pressure as the sample loop pressurized. Feature 2 is the baseline disturbance caused by venting the column flow to the atmosphere and making up the flow through the catalysts and detector with a separate N₂ carrier stream. Two possible reasons for this disturbance are 1) the back pressure of the column flow through the Pd catalyst is not exactly matched to that of the make-up flow, or 2) the impurities in the column and make-up flows are different and this causes different responses in the detector. Feature 3 shows that the separation between O₂ and COS is adequate because after the valve switches back to column flow through the catalysts, there is ample time for the baseline to return to approximately its starting level. Feature 4 is the COS peak, quantified at 562 ppt with the high concentration tank standard. It is tall and sharp, with minimal tailing, and represents an SNR of 12, which is excellent. Feature 5 is the height of the noise used to calculate the SNR. Feature 6 is an unknown peak that gives a large response in the ECD-S. This peak has been named LEP for "late-eluting-peak" and its identity remains a mystery. Details of the LEP will be discussed later.

Water has a strong detrimental effect on the chemistry of the Carbopack XE-60. Since Carbopack is 1% H₃PO₄, which is quite polar, water elutes very slowly and causes periods of extended downtime after an accidental injection of a humid sample. The column always returns to normal operation, however, after heating to 100°C for several hours to drive off all water.

The Chromasil 310 column was used primarily on the first cruise, but the results were only marginally acceptable. This was primarily due to the fact that separation between COS and LEP was poorer, column bleed was higher, and COS peak heights were generally smaller than the Carbopack XE-60 results. Also, in order to attain the necessary separation, a 12' column was used which meant less flow through the column for an equivalent column head pressure as with the Carbopack. This was observed to decrease the efficiency of the system.

The other columns tested (Porapack, Hayes, and Deactigel) were not acceptable for automated use in the ECD-S. The only redeeming qualities of the Porapack and Hayes polymers is that they strongly retain COS allowing the use of a 4 ft long column, which minimizes flow resistances and analysis times. They are also rather impervious to water, which is a benefit. However, the separation between COS, LEP, and O₂ is poor, in addition to there being substantial column bleed.

3.3.5 Integration and Data Acquisition

The signal from the ECD was wired to a 3393A Hewlett-Packard Integrator-Chart Recorder, which produced peaks on thermal paper. BASIC programs can be written on this integrator which allow saving the results to floppy disk, via a 9122 HP disk drive. This could then be interfaced to a PC-type computer and the data transferred and put into spreadsheet form. Digital chromatograms were stored on floppy disks and could be reintegrated for further analysis. Controlling the VICI valves was done through a 19405A HP Sampler/Event Control Module and establishing an external event time table on the integrator.

3.3.6 Summary of Operating Parameters

Table 3.2 summarizes the operating parameters of the ECD-S system used on cruise 2, which represents the optimal state achieved in this study.

3.4 Specific Problems Associated with the ECD-S

Several problems were encountered during routine analysis of ambient levels (500 ppt) of COS: 1) a blank peak with a similar retention time as COS, 2) other later eluting peaks (LEPs) that were unidentifiable, 3) a large and interfering switch-out disturbance,

Table 3.2. Summary of Operating Parameters

PARAMETER	VALUE	PARAMETER	VALUE
Column:		Detector	
Type	Carbopack 60/80 1.5% XE-60 1.0% H ₃ PO ₄	Baseline Adjust	335
Dimensions	9 feet x 1/8" OD TFE tubing	Attenuation	2 ¹⁰
Flows:	(mL/min)	Integrator	
Out Detector	61	Attenuation	6
Make-up	26	Chart Speed	0.5
Out Column	21	Area Reject	10,000
F ₂ Source	40	Threshold	5
Over Perm Tube	200-400	Peak Width	0.2
Hydrogen	2-3	External Valve	(minutes)
Pressures:	(psi)	Switching Times	
Catalysts	11-12	Ext +1	1
Make-up	11-12	Ext -7	1
Column Head	35-40	Ext -1	1.5
N ₂ Tank Regulator	45-50	Ext -2	1.8
Permeation Block	10	Ext +2	2.8
Temperatures:	°C	Time Table	(minutes)
Column	50	Intg +8	0
Detector	290	Intg +9	0
Ag	30	Intg -9	2.6
Pd	30	Intg +9	5
Permeation Block	40	Intg -9	9
		Stop Run	10

and 4) poor catalyst performances resulting in falling or increasing standard peak heights over time.

3.4.1 The Blank

The blank was found to be caused by small amounts of COS that were associated with valve or zero-air contamination. Laboratory work after the first cruise showed that the type "P" rotor material used in my VICI sample injection valve was adding on average, 115 ppt of COS to every injection. The results during the first cruise were presumably unaffected by this contamination since it contaminated sample and standard runs equally. However, similar VICI valve with a "P" rotor was used just on the samples only as a cryo-loop switch, and this added an estimated 6% contamination to each sample, which was subtracted out, described in chapter 5. A replacement rotor (type "M") was ordered from VICI and this was found to be completely "clean" for COS. Thus a large portion of the blank was eliminated before the second cruise, which improved the overall measurement precision by nearly a factor of 2. Midway during the second cruise, however, it was discovered that the zero-air generator (Peak Scientific) was incompletely destroying COS, and adding about 18 ppt to each standard injection. This was accounted for in the final analysis.

Caution must be used when pressure regulators on carrier gas tanks are stored outside on the deck of the ship and exposed to the hot sun. Any hydrocarbon impurities often contain trace amounts of sulfur, which can permeate out of the regulator and into the gas lines, as a function of temperature. It is important to use pressure regulators with stainless-steel diaphragms, containing no rubber parts at all. Even with stainless, a hot (40-50°C) regulator can emit an unacceptable level of impurities that can load up the column and/or poison the catalyst. An obvious solution is to keep the gas cylinders cool, but if this cannot be done, then a clean-up column between the cylinder and the instrument should be used. On the two cruises, both a molesieve column (conditioned at 350°C for 1 hour) and a carrier gas purifier (Supelco, heated catalyst tube) were used, both giving good results.

3.4.2 The LEPs

The nature of the LEPs was investigated by: 1) testing the retention time of several compounds known to produce a response in the ECD-S, and 2) by testing the effect of heating the Pd catalyst on LEP response. The first test was designed to see if CFC's, which are known to give a response in the ECD-S at cool Pd temperatures (Johnson and Lovelock, 1988) were present in the sample and standard air. None of the following compounds tested, matched the retention time of the LEP (Table 3.3).

The second test was designed to understand if the LEPs were associated with COS decomposition and somehow dependent on catalyst reaction conditions. The results shown in Figure 3.6 clearly shows that COS (at ambient levels) and LEP behave like two distinct compounds. Runs were performed at different Pd temperatures, while focusing on the peak heights of COS and LEP. As the temperature of the Pd increased along with its ability to destroy any reducible species (Johnson and Lovelock, 1988) the peak height of LEP decreased, indicating that it probably is an incompletely fluorinated compound. COS, on the other hand, which is actually in the form of SF_6 , is practically unaffected by temperature. Other evidence that indicates that LEP and COS are uncoupled and distinct compounds is the often fluctuating nature of LEP, during a period of COS standard analysis, when peak heights are very consistent.

Other unknown peaks with retention times much later than the LEP in Figure 3.5 were sometimes a problem in routine analyses aboard the ship. Their retention times would often be longer than the time between runs, so that the following run would have a contaminant peak from the previous. DMS has a retention time of 21 minutes through Carboxpack at the flow rates and temperatures used and F-11 has an retention time of about 27 minutes. Both of these compounds can be at levels large enough to produce a

Table 3.3. Retention Times of Various Compounds on 12 ft Chromisil 310, 45°C isothermal, 23 mL/min N₂

Compound	Retention Time
COS	3.988
LEP	4.735
F-11	9.990
F-22	5.589
CS ₂	6.840
DMS	Does not elute

sizable response either as natural or ship-related contaminants. Operationally, having runs every 15 minutes seemed to prevent any LEP's from overlapping with COS.

3.4.3 Switch-Out Disturbance

The valve switch that is performed at about 2 minutes into every run to vent oxygen from the system before it poisons the catalysts, routinely causes a baseline disturbance. The cause of the disturbance is suspected to be unmatched pressures or flows and/or different impurity levels between the two streams. When the switch-out (SO) disturbance is minimized, the baseline is at its starting level before the COS peak starts to register. Often, however, the SO disturbance cannot be minimized and the COS elutes on a sloping baseline which contributes noise and imprecision to the analysis. Two

Figure 3.6. Effect of Pd catalyst temperature on COS and LEP peak heights.

strategies were used to minimize the SO disturbance: 1) measure the flows coming out of the column and the make-up, to make sure they are balanced. Also make sure the back pressures are the same. A rule of thumb is that if the signal goes slowly up during an SO, then more make-up flow is needed, and vice-versa. If there is a sharp spike at the beginning of the switch, then the pressures are not matched. This only applies providing that the chemistries of the two flows are the same, which is the next point. 2) Column bleed is a common reason for an large SO disturbance, since the make-up flow is just N_2 and has a different chemistry than the column flow. Heating the column to its conditioning temperature specified by the manufacturer usually remedies this problem. On cruise 2 a steadily increasing SO disturbance was a persistent problem that was only temporarily fixed by conditioning the column. The problem most likely stemmed from repeated injections of dirty or humid air that was causing the column to load up, although the exact cause was never determined.

3.4.4 Catalyst Performances

If either the Ag or Pd catalysts are not working properly, the analyses will be of very poor quality. A common problem is inconsistent fluorination efficiencies which can be partially mitigated by running standards before and after each run. The instrument response is nearly continually measured, and any real changes in ambient concentrations can be tracked with reasonable accuracy. However, the ECD-S is capable of having a consistent response when the catalysts are operating at optimal conditions. Reconditioning of each catalyst, as described in sections 3.3.2 and 3.3.3, is sometimes the only way to insure that they are working properly, although conditioning takes considerable time, and thus it should only be done as a last resort. Techniques have been developed to diagnose the condition of each catalyst, which are very useful to quickly

determine the next course of action. Injection of a standard mixture of ~100 ppb SF₆ and 600 ppb COS (called PM standard) is used to qualitatively determine the state of the Ag catalyst. At proper working conditions the COS peak should be equivalent in height to the SF₆ peak. If incomplete fluorination is occurring then only the SF₆ peak would be detected. If this is the case, the next course of action would be reconditioning the catalyst.

Assessing the state of the Pd catalyst involves tracking the reading on the back pressure gauge (component 26 on Figure 3.1). A rise in pressure can mean a degrading catalyst, although, other tubing sections in the post-column system should be checked for blockages before the Pd catalyst is replaced. A sure indicator of a degrading Pd catalyst is increase in baseline noise, and that which persists for several days. Normally, the system will rebound after an accidental injection of oxygen in several hours. If this is not the case, the Pd catalyst may need to be replaced.

3.5 Sampling

COS was sampled in four different ways on board the ship: 1) ambient atmospheric air was pumped from the mast of the ship and into the sample loop, 2) headspace air from the Weiss equilibrator was pumped into the sample loop, 3) headspace air from the Ferek equilibrator was pumped into the sample loop, and 4) COS was purged from a known volume of water and collected at liquid nitrogen temperature on an adsorbent and injected directly onto the column. Following is a description of each of these sampling setups, and an evaluation of the associated pumps, tubing and accessories.

3.5.1 Ambient Atmospheric Air

Air was sampled from the top of the mast on the flying bridge about 20 meters above the sea surface, using an Air-Cadet (Cole Parmer) pump (component 7 on Fig. 3.1) and Teflon tubing (1/4" ID), and dried using a loop held at -40°C (component 14 on Fig. 3.1). Flow through the pump was about 5 L/min and a pressure of ~ 5 psi was maintained with the back pressure regulator (component 9, Fig. 3.1). Air sampling was done only when wind directions were forward of the beam of the ship, although no appreciable contamination from stack gases was detected when the winds were considered "bad".

No contamination or losses of COS in any component of the sampling system was detected. Zero-air was pumped through 100 meters of Teflon tubing and no COS was detected, as was none detected flowing through the pump with a Fluorel-type diaphragm. The Nitrile-type diaphragm after reaching its operating temperature of about 40°C emitted traces of COS and was not used in this study. Dekoron Tubing was tested and found to contaminate with COS, but only when over 100 feet were used. Less than 100 feet, and the contamination was not detectable. Passing standards through each of these components showed that COS was not being destroyed since yields were consistently $100 \pm 5\%$. Components 11 and 13 (Fig 3.1) are solenoid valves and did not contaminate for COS, since the inner materials are all Teflon.

Proper dehydration of the sample air is very important in maintaining a consistent response of the ECD-S to COS. As was previously mentioned, water affects the column and increases column bleed and also poisons the catalyst causing increased baseline noise, and erratic fluorination efficiencies. Component 14 on Fig. 3.1 shows a schematic of a loop immersed in a dewar filled with isopropyl alcohol held at -40°C . The loop was either 1/8" or 1/4" OD stainless or Teflon-lined stainless with a periodic sample flow of about 100 mL/min. This was found to effectively dehydrate the samples by freezing out the water vapor and collecting the ice in the loop. The problem is that ice would

periodically plug the loop, often cutting off the flow of sample. To minimize down-time from this problem, two loops were used, one in the cold bath, and the other connected to a purge gas that would blow the water and ice out, keeping it dry until use. A VICI valve (component 10, Fig. 3.1) was used to manually switch between loops.

3.5.2 The Weiss Equilibrator

COS dissolved in surface water was partitioned continuously using a Weiss equilibrator (Fig 3.7). Developed by Ray Weiss (Scripps Institute of Oceanography) and described by Butler et al. (1988) this equilibrator is constructed of clear acrylic and uses a "shower head" to spray sea water through the headspace, maintaining an equilibrator atmosphere that is representative of surface water concentrations. Water from a depth of 5 meters was pumped from the bow of the ship at a rate of 15-20 LPM, minimizing water temperature perturbations. Two mercury thermometers were used to track temperatures inside the equilibrator, which showed an average warming of 0.26°C compared to surface water. An estimated headspace volume of 20 L was circulated at 4-6 LPM with a pumping system similar to that used for air sampling from the flying bridge. The lower half of the main chamber serves as an airlock, allowing sample water to move freely through the equilibrator, and trapping the headspace air within the equilibrator. Less than 1% of the headspace volume was removed for sampling, thus minimizing the amount of ambient air needed to maintain atmospheric pressure inside the equilibrator. The equilibrator and tubing were tested for inertness to COS and no appreciable losses (or increases) were observed.

3.5.2.1 Equilibrator Response Time

On several occasions during the cruises, tests were performed to measure the response of the headspace concentrations to perturbations in the equilibrator. One such

Figure 3.7. Schematic of the Weiss equilibrator.

test is shown in Figure 3.8. During periods when headspace concentrations were low (saturation ratio < 0.5) the circulation loop was broken and ambient air from the bow was allowed to flush the headspace. OCS in the headspace increased as can be seen Figure 3.8A. By fitting these points to an exponential, a time constant of 2.4 minutes is obtained, which indicates the residence time of air in the headspace. This is compared with a residence time of 3.6 minutes, obtained using the measured air circulation rate (5.5LPM) and an estimated headspace volume (20L). In all tests (N=5), headspace concentrations rose to only about 70-95% of the atmospheric concentration suggesting that some of the OCS was exchanging into the undersaturated water in the equilibrator.

When the headspace circulation line was reattached, OCS levels in the equilibrator fell approximately exponentially back to their starting levels, due to the process of equilibration of undersaturated water with the headspace (Figure 3.8B). This can also be fitted to an exponential decay and a time constant of 7.6 minutes is obtained. This represents the response time of the equilibrator to a rapid OCS concentration change in the sea water.

3.5.2.2 Equilibrator Model

A simple model was developed by Jim Johnson (NOAA/PMEL) in order to describe the parameters that control the operation of the Weiss equilibrator. Using the equations outlined below, it is also possible to predict a response time of the headspace concentration to a rapid concentration change in the incoming water, and compare that prediction to the experimental results shown in Fig. 3.8B.

In all equilibrators it is assumed that given sufficient time, the headspace air comes into equilibrium with the trace gas concentration in the water stream, C_w , which can be determined from the measured headspace concentration, C_e , using:

Figure 3.8. Equilibrator response time experiment.

$$C_w = \frac{C_e}{H} \quad (3.11)$$

where H is the Henry's law coefficient. H is a function of temperature and salinity, so these quantities must be known along with C_e in order to calculate C_w . To introduce time-dependent terms into equation 3.11, the flux of gas between the headspace and water stream must be parameterized:

$$V_e \frac{dC_e}{dt} = Q_w (C_w - C_{w0}) \quad (3.12)$$

where V_e is the volume of the headspace, C_e is the concentration of the trace gas in the headspace, Q_w is the volumetric flow rate of the sample water stream through the equilibrator, C_w is the concentration of trace gas in the water stream as it enters the equilibrator, and C_{w0} is the concentration of the trace in the water stream as it exits the equilibrator. This equation is a statement of the conservation of mass within the equilibrator, such that all of the trace gas can be accounted for in both the headspace and the water, with losses or gains in concentration of each reservoir being exactly matched by gains or losses in the other reservoir. For equation 3.12 to be valid, however, it must be assumed that the equilibrator is a closed system with no leaks or vents of outside air, and that there are no losses or gains in trace gas concentration within the equilibrator, either through biological or chemical mechanisms. For COS, I have found that the Weiss equilibrator is quite inert and does not contaminate, so I am reasonably sure that the second criteria is met. The first criteria requires a larger leap of faith, but one which has a lot of validity. Although there is a vent line attached to the equilibrator to insure atmospheric pressure in the headspace, the vent flow is very small (< 15 mL/min) and given a headspace volume of 20L, it would take the vent flow alone over 22 hours to flush the headspace, which is much less than a 1% error. Jim Johnson's work (Johnson et al., 1995) with a more sophisticated model including terms parameterizing the vent flow,

suggests that the vent flow is insignificant for COS, since the predicted difference in model results between using and ignoring vent flow terms is about 1%. Thus, for the purposes of this study, I will use the simple "level one" model, which ignores a vent flow.

If the sample water comes into full equilibration with the headspace as it showers through it then C_{w0} will be a function of C_e as in eqn. 3.11, so that eqn. 3.12 can be expressed as:

$$V_e \frac{dC_e}{dt} = Q_w \left(C_w - \frac{C_e}{H} \right) \quad (3.13)$$

The right hand side of (3.13) represents the maximum amount of COS that can be exchanged during the residence time of the water in the equilibrator. However, this quantity is controlled by thermodynamics and says nothing of the kinetics of gas exchange, which often prevents full equilibration. Thus, a term called the equilibrator coefficient, E , is introduced which is a scaling factor that indicates the fraction of full equilibration that occurs during the amount of time that the sample water is in contact with the headspace. Equation 3.13 then becomes:

$$V_e \frac{dC_e}{dt} = E \times Q_w \left(C_w - \frac{C_e}{H} \right) \quad (3.14)$$

with E having a value between 0 and 1. A time dependent solution of 3.14 for C_e , assuming an initial C_e of C_{ei} that is not in equilibrium with C_w is:

$$C_{e(t)} = (C_{ei} - HC_w) e^{-\left(\frac{t}{\tau}\right)} + HC_w \quad (3.15)$$

where t is the equilibration time constant and is equal to:

$$\tau = \frac{V_e H}{Q_w E} \quad (3.16)$$

The solution (3.15) shows that C_e relaxes to a steady-state concentration HC_w with a time constant τ .

Using equation 3.16 and the value for τ obtained from the exponential fit to the data in Fig. 3.7, an estimate of E can be obtained. Allowing $V_e = 20$ L, $Q_w = 16$ L/min, $\tau = 7.6$ minutes, and $H = 2.1$, gives $E = 0.35$, which says that on average, each droplet of water is about 35% equilibrated with the headspace before it exits the equilibrator. The question to be asked then, is how long would it take the headspace to come to equilibrium with a sharp change (i.e. step-function) in sea water concentration? Three e-folding times are necessary to obtain 95% equilibration, which would be $(7.6 \times 3) = 23$ minutes, during which time the ship would travel about 4.6 nautical miles at normal speeds. From this I can assume that it is unlikely that significant disequilibrium is adversely affecting the measurements of COS saturation ratio. A concentration "hot spot" in the ocean would have to be larger than 4.6 nautical miles across, before the measured saturation ratio would approach the actual concentration in the water. This kind of resolution for COS measurement is entirely acceptable for the purposes of calculating regional or global fluxes.

3.5.3 The Ferek Equilibrator

This equilibrator was used during three experiments on the second cruise for the purposes of comparing the results with the Weiss equilibrator. Since many of the measurements from this work show saturation ratios (SRs) < 1 , it was necessary to show that the Weiss equilibrator was not producing artificially low values. Early seawater COS measurements were made using the Ferek equilibrator by Ferek and Andreae (1983), and they reported very high concentrations (saturation ratios > 5) in coastal waters off Peru.

The design of the Ferek equilibrator is simpler than the Weiss equilibrator, and is patterned after the apparatus used by Conrad et al. (1982) for CO measurements in seawater. Shown schematically in Figure 3.9 the Ferek equilibrator is constructed of glass with Teflon fittings attached to 1/4" sidearms. Teflon tubing and a Metal Bellows

Figure 3.9. Schematic of the Ferek equilibrator.

pump (MB-11) were used to circulate the headspace. Seawater was delivered from the ship's bow at an average rate of 0.73 L/min, and the headspace was pumped at approximately 1.3 L/min. The dimensions of the equilibrator are 5 cm diameter by 70 cm in height, giving an average headspace volume of 700 mL when the water level is maintained at 35 cm. Approximately 100 mLs of headspace air were withdrawn periodically for analysis by filling the sample the sample loop and injecting. Because there is no vent line, this withdrawal of air caused a rather large perturbation in the headspace by lowering the pressure and causing the water level to slowly rise. The water level would return to normal after several minutes, presumably due to leaks in the plumbing, or dissolved air in the seawater. It was assumed, however, that by analyzing the headspace infrequently (> 30 minutes between samples) the initial conditions would represent equilibrated seawater, with little contamination from ambient air.

3.5.4 The Purge and Trap System

A purge and trap system was employed on the second cruise as a further check of the accuracy of the Weiss equilibrator. Purge and trap was also used for COS analysis in irradiated seawater samples, as described in Chapter 4. The apparatus used was modified from an apparatus constructed by Jim Johnson and Tim Bates (NOAA/PMEL) for analysis of CH₄, CO, and DMS. Modifications included replacing the VICI valve rotors with type "M" material and installing all stainless steel or Teflon tubing. The only exception is a short (< 10 cm) piece of PEEK tubing (Alltech) used to fill the stripping vessel.

Sometimes called a cryogenic collection system (Johnson, 1985), the purge and trap is shown schematically in Figures 3.10 and 3.11. Fig. 3.10 shows the apparatus in the stripping and cryo-collection mode. In this mode, about 10 mLs of seawater are purged with a flow of about 100 mL/min of helium, which bubbles through a glass frit.

Figure 3.10. Schematic of the purge and trap system shown in sample collection mode.

Figure 3.11. Purge and Trap system shown in sample injection mode.

The stripper vessel is a modified graduated cylinder, with 1/4" glass arms for connecting Swagelock fittings. The purge flow is directed through valve 2 (in the strip position) and then through a loop held at -40°C in 2-propanol to dehydrate the sample stream. Condensable gases are then collected at liquid nitrogen temperature on a column containing Porapak Q (80/100) (Alltech) after passing through valve 3 (in the load position). After about a 10 minute purge valve 3 is switched to the inject mode simultaneous with the loop being transferred from the dewar of LN_2 to the container of room temperature water. This configuration is shown in Figure 3.11. The contents of the cryo-loop are then swept into the GC and the ECD-S, with valve 2 switched to the bypass position and the stripper vented to the atmosphere using a 4-way ball valve (Whitney). Standards were introduced through valve 1, swept through the cryocool loop and collected in similar fashion as the samples.

Various methods of dehydration were used including MgClO_4 , silica gel, and Drierite, all contained in a glass tube with stainless steel fittings. Of the three, Drierite gave the best results, because it did not contaminate for COS, nor did it destroy it, and it is relatively easy to handle. MgClO_4 also gave a clean background, but its oxidizing nature made it undesirable. Silica gel was not acceptable because of its large background of contaminants. All these methods were not as convenient as passing the purge gas through the cryo-cooled 2-propanol bath, which could handle much more water before it would become plugged.

Throughout the use of the purge and trap system, a non-zero background persisted in the helium stream at about a level of 1 picomolar in a 12 mL water sample. The blank through the stripper was higher than the blank through just the cryocool. It is unknown the exact source of this blank, but permeation through Teflon tubing, and production from a dirty stripper and/or tubing are possibilities. Stripping times were held consistently at 10 minutes to attempt to minimize imprecision if the source of the blank was associated

with the stripper. Blank values were not subtracted from sample concentrations, assuming that equal blanks in both sample and standards would cancel out.

3.5.5 Sample Loops

A loop made of Teflon with an ID of 1/16" and an internal volume of 4.53 mL was used as the sample loop. The volume of this loop was chosen as being a trade-off of obtaining maximum signal with a large sample size without overloading the column. The response of the ECD-S appeared to be linear to loop size up through a 5 mL loop. Before the source of the blank was determined to be from the Valco valve rotor material, permeation through the Teflon loop was a suspected source. However, stainless steel and Teflon-lined stainless loops were used and both gave the same results, concluding that permeation is negligible through this amount of Teflon.

3.6 Standards

This section will focus on the methods used to generate an ambient level standard (~500 pptv). Three different methods were used: dynamic dilution of a 1000x ambient high pressure cylinder, dynamic dilution of a COS permeation device, and analysis of a high pressure cylinder containing approximately ambient levels of COS.

3.6.1 High Concentration Tank Standard

All reported measurements have been quantified using a 2000 psi cylinder of COS at 495 ppb purchased from Scott Specialty Gases, November, 1992 (component 4 in Fig. 3.1). A thousand-fold dynamic dilution was accomplished by mixing a small flow (about 4 mL/min) from the COS tank with a large flow (4 L/min) of COS-free air, generated by two different commercial devices (Aadco or Peak Scientific). Mass flow controllers (Tylan FC-260) were used to produce consistent flows to better than 1%, as determined with an electronic bubble flow meter (Gilibrator).

The stability of the Scott standard over a two year period has been monitored and appears to have remained quite stable. Figure 3.12 is a plot of the calibration history of the Scott standard. Three different permeation tubes and quantification by the manufacturer show agreement to within 8%, with a mean and standard deviation of 504 ± 40 ppbv. The two triangles in Figure 3.12 are calibrations from the first cruise, and the large cluster of points around 1994 are from the second cruise. Many more calibrations were performed on the second cruise because it was suspected that the tank standard was increasing in concentration and making ambient atmospheric levels too low. Post-cruise recertification by Scott and further permeation tube analysis showed this not to be the case, and thus the quantification problem was blamed on dirty zero-air from the Peak Scientific device. However, a best estimate of contamination levels still makes ambient atmospheric data from cruise 2 lower than cruise 1, which is not an expected natural phenomena.

3.6.2 Permeation Tubes

"Perm" tubes containing various sulfur compounds have been used and maintained by the Tim Bates / Jim Johnson group (NOAA/PMEL) since the early 1980's. The first tube used (Perm 1) was filled in 1991 (Metronics Inc.) and tubes 2 and 3 were filled in the lab using COS in a lecture bottle (minimum purity 96%, Hydrocarbon Technologies) in 1992. Permeation tubes are small (5 cm) stainless steel cylinders that contain liquid COS under several atmospheres of pressure. A permeable wafer of Teflon forms part of the cap and allows COS to permeate at a fixed rate based on temperature. The partial pressure of COS outside the perm tube is assumed to be much less than that inside the tube, and is not important in controlling the flux across the membrane. The tubes are held at a constant temperature of 40°C, either in an oven block or in a tube immersed in a water bath, with a flow of N₂ or air over them. These particular

Figure 3.12. Calibration history of Scott standard purchased 11/92.

permeation tubes are designed to be "low loss", since it is possible using a two-step dilution, to generate an ambient level standard. Standards are generated by the setup shown in Figure 3.13. The high concentration COS stream is diluted with zero-air using the same mass flow controllers as were used for the tank standard. Typical flows through the perm tube block were 200-400 mL/min.

These perm tubes are weighed approximately every two months in order to determine the amount of COS that has been lost over a known amount of time. From these data, an average weight-loss rate in ng COS / min is assigned to the tube and used to calculate the concentration of COS in the diluted flow. Table 3.4 shows the average weight losses and uncertainties of each permeation tube. Perm 3 has a much lower loss rate because of a stainless steel disk with a very small (1/64") hole in the middle that is part of the cap, sitting on the inside of the Teflon wafer, as opposed to just Teflon in the other tubes. This tube was constructed with the hope that COS emission would be significantly less and make possible a one-step dilution for the generation of an ambient level standard. Although the loss rate of perm is less, two stages of dilution are still required. All air-flow measurements are corrected to STP so that the conversion factor 22.4 nL / nmole can be used.

Unfortunately, the lifetime of these perm tubes appears to be about 2 years, although perm 3 has a lifetime longer than 2 years presumably because its loss rate is much lower. It is important to fill new ones before the primary tube dies in order to have several weighings and a loss rate that is reasonably accurate. Perm 1 was the primary tube on cruise 1, but then lost its emission shortly after returning. Perm 2 died shortly after cruise 2. From Figure 3.12 it can be seen that the results from each tube agree only to within 5% of each other so that switching tubes in the middle of field measurements can introduce unwanted systematic error. Ideally, several tubes should be tested simultaneously and their results averaged. The use of perm tubes is still seen as essential

Figure 3.13. Schematic of the permeation tube system.

Table 3.4: Loss Rates of Permeation Tubes used for COS Quantification

Device	Loss Rate (ng COS / minute)
Perm 1	529.76 $\pm$ 21.81
Perm 2	527.12 $\pm$ 56.40
Perm 3	339.25 $\pm$ 29.60

because the stability of COS in a cylinder, even at 0.5 ppm, is not well known or trusted. Perm tubes provide an absolute concentration based on gravimetry. Further work should be done to determine perm tube loss rates with better precision and accuracy.

3.6.3 Ambient Level Tank Standard

The most convenient way to generate a standard of COS would be to fill a cylinder to ~2000 psi with ambient atmospheric air and inject it directly in the GC with no dilution. Unfortunately, this is not feasible since COS has a limited stability in a cylinder at these concentrations. On the second cruise a Spectra Seal aluminum cylinder was filled to 2000 psi with ambient air and dried using an acrylic tube filled with indicating silica gel. Analyses of this cylinder showed that the concentration was stable for about 2 weeks, and then fell off quite rapidly to below detection limit (Figure 3.14). A possible reason for the instability could be incomplete dehydration of the sample, which may accelerate base-catalyzed hydrolysis of COS on the walls of the inside of the cylinder. Better drying agents may provide a solution, as could water trapping with

Figure 3.14: COS concentration trend in an ambient level tank standard filled on the second cruise.

cryogenics, although the amount of water needed to be trapped in a 30 L cylinder at 2000 psi would cause a lot of ice build-up.

COS appears to be stable in smaller canisters for periods longer than 2 weeks. Several small "eggs" (2 L canisters) and a larger (10 L) canister were analyzed about 1 month after filling by Paul Quay (University of Washington) at Cheeka Peak, Washington. Concentrations ranged from 398 ppt to 877 ppt. These samples were not dried before being filled and were thus passed through a cryocool alcohol bath before injection. Also, a large 30 L Spectra Seal tank was analyzed a month after filling at Cheeka Peak, dried using MgClO_4 and it showed a concentration of 448 ppt. It is not clear why COS was stable in these tanks and not the one filled on the second cruise. These results seem to indicate, however, that ambient level COS can be stable for periods long enough to make tank filling a viable way to generate a standard. By using an ambient level standard with no dilution, it may be possible to improve the precision of the measurements by decreasing the scatter of the permeation tube data shown in Figure 3.12. Clearly, more work needs to be done in determining the proper container, desiccant, pump, and flow parameters.

3.7 Quantification and Instrument Performance

This section discussed the methods used to quantify unknown concentrations in field samples and performance of the instrument as measured by accuracy, precision, and linearity of response.

3.7.1 Quantification

On both cruises, the normal cycle of analyses were: standard, ambient air, equilibrator head space, standard, etc. Concentration of COS in the standard was determined by knowing the concentration in the cylinder (or loss rate of the permeation

tube), and be measuring the flows. Standard concentrations were typically 400-600 ppt. Sample concentration was determined by the following equation:

$$\frac{(\text{IntegratorResponse})_{\text{sample}}}{(\text{IntegratorResponse})_{\text{standard}}} \times [\text{COS}]_{\text{standard}} \quad (3.17)$$

The integrator response of the sample is simply the average of the responses of the standard runs before and after the sample. Quantification in this way can be called a 2-point calibration curve, where it is assumed that the instrument response is zero when COS is at 0 ppt. In other words, by running just one standard, a standard curve (line) is then drawn through the sample point and the (0,0) point. The integrator response of the sample in equation 3.17, is actually divided by the slope ($\Delta y/\Delta x$) of the standard response curve. This method of quantification would make some analysts uneasy, but for the purposes of shipboard measurements, it works quite well. The biggest advantage to running just one standard concentration instead of a multipoint standard curve is the savings in time, so that more analyses of samples may be performed. Also, in order to have automated runs of standards of different concentrations, it is necessary to automatically change the mass flow controller settings, which we were not able to do

The ECD-S allows accurate measurements using a 2-point calibration because of its high degree of linearity. Figure 3.15 shows typical calibration curves from different times and locations. In every case, except 3.15C, the r^2 is at least 0.990, indicating a high degree of linearity in the concentration region of 0-2000 ppt, which covers at least 95% of the measurements in air or water on both cruises. A systematic error resulting from non-linearity is estimated to be only 1% (Johnson and Bates, 1993). Two of the standard curves (A and C) show a non-zero blank, which was the result of contaminations described earlier. These blanks were assumed to be influencing both the sample and standard injections so that the 2-point calibration technique just described is still valid as long as the responses of the standard and the sample were identical, which was the case

Figure 3.15: Calibration curves indicating instrument response as a function of COS concentration. A) Standard curve from purge and trap system, cruise 2. B) Standard curve from second cruise. C) Standard curve from first cruise. D) Standard curve from laboratory between first and second cruises.

for ambient atmospheric air measurements. When the response of the unknown is significantly different from the standard, as was often the case with the equilibrator measurements, then a small error arises from not subtracting the blank from both standard and sample before taking their ratio. This error is estimated to be at most 5% for only the very highest or lowest samples, and probably averages about 1%.

3.7.2 Accuracy and Precision

The original goal of this project was to make long term atmospheric concentration measurements at the 1% precision level. Precision, or the degree of tightness of the data around a central value, is important when trying to detect small trends, like seasonal variations of atmospheric COS. Unfortunately, this was not possible with the current analytical system due to a number of factors that pushed the instrument precision to between 5-20%. However, this degree of precision was sufficient to detect variations in seawater COS, which often undergoes large diurnal variations of an order of magnitude or more. Thus the trends in the atmospheric data in chapter 5, such as information on seasonal and hemispheric differences are greatly clouded by the imprecision of the measurements, whereas the seawater data is quite useful.

Accuracy is a measure of how close the data are to the true value. It is diminished by all the factors that contribute to imprecision in the data, in addition to the factors that affect how well the standards are known. In this project the uncertainty in reliably generating a known standard with which to calibrate unknown samples was a major contributor to inaccuracy.

To quantify the total uncertainty, the contribution of each factor in the measurement process to the total error must be known or estimated. Table 3.5 is a list of every factor and an estimate of each uncertainty expressed as a percentage of the mean

value. Total uncertainty can then be expressed as $\pm(AC+B)$, after Johnson and Bates (1993).

Table 3.5: Factors Contributing to Measurement Uncertainty

Measurement Component	Percent Uncertainty	Comments
Flow Controllers	1%	For each controller
Tank Standard	8%	From perm tube calibrations
Detector Non-linearity	1%	From Johnson and Bates (1993)
Not Subtracting the Blank	1%	Occurs when the standard response is very different from the unknown response
Permeation Standard	5%	% agreement between tubes, from Fig. 3.11
Peak Height, Sample	4%	From replicate standard analyses
Peak Height, Standard	4%	From replicate standard analyses
Instrument Drift Between Calibrations	5%	
Unknown Errors	5%	
Total Error	13%	Summed in quadrature

Chapter 4

Photoproduction of Carbonyl Sulfide in South Pacific Ocean Waters as a Function of Irradiation Wavelength

Published in *Geophysical Research Letters*, 22, 215-218, 1995

Peter S. Weiss,^{1,2} Steven S. Andrews,³ James E. Johnson,^{2,4} and

Oliver C. Zafiriou³

4.1 Abstract

Carbonyl sulfide (OCS) photoproduction rates were measured at selected wavelengths of ultraviolet light between 297 and 405 nm in sea water samples from the Southern Pacific Ocean. Near-surface and column production rate spectra for natural sunlit waters were calculated using sea-surface sunlight data measured near the austral summer solstice. These plots show that photoproduction rates are at a maximum at 313 nm in tropical waters and at 336 nm in Antarctic waters. Tropical surface and column rates were found to be 68 pM/day and 360 nmol/m²/day, respectively, and Antarctic surface and column rates were found to be 101 pM/day and 620 nmol/m²/day, respectively. A high degree of variability was observed between photoproduction rates from different ocean regions, with coastal rates being the highest, suggesting that natural environmental variability is an important factor. Photoproduction rates at 297 nm were found to be constant at individual locations with increasing irradiation time. Relative photoproduction rates from this work are compared to previously measured rates from coastal sea water.

¹University of Washington, Department of Chemistry, Seattle, Washington.

²NOAA Pacific Marine Environmental Laboratory, Seattle, Washington.

³Woods Hole Oceanographic Institution, Woods Hole, Massachusetts.

⁴Joint Institute for the Study of Atmosphere and Ocean, University of Washington, Seattle, Washington.

4.2 Introduction

Carbonyl sulfide (OCS) is naturally present in the earth's atmosphere at an average concentration of 500 pptv and a residence time of greater than 1 year (Khalil and Rasmussen, 1984). This long lifetime allows it to enter the stratosphere and act as the major non-volcanic source of stratospheric sulfate aerosols (Crutzen, 1976). Considerable research has focused on the role of these stratospheric aerosols in enhancing ozone destruction through heterogeneous chemistry with chlorine and nitrogen species (Rodriguez et al., 1991; Hofmann and Oltmans, 1992; Solomon et al., 1993). Presently, the proposed atmospheric budget for OCS is quite unbalanced, with the total sources exceeding the total sinks by a factor of near 2 (Chin and Davis, 1993). The oceans are believed to be an important source of atmospheric OCS (Andreae and Ferek, 1992), but the magnitude is still uncertain (0.16 - 0.64 Tg OCS/yr, or 20-40% of total flux) (Chin and Davis, 1993).

OCS is produced in marine surface waters from photolysis of dissolved organic material (DOM) (Ferek and Andreae, 1984). Zepp and Andreae (1990) have postulated that OCS formation results from DOM chromophores acting as photosensitizing agents in the oxidation of dissolved organic sulfur (DOS) compounds. Since photosensitized reactions are generally more rapid in coastal waters than in the open ocean, their results may explain why dissolved OCS concentrations are usually highest in coastal, sunlit waters. However, photoproduction rates of OCS from open ocean waters have not previously been reported.

We present here the first OCS action spectra measurements for surface waters of the open ocean. These data provide a basis for estimating total photochemical production rates under natural sunlight conditions. With the observed losses of stratospheric ozone, especially over the Antarctic region, a knowledge of the action spectra of OCS is

essential for determining the enhancement of OCS production from increased UV-B flux to the surface ocean.

4.3 Experimental

Photoproduction rates were measured on a cruise aboard the NOAA Ship Surveyor during the '93 - '94 austral summer (Figure 4.1). Surface water was sampled from the ship's "clean" seawater pumping system with an intake about 5 meters below the surface. Samples were taken only while underway to reduce contamination by the ship. Irradiations were performed with a Spectral Energy 1-kW Monochromatic Illumination System with a mercury-xenon lamp and a monochromator with a 10.0 nm bandwidth. Samples were held in a gas-tight, cylindrical quartz cell with a 31 cm pathlength and a 2.2 cm inside diameter. Relative light intensity was measured with an International Light model IL1700 radiometer and corrected to absolute light doses by ferrioxalate actinometry (Hatchard and Parker, 1956). Sea water absorption, referenced to Milli-Q water (Millipore Corp), was measured on 0.2 mm filtered water with a Hewlett-Packard model 8452A diode array spectrophotometer, using a 10 cm pathlength quartz cell. Spectra were corrected for refractive index effects by subtracting the average apparent absorption from 700 to 800 nm from each spectrum (Blough et al., 1993; Green, 1992). All samples were found to be optically thin with $A_{350\text{nm}} < 0.05 \text{ cm}^{-1}$ (Valentine and Zepp, 1993). Sea surface light intensity was measured with a LI-1800UW spectroradiometer (LI-COR, inc.) at 2 nm intervals between 300 nm and 850 nm, with an 8 nm bandwidth, and also with an Epply radiometer.

Duplicate samples were analyzed without UV-irradiation to determine initial OCS concentrations; some irradiations were performed on sea water that was degassed with OCS-free air in a 1-liter sparging vessel. Degassed samples showed no significant difference in photoproduction versus unmodified sea water. Sample temperatures were

Fig. 4.1. Cruise track of the NOAA Ship Surveyor from Seattle, Washington USA to Punta Arenas, Chile (November 20, 1993 to January 7, 1994). Sampling locations are denoted by numbers and N refers to the number of samples taken at each location.

initially between -1 and 28°C, and warmed during irradiations to near room temperature based on Kieber et al. (1990). Typical irradiation times were 30 min at 297 nm, 306 nm, and 313 nm, 60 min at 336 nm and 365 nm, and 12 hours at 405 nm. These wavelengths were selected for high energy output from the lamp.

Hydrolysis of dissolved OCS (Elliot et al., 1987) did not significantly affect photoproduction rate measurements between 297 and 365 nm since irradiation times were one hour or less and OCS concentrations in dark control samples decreased by less than 10% (<1 pM) during this time. For the measurements at 405 nm (using degassed water only), it was necessary to subtract a significant concentration increase (~50% of OCS concentration after irradiation) which occurred in the dark control samples after ~12 hour incubations. The reason for this increase is unclear since there was no measurable room light below 415 nm. OCS production by a mechanism other than UV photolysis cannot be ruled out, however, on the basis of this study.

Water samples were transferred by ground-glass syringe to a purge-and-trap system, described in detail by Johnson and Harrison (1986). Differences in the present system include using about 12 mls of sample water, a stainless steel cold finger held at -40°C to dehydrate the sample, and a cryotrap loop filled with Porapak Q (80/100, Alltech). Condensed gases were then injected onto a gas chromatograph with an electron capture detector (VICI, 140BN), referred to as the electron capture sulfur detector (ECD-S). The instrument is described in detail in Johnson and Lovelock (1988) and Johnson and Bates (1993); the operating temperature of the catalysts was lowered from 150°C to 40°C to improve the signal-to-noise ratio without loss of selectivity.

OCS levels ranged from 2 to 200 pM in irradiated samples where the ECD-S showed a linear response to standards of better than 96%. Standards were made by diluting a 512 ± 38 ppbv tank standard (Scott Specialty Gases) with OCS-free air, to make a secondary standard of about 1 ppbv OCS in dry air. The tank standard was

calibrated using two permeation devices whose weight loss histories are known from bi-monthly weighings. The instrument blank was about 4% of the standard peak, or about 1 pM in a 12-ml water sample. Measurement accuracy was about 15% based on the permeation tube weight-loss data and the precision was about 15% based on the reproducibility of standard peak heights over a 1-day period.

4.4 Results and Discussion

Table 4.1 shows the mean of all measurements of photoproduction rates of OCS as a function of wavelength. Figure 4.2A is a plot of the average action spectra from tropical and Antarctic regions (on Fig. 4.1, locations 1-2 and 3-10, respectively). These rates fall off approximately exponentially with increasing wavelength, as noted previously for OCS (Zepp and Andreae, 1990), CO (Valentine and Zepp, 1993) and formaldehyde (Kieber et al., 1990). Additionally, photoproduction rates from Antarctic waters are consistently higher than those from tropical waters. By normalizing these action spectra with available UV sunlight measured at local noon at the sea-surface (Fig. 4.2B), the result is the near-surface production rate spectra shown in Figure 4.2C. Note that in the tropics, production rates are at a maximum around 313 nm, whereas in Antarctic waters the maximum is closer to 340 nm. Figure 4.2D shows column production rate spectra that were obtained using quantum yields and assuming that all incident light is absorbed in the water column. Figure 4.2D represents an upper limit for production rates since in "blue waters", a significant fraction of the total absorption of light includes sea water absorption and backscattering of light out of the ocean. However, these curves do show that column integrated production rates are enhanced at longer wavelengths compared to surface rates.

To estimate daily near-surface and column photoproduction rates, it was assumed that 6.5 and 8 hours of noon sunlight at the tropical and Antarctic locations, respectively,

Table 4.1. Photoproduction of OCS in sea water (mean $\pm 1\sigma$)

<u>Wavelength</u> (nm)	<u>N</u> ¹	<u>Production Rate</u> (pM OCS / J/cm ²)	<u>Relative Production Rate</u> ²	<u>Absorption Coefficient</u> ³ (a _l) (meter ⁻¹)	<u>Quantum Yield</u> ⁴
297	26	4.96 $\pm$ 1.93	1.00	0.36 $\pm$ 0.02	5.80e-7 $\pm$ 2.26e-7
306	2	2.63 $\pm$ 0.51	0.53	0.30 $\pm$ 0.02	3.71e-7 $\pm$ 0.72e-7
313	8	1.59 $\pm$ 0.73	0.32	0.25 $\pm$ 0.01	2.46e-7 $\pm$ 1.13e-7
336	7	0.78 $\pm$ 0.79	0.16	0.17 $\pm$ 0.01	1.64e-7 $\pm$ 1.66e-7
365	8	0.34 $\pm$ 0.29	0.069	0.12 $\pm$ 0.01	9.33e-8 $\pm$ 8.02e-8
405	2	0.058 $\pm$ 0.008	0.012	0.09 $\pm$ 0.02	1.94e-8 $\pm$ 0.26e-8

¹ N is the number of distinct samples irradiated at each wavelength. ² Relative production rate = prod. rate / prod. rate at 297 nm in pM/J/cm². ³ a_l = 2.303 A_l / r, where A_l is absorbance and r is the pathlength in meters. a_l was measured (mean $\pm 1\sigma$, N = 6 for each λ) in the same water types but not the exact locations as samples taken for irradiations. ⁴ quantum yield = μ mole OCS produced / μ einstein absorbed.

were equivalent to an entire day's radiation. These times result from dividing the measured total insolation at each location by the maximum insolation intensity, occurring around local noon, depending on cloud cover. No corrections were made for high albedo at the sea-surface at large zenith angles, and the fact that a higher fraction of UV light is diffuse than that of the rest of the spectrum. However, to a first approximation, these effects will cancel, giving an estimate of tropical surface and column rates of 68 pM/day

Fig. 4.2. (A) Average action spectra of OCS in sea water from tropical (10° - 22° S) and Antarctic (58° - 70° S) regions, not including coastal data. Lines are exponential fits to the data (*tropical*: $y = 2.87e^{-(0.049(x-300))}$; *Antarctic*: $y = 4.08e^{-(0.055(x-300))}$). (B) Measured downward solar irradiance at the sea surface (*tropical*: local noon, 4° S, 19° zenith angle; *Antarctic*: local noon, 61° S, 38° zenith angle). (C) Surface production rate spectra with estimated areas under the curves. (D) Column production rate spectra with estimated areas under the curves. The points at 405 nm for the tropical curves in C and D are from the exponential fit data in (A).

and 360 nmol/m²/day, respectively, and Antarctic surface and column rates of 101 pM/day and 620 nmol/m²/day, respectively.

Photoproduction was measured on samples from different locations as a function of 297 nm irradiation time, up to 75 minutes (Figure 4.3). Irradiation intensity remained constant during these studies. No significant departure from linearity was observed, indicating that only a small fraction of the DOS pool was being photolyzed and significant photobleaching was not occurring. The distinctly different slopes of the lines demonstrate the natural variability of OCS photoproduction rates. Note that the highest production occurred in the coastal sample, consistent with previous speculation (Zepp and Andreae, 1990). Figure 4.4A shows action spectra from different locations plotted on a log scale to facilitate slope comparisons. Although the lines are offset from each other, the slopes are relatively constant, suggesting that photochemical mechanisms are similar between locations, and other factors such as OCS precursor concentrations are influencing production rates. Weak correlations between photoproduction rates and dissolved dimethyl sulfide and chlorophyll-a concentrations ($R^2 = 0.41$ and 0.46 , respectively), indicate that these species are not directly involved in OCS formation.

The average action spectrum from this work (data from Table 4.1) is compared to that for OCS from a coastal North Sea sample (Zepp and Andreae, 1990), in Figure 4.4B. An exponential fit to each data set gives log slopes of -0.017 and -0.048 nm^{-1} for this work and Zepp and Andreae (1990), respectively. Differences in DOM origins between the two works may explain this pronounced discrepancy. Zepp and Andreae (1990) collected samples in an area influenced by riverine inputs, rich in terrestrial DOM, whereas this work was dominated by measurements in open waters presumably containing mostly marine DOM. Because the two types of DOM are suspected to have very different photoresponses (Mopper et al., 1991), this difference is not surprising. Further studies should focus on the dependence of action spectra on sampling site with

Fig. 4.3. Photoproduction of OCS with 297 nm radiation in samples from five locations (see Fig. 4.1). Linear fits to each sample set, with an origin point added, are also shown.

Fig. 4.4. (A) Action spectra from four locations, denoted in Fig. 4.1. (B) Action spectra expressed as relative production rates from this work compared to Zepp and Andreae (1990), with exponential fits. Absolute production rates were not reported in Zepp and Andreae (1990).

the intention of understanding the number and origins of OCS-forming DOM pool(s) and their relationship(s) to the DOM pools involved in other photophysical (absorption, fluorescence) and photochemical processes.

Acknowledgments. We appreciate the support of the officers and crew of the NOAA Ship Surveyor. PSW is supported by the U.S. DOE Graduate Fellowship for Global Change administered by ORISE. We thank Drs. Timothy Bates and Richard Gammon for helpful discussions, and the Radiatively Important Trace Species (RITS) and Marine Sulfur and Climate Components of the NOAA Climate and Global Change Program for general support. The WHOI work was supported by NSF grant OCE-915608, ONR grant N00014-91-5-1258, and NASA grant NAGW-2431. This is contribution number 1524 for NOAA/PMEL, 267 for JISAO, and 8699 for WHOI.

Chapter 5

A Reevaluation of the Open Ocean Source of Carbonyl Sulfide to the Atmosphere

Accepted by *Journal of Geophysical Research*, June 16, 1995

Peter S. Weiss^{1,2}, James E. Johnson^{2,3}, Richard H. Gammon^{1,4}, and Timothy S. Bates^{2,3}

5.1 Abstract

Carbonyl sulfide (COS) concentrations were measured in surface seawater samples and the overlying marine boundary layer of the Pacific Ocean using gas chromatography (GC) and electron capture sulfur detection (ECD-S). A wide latitudinal range was covered (55°N-70°S) on two cruises nine months apart. COS saturation ratios (SR's) in seawater were found to be less than 1 (undersaturated) across wide regions of the open ocean, especially in the subtropical gyres and wintertime subpolar waters. SR's were highest in coastal/shelf regions and in spring/summertime temperate waters. Extensive undersaturation is attributed to a low COS photoproduction potential of the water, limited sunlight, and/or a rapid hydrolysis rate constant. Decreasing COS concentrations during diurnal cycles in tropical waters were fit to first-order exponentials, with resulting decay times agreeing with calculated hydrolysis lifetimes to within 15%. Air-sea fluxes of COS from the open ocean were calculated using two different expressions for the transfer velocity and averaged into 6 latitude bands and three seasons. Based on these data, we report a global open ocean sea-air flux of -0.032 (-0.010 to -0.054) Tg COS / yr, which is much lower and of different sign than the current global estimate (0.14-0.58 Tg COS / yr). Atmospheric COS mixing ratios averaged 470 pptv on

¹University of Washington, Department of Chemistry, Seattle, Washington.

²NOAA Pacific Marine Environmental Laboratory, Seattle, Washington.

³Joint Institute for the Study of Atmosphere and Ocean, University of Washington, Seattle Washington.

⁴University of Washington, School of Oceanography, Seattle, Washington.

the first cruise and 442 pptv on the second cruise, with much of the difference possibly a result of a seasonal decrease in the northern hemisphere COS mixing ratio of up to 10%.

5.2 Introduction

Carbonyl sulfide (COS) is unique among naturally occurring sulfur gases in the atmosphere because of its relatively slow reaction with the OH radical (Wahner and Ravishankara, 1987), giving it a tropospheric lifetime of one year or more, and an average mixing ratio of 500 pptv $\pm$ 10% (Khalil and Rasmussen, 1984). The long lifetime allows substantial transport of COS to the stratosphere where it is believed to sustain the Junge layer with sulfate aerosol particles during volcanically quiescent periods (Engel and Schmidt, 1994; Crutzen, 1976). These high-altitude aerosols influence the Earth's radiation budget by interacting with incoming solar radiation (Turco et al., 1982), and could partially offset the warming effect of increased greenhouse gases through higher stratospheric optical depths (Turco et al., 1980). Stratospheric aerosols are also believed to enhance ozone depletion, with the most recent evidence coming from record stratospheric ozone losses over Antarctica following the injection of large amounts of SO₂ from the eruption of Mount Pinatubo (Solomon et al., 1993). Ozone depletion appears to be a result of heterogeneous reactions of N₂O₅ on sulfuric acid aerosol surfaces, which effectively sequesters active nitrogen and leads to increased levels of ClO, which reacts to destroy ozone (Fahey et al., 1993; Rodriguez et al., 1991). These reactions have the potential to influence stratospheric ozone levels on a global scale, since the very low temperatures found only in polar stratospheric clouds are not necessary for removal of N₂O₅. A small secular increase in background stratospheric aerosol mass in the northern mid-latitudes, raises the possibility that ozone depletion could be accelerated above populated areas of the northern hemisphere (Hofmann, 1990). The cause of the

aerosol increase remains uncertain largely a result of inadequate information on COS sources and sinks.

There has been no detectable change in the average atmospheric concentration of COS since 1977 (Rinsland et al., 1992; Bandy et al., 1992), which implies that sources of COS have been approximately balanced by the sinks. However, most COS budget estimates have sources exceeding sinks by a factor of 2 or more (Khalil and Rasmussen, 1984; Goldan et al., 1988; Chin and Davis, 1993). Table 5.1 shows a recent budget estimate (Chin and Davis, 1993), along with our proposed revised budget. The "missing sink", which is often used to bring the budget into balance, is speculated to be COS deposition to land plants. Laboratory studies have shown the uptake resistances for COS and CO₂ to be similar (Goldan et al., 1988). Limited field measurements, however, have not supported such a large plant sink (Mihalopolous et al., 1989; Berresheim and Vulcan, 1993; Fried et al., 1993; deMello and Hines, 1994), raising the possibility that some COS source terms have been overestimated. Major sources are believed to be emission by soils, the oceans, biomass burning, and tropospheric oxidation of CS₂ (Chin and Davis, 1993). Additionally, recent laboratory work by Barnes et al. (1994) suggests that gas-phase OH initiated oxidation of dimethyl sulfide (DMS) forms appreciable quantities of COS and may represent a significant global source, leading to an even larger imbalance in the global budget.

The most extensively studied source has been the ocean. COS production is believed to result from photo-sensitized oxidation of sulfur-containing dissolved organic matter (DOM) in surface seawater (Ferek and Andreae, 1984; Andreae and Ferek, 1992; Zepp and Andreae, 1994). Coastal and shelf regions, being richer in photo-sensitizing agents than the open ocean, are thought to make up about 60% of the total ocean flux (Andreae and Ferek, 1992), even though by area, the coastal ocean accounts for only about 13% of the world's ocean (Andreae, 1986). Weiss et al. (1995) have reported that COS

Table 5.1. Global sources and sinks of COS¹: Previous and revised estimates

	Previous Estimate	Revised Estimate
Sources	Tg COS per year	Tg COS per year
ocean		
coastal	0.32 (0.17-0.47)	0.32
open	0.29 (0.14-0.58)	—
CS ₂ oxidation	0.34 (0.17-0.61)	0.34
soil and marsh	0.27 (0.14-0.52)	0.27
DMS oxidation	0.17 (0.10-0.28)	0.17
biomass burning	0.14 (0.04-0.26)	0.14
anthropogenic	0.05 (0.03-0.07)	0.05
volcano	0.02 (0.006-0.09)	0.02
total sources	1.6 (0.81-3.0)	1.3 (0.67-2.5)
Sinks	Previous	Revised
vegetation uptake	0.43 (0.16-0.91)	0.43
reaction with OH	0.13 (0.02-0.80)	0.13
open ocean	---	0.032 (0.010-0.054)
photolysis	0.029 (0.020-0.040)	0.029
reaction with O	0.015 (0.009-0.026)	0.015
total sinks	0.60 (0.19-1.8)	0.63 (0.22-1.9)

¹Data from Chin and Davis (1993), except for ocean source, which is an average from Andreae and Ferek (1992) and Mihalopolous et al. (1992), and DMS source is from Barnes et al. (1994).

photoproduction rates are up to an order of magnitude larger in coastal water compared with the open ocean. COS removal from the water column is believed to occur both by sea-air exchange and by reaction with hydroxide ion in the water (Elliot et al., 1989; Radford-Knoery and Cutter, 1994), with a rate that depends on temperature and pH. Before measurements of dissolved COS were made, Johnson (1981) proposed that the oceans could be a major sink for atmospheric COS based on hydrolysis rate constants determined for fresh water. However, subsequent measurements in selected regions showed that COS was supersaturated with respect to atmospheric equilibrium, leading to the conclusion that the oceans were a major source of COS to the atmosphere (Rasmussen et al., 1982; Ferek and Andreae, 1983; Turner and Liss, 1985; Johnson and Harrison, 1986; Mihalopolous et al., 1992). On the other hand, data have been sparse from ocean regions that are expected to have the lowest concentrations of dissolved COS (i.e. high latitude, wintertime, or waters with low COS precursor concentrations). In this paper we report the discovery of extensive regions of undersaturation in surface seawaters of the Pacific Ocean. This phenomenon has not been previously reported perhaps because the majority of dissolved COS measurements in the past have been carried out either in coastal regions where production rates are very high, or during spring and summer months in the midlatitude open ocean where sunlight is abundant and biological activity is high. Previous global ocean fluxes may be overestimated because they do not adequately address the seasonal and spatial variability in seawater COS concentrations, which have been observed to vary by at least two orders of magnitude. In particular, coastal and open ocean regions have very different dissolved COS concentrations, yet only two studies (Mihalopolous et al., 1992; Andreae and Ferek, 1992) report separate fluxes for these regions. We have collected an extensive open ocean data set of COS concentrations in surface waters and from the overlying marine boundary layer, and the global open ocean flux we present here indicates that the open ocean acts as a weak sink

to atmospheric COS. This revision slightly improves the unbalanced budget of global sources and sinks.

5.3 Experimental

Air and Water Sampling

Air was sampled from the top of the mast on the flying bridge about 20 meters above the sea surface, using an Air-Cadet (Cole Parmer) pump and Teflon tubing (1/4" ID), and dried using a stainless-steel loop held at -40°C. COS dissolved in surface water was partitioned continuously using a Ray Weiss-type (Scripps Oceanographic Institute) equilibrator. Described by Butler et al. (1988), the Weiss equilibrator is constructed of clear acrylic and uses a "shower head" to spray sea water through the headspace, maintaining an equilibrator atmosphere that is representative of surface water concentrations. Water from a depth of 5 meters was pumped from a forward intake of the ship at a rate of 15-20 LPM. Based on results for CO (Bates et al., 1995), another photochemically produced dissolved gas, it was assumed that there was no consistent COS concentration gradient between the surface and the sampling depth of 5 meters. The temperature in the equilibrator was continuously monitored by a calibrated thermistor connected to an automated data system, which showed that the water had warmed an average of 0.26°C compared to surface water at the intake. A correction for this warming in the solubility coefficient (H) was made. An estimated gas headspace volume of 20 L was circulated at 4-6 LPM with a pumping system similar to that used for air sampling from the flying bridge. Less than 1% of the headspace volume was removed for each sampling, thus minimizing the amount of ambient air needed to maintain atmospheric pressure inside the equilibrator. The equilibrator and tubing were tested for inertness to COS and no appreciable losses (or increases) were observed.

Analysis

COS was analyzed using the electron capture sulfur detector for gas chromatography (ECD-S) described in detail in Johnson and Lovelock (1988) and Johnson and Bates (1993). Modifications of the instrument are described in Weiss et al. (1995). The ECD-S has sensitivity down to the femtomole level without sample preconcentration, making it possible to inject 5 mls of sample air directly to the GC. COS levels ranged from 0.2 to 4.5 ppb in equilibrated seawater samples where the ECD-S showed a linear response to standards of better than 96%. Standards were made by diluting a 1000-times ambient level (~ 500 ppbv) high pressure gas cylinder standard (Scott Specialty Gases) with COS-free air, to make a continuously-flowing secondary standard in the 0.5 ppbv range. The primary tank standard was calibrated from analyses by the manufacturer (Scott), and by using permeation tubes whose weight loss histories were known from bi-monthly weighings. The average of all permeation tube calibrations was 504 ± 40 ppbv, which compared well to the Scott calibration of 495 ± 25 ppbv. Over the two year period there was no detectable ($>1\sigma$) systematic trend in concentration loss or gain of the high pressure cylinder. A value of 504 ppb was used for the tank standard calibration for both cruises.

The lower limit of detection, defined as the mixing ratio of COS where signal/noise = 2 was 115 ppt during cruise 1 and 23 ppt during cruise 2. The primary reasons for improvement during cruise 2 were optimization of the fluorination catalyst through occasional conditioning with 1% F_2 in N_2 at $250^\circ C$ for 1 hour, and a reduction of the blank. The majority of the blank during cruise 1 was caused by contamination from the sample injection valve, affecting all injections similarly and canceling out most of the systematic error. About 28 ppt, however, was systematically added to each ambient- and equilibrated-air injection from a valve used to switch between sample dehydration loops, and this amount was subtracted from each of these analyses. During cruise 2 the valve

rotors were replaced with a non-contaminating material and the blank was reduced to about 23 ppt. This residual contamination was a result of incomplete cleanup of ambient air through the zero-air generator (Peak Scientific), making an addition of 23 ppt to each ambient air analysis necessary. The reproducibility of the blanks in both cruises was observed to be about 7%.

The overall accuracy of the measurements, estimated by calculating the root mean square of the standard deviations of the standard calibration and the blank determinations, was 11%. The precision of the measurements was 6-10% based on the reproducibility of the standard over a 6-hour period.

5.4 Results and Discussion

Sea Water Measurements

Measurements of COS in air and sea water were made along two meridional sections (55°N - 70°S) (Fig. 5.1) aboard the NOAA Ship Surveyor from March 20, 1993 to May 7, 1993 (cruise 1) and November 20, 1993 to January 7, 1994 (cruise 2).

COS sea water saturation ratios (Fig. 5.2) were calculated from the surface seawater COS partial pressure, P_s , and the atmospheric partial pressure, P_a , and are defined as:

$$SR = \frac{P_s}{P_a} \quad (5.1)$$

where,

$$P_s = (P - P_{we}) X_e \frac{H_s}{H_e} \quad (5.2)$$

and,

$$P_a = (P - P_{wa}) X_a \quad (5.3)$$

Figure 5.1. Cruise tracks of the NOAA Ship Surveyor during the March 20 - May 7, 1993 and November 20, 1993 - January 7, 1994 RITS (radiatively important trace species) cruises. Cruise 1 (RITS93) began in Punta Arenas, Chile, and cruise 2 (RITS94) began in Seattle, Washington.

Figure 5.2. Latitudinal dependence of COS saturation ratios in seawater from both cruises. Horizontal dashed lines indicate a saturation ratio of 1, or seawater in equilibrium with atmospheric COS.

P is the atmospheric pressure at the time of the measurement, P_{wa} is the saturation vapor pressure of seawater at the sea-surface temperature and salinity, P_{we} is the saturation vapor pressure of seawater in the equilibrator (calculated from the equilibrator temperature and assuming 100% relative humidity) (Weiss and Price, 1980), X_a is the measured mixing ratio of COS in dry air, X_e is the measured mixing ratio of COS in the equilibrator headspace air after removal of water vapor, H_s is the Henry's Law solubility constant for COS in seawater at the sea surface temperature, and H_e is the Henry's Law solubility constant for COS at the equilibrator temperature.

The SRs along the cruise track ranged from about 0.2 to 4.5 and were highly variable, especially between low latitude oligotrophic waters and summertime temperate and polar waters (Fig. 5.2). Such variability reflects changing source and sink strengths in the water column. As suggested by Andreae and Ferek (1992), COS concentrations in seawater are controlled by photochemical production which depends on both light intensity and COS precursor concentration, and a removal term which is first order (hydrolysis) with respect to COS concentration. The ocean regions with the highest concentrations of dissolved COS (high latitude, summertime) had abundant sunlight and low water temperatures (slow hydrolysis rates). Although there are no direct measurements, it is likely that COS precursor concentrations were elevated, given the higher photoproduction rates found by Weiss et al. (1995) in these regions compared to the rest of the open ocean, and the large amounts of biomass in the water reflected by chlorophyll-a measurements. Low latitude oligotrophic waters had the lowest COS concentrations presumably resulting from relatively warm water temperatures (rapid hydrolysis) and low photoproduction rates (Weiss et al., 1995), in spite of ample solar radiation in these regions.

The importance of season on seawater COS concentration can also be seen in Figure 5.2. In the temperate and sub-polar latitudes (35° - 65°) there is roughly a factor of

2 increase in the average SR between cruise 2 (boreal winter) and cruise 1 (boreal spring), and similarly between austral autumn and summer. The magnitude of this seasonal variation is also consistent with the findings of Mihalopolous et al. (1992). Factors such as changes in available sunlight and precursor concentrations in the surface waters are probable causes of such variability.

Diurnal Cycles

In addition to the seasonal and regional variations in COS SRs, the SRs also exhibit a strong diurnal variation. Data from three consecutive days in the subtropical gyre region (13° - 29°) of the northern hemisphere are shown in Figure 5.3. Note that the maximum concentrations each day barely reach saturation, indicating that this region of the ocean was a net sink for atmospheric COS. Also, the 2-4 hour time lag between the maximum light intensity and maximum COS concentrations is consistent with the observations of Andreae and Ferek (1992). Turnover times of COS in surface waters were calculated by fitting the post-sunset concentration decreases to first order exponential functions, and are listed in Table 5.2. These turnover times show a good agreement to the hydrolysis lifetimes predicted from rate constants from Radford-Knoery and Cutter (1994) indicating that hydrolysis is the dominant removal pathway for seawater COS as was speculated by Andreae and Ferek (1992). Predicted lifetimes from Elliot et al. (1989) are consistently shorter than our observed turnover times perhaps indicating that dark production of COS is a significant source in seawater. The rate constants from Elliot et al. (1989) were determined in artificial solutions that likely had no dark production, whereas Radford-Knoery and Cutter (1994) used ambient seawater. Dark production, which has been observed previously by Ulshofer et al. (1995) and Weiss et al. (1995), would increase the observed turnover time of COS relative to the hydrolysis lifetime. Our results suggest that dark production increases the COS lifetime

Figure 5.3. Three consecutive diurnal cycles of dissolved COS concentrations (as saturation ratios) from each cruise 1 (13°-29°N). First-order exponentials have been fit to the concentration losses each afternoon. Sunlight intensity is also plotted and has a maxima at local noon each day.

Table 5.2. Comparison of Measured Decay Times of COS Concentration in Seawater with Hydrolysis Lifetimes¹

Curve # in Figure 5.3	Date (Cruise 1, 1993)	Temperature of Equilibrator	τ Hydrolysis (hours) Radford-Knoery and Cutter (1994)	τ Hydrolysis (hours) Elliot et al. (1989)	τ Fit ² (hours)
1	April 27	23.2	10	8	11 $\pm$ 3
2	April 28	21.7	12	10	12 $\pm$ 2
3	April 29	18.4	17	13	20 $\pm$ 4

¹ Hydrolysis lifetimes at specified temperature, and a 3-day averaged pH of 8.17, measured at the same locations during cruise 2 (Nov. 30-Dec 2).

² Exponential fits to curves in Figure 5.3, with the error of the fit.

at the surface by at least 15% under the wind and temperature conditions that prevailed during this study. This is a lower limit since COS concentrations decrease with depth in the top 100-200 meters (Radford-Knoery and Cutter, 1994) and vertical mixing, which would show a decrease in the observed lifetime at the 5 meter depth, was not considered here.

A kinetic model for COS diurnal cycles ($SR > 1$) in surface waters can be parameterized:

$$\frac{d[\text{COS}]}{dt} = k_1 E(t) [\text{DOS}] + P_{\text{dark}} - k_2 [\text{COS}(t)] - L_{\text{mix}} - L_{\text{vent}} \quad (5.4)$$

where k_1 is the photoproduction rate, $E(t)$ is proportional to sunlight intensity, $[\text{DOS}]$ is a measure of the COS precursor concentration, P_{dark} is the dark production rate, k_2 is the

hydrolysis rate constant, L_{mix} is the loss due to mixing and L_{vent} is the loss due to gas exchange.

Comparison of the Weiss Equilibrator with Other Sampling Techniques

As a check of the efficiency of the Weiss equilibrator, we compared its performance with two other techniques, a bubbling equilibrator and a conventional purge and trap system. The bubbling equilibrator was constructed of glass and is the same dimensions and design as that used by Ferek and Andreae (1983). This type of equilibrator was originally developed by Conrad et al. (1982) for dissolved CO in seawater, and relies on air bubbled through continuously flowing seawater to obtain equilibrium in the headspace. The headspace is circulated continuously, in similar fashion as the Weiss equilibrator. Having no materials other than glass and Teflon, which are inert to COS, the bubbling equilibrator provided a good check to see if wall losses were occurring in the Weiss equilibrator (made of acrylic).

Purge and trap analysis has been the most common technique for sampling dissolved COS, and the apparatus used here is described in Weiss et al. (1995). Table 5.3 presents the results of the intercomparisons. The uncertainty values represent 1σ of the mean for the number of measurements (N). Comparisons were made in a variety of water types with different ambient levels of dissolved COS, usually at night to minimize diurnal variability. The measurements with the Weiss equilibrator fall within the uncertainty ranges of the other techniques, indicating that there are no systematic differences between the three techniques. The advantage in using the Weiss equilibrator over the other methods is that an automated system is much easier to setup and maintain. The bubbling equilibrator is sensitive to losses of headspace gas through bubbles escaping into the seawater drain, which causes the water level to slowly rise. For the purge and trap

Table 5.3. Comparison of Weiss Equilibrator with Bubbling Equilibrator and Purge and Trap

Weiss Equilibrator			Bubbling Equilibrator	
Location	N	Headspace Concentration (ppt)	N	Headspace Concentration (ppt)
55°N, 140°W	7	580 ± 54	5	631 ± 61
20°N, 140°W	10	276 ± 53	12	297 ± 59
44°S, 144°W	15	826 ± 85	14	823 ± 82

Weiss Equilibrator			Purge and Trap	
Location	N	Seawater Concentration (pmole / L)	N	Seawater Concentration (pmole / L)
7°S, 140°W	15	5.8 ± 1.0	23	5.3 ± 1.2
21°S, 149°W	3	4.6 ± 1.0	5	3.5 ± 1.7
64°S, 134°W	50	31.7 ± 6.7	11	29.7 ± 7.3

system, manual injections make this technique very labor intensive and the hardest to automate.

Saturation Ratio Comparisons with other Studies

Where open ocean measurements from this work overlap with previous studies in region and season, the agreement is usually within measurement uncertainties. For example, our average springtime SR from the temperate North Pacific (cruise 1) is 1.2, compared to Andreae and Ferek (1992), who report an SR of 1.9 from the North Atlantic and Rasmussen et al. (1982) who report an SR of 1.4 from the North Pacific. Staubes and Georgii (1993) report SR's of 3-6 in the South Atlantic (50°-70°S) during the austral summer solstice, compared to our SR's of 1-4 from cruise 2. The only previously reported wintertime open ocean data come from the Sargasso Sea during November (Andreae and Ferek, 1992). They report an average SR of 1.5, which is 2-3 times larger than our findings in the Pacific, but may reflect the higher productivity of the Sargasso Sea in winter compared to the subtropical Pacific. Coastal ocean SR's from this work (from off Washington/Oregon coast, and the eastern side of Tierra del Fuego) average 2.6 which is on the low end of the range from other studies from temperate coastal regions (SR = 2-20) (Mihalopolous et al., 1992). Such a discrepancy could originate from the type of coastal areas studied, since COS concentrations in bays and inlets, rich in terrigenous runoff, are likely to be higher than off of rocky coastlines where most of our coastal measurements were taken. Consequently, we have chosen to separate our data into open ocean and coastal/shelf (<400m depth) categories and calculate an open ocean flux of COS to compare with previous studies.

Air-Sea Flux Calculations

The oceanic flux of COS can be estimated using the model of Liss and Slater (1974):

$$F = K_w \left(C_w - \frac{C_a}{H_d} \right) \quad (5.5)$$

where C_w and C_a are the COS concentrations in seawater and air, respectively, K_w is the sea-air transfer velocity, and H_d is the dimensionless Henry's Law solubility constant from Johnson and Harrison (1986). Expression 5.5 can be also written:

$$F = K_w \left(\frac{P_a}{H_p} \right) (SR - 1) \quad (5.6)$$

where P_a is the atmospheric partial pressure of COS and H_p is the Henry's Law solubility constant in units of liter-atm-mole⁻¹ ($H_p = H_d RT$). K_w is a function of wind speed and the Schmidt number which is the ratio of sea water viscosity to COS molecular diffusivity, both being functions of temperature.

Two methods for calculating the transfer velocity were used in the subsequent data analyses. The first is based on the equations developed by Liss and Merlivat (1986) which are linear fits of wind speed to transfer velocities determined by tracer experiments under three different wind speed regimes (Mihalopolous et al, 1992):

$$K = 0.17 (A(\theta))^{-2/3} u \quad (\text{for } u < 3.6 \text{ m s}^{-1}) \quad (5.7)$$

$$K = 0.17 (A(\theta))^{-2/3} u + 2.68 (A(\theta))^{-1/2} (u - 3.6) \quad (\text{for } 3.6 < u < 13 \text{ m s}^{-1}) \quad (5.8)$$

$$K = 0.17 (A(\theta))^{-2/3} u + 2.68 (A(\theta))^{-1/2} (u - 3.6) + 3.05 (A(\theta))^{-1/2} (u - 13) \quad (\text{for } u > 13 \text{ m s}^{-1}) \quad (5.9)$$

where K is the transfer velocity in cm/hr, u is wind speed in m/s, $A(\theta)$ is the ratio $Sc(\theta)/Sc(20)$, where $Sc(\theta)$ is the Schmidt number of COS and $Sc(20)$ is the Schmidt number of CO₂ in seawater at 20°C, equal to 595 (Mihalopolous et al, 1992).

The second method for calculating the transfer velocity comes from Wanninkhof (1992) and is a quadratic fit of climatological wind speeds to transfer velocities determined from ¹⁴C disequilibria in the ocean:

$$K = 0.39 u^2 (A(\theta))^{-1/2} \quad (5.10)$$

where K , u , and $A(\theta)$ are defined above except that $Sc(20) = 660$ (Wanninkhof, 1992). The factor 0.39 is used for climatological winds, as opposed to 0.31 which is appropriate for instantaneous (ship's) winds. Since there is no current consensus over which

relationship (Wanninkhof vs. Liss and Merlivat) provides the most accurate values for transfer velocity, we use the two relationships to bound the range of potential values.

Another source of uncertainty in transfer velocity calculations is in choosing values for wind speed. Two wind fields were compared in this study, winds measured aboard the ship at a height of 18 meters above sea-level, and 40-year climatological winds obtained from COADS (Comprehensive Ocean-Atmosphere Data Set), which are monthly averages on a latitude-longitude grid of $2^\circ \times 2^\circ$. Ship winds gave larger transfer velocities using the Liss and Merlivat relationship by nearly a factor of two because of high wind speeds associated with particular storm events and the non-linearity of the transfer velocity expressions. Transfer velocities calculated using the ship-board winds provide the best estimate of the instantaneous flux, although these calculations are not necessarily representative of the zonal average flux. Additionally, we have observed no significant anti-correlation between ship's wind speed and our measured seawater COS concentrations, indicating that COS concentrations in the mixed layer are not very sensitive to rapid changes in wind speed. This is not surprising, since the venting of COS to the atmosphere is a minor loss term in the cycling of dissolved COS in the mixed layer. Thus, for the purposes of estimating a regional and seasonal flux we have chosen to use the COADS winds. It should be noted that there is no standard observational height for COADS winds. However, by assuming a height of 10 meters, we estimate (using a drag coefficient of 1.5×10^{-3} (Liss and Merlivat, 1986)) an added uncertainty to the transfer coefficients of only 2%.

Using equation 5.6 a local flux was calculated at each SR measurement location. Local fluxes were then averaged into 6 latitude bands for the open ocean and three seasons: summer, winter, and equinox. Separating the data into 3 seasons was based on the fact that the first cruise was entirely during the spring/fall seasons and the second cruise was entirely during the winter/summer seasons, for northern and southern

hemispheres, respectively. These seasons were defined so that their midpoints coincide with the equinox (for fall/spring) or the solstice (for winter/summer), corresponding to the midpoint in the solar cycle for a particular season. Since COS production is a strong function of available sunlight, this redefinition of seasons seems justified. A summary of the flux calculations based on seasons and regions is given in Table 5.4. Note that the regionally averaged values for K , P_a , H , and SR were not used for the regionally averaged flux calculation, but instead the local values for these parameters were used to obtain a local flux which was then averaged into regions. Thus, a regionally averaged SR of 1.0 does not necessarily give a regionally averaged flux of 0. The total open ocean flux of COS to the atmosphere is -0.022 Tg/yr, using monthly averaged winds from COADS and transfer velocity relationships from Liss and Merlivat (1986). If the Wanninkhof (1992) transfer velocity relationship is used, the result is a flux of -0.041 Tg COS/yr. Thus, we have chosen to report our open ocean flux as -0.032 Tg/yr, which is the average of the two extremes. Figure 5.4 shows a comparison of the regionally and seasonally averaged fluxes calculated using the two different expressions for transfer velocity. Wanninkhof (1992) fluxes are consistently larger in each season, in both the positive and negative direction. It is also interesting to note that no amount of uncertainty in K can change the fact that the wintertime open ocean is a sink for atmospheric COS. Including the uncertainties in the SR s, P_a , K , and H , into the flux by calculating the root mean square of the percent errors in each parameter gives a range of fluxes from -0.010 to -0.054 Tg COS/yr.

With regard to the atmospheric budget of COS, designating the open ocean as a sink rather than a source, makes the sum of the sources only ~50% larger than the sum of the sinks (Table 5.1). However, even if this revised budget were accurate, atmospheric COS would still be increasing by about 11%/yr, given a global atmospheric burden of 4.6 Tg. This is directly contradictory to the findings of Rinsland et al. (1992) and Bandy et

Table 5.4. Calculation of seasonal, regional, and global COS sea-air flux using climatological winds, transfer velocities (K) from Liss and Merlivat (1986), and H from Johnson and Harrison, (1986).

Region	Latitude	†Area m ²	Schmidt Number	Wind Speed (meter/sec)	K (meter/day)	P _a (natm)	H	SR	Flux (Gg COS/yr)*
Equinox									
polar	65-80°	9.50E+12	2,665	7.2	1.3	0.445	1.0	1.0	-0.3
subpolar	50-65°	9.50E+12	1,862	8.5	2.1	0.451	1.3	1.2	0.9
temperate	35-50°	2.40E+13	1,360	8.0	2.2	0.466	1.6	1.2	2.4
subtropical	20-35°	3.35E+13	825	6.8	2.1	0.472	2.3	0.6	-5.4
tropical	5-20°	3.85E+13	610	6.7	2.3	0.481	3.0	1.0	-0.4
equatorial	0-5°	4.60E+13	569	5.3	1.4	0.430	3.1	0.9	-0.5
total									-3.4
Summer									
polar	65-80°	9.50E+12	2,886	6.7	1.1	0.443	0.9	1.7	3.2
subpolar	50-65°	2.40E+13	2,285	7.6	1.6	0.444	1.1	1.9	10.0
temperate	35-50°	3.35E+13	1,205	7.1	1.9	0.435	1.7	1.4	6.1
subtropical	20-35°	3.85E+13	882	6.5	1.8	0.408	2.2	0.7	-4.4
tropical	5-20°	4.60E+13	597	6.5	2.2	0.394	3.0	0.9	-1.9
equatorial	0-5°	1.60E+13	622	7.0	2.6	0.391	2.9	0.9	-0.7
total									12.3
Winter									
polar‡	65-80°	--	--	--	--	--	--	--	--
subpolar	50-65°	9.50E+12	1,511	10.2	3.0	0.488	1.4	0.7	-2.6
temperate	35-50°	2.40E+13	1,139	10.0	3.4	0.414	1.8	0.6	-8.3
subtropical	20-35°	3.35E+13	822	7.6	2.6	0.424	2.3	0.5	-8.2
tropical	5-20°	3.85E+13	624	7.9	3.2	0.429	2.9	0.6	-7.3
equatorial	0-5°	4.60E+13	618	6.9	2.5	0.427	2.9	0.7	-4.3
total									-30.7
total									-0.022
									Tg
									COS/yr

† Areas from Bates et al. (1987).

‡ Wintertime polar ocean assumed to be ice-covered.

* Regional fluxes were obtained from the average of local fluxes in that region, calculated from local SR, H, K, and P_a values, not from the regionally averaged parameters listed. Seasons are defined as: Equinox = Feb. 5 - May 7 and Aug. 5 - Nov. 7; Summer = May 8 - Aug. 4 (northern hemisphere); Winter = Nov. 8 - Feb. 4 (northern hemisphere).

Figure 5.4. Regional and seasonal distribution of COS sea-air flux in both northern and southern hemispheres. Solid lines are fluxes calculated using transfer velocity-wind speed relationships from Liss and Merlivat (1986) (L & M) and dotted lines are fluxes using transfer velocity-wind speed relationships from Wanninkhof (1992) (Wann). Symbols represent the midpoint of each region defined in Table 5.4. Seasons are also defined in Table 5.4.

al. (1992), who have observed that atmospheric COS has changed by less than 1%/yr since 1977. Other sources must be investigated with the possibility that they are overestimated. One possibility is the proposed soil source. Castro and Galloway (1991) found that the enclosure technique used to generate previous data may have produced artificially high COS fluxes as a result of using sulfur-free purge gas. Recent work by de Mello and Hines (1994) also suggests that the magnitude of COS fluxes from soils and wetlands depends on whether a static or dynamic enclosure system is employed. Most budgets also have CS₂ conversion as a major source of COS while knowledge of sources and sinks of CS₂ is even more limited than for COS. Finally, the magnitude of the coastal ocean flux should be the focus of future COS measurements in the marine environment. Table 5.5 shows a comparison of average SR's for coastal regions, including our work, which is significantly lower. The discrepancy is probably a result of different measurement locations, as mentioned earlier, indicating that more measurements need to be made in various coastal environments in order to better resolve the spatial and seasonal variations.

Atmospheric COS Concentrations

Ambient atmospheric measurements from both cruises are shown in Figure 5.5 averaged in 5° bins as a function of latitude. Averages by hemisphere and cruise are shown in Table 5.6. Linear fits to the concentration data from each cruise show an interhemispheric gradient that changes direction between the two cruises. Interhemispheric ratios shown in Table 5.6 are less than the standard deviation of the average concentrations from each hemisphere, however, these trends are statistically significant at the 95% confidence level based on a t-test. Average concentrations in the northern hemisphere appeared to change by about 10% between cruises compared to only a 5% change in the southern hemisphere. Although the magnitude of the seasonal

Table 5.5. Observed Coastal Ocean Saturation Ratios

Reference	SR
This Work	2.6 ± 0.8 (N=45)
Mihalopolous et al., 1992	9
Andreae and Ferek, 1992	9
Johnson, 1985	4
Turner and Liss, 1985	4.6
Rasmussen et al., 1982	4.2

changes observed in this work is less than the overall measurement accuracy, estimated at 11%, the data trends suggest that the northern hemisphere experiences a more pronounced seasonal cycle of atmospheric COS than the southern hemisphere. Mihalopolous et al. (1991) have observed a seasonal cycle of similar magnitude in the southern hemisphere (<5.4%). An increase in northern hemisphere COS concentrations of order 5-10% in the spring/summer months has also been observed by Rinsland et al. (1992) using total column infrared spectroscopy from two temperate northern hemisphere sites. Some of their seasonal signal was attributed to seasonal changes in tropopause height, although by accounting for this correction, they still report a seasonality of about 5%, with a distinct maximum during the late summer. The magnitude of this seasonality is in general agreement with our findings. Our lack of northern hemisphere data during the summer and autumn months make a complete comparison not possible.

Figure 5.5. Ambient atmospheric measurements of COS mixing ratio, in parts-per-trillion by volume (pptv), presented as 5 degree averages. Linear fits to the data sets are also shown. The error bars indicate the average of the standard deviations from each latitude bin.

Table 5.6. Ambient Atmospheric Data from both Cruises

	Cruise 1	Cruise 2
<i>Northern Hemisphere</i>		
mean	477 ppt	431 ppt
σ	40 ppt	37 ppt
σ/mean	0.08	0.08
N	382	185
$\sigma/N^{1/2}$	2 ppt	3 ppt
<i>Southern Hemisphere</i>		
mean	463 ppt	448 ppt
σ	67 ppt	25 ppt
σ/mean	0.14	0.06
N	360	353
$\sigma/N^{1/2}$	4 ppt	1 ppt
<i>Total</i>		
mean	470 ppt	442 ppt
σ	55 ppt	31 ppt
σ/mean	0.12	0.07
gradient	0.30 ppt/°lat	-0.24 ppt/°lat
IHR ¹	3.0%	-3.8%

¹Interhemispheric ratio = (northern average - southern average) / southern average

The magnitude of the interhemispheric gradients from each cruise are less than 5%, which is in agreement with past measurements over the Pacific (Torres et al., 1980; Johnson and Harrison, 1986). This distribution suggests that the COS lifetime is greater than the interhemispheric mixing time (~1 year) or that the sources and sinks are nearly the same in the two hemispheres. The Pacific data are not consistent with the large inter-

hemispheric gradients (15-25%, north>south) observed by Bingemer et al. (1990) and Johnson et al. (1993) over the Atlantic in the boreal spring and summer. Given the long lifetime of COS, the interhemispheric gradient of COS over the Atlantic should be similar to that of the Pacific during the same season. Bingemer et al. (1990) suggest that their gradient and correlations with CO and CH₄ concentrations are evidence for anthropogenic sources of COS from Europe and North America, which may be increasing due to a world-wide increase in industrialization. This is not consistent, however, with the upper limit of 0.2%/yr global increase in COS set by Rinsland et al. (1992). More high precision measurements of atmospheric COS are needed to help resolve this discrepancy.

5.5 Conclusions

With the global budget of COS greatly out of balance, the magnitude of the open ocean source was reevaluated based on measurements in many ocean regions and in seasons not previously sampled. COS concentrations were measured in surface waters of the Pacific and the overlying boundary layer between 55°N to 70°S on two cruises covering three seasons. Seawater COS concentrations were observed to be dependent on water type, time of day, and season. Highest concentrations (saturation ratios 1-4.5) were observed in coastal waters and in polar and subpolar waters that had continuous sunlight. Dissolved COS concentrations were lowest (saturation ratios 0.2-1.5) in subtropical gyre regions of low biomass (determined by chlorophyll fluorescence) and limited sunlight (subpolar, wintertime waters). Extensive regions of the open ocean were observed to be undersaturated with respect to atmospheric equilibrium of COS and thus act as a sink for atmospheric COS. First order decay times of dissolved COS concentrations in surface seawater agreed with predicted hydrolysis lifetimes from seawater solutions. This suggests that hydrolysis was the dominant sink mechanism under the wind and temperature conditions that prevailed during this study. Dark

production may have played a significant role in lengthening the observed lifetime of COS at the surface relative to laboratory measurements of hydrolysis lifetimes on artificial solutions.

A global open ocean flux for COS, calculated using monthly averaged wind speeds and the Liss and Merlivat (1986) expressions for transfer velocity, gave a net sink of 0.022 Tg COS/yr. The open ocean COS sink, calculated using the Wanninkhof (1992) expression for transfer velocity, was significantly larger, 0.041 Tg COS/yr. Averaging the two, we report an average sink of 0.032 Tg COS/yr (0.010-0.054) which includes uncertainties due to the transfer velocity relationships, wind fields, atmospheric mixing ratio measurements, Henry's constants, and regionally averaged saturation ratios. These results indicate that the open oceans are a relatively unimportant factor in the global COS budget. Furthermore, there is considerable uncertainty in the global flux from the coastal ocean, which could very likely be overestimated. Future COS measurements in the marine environment should focus on coastal/shelf regions, where understanding of mechanisms of COS photoproduction is still limited. Also, since all of the above observations have been done in the Pacific Ocean, data from other oceanic regions, especially in wintertime are clearly needed.

Atmospheric COS mixing ratios appeared to increase from south-to-north during the equinox cruise and decrease from south-to-north during the summer/winter cruise. This reversal in gradient direction implies a seasonal cycle on the order of 10% in the northern hemisphere with a maximum during the boreal springtime. The difference in average COS mixing ratios between hemispheres was less than 5%, in agreement with previous measurements, but inconsistent with measurements over the Atlantic Ocean during similar seasons.

Acknowledgments. We appreciate the support of the officers and crew of the NOAA Ship Surveyor and the help of Jerry Davison and Steve Hankin with the COADS wind data. PSW is supported by the U.S. DOE Graduate Fellowship for Global Change administered by ORISE. We thank the Radiatively Important Trace Species (RITS) and Aerosol and Climate Components of the NOAA Climate and Global Change Program for general support. This is contribution number 1611 for NOAA/PMEL, and 305 for JISAO.

Chapter 6

Modeling the Seasonality of Atmospheric COS

6.1 Introduction

In this chapter I describe the details of a simple global model for estimating the seasonality of COS in the atmosphere. The model is based on assuming an annual balance of sources and sinks, which can be justified given the fact that the atmospheric concentration of COS has remained stable for nearly two decades. The main motivation for such a model is that it can serve to constrain the magnitude and/or location of sources and sinks, by testing whether or not a given seasonality of the fluxes produces the seasonal trends in COS that have been observed by previous studies such as Rinsland et al. (1992), Bandy et al. (1992), Mihalopolous et al. (1991), and the data shown in Chapter 5. Because the budget does not currently balance, it is very likely that some sources have been overestimated, and/or the "missing" sink is poorly understood. Through the use of a model to try different flux scenarios, fluxes that have been previously suggested in the literature can be verified. There is, however, a large amount of uncertainty involved in estimating not only the seasonal distribution of the fluxes, but also the hemispheric distribution. More information on the magnitude of sources and sinks is clearly needed.

6.2 The Model

The quick BASIC code for the model named SEASBURD.BAS is shown in the appendix. The fundamental equation used to model the cycle of COS is:

$$\frac{d[COS]}{dt} = S_1 + S_2 + \dots S_n - Q_1 - Q_2 - \dots Q_n \quad (6.1)$$

where S is a source in amount per year and Q is a sink with the same units. Equation 6.1 is a time-dependent differential equation with an approximate solution of:

$$[COS]_t = [COS]_{t-1} + \left(\frac{\Delta[COS]}{\Delta t} \right) \times \Delta t \quad (6.2)$$

where $[COS]_t$ is the COS atmospheric concentration at time t , $[COS]_{t-1}$ is the previous concentration and $\left[\left(\frac{\Delta[COS]}{\Delta t} \right) \times \Delta t \right]$ is the change in COS concentration in a time-step Δt , also known as the input flux. By using the computer program to 'step through' a time dependent input flux, an output of $[COS]$ as a function of time can be generated.

The input flux function was generated by taking magnitudes of the annual fluxes for each source and sink from the literature and assuming a magnitude of an "other" sink that makes the annual budget balance. Input flux functions were generated for summer and winter, and the northern and southern hemispheres. In most cases, partitioning fluxes into their seasonal and hemispheric components was done in spite of any data. However, best guesses were obtained by using analogies to other gases, and by assuming dependencies based on temperature, sunlight, and land/ocean area. Many of the source or sink strengths of COS are dependent on the COS concentration gradient between the source or sink and the atmosphere. Thus, as $[COS]$ varies seasonally, so should the fluxes in a negative feedback manner. For example, the air-sea flux is dependent on the concentration across the air-sea interface and as atmospheric COS increases, the corresponding sea-air flux will decrease. This type of feedback was parameterized:

$$\text{NewFlux} = \text{OldFlux}([COS]_o/[COS]_t) \quad (6.3)$$

where the ratio $[COS]_o/[COS]_t$ is the fraction that the current COS concentration ($[COS]_t$) has changed compared to the original COS concentration ($[COS]_o$). For a sink like OH oxidation in the atmosphere, the feedback fraction is the reciprocal: $[COS]_t/[COS]_o$, which allows the sink strength to increase as the atmospheric concentration increases.

Mixing between hemispheres was parameterized by the equation:

$$F_{NS} = k\Delta C \quad (6.4)$$

where F_{NS} is the flux between the northern and southern hemispheres, k is the exchange coefficient equal to $1/\tau$ (τ = the hemispheric mixing time) and ΔC is the concentration difference between hemispheres.

It was assumed that the input flux functions for each hemisphere were not simply a square wave of two distinct values per year (summer and winter), but rather a continuously changing periodic function based on the periodic nature of the seasons. The average values for summer and winter were assumed to represent the peak-to-peak amplitude of a sine wave that has a period of one year. This was parameterized with the expressions for A and R :

$$A_{nh} = (\text{ABS}(\text{nflxsum}(j\%)) + \text{ABS}(\text{nflxwin}(j\%))) / 2 \quad (6.5)$$

$$A_{sh} = (\text{ABS}(\text{sflxsum}(j\%)) + \text{ABS}(\text{sflxwin}(j\%))) / 2 \quad (6.6)$$

$$R_{nh} = (\text{ABS}(\text{nflxsum}(j\%)) - \text{ABS}(\text{nflxwin}(j\%))) / 2 \quad (6.7)$$

$$R_{sh} = (\text{ABS}(\text{sflxsum}(j\%)) - \text{ABS}(\text{sflxwin}(j\%))) / 2 \quad (6.8)$$

where nh and sh refer to northern and southern hemispheres, respectively, ABS is the absolute value function, nflxsum and nflxwin are the northern hemisphere average fluxes in summer and winter, respectively, sflxsum and sflxwin are the southern hemisphere average fluxes in summer and winter, respectively, and $j\%$ is a variable for counting as the program steps through each Δt . The quantity A represents the average of the summer and winter extremes, and R represents the absolute value between the average and the peak of the curve. By incorporating these variables into a cosine function, a periodic expression for the flux is obtained. Using the northern hemisphere winter flux as an example:

$$\text{nflxwin}(j\%) = A_{nh} * \cos(j\% / (dt * 2) * 2\pi) + R_{nh} \quad (6.9)$$

where nflxwin is the new flux at each point in time, $j\%$, and dt is the number of time-steps per season.

Seasons were defined as summer = May 1 - Oct. 31 (northern hemisphere)

Nov. 1 - April 30 (southern hemisphere)

winter = Nov. 1 - April 30 (northern hemisphere)

May 1 - Oct. 31 (southern hemisphere)

These definitions comes from Bates et al. (1987). The starting COS concentration was assumed to be 2.3 Tg in each hemisphere, based on a total atmospheric burden of 4.6 Tg globally (Chin and Davis, 1993). The time-step used in the model runs was 1.825 days, which gives 200 data points per year, or 100 points per season.

6.3 Flux Scenarios

Two different flux scenarios were run and the output of COS burdens as a function of time was compared with actual measurements in the atmosphere. The magnitude of the fluxes are shown in Table 6.1 and illustrated in Figures 6.1 and 6.2. Scenario 1 represents fluxes that are taken directly from the literature, and represents our best current understanding of the budget. The ocean source is from Chapter 5, with coastal data included from this work, assuming wind fields and exchange coefficients from Mihalopolous et al. (1992). The ocean estimate from this work is lower than all previous estimates, but includes a higher percentage of open ocean measurements, and higher latitude coastal data. I believe that this ocean estimate is more accurate than previous estimates. The soil source is from Chin and Davis (1993) and is partitioned hemispherically with land area by assuming that 72% of the soil source is in the northern hemisphere. It was also assumed that the soil source is twice as large in the summer than the winter based on the dependence of sulfur gas emissions from soils with temperature (Goldan et al., 1987; Guenther et al., 1989). CS₂ sources were taken from Chin and Davis (1993) and are shown in Table 6.2. Hemispherically, the sources were partitioned as: ocean - 43% NH, 57% SH (Sverdrup, 1940); soils - 72% NH, 28% SH (land area); volcano - 72% NH, 28% SH (land area); anthropogenic - 80% NH, 20% SH (land area +

Table 6.1. Seasonally and hemispherically estimated fluxes (Tg) for COS used as input for modeling the seasonal cycle of atmospheric COS. Scenario 1 represents the currently accepted magnitudes and phases for each source and sink. Scenario 2 is assumes non-seasonal sinks, and a greatly reduced soil source.

Scenario 1

	ocean	soil	CS ₂	volc	biomass	anthro	OH	other	total
NH sum	0.024	0.129	0.127	0.005	0.067	0.015	-0.043	-0.314	0.010
NH win	0.002	0.064	0.094	0.005	0.034	0.015	-0.029	-0.157	0.029
SH sum	0.013	0.049	0.077	0.005	0.026	0.006	-0.065	-0.121	-0.009
SH win	-0.012	0.025	0.037	0.005	0.013	0.006	-0.043	-0.060	-0.030
total	0.026	0.267	0.335	0.020	0.140	0.042	-0.180	-0.651	0

Scenario 2

	ocean	soil	CS ₂	volc	biomass	anthro	OH	other	total
NH sum	0.024	0.062	0.127	0.005	0.067	0.015	-0.045	-0.185	0.072
NH win	0.002	0.031	0.094	0.005	0.034	0.015	-0.045	-0.185	-0.052
SH sum	0.013	0.024	0.077	0.005	0.026	0.006	-0.045	-0.071	0.033
SH win	-0.012	0.012	0.037	0.005	0.013	0.006	-0.045	-0.071	-0.048
total	0.026	0.129	0.335	0.020	0.140	0.042	-0.180	-0.513	0

Figure 6.1. Scenario 1. Seasonal and hemispheric distribution of the fluxes for each source and sink of COS. Data are shown in Table 6.1. Magnitude of soil source is taken from Chin and Davis (1993). OH sink is assumed to be stronger in the southern hemisphere vs. the northern hemisphere (60% vs. 40%) and stronger in summer vs. winter (60% vs. 40%). The other sink is assumed to be land plants and scales with land area (NH=72%, SH=28%) and assumes that there is twice as much photosynthetic uptake in the summer vs. the winter (summer=67%, winter=33%).

Figure 6.2. Scenario 2. Seasonal and hemispheric distribution of the fluxes for each source and sink of COS. Data are shown in Table 6.1. Magnitude of soil source is assumed to be half of that reported by Chin and Davis (1993). OH sink is assumed to not be dependent on season or hemisphere. The other sink controlled by the land area (72% in northern hemisphere), but is not dependent on season.

Table 6.2: The Distribution of CS₂ Emissions (Tg)

Source	CS ₂ ¹	COS	NH	SH	NH sum	NH win	SH sum	SH win
ocean	0.180	0.113	0.049	0.065	0.039	0.010	0.052	0.013
soil	0.023	0.014	0.010	0.004	0.007	0.003	0.003	0.001
volcano	0.020	0.013	0.006	0.006	0.003	0.003	0.003	0.003
anthro	0.310	0.195	0.156	0.039	0.078	0.078	0.020	0.020
totals	0.533	0.336 ²	0.222	0.114	0.127	0.094	0.077	0.037

¹CS₂ sources from Chin and Davis (1993)

²CS₂ contribution to COS is from Chin and Davis (1993)

population). Seasonally the sources were partitioned as: ocean - 80% summer, 20% winter (based on my COS data); soils - 0.67% summer, 0.33% winter (temperature dependence); volcano and anthropogenic - no seasonal dependence. COS from biomass burning (Crutzen and Andreae, 1990) was assumed to have the same hemispheric and seasonal distribution as the soil source, with 72% in the northern hemisphere and 66% in the summer. The anthropogenic source (Chin and Davis, 1993) was assumed to be partitioned 80%:20% for the northern and southern hemispheres, respectively, and was assumed to have no seasonality.

Loss of COS by oxidation with OH, other radicals, and photolysis in the troposphere and stratosphere (Chin and Davis, 1993) was partitioned as follows: 40% NH, 60% SH (higher OH in southern hemisphere due to less CO and CH₄ scavenging, although this hemispheric asymmetry in OH may be too high); 60% summer, 40% winter (more sunlight and photochemical production of OH in summer). The 'other' sink was

assumed to associated with land plants which have a very uneven hemispheric distribution and a strong seasonality. I assumed: 72% NH, 28% SH (land area); 67% summer, 33% winter. The seasonal distribution is assuming that a large fraction of photosynthesis occurs in the summer months, and based on the seasonality of CO_2 (Fung et al., 1987), the sink strength is about two times stronger in the summer.

The fluxes for scenario 2 are given in Table 6.1, and shown graphically in Figure 6.2. The idea behind scenario 2 was to have the resulting atmospheric cycle more closely resemble the measurements than the results obtained using scenario 1. Because of the uncertainty involved in all the fluxes, many different combinations could be used to construct a new scenario and scenario 2 just represents one possible combination. Scenario 2 left all the sources the same except for the soil source, which was reduced by a factor of two. Recent work by Castro and Galloway (1991) and de Mello and Hines (1994) suggests that previous estimates of the soil sources of COS and CS_2 could be overestimated because of questionable flux measurement techniques. My adjustment of a factor of two reflects this possibility. The seasonal and hemispheric distributions are the same as in scenario 1. The OH oxidation sink for scenario 2 is the same magnitude as scenario 1, except that there is no hemispheric asymmetry or seasonality. The 'other' sink is assumed to scale hemispherically with land area, but has no seasonality.

6.4 Model Results and Discussion

Model output from flux scenario 1 is shown in Figure 6.3 and represents a seasonal amplitude variation (peak to peak) of only about 0.3%, with a summer minimum and winter maximum in the northern hemisphere. The reason for the lack of seasonality in scenario 1 is mainly due to the fact that the source and sink strengths are strongest at the same time of year (summer). The large seasonality in the sources and sinks is nearly canceled out. The response time of the atmosphere to the input flux appears to be about

Figure 6.3. Seasonally distributed COS burdens and fluxes for each hemisphere, based on flux inputs for scenario 1. The top two curves represent the burdens, and the lower two curves represent the fluxes per 1.825 days (200 time-steps per year). The value of 0.0 on the x-axis refers to Jan 1.

3.5 months, from Figure 6.3. The interhemispheric gradient (IHR) appears to be about 1.6%, with higher levels in the northern hemisphere.

Model output from flux scenario 2 is shown in Figure 6.4 and represents a seasonal amplitude of about 1.6%, which is about five times larger than the amplitude from scenario 1. The primary reason for this increase is that the seasonality was removed from the sinks in scenario 2 and did not act to cancel the seasonality in the sources, as was the case above. This scenario was devised with the purpose of creating output that showed a northern hemisphere summer maximum, in phase agreement with observations shown in Chapter 5 and those by Rinsland et al. (1992). Another feature from Figure 6.4 that resembles observations from Chapter 5, is that the IHR changes sign from summer to winter. In the month of July the modeled IHR is about 2.3%, whereas during January, the IHR is about -0.7%, with the negative sign indicating a higher average burden in the southern hemisphere. The results from Chapter 5 showed a changing IHR from 3.0% in April to -3.8% in December, which is about a factor of two larger than the model results.

Figure 6.5 shows a comparison of the model output for the northern hemisphere from scenario 2, and measurements of COS from different seasons. Although there is considerable offset in the absolute magnitudes of the data, there can be seen distinct summer maximum in each case. The existence of a summer maximum points to the conclusion that the seasonality of atmospheric COS is dominated by the seasonality of its sources, as was the case for flux scenario 2. If the sinks also contribute a strong seasonality, then their phase must be opposite to that of the sources, or else atmospheric COS would display very little seasonality, as was the case for scenario 1. This conclusion helps constrain the budget, which was the original goal of this exercise, in that it makes the existence of a large plant sink nearly impossible (if the phase of the plant sink is that of photosynthetic uptake. Speculation by Johnson et al. (1993) and Bingemer et al. (1990) agrees with this conclusion that it is difficult to explain the observed

Figure 6.4. Seasonally distributed COS burdens and fluxes for each hemisphere, based on flux inputs for scenario 2. The top two curves represent the burdens, and the lower two curves represent the fluxes per 1.825 days (200 time-steps per year). The value of 0.0 on the x-axis refers to Jan 1.

Figure 6.5. Comparison of model output from northern hemisphere, scenario 2 (solid line) with data from Rinsland et al. (1992) fit to a polynomial (dashed line). Also shown are northern hemisphere average COS concentrations from this work (Chap. 5) and CITE-3 (Johnson et al., 1993).

seasonal and hemispheric trends in atmospheric COS while assuming a large land plant sink. On the other hand, in this work, I have assumed that the seasonality of the sources is relatively well understood, especially the main ones like CS₂, soils, and biomass burning. These sources are, in fact, very poorly characterized, and are most likely overestimated. Thus, given the large degree of uncertainty with which all COS flux processes are known, no firm conclusions can be drawn on the existence or importance of the plant sink on the basis of this study.

Chapter 7

COS in Polar Ice Cores

7.1 Introduction

This phase of my research involved attempting to measure the paleo-record of carbonyl sulfide trapped in polar ice cores. The main motivation for this project was to determine pre-industrial and glacial levels of COS in the atmosphere and use these levels as a proxy for historical trends in the stratospheric sulfate aerosol burden. Historical information on stratospheric sulfate aerosols could lead to a greater understanding of trends in the Earth's radiation budget and stratospheric ozone.

Work was carried out at CNRS, Laboratoire de Glaciologie et Geophysique de l'Environnement in St. Martin d'Heres (Grenoble), France, under the direction of Robert Delmas, Dominique Raynaud and Richard Gammon. Ice core samples were previously collected from Greenland and Antarctica.

7.2 Climate Information from Ice Cores

Measurements of trapped atmospheric gases such as carbon dioxide and methane, and various ion species in polar ice cores have provided a unique record of paleoatmospheric chemistry dating back at least 160,000 years (Raynaud and Barnola, 1985; Barnola et al., 1987; Chappellaz et al., 1990; Legrand and Delmas, 1987; Etheridge et al., 1988). This record provides a critical basis for investigating the relationship between the composition of the atmosphere and the causes and consequences of climate change. Figure 7.1 shows the paleo-record of some important species that have been measured in the Vostok core. A comparison of temperature (which is a proxy for climate, determined from $^{18}\text{O}/^{16}\text{O}$ ratios) with the greenhouse gases CO_2 and CH_4 shows a very good correlation, which indicates that these phenomena are highly coupled. Glacial and interglacial periods are clearly delineated with a spacing of roughly 100 kyrs. The record

Fig. 7.1. Ice core records from Vostok (Antarctica) of atmospheric carbon dioxide (Barnola et al., 1987), methane (Chappellaz et al., 1990), non-seasalt sulfate (Legrand et al., 1991), and the temperature record inferred from hydrogen isotopes (Jouzel et al., 1987).

for non-seasalt sulfate ions appears to be anti-correlated with climate, with enhanced levels during cooler periods, and much noisier. Legrand et al. (1988) suggest that if sulfate is proportional to cloud condensation nuclei in the atmosphere, then a significant cooling is expected from such enhanced levels of sulfate, consistent with the temperature record. It is unclear, however, what causes the climate system to oscillate from glacial to interglacial states.

The mechanics of gases being incorporated into bubbles trapped into ice has been well documented (Delmas, 1992; Raynaud et al., 1993). The gas record in these bubbles appears to be an accurate measure of the composition of the original atmosphere, although there are a number of uncertainties. Figure 7.2 schematically shows the physical processes involved in the formation of an ice record. Snow falling in very cold regions accumulates slowly, and does not melt by warming (sublimation does occur, but will not be considered here). With time and weight of new snow above, the fallen snow becomes more compact and is transformed into firn, a porous material with a density of 0.5-0.8 (Delmas, 1992). The interstitial air in the firn communicates with the atmosphere above and can be considered well-mixed, until a certain depth (close off zone) where bubbles begin to form. At a density of about 0.83, the firn is entirely transformed into ice, with the rate transformation being a function of temperature and snow accumulation. Unlike the porous firn, ice is an air-tight material. The amount of air entrapped by the close off process is about 10 mL/100 g of ice, less when the ice is formed at high elevations, more at low-elevation sites (Raynaud and Lebel, 1979). Martinerie et al. (1994) suggest that in addition to elevation, which is often a result of ice sheet thickness, climatic parameters such as wind could also influence ice pore volumes. In addition, certain trace gases within the ice pores may be enriched or depleted relative to levels in the free atmosphere during the process of firn transformation into ice. This source of uncertainty in the ice record is primarily due to gravitational enrichment of heavier

Fig. 7.2. Schematic of the formation of ice records, adapted from Delmas (1992). Aerosols and gases are incorporated into falling snow, which gets compacted into a firn layer and finally becomes closed off to the atmosphere and forms bubbles in the ice.

compounds in the firm when a state of diffusive equilibrium is reached after the close off process. Chemical adsorption of gases on surfaces of snow and ice crystals, as well as clathrate formation, may also be occurring. Current research involves using tracers to take into account various dynamical and chemical effects of air in the firm (Raynaud et al., 1993). All these uncertainties appear to be minor for greenhouse gases, however, since the recent ice records of CO_2 and CH_4 from Antarctica up through the late 1900's show a very close agreement to the corresponding high-precision atmospheric measurements which began in 1958 and 1978 for CO_2 and CH_4 , respectively.

7.3 COS as a Proxy for Stratospheric Sulfate and Trace Sulfur Gases

Carbonyl sulfide (COS) concentrations from depths in the ice may provide information on the historical trends of this climatically important trace gas. Its historical record is most likely well preserved in ice cores because COS is very stable in the atmosphere and is inert to most substances, especially at low temperatures. While it is not known what effect COS currently has on forcing climate change, there is a potential for the global COS cycle to be part of a climate feedback mechanism through influencing stratospheric chemistry. There is limited information on paleoconcentrations of stratospheric aerosols because they cannot be directly measured in ice core samples. This necessitates the use of a proxy for stratospheric aerosols that is preserved in the ice cores, with COS being the logical choice. A historical record of COS can be used in conjunction with the record of volcanic eruptions, which also contribute large amounts of sulfur to the stratosphere, as input for climate models in assessing the impact of heterogeneous chemistry on ozone changes (Granier and Brasseur, 1992).

COS information in ice cores may also be used as a proxy for other reduced sulfur gases that have their biogeochemical cycles linked with COS but are not preserved in the ice because of their short atmospheric lifetimes. DMS is perhaps the most climatically

important sulfur gas for which there is no paleo-record. DMS has the largest non-anthropogenic flux to the atmosphere of all sulfur gases and thus is the main source of cloud condensation nuclei (CCN) to the remote atmosphere. CCN have light scattering properties, which affect planetary albedo and cause climate forcing (Charlson et al., 1987). A direct oxidation product of DMS in the atmosphere is methanesulfonic acid (MSA), for which a paleo-record exists (Legrand et al., 1987). This paleo-record indicates that MSA and sulfate ions were enhanced during glacial periods, further validating their correlation to a cooler climate. However, it is not possible to know if DMS fluxes were also enhanced during this period because MSA is only indirectly related to DMS. Gas phase MSA formation rates could have been different as well as MSA deposition rates in snow during glacial times. Thus, a gaseous sulfur compound like COS may give a clue at paleoconcentrations of DMS. Many natural processes that produce COS, also are sources of DMS, like soil respiration and ocean biology. Some researchers have noticed moderate correlations with dissolved COS and DMS concentrations in surface ocean waters (Ferek and Andreae, 1983; Weiss et al., 1995a), whereas Johnson and Harrison (1986) observed an anticorrelation. However, even though DMS and COS sources may not be totally synchronous across the planet, it is possible that the change in ecosystems caused by glaciation, would have similar effects on the cycling of both compounds.

7.4 Analytical Methods

Work was carried out in Grenoble, France between February and April, 1995, with the electron capture sulfur detector (ECD-S) described in Chapter 3. The ECD-S can make measurements in two different modes: injection of up to 5 mLs of dry air, or preconcentration of dry air on a packed loop at liquid nitrogen temperature with a helium flush. Because extraction of COS from the ice involved purging sample containers with

several volumes of flush gas, the cryotrapping mode of the ECD-S was used throughout this study.

Two different ice-extraction techniques were employed: crushing and melting/stripping, shown in Figure 7.3. The crushing method was based on procedures developed for the extraction of CO₂ (Barnola et al., 1987). This involved placing a 30-50 g piece of ice into a vacuum-tight stainless steel vessel at -50°C containing about 10 steel balls and evacuating the crusher and sample lines to a pressure of less than 10⁻⁴ torr. A vacuum tight seal was made with indium wire. The vessel was then agitated violently for 1.25 minutes, creating a fine ice powder inside the crusher, and liberating the trapped gases from the interstitial pores into the headspace. The ~50 mL headspace was then expanded into a much larger volume (500 mL), which was also evacuated, giving an extraction efficiency of about 90%, assuming perfect crushing. The large sample cylinder was then flushed with several volumes of COS-free helium, which was subsequently dehydrated in an alcohol bath at -50°C and trapped in a packed loop (Porapak QS, Alltech) at liquid N₂ temperature. The air content within the ice sample is known from pressure measurements by a barometer after crushing, and by assuming an average volume of air to mass of ice ratio.

The melting/stripping procedure was much simpler to perform, and seemed to give better results than crushing. This technique was based on stripping COS from seawater, analogous to the method used in Chapter 4. A stripping vessel was designed and constructed based on vessels used for methane extraction by the melting/refreezing technique (Chappellaz et al., 1990). A 30-50 g piece of ice was placed inside the stripper and a leak-tight seal was made with indium wire. The vessel was then purged with several volumes of helium, after which the ice was allowed to slowly melt. The melt water was purged with more helium and this was dehydrated in a cold alcohol bath and

COLD CRUSHING

MELTING/STRIPPING

Fig. 7.3. Schematic of the crushing and melting/stripping experimental setups used for COS extraction from ice-core samples.

trapped on the cryoloop. The quantity of gas in the ice was inferred from the weight of ice used and the mean volume of air to mass of ice ratio for that particular core and depth from previous measurements.

7.5 Results and Discussion

Measurements with the crushing vessel were plagued with heavy contamination (about 2 times ambient atmospheric signal), likely emanating from the walls of the crusher. Two lines of evidence support this view: one is that crushing cannot be used for methane extraction because the striking of the balls against the vessel walls is a source of methane. Steel probably contains impurities of sulfur as well as methane. Two is that the contamination level was observed to be temperature dependent, with less contamination at colder temperatures. This is consistent with results for methane (J. M. Barnola, private communication). Another major limitation of this technique is the very high gas volumes required to flush the 500 mL sample cylinder after crushing. A constantly emitting contamination source anywhere in the flush gas line will be concentrated on the cryotrap, leading to a huge blank. Even when no crushing was performed, blank levels were not lower than an ambient atmospheric signal (equivalent to 5 mL STP of air containing 500 pptv COS).

Melting/stripping gave some promising preliminary results that deserve more investigation. The blank associated with the extraction line appeared to be much lower than the crushing system, and much less flush gas volumes were required. Initially, it was thought that COS may be susceptible to pH-dependent hydrolysis in the aqueous meltwater solutions that could give artificially low results. This appeared not to be the case, presumably because hydrolysis reactions at the temperatures and time-scales (~20 min) of the analyses are too slow to impact the natural COS levels. There did appear to be, however, a problem with stripping the melted sample down to the blank level that was

obtained before the ice was placed inside the stripper. One explanation is poor stripping efficiency, which is likely, given the wide and short design of the stripper. Another explanation is that COS was being produced in the stripper during analysis, either photochemically, or through dark production mechanisms. My experience with COS stripping from fresh and seawater is that it is often difficult to strip to a clean blank level. Also, if a solution is allowed to sit for several hours after being stripped to a blank level, and then restripped, the restripped COS values will often be quite elevated. This implies an unexplained production pathway that should be considered in future studies with ice extraction.

Discouraging results were obtained with so-called bubble-free ice that had been prepared at LGGE and was supposedly free of contaminants. This ice gave very high levels of COS for both the crushing and stripping methods. Clearly, zero ice for COS has different cleanliness requirements than the zero ice used, which had been made for CO₂ and CH₄ analyses. However, even for these carbon-cycle gases, contamination levels were not zero (5-10 ppm for CO₂, 5 ppb for CH₄, and 1-5 ppb for CO) and needed to be subtracted out.

A worthwhile question to ask is whether or not atmospheric levels of COS were significantly different in pre-industrial and glacial times than they are today? Because of the major uncertainties in the COS budget, it may not be possible to speculate on how the various sources and sinks of COS would have been different in ancient times. However, a few things can be mentioned. Other trace gases that have a significant anthropogenic component were significantly lower during pre-industrial and glacial times (CO₂, CH₄, N₂O). If direct or indirect (CS₂) human sources of COS are significant, then paleo-levels of COS would be lower. However, the glacial record of sulfur species, MSA and SO₄²⁻, shows increased values during glacial times, which are potentially the result of greater sulfur gas emissions. If this is the case, then COS levels may have been higher in glacial

epochs. We know that the oceans were colder during the ice ages, which would make hydrolysis slower. However, because of decreased levels of atmospheric CO_2 , the oceans were slightly more alkaline, which would make hydrolysis faster. Additionally, there may have been more atmospheric dust which would limit the UV light flux to the surface ocean and decrease the marine photochemical source. This points towards a slightly lower ocean source overall. COS from soils would have been less during ice ages because of the possibility that soils would have been drier, and the temperature dependence of COS emission from soils. If boreal forests are a large sink, then atmospheric COS would have been higher during glacial times as the glaciers covered wide regions of the northern high latitudes. Changes in the atmospheric OH field should also have a significant effect of paleo-levels of COS, although these changes are thought to be small (P. Martinerie, pers. comm.). The elimination of the pollution source of COS to the atmosphere, however, would probably be the largest difference in ancient COS levels. Current estimates are that 25-40% of COS sources are anthropogenic (Chin and Davis, 1993), although this is not universally accepted. In all probability, however, paleo-levels of COS in ice cores are probably not orders of magnitude different than present atmospheric values, which puts severe constraints on the measurement system, in terms of tolerances towards blanks and system fluctuations.

Chapter 8

Miscellaneous findings: COS incubation experiments and a reevaluation of the pollution source of COS

8.1 Introduction

Two research findings regarding the biogeochemistry of COS, that were left out of the publications (Chapters 4 and 5), will be discussed in this chapter. The first is an incubation experiment that was performed during RITS 94 (cruise 2), at which time COS in seawater samples was measured as a function of time and compared to concentration losses predicted from hydrolysis equations. The second is an analysis of my atmospheric measurements that were taken in so-called polluted environments, with the premise that COS levels are not appreciably affected by anthropogenic inputs. The results from both of these studies cast some light on currently unclear aspects of the COS cycle, and suggest areas for future work. However, because of lack of data, these findings are only considered preliminary.

8.2 COS Incubation Experiments

During the second leg of RITS 94 very high and variable concentrations of COS were encountered in the water along the ice-edge near 67°S (20-80 pM COS). This observation was somewhat surprising since there was very little UV light reaching the sea-surface due to thick cloud coverage, and presumably little photoproduction. The water in this region was very cold (-0.5 to 0.5°C), which would give COS a long lifetime in the water (4-6 days, Elliot et al., 1989), but it was not certain whether this was the only cause of elevated COS levels. Dark production was a possibility based on the results of Radford-Knoery and Cutter (1994) and Ulshofer et al. (1995).

Incubations were performed (December 27, 1993-January 1, 1994) with the help of Oliver Zafiriou, using several 20 mL glass tubes and Teflon caps. The tubes were

filled with either unfiltered seawater, 0.2 μm filtered and purged "zero" seawater, or seawater spiked with 1/4 mL of saturated HgCl_2 solution. Samples were kept at ambient seawater temperatures and not exposed to outside light. Initial concentrations of the samples were determined at the time of filling. COS concentrations were determined using a purge and trap and ECD-S, described in Chapter 4.

The results of two different incubation experiments are shown in Figure 8.1, along with exponential decays based on hydrolysis rate constants (Elliot et al., 1989). Exponential decays follow the form:

$$[\text{COS}]_t = [\text{COS}]_0 e^{-k_{\text{hyd}} t} \quad (8.1)$$

where $[\text{COS}]_t$ and $[\text{COS}]_0$ are the concentrations at time t and time 0, respectively, and k_{hyd} is the hydrolysis rate constant. Since k_{hyd} is pH and temperature dependent, these quantities were needed with some accuracy. Seawater temperature was determined to be $-0.33 \pm 0.02^\circ\text{C}$ and $0.54 \pm 0.02^\circ\text{C}$ for the first and second incubations, respectively, on board the ship and pH was 7.90 ± 0.06 , as determined by pH meter at PMEL in Seattle, Jan 19, 1994 from samples taken during the experiment. The pH determination may be affected by significant warming between the ocean and laboratory environments, however, a rough measure of pH while underway was about 7.7, so it seems that the lab result is not too far off. Hydrolysis decays for both pH 7.7 and 7.9 are shown in Figure 8.1 to demonstrate the sensitivity of these functions to pH. In general, the COS levels in the incubated samples are higher than the hydrolysis curves, especially incubation 2, which is higher by about 20%. These results suggest that hydrolysis reactions are the primary processes affecting COS concentrations in these incubated samples, but that dark production cannot be ignored. The results with HgCl_2 -spiked samples in incubation 2 suggest that biologically controlled dark production is not a factor since HgCl_2 is known to be toxic to organisms. Dark production through abiotic pathways cannot be ruled out,

Fig. 8.1. Comparison of two separate incubation experiments carried out during the RITS 94 cruise. The COS concentration loss rates are compared to the rates predicted from hydrolysis expressions at two different pHs: Elliot = Elliot et al. (1989). Hg refers to samples treated with mercuric chloride. The upper curves had a higher initial COS concentration, perhaps a function of our closer proximity to the ice edge near Antarctica. Concentrations in the dark control sample increased dramatically and are shown by the solid line.

however, and can even be supported based on incubation results on zero water spiked with HgCl_2 . This sample increased from 7.0 to 22 pM COS in the ~100 hour period of the second incubation. If this increase were subtracted from the last points of incubation 2, then the agreement with the hydrolysis curves would be a lot closer. An explanation of an abiotic production mechanism is still needed. In both experiments, each cluster of two points represents a sample and duplicate of the same sample. Analytical precision can be estimated from these duplicates at ~15%. The goodness of fit between the data points and the hydrolysis curves is largely dependent on how well the pH of the samples were known. The average pH of seawater is closer to 8.2 and if this value is used, then the hydrolysis curves fall off much more steeply than the data points and one could conclude that significant dark production is occurring. Future attempts at this experiment should focus on taking more samples in a variety of waters, and making a more accurate determination of the pH at the time of the measurement.

8.3 A Reevaluation of the Pollution Source of COS

Presently, it is unclear what the contribution is of anthropogenic sources to the COS budget. Before 1990 it was generally accepted that anthropogenic sources were less than 25% of the total sources, including the contribution from CS_2 (Khalil and Rasmussen, 1984). There were two lines of evidence that supported a limited pollution source. One is the lack of latitudinal gradients in atmospheric COS that were reported by Torres et al. (1980) and Johnson and Harrison (1986). Since pollution is more intense in the northern hemisphere, a pollution source of COS would lead to a strong north-south gradient, similar to the gradients for gases like methane and CO. The other piece of evidence is that several measurements of COS have been made in polluted urban environments and have shown concentrations that are not too different from the global

average of 500 ppt. Sandalls and Penkett (1977) found COS levels to be 510 ppt in England and Torres et al. (1980) reported 533 ppt in Philadelphia.

In 1990, Bingemer et al. reported a large hemispheric gradient in atmospheric COS over the north Atlantic Ocean and showed that this gradient was consistent with large pollution sources of COS on the continents of Europe and North America. Other researchers began to observe elevated concentrations of COS and attribute them to influence from pollution sources. Mihalopolous et al. (1989) found a COS level of 713 ppt above coastal France and correlated it with elevated CO₂. Staubes and Georgii (1993) observed COS concentrations as high as 700 ppt (average 628 ± 42 ppt) in the marine boundary layer above the Drake Passage. From back trajectory analysis they concluded that their air samples had been influenced by the South American continent. However, if pollution episodes marked by elevated levels of other trace gases result in increases in COS, then atmospheric trends in COS should more closely match the trends in other trace gases. In particular, COS levels have not increased measurably since 1977, contrary to the trends in CO₂, CH₄, and CO. Also, except for biomass burning, specific pollution sources of COS have yet to be definitively identified.

Table 8.1 shows a compilation of my atmospheric COS measurements from so-called polluted environments. The mixing ratios reported do not vary significantly from the global average. The first location was in Seattle, outside the laboratory, where two days of continuous measurements were made. The second location was aboard the Surveyor during periods when the winds were behind the beam, meaning that the relative wind direction was from the rear of the ship, which caused ship exhaust to influence the sampling lines above the bow. The third location is similar in season and location to the measurements from Staubes and Georgii (1993), who found concentrations up to 700 ppt. The fourth and fifth locations were at the Glaciological Laboratory in Grenoble, France, which has nearly the worst air quality of any city in France. The first day was windy and

Table 8.1: Atmospheric mixing ratios of COS in "polluted environments"

Location	Date	Mixing Ratio
NOAA, Seattle, WA	Oct. 7, 1992	440 ± 40 ppt
Near Palmer Station, air influenced by stack gases	Jan 1-3, 1994	460 ± 17 ppt
Straits of Magellan, air influenced by continental pollution	Jan. 7, 1994	451 ± 19 ppt
Grenoble, France, raining	Feb. 27, 1995	469 ± 27 ppt
Grenoble, France, inversion	Feb. 28, 1995	533 ± 30 ppt

raining, so a well mixed boundary layer was assumed. The second day was influenced by a strong inversion near the ground and presumably trapped more pollutants closer to the surface. Because the second day shows significantly higher results than the previous day, this suggests that pollution sources are not zero. However, one would expect concentrations much higher than 533 ppt in polluted France in order to cause the 800-900 ppt levels observed by Bingemer et al. (1990) off the coast of Europe in the Atlantic.

These data suggest that pollution sources are not negligible, but do not drastically affect the atmospheric distribution of COS. It also seems that there is more evidence in favor of a small anthropogenic input and that elevated concentrations of COS could be

explained in terms of other source/sink processes. The data of Bingemer et al. (1990), for example, could be influenced by strong marine sources that were likely occurring during the period of their measurements (boreal springtime). Another possibility is that since most anthropogenic COS arises from anthropogenic CS₂, which has an atmospheric lifetime of around 12 days, enhanced COS would be found a great deal away from the source region. This may explain why elevated COS levels were not found downwind of the ship's smokestack, for instance.

Chapter 9

Conclusion

9.1 Conclusions of This Study

The major findings of this research can be summarized:

1. Photoproduction vs. wavelength of irradiation plots (action spectra) were determined by measuring the COS concentration increase as a function of wavelength. These action spectra were used with sea-surface sunlight data to calculate near-surface and column production rates. Photoproduction of COS is at a maximum between 313 and 336 nm in natural sunlit waters. Tropical water surface and column production rates are 68 pM/day and 360 nmol/m²/day, respectively. Antarctic surface and column production rates are 101 pM/day and 620 nmol/m²/day, respectively.
2. A high degree of variability was observed between photoproduction rates from different ocean regions, with coastal waters the highest, suggesting that natural variability in seawater is an important factor.
3. Photoproduction rates at 297 nm were found to be linear with light flux at all locations sampled indicating that only a small fraction of the dissolved organic sulfur pool was being photolyzed.
4. Extensive undersaturation of COS was observed especially in subtropical and subpolar waters during the winter. Highest COS saturation ratios were found in coastal/shelf regions and in spring/summertime temperate waters.
5. The globally averaged open ocean flux was found to be -0.032 (-0.010 to -0.054) which represents a very weak sink of atmospheric COS. This revised flux slightly improves the global atmospheric budget, which is currently out of balance by at least a factor of two.

6. Hydrolysis of COS appears to be the dominant sink mechanism in surface waters. Published rate constants give lifetimes that agreed to within 15% of observed decay times of COS concentrations during diurnal cycles.

7. Atmospheric COS mixing ratios averaged 470 pptv on the first cruise and 442 pptv on the second cruise, with much of the difference possibly a result of a seasonal decrease in the northern hemisphere COS mixing ratio of up to 10%. Interhemispheric ratios were found to be 3.0% during the equinox cruise (RITS 93) and -3.8% during the solstice cruise (RITS 94).

8. Using a simple steady-state atmospheric model to calculate the seasonality of COS it was found that by assuming a missing sink with no seasonality, the predicted cycle more closely matched the observed seasonal cycle compared to when a large plant sink was assumed. This implies that the missing sink is not land plants.

9. Preliminary attempts to measure COS trapped in ice-cores showed that the melting/stripping technique is much more viable than the crushing technique because of relative contaminations.

10. Results from dark-incubated seawater samples showed that COS concentration losses followed hydrolysis loss rates to within 30%. Dark production of COS may have been occurring, but was probably not biologically controlled, since mercury spiked samples showed the same decay rates as the control samples.

11. A large pollution source of COS is unlikely since elevated concentrations have never been measured in so-called polluted environments.

9.2 Areas for Future Work

Much work still needs to be done on the analytical system with the goal of making it more stable over the long term. Currently, the system suffers from a wandering baseline, and inconsistent fluorination, which lead to imprecision. Both the silver

palladium catalysts should be redesigned to make them more efficient. One idea for the silver is to provide more surface area for the $\text{COS} + \text{AgF}_2$ reaction to occur without increasing dead volume. A long (50 cm) and thin (1/16" OD) tube filled with AgF_2 may be a possibility. AgF_2 was tried previously without success, but more effort should be made to thoroughly test this fluorinating agent. Currently the details of the $\text{COS} + \text{AgF}_2$ reaction are unknown and need to be optimized. The Pd catalyst should be run hot (up to 350°C) for optimal cleanup, based on previous work by Benner and Lamb (1985) and others, but this has never produced acceptable results in this study. More emphasis should be placed on redesigning the Pd tube, heater block and Pd substrate to allow higher temperatures with a minimal increase in baseline noise. Attempts should be made to temperature program the column, and use a capillary column for more efficient separation.

There is a need for a stable standard at ambient concentration (500 ppt) in order to improve the precision of quantification. Different cylinder filling and storage techniques should be employed, in order to reduce the dependence on permeation tubes, which are only accurate to 5-10%.

Long-term continuous atmospheric measurements of COS are needed to investigate seasonal cycles and help constrain the budget. This requires a very stable standard, in addition to a stable instrument.

From the investigations of photoproduction rates, I was unable to explain the controlling factor in determining the photoproduction potential of seawater. Further studies should focus on the characteristics of the COS-forming DOM pools and their relationship to DOM pools involved in other photochemical processes (e.g. CO formation). Also, mechanism for dark production has yet to be postulated. My data suggest that it is abiotic.

The open ocean is not very significant in the global COS flux, and future studies in the marine environment should focus on coastal regions. My preliminary work suggests that fluxes from these regions have been overestimated and based on a few elevated measurements from selected regions.

The problem of a missing sink still exists, with the currently accepted view that it is land plants. Vertical measurements of COS in the forest canopy, similar to Berresheim and Vulcan (1992), should be carried out in a variety of forests, especially boreal, to determine the magnitude of this potentially large sink (or source). Soil sources and/or sinks should be reanalyzed as well. The contribution of pollution sources should be reevaluated also, based on my lack of any elevated values in polluted areas.

The potential use of COS as a proxy for stratospheric sulfate in ice core samples is very exciting and more work should be done to optimize an analytical system for this task. Currently, contamination is a problem, but can probably be minimized by using specific materials and making the gas extraction equipment more compact (i.e. use less tubing). It would also be useful to design the instrument to measure methyl halides (ECD-detectable) as well as COS on the same ice-core sample.

Bibliography

Adams, D.F, S.O. Farwell, E. Robinson, M.R. Pack, and W.L. Barnesberger, Biogenic sulfur source strengths. *Environ. Sci. Tech.*, 15, 1493-1498, 1981.

Andreae, M. O., and R. J. Ferek, Photochemical production of carbonyl sulfide in seawater and its emission to the atmosphere. *Glob. Biogeo. Cycl.*, 6, 175-183, 1992.

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

Andreae M. O. The ocean as a source of atmospheric sulfur compounds, in The Role of Air-Sea Exchange in Geochemical Cycling, Edited by p. Buat-Menard, pp. 331-362, D. Reidel, Hingham, Mass., 1986.

Baker K. S., R. C. Smith, Bio-optical classification and model of natural waters, 2. *Limnol. Oceanogr.*, 27, 500-509, 1982.

Baker, K. S., R. C. Smith, and A. E. S. Green, Middle ultraviolet irradiance at the ocean surface: Measurements and models, In The role of solar ultraviolet radiation in marine ecosystems. NATO Conf. Ser. 4, Mar. Sci. V. 7. Plenum, 79-91, 1982.

Bandy, A. R., D. C. Thornton, D. L. Scott, M. Lalevic, E. E. Lewin, and A. R Driedger III, A time series for carbonyl sulfide in the northern hemisphere. *J. Atmos. Chem.*, 14, 527-534, 1992.

Barnes, I., K. H. Becker, E. H. Fink, A. Reimer, F. Zabel, and H. Niki, Rate constant and products of the reaction $\text{CS}_2 + \text{OH}$ in the presence of O_2 . *Int. H. Chem. Kinet.*, 15, 631-645, 1983.

Barnes, I., V. Bastian, K. H. Becker, and K. Wirtz, Atmospheric sulfur compounds: Sources and tropospheric oxidation processes, In Formation, Distribution and Chemical Transformation of Air Pollutants, ed. R. Zellner, pp. 59-73, Dechema Monographie Vol. 104, VCH Verlagsgesellschaft, 1987.

Barnes, I., K. H. Becker, and I. Patroescu, The tropospheric oxidation of dimethyl sulfide: A new source of carbonyl sulfide. *Geophys. Res. Lett.*, 21, 2389-2392, 1994.

Barnola, J. M., D. Raynaud, Y. S. Korotkevich, and C. Lorius, Vostok ice provides 160000 year record of atmospheric CO_2 . *Nature*, 329, 408-414, 1987.

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

Bates, T.S., K.C. Kelly, J.E. Johnson, and R.H. Gammon, Regional and seasonal variations in the flux of oceanic carbon monoxide to the atmosphere. Submitted to *J. Geophys. Res.*, 1995.

Bates, T.S., B.K. Lamb, A. Guenther, J. Dignon, and R.E. Stoiber, Sulfur emissions to the atmosphere from natural sources. *J. Atmos. Chem.*, 14, 315-337, 1992.

Belviso, S., B.C. Nguyen, and P. Allard, Estimate of Carbonyl Sulfide (OCS) Volcanic Source Strength Deduced from OCS/CO₂ Ratios in Volcanic Gases. *Geophys. Res. Lett.*, 3, 133-136, 1986.

Benner, B.L., and B. Lamb, A fast response continuous analyzer for halogenated atmospheric tracers. *J. Atmos. Ocean. Tech.*, 2, 582-589, 1985.

Berresheim, H. and V. D. Vulcan, Vertical distribution of COS, CS₂, DMS, and other sulfur compounds in a loblolly pine forest. *Atmos. Environ.* 11, 2031-2036, 1991.

Bingemer, H. G., S. Burgermeister, R. L. Zimmermann, and H. W. Georgii, Atmospheric OCS: evidence for a contribution of anthropogenic sources? *J. Geophys. Res.*, 95, 20,617-20,622, 1990.

Bolin, B., On the exchange of carbon dioxide between the atmosphere and the sea. *Tellus*, 12, 274-281, 1960.

Blough, N.V., O.C. Zafiriou, and J. Bonilla, Optical absorption spectra of waters from the Orinoco River outflow: terrestrial input of colored organic matter to the Caribbean. *J. Geophys. Res.*, 98, 2271-2278, 1993.

Broecker, W. S., An application of natural radon to problems in ocean circulation. In: Symposium on diffusion in oceans and fresh waters. Lamont-Doherty Geological Observatory, Palisades, NY, 116-145, 1965.

Broecker, W. S., and T. H. Peng, The vertical distribution of radon in the BOMEX area. *Earth Planet. Sci. Lett.*, 11, 99-108, 1971.

Broecker, W. S., and T. H. Peng, Tracers in the Sea. Lamont-Doherty Geological Observatory, 1982.

Brown, K., and J. Bell, Vegetation--The missing sink in the global cycle of carbonyl sulfide (OCS). *Atmos. Environ.*, 20, 537-540, 1986.

Butler, J. H., J. W. Elkins, C. M. Brunson, K. B. Egan, T. M. Thompson, T. J. Conway, and B. D. Hall, Trace gases in and over the West Pacific and East Indian Oceans during the El Nino Southern Oscillation Event of 1987. NOAA Data Rep. ERL ARL-16, 104 pp., Air Resour. Lab., Silver Spring, Md., 1988.

Castro, M. S., and J. N. Galloway, A comparison of sulfur-free and ambient air enclosure techniques for measuring the exchange of reduced sulfur gases between soils and the atmosphere. *J. Geophys. Res.*, 96, 15427-15437, 1991.

Chappellaz, J., J. M. Barnola, D. Raynaud, Y. S. Korotkevich, and C. Lorius, Ice-core record of atmospheric methane over the past 160,000 years. *Nature*, 345, 127-131, 1990.

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

Cheng, B-M., and Y-P. Lee, Rate Constant of OH + OCS Reaction Over the Temperature Range 255-483 K. *Int. J. Chem. Kinet.*, 15, 631, 1986.

Chin M., and D. D. Davis, Global sources and sinks of OCS and CS₂ and their distributions. *J. Biogeochem. Cycl.*, 7, 321-327, 1993.

Chin M., and D. D. Davis, A reanalysis of carbonyl sulfide as a source of stratospheric background sulfur aerosol. *J. Geophys. Res.*, 100, 8993-9005, 1995.

Climate Monitoring and Diagnostics Laboratory (CMDL) Summary Report No. 22, Edited by James T. Peterson, NOAA, Department of Commerce, 1995.

Conrad, R., W. Seiler, G. Bunse, and H. Giehl, Carbon monoxide in seawater (Atlantic Ocean). *J. Geophys. Res.*, 87, 8839-8852, 1982.

Craig, H., The natural distribution of radiocarbon and the exchange time of carbon dioxide between the atmosphere and the sea. *Tellus*, 9, 1-17, 1957.

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

Crutzen, P. J., Atmospheric interaction - Homogeneous gas reactions of C, N, and S containing compounds, in The Major Biogeochemical Cycles and Their Interaction, edited by B. Bolin, and R. B. Cook, pp. 63-114, SCOPE 21, John Wiley and Sons, New York, 1983.

Crutzen, P.J. and M.O. Andreae, Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. *Science*, 250, 1669-1678, 1990.

Cutter, G. A., and J. Radford-Knoery, Carbonyl sulfide in two estuaries and shelf waters of the western North Atlantic Ocean. *Mar. Chem.*, 43, 225-233, 1993.

David, D. J., Gas Chromatographic Detectors. John Wiley and Sons, pp. 76-113, 1974.

Deacon, E. L., Gas transfer to and across an air-water interface. *Tellus*, 29, 363-374, 1977.

Delmas, R. J., Environmental information from ice cores. *Rev. Geophys.*, 30, 1-21.

de Mello, W. Z., and M. E. Hines, Application of static and dynamic enclosures for determining dimethyl sulfide and carbonyl sulfide exchange in sphagnum peatlands: implications for the magnitude and direction of flux. *J. Geophys. res.*, 99, 14601-14607, 1994.

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

Elliot, S., E. Lu, and F. S. Rowland, Rates and mechanisms for the hydrolysis of carbonyl sulfide in natural waters. *Environ. Sci. Technol.*, 23, 458-461, 1989.

Engel, A., U. Schmidt, Vertical profile measurements of Carbonylsulfide in the stratosphere. *Geophys. Res. Lett.*, 21, 2219-2222, 1994.

Etheridge, D. M., G. I. Pearman, and F. De Silva, atmospheric trace gas variations as revealed by air trapped in an ice core from Law Dome, Antarctica. *Ann. Glaciol.*, 10, 28-33, 1988.

Fahey, D. H., S. R. Kawa, E. L. Woodbridge, P. Tin, J. C. Wilson, H. H. Jonsson, J. E. Dye, D. Baumgardner, S. Bormann, D. W. Toohey, L. M. Avallone, M. H. Proffitt, J. Margitan, M. Loewenstein, J. R. Podolske, R. J. Salawitch, S. C. Wofsy, M. W. K. Ko, D. E. Anderson, M. R. Schoeberl, K. R. Chan, In situ measurements constraining the role of sulphate aerosols in mid-latitude ozone depletion. *Nature*, 363, 509-514, 1993.

Fall, R., D. Albritton, F. Fehsenfeld, W. Kuster, and P. Goldan, Laboratory Studies of Some Environmental Variables Controlling Sulfur Emissions from Plants. *J. Atmos. Chem.*, 6, 341-362, 1988.

Farman, J. C., B. G. Gardiner, and J. D. Shanklin, Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction. *Nature*, 315, 207-210, 1985.

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

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

Fried, A., B. Henry, R.A. Ragazzi, M. Merrick, J. Stokes, T. Pyzdrowski, and R. Sams, Measurements of Carbonyl Sulfide in Automotive Emissions and an Assessment of its Importance to the Global Sulfur Cycle. *J. Geophys. Res.*, 97, 14621-14634, 1992.

Fried, A., L. F. Klinger, and D. J. Erickson III, Atmospheric carbonyl sulfide exchange in bog microcosms. *Geophys. Res. Lett.*, 20, 129-132, 1993.

Gammon, R.H., and R.J. Charlson, Origins, Atmospheric Transformations, and Fate of Biologically Exchanged C, N, and S Gases. in Interactions of C, N, P, and S Biogeochemical Cycles and Global Change. R.Wollast, F.T. Mackenzie, and L. Chou Eds., Springer-Verlag, 1993.

Goldan, P.D., W.C. Kuster, D.L. Albritton and F.C. Fehsenfeld, The measurement of natural sulfur emissions from soils and vegetation: three sites in the eastern united states revisited. *J. Atmos. Chem.*, 5, 439-467, 1987.

Goldan, P., R. Fall, W. Kuster, and F. Fehsenfeld, Uptake of OCS by growing vegetation: a major tropospheric sink. *J. Geophys. Res.* 93, 14186-14192, 1988.

Granier, C., and G. Brasseur, Impact of heterogeneous chemistry on model predictions of ozone changes. *J. Geophys. Res.* 97, 18015-18033, 1992.

Green, S.A., Applications of fluorescence spectroscopy to environmental chemistry. Ph.D. Thesis. MIT/WHOI, WHOI-92-24, 1992 .

Gruner, P., and H. Kleinert, Die dammerungerscheinen, *Probl. Kosm. Phys.*, 10, 1-113, 1927.

Guenther, A., B. Lamb, and H. Westburg, U.S. National Biogenic Sulfur Emissions Inventory. In: Biogenic Sulfur in the Environment. Saltzman, E.S., and Cooper, W.J., eds., 14-30, 1989.

Hatchard, C.G., and C.A. Parker, A new sensitive chemical actinometer. II. potassium ferrioxalate as a standard chemical actinometer. *Proc. Royal Soc. London*, 235A, 518, 1956.

Hanst, P.L., L.L. Spiller, D.M. Watts, J.W. Spence, and M.F. Miller, Improved Measurements of Fluorocarbons, Carbon Tetrachloride, Carbonyl Sulfide and other Atmospheric Trace Gases. *J. Air Pollut. Control Ass.* 25, 1220-1226, 1975.

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

Hofmann, D. J., and S. Solomon, Ozone destruction through heterogeneous chemistry following the eruption of El Chichon. *J. Geophys. Res.* 94, 5029-5041, 1989.

Hofmann D.J., and S.J. Oltmans, The Effect of Stratospheric Water Vapor on the Heterogeneous Reaction Rate of ClONO_2 and H_2O for Sulfuric Acid Aerosol. *Geophys. Res. Lett.*, 19, 2211-2214, 1992.

Hynes, A. J., P. H. Wine, and J. M. Nicovich, Kinetics and mechanism of the reaction of OH with CS_2 under atmospheric conditions. *J. Phys. Chem.*, 92, 3846-3852, 1988.

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

Inn, E. C. Y., J. F. Vedder, and D. O'Hara, Measurements of stratospheric sulfur constituents. *Geophys. Res. Lett.*, 8, 5-8 1981.

Johnson, J. E., T. S. Bates, and P. S. Weiss, Factors affecting dissolved trace gas measurements using equilibrator techniques. *Manuscript In Preparation*, 1995.

Johnson, J. E. and T. S. Bates, Atmospheric measurements of carbonyl sulfide, dimethyl sulfide, and carbon disulfide using the electron capture sulfur detector. *J. Geophys. Res.*, 98, 23411-23421, 1993.

Johnson, J. E., A. R. Bandy, D. C. Thornton, and T. S. Bates, Measurements of atmospheric carbonyl sulfide during the NASA chemical instrumentation test and evaluation project: implications for the global COS budget. *J. Geophys. Res.*, 98, 22,443-22,448, 1993.

Johnson, J. E., and J. E. Lovelock, Electron capture sulfur detector: reduced sulfur species at the femtomole level. *Anal. Chem.*, 60, 812-816, 1988.

Johnson, J. E., and H. Harrison, Carbonyl sulfide concentrations in the surface waters and above the Pacific Ocean. *J. Geophys. Res.*, 91, 7883-7888, 1986.

Johnson, J. E., The role of the oceans in the atmospheric cycle of carbonyl sulfide. Ph.D. Dissertation, University of Washington, 1985.

Johnson, J. E., The lifetime of carbonyl sulfide in the troposphere. *Geophys. Res. Lett.*, 8, 938-940, 1981.

Jones, B. M. R., J. P. Burrows, R. A. Cox, and S. A. Penkett, OCS formation in the reaction OH with CS_2 . *Chem. Phys. Lett.*, 88, 372-376, 1982.

Jouzel, J., C. Lorius, J. R. Petit, C. Genthon, N. I. Barkov, V. M. Kotlyakov, and V. N. Petrov, Vostok ice core: a continuous isotope temperature record over the last climatic cycle (160,000 years). *Nature*, 329, 403-409, 1987.

Junge, C.E., C.W. Chagnon, and J.E. Manson, Stratospheric Aerosols. *J. Meteor.*, 18, 81-108, 1961.

Junge, C. E., Sulfur budget of the stratospheric aerosol layer, review paper presented at the International Conference of Structure, Composition and General Circulation of the Upper and Lower Atmospheres and Possible Anthropogenic Perturbations, Jan 14-25, 1974, Melbourne, Australia, published in the Proceedings.

Kanwisher, J., On the exchange of gases between the atmosphere and the sea. *Deep sea Res.*, 10, 195-207, 1963.

Kaufman, Y. J., Aerosol optical thickness and atmospheric path radiance. *J. Geophys. Res.*, 98, 2677-2692, 1993.

Kieber, D. J., J. A. McDaniel, and K. Mopper, Photochemical source of biological substrates in seawater: Implications for carbon cycling. *Nature*, 341, 637-639, 1989.

Kieber, R.J., X. Zhou, and K. Mopper, Formation of carbonyl compounds from uv-induced photodegradation of humic substances in natural water: fate of riverine carbon in the sea. *Limnol. Oceanogr.*, 35, 1503-1515, 1990.

Khalil, M. A. K., and R. A. Rasmussen, Global sources, lifetimes, and mass balances of carbonyl sulfide (OCS) and carbon disulfide (CS₂) in the earth's atmosphere. *Atmos. Environ.* 18, 1805-1813, 1984.

Kim, K-H., and M. O. Andreae, Carbon disulfide in seawater and the marine atmosphere over the North Atlantic. *J. Geophys. Res.*, 92, 14733-14738, 1987.

Kurylo, M. J., Flash photolysis resonance fluorescence investigations of the reactions of OH radicals with OCS and CS₂. *Chem. Phys. Lett.*, 58, 238-242, 1978.

Lamb, B. H., H. Westberth, G. Allwine, L. Barnesberger, and A. Guenther, Measurement of biogenic sulfur emissions from soil and vegetation: Application of dynamic enclosure methods with Natusch filter and GC/FPD analysis, *J. Atmos. Chem.*, 5, 417-437, 1987.

Legrand, M., and R. J. Delmas, A 220yr continuous record of volcanic H₂SO₄ in the Antarctic ice sheet. *Nature*, 328, 671-676, 1987.

Legrand, M., R. J. Delmas, and R. J. Charlson, Climatic forcing implications from Vostok ice core sulphate data. *Nature*, 334, 418-420, 1988.

Legrand, M., C. Feniet-Saigne, E. Saltzman, C. Germain, N. Barkov, and V. Petrov, Ice-core record of oceanic emissions of dimethylsulphide during the last climate cycle. *Nature*, 350, 144, 1991.

Liss, P. S., Gas transfer: experiments and geochemical implications. in Air-Sea Exchange of Gases and Particles, edited by P. S. Liss and W. G. N. Slinn, pp. 241-298, 1982.

Liss, P. S., and L. Merlivat, Air-sea gas exchange rates: introduction and synthesis, in The Role of Air-Sea Exchange in Geochemical Cycling, edited by P. Buat-Menard, pp. 113-129, 1986.

Liss, P. S., and P. G. Slater, Flux of gases across the air-sea interface. *Nature*, 247, 181-184, 1974.

Lovelock, J. E., A sensitive detector for gas chromatography. *J. Chromatogr.*, 1, 35, 1958.

Lovelock, J. E., United States Patent 3 725 009, 1973.

Lovelock, J. E., Gaia, a new look at life on earth. Oxford University Press, 1989.

Lovelock, J. E., and S. R. Lipsky, *J. Am. Chem. Soc.*, 82, 431, 1960.

Maroulis, P. J., and A. R. Bandy, Measurements of atmospheric concentrations of CS₂ in the Eastern United States. *Geophys. Res. Lett.*, 7, 681-684, 1980.

Martinerie, P., V. Y. Lipenkov, D. Raynaud, J. Chappellaz, N. I. Barkov, and C. Lorius, Air content paleo record in the Vostok ice core (Antarctica): A mixed record of climatic and glaciological parameters. *J. Geophys. Res.*, 99, 10565-10576, 1994.

McCormick, M. P., SAGE aerosol measurements. NASA reference publication, vol II, Jan. 1, 1980 to Dec. 31, 1980, 1986.

McElroy, M. B., R. J. Salawitch, and S. C. Wofsy, Antarctic O₃: Chemical mechanisms for the spring decrease. *Geophys. Res. Lett.*, 13, 1296, 1986.

Meshri, D. T., The modern inorganic fluorochemical industry. *J. Fluorine Chem.*, 33, 195-226, 1986.

Mihalopolous, N., B. C. Nguyen, J. P. Putaud, and S. Belviso, The oceanic source of carbonyl sulfide (OCS). *Atmos. Environ.*, 26A, 1383-1394, 1992.

Mihalopolous, N., J. P. Putaud, B. C. Nguyen, and S. Belviso, Annual variation of atmospheric carbonyl sulfide in the marine atmosphere in the southern Indian Ocean. *J. Atmos. Chem.*, 13, 73-82, 1991.

Mihalopolous, N., B. Bonsang, B. C. Nguyen, M. Kanakidou, and S. Belviso, Field observations of carbonyl sulfide deficit near the ground: possible implication of vegetation. *Atmos. Environ.*, 23, 2159-2166, 1989.

- Molina, M. J., and F. S. Rowland, Stratospheric sink for chlorofluoromethanes: chlorine-atom catalyzed destruction of ozone. *Nature*, 249, 810, 1974.
- Mopper, K., and E. T. Degens, in *The Global Carbon Cycle*, eds. B. Bolin, E. T. Degens, S. Kempe, and P. Ketner, 293-316, Wiley, New York, 1979.
- Mopper, K., and X. Zhou, Hydroxyl radical photoproduction in the sea and its potential impact on marine processes. *Science*, 250, 661-664, 1990.
- Mopper, K., X. Zhou, R.J. Kieber, D.J. Kieber, R.J. Sikorski, and R.D. Jones, Photochemical degradation of dissolved organic carbon and its impact on the oceanic carbon cycle. *Nature*, 353, 60-62, 1991.
- O'Brien, M. J., Detectors, In *Modern Practice of Gas Chromatography*, John Wiley and Sons, 254-265, 1977.
- Peng, T. H., T. Takahashi, and W. S. Broecker, Surface radon measurements in the North Pacific Ocean station Papa. *J. Geophys. Res.*, 79, 1772-1780, 1974.
- Philip, B., and H. Dautzenberg, Kinetic investigations of the formation and decomposition of monothiocarbonate in aqueous solution. *Z. Phys. Chem.*, 229, 210-224, 1965.
- Pos, W. H., and H. Berresheim, Automotive tire wear as a source for atmospheric OCS and CS₂. *Geophys. Res. Lett.*, 20, 815-817, 1993.
- Prather, M., Catastrophic loss of stratospheric ozone in dense volcanic clouds. *J. Geophys. Res.*, 97, 10187-10191, 1992.
- Prinn, R. G., R. F. Weiss, B. R. Miller, J. Huang, F. N. Alyea, D. M. Cunnold, P. J. Fraser, D. E. Hartley, and P. G. Simmonds, Atmospheric trends and lifetime of CH₃CCl₃ and global OH concentrations. *Science*, 269, 187-192, 1995.
- Radford-Knoery, J., and G. A. Cutter, Biogeochemistry of dissolved hydrogen sulfide species and carbonyl sulfide in the western North Atlantic Ocean. *Geochim. Cosmochim. Acta*, 58, 5421-5431, 1993.
- Rasmussen, R. A., M. A. K. Khalil, and S. D. Hoyt, The oceanic source of carbonyl sulfide. *Atmos. Environ.*, 16, 1591-1594, 1982.
- Raynaud, D., and B. Lebel, Total gas content and surface elevation of polar ice sheets. *Nature*, 281, 289-291, 1979.

- Raynaud, D., and J. M. Barnola, An Antarctic ice core reveals atmospheric CO₂ variations over the past few centuries. *Nature*, 315, 309-311, 1985.
- Raynaud, D., J. Jouzel, J. M. Barnola, J. Chappellaz, R. J. Delmas, C. Lorius, The ice record of greenhouse gases. *Science*, 259, 926-934, 1993.
- Rinsland, C. P., R. Zander, E. Mahieu, P. Demoulin, A. Goldman, D. H. Ehhalt, and J. Rudolph, Ground-based infrared measurements of carbonyl sulfide total column abundances: long-term trends and variability. *J. Geophys. Res.*, 97, 6995-6002, 1992.
- Rodriguez, J. M., M. K. W. Ko, and N. D. Sze, Role of heterogeneous conversion of N₂O₅ on sulphate aerosols in global ozone losses. *Nature*, 352, 134-137, 1991.
- Sandalls, F.J. and S.A. Penkett, Measurements of carbonyl sulfide and carbon disulfide in the atmosphere. *Atmos. Environ.*, 11, 197-199, 1977.
- Servant, J., The burden of the sulfate layer of the stratosphere during volcanic quiescent periods. *Tellus* 38B, 74-79, 1986.
- Sikorski, R. J., and R. G. Zika, Modeling mixed layer photochemistry of H₂O₂: Optical and chemical modeling of production. *J. Geophys. Res.*, 98, 2315-2328, 1993.
- Simmonds, P.G., A.J. Lovelock, and J.E. Lovelock, Continuous and ultrasensitive apparatus for the measurement of air-borne tracer substances. *J. Chromatog.*, 126, 3-9, 1976
- Smethie, W. M., T. T. Takahashi, D. W. Chapman, and J. R. Ledwell, Gas exchange and CO₂ flux in the tropical Atlantic Ocean determined from ²²²Rn and pCO₂ measurements. *J. Geophys. Res.*, 90, 7005-7022, 1985.
- Solomon, S., R. R. Garcia, F. S. Rowland, and D. J. Wuebbles, On the depletion of Antarctic ozone. *Nature*, 321, 755, 1986.
- Solomon, S., The mystery of the Antarctic ozone "hole". *Rev. Geophys.*, 26, 131-148, 1988.
- Solomon, S., R. W. Sanders, R. R. Garcia, and J. G. Keys, Increased chlorine dioxide over Antarctica caused by volcanic aerosols from Mount Pinatubo. *Nature*, 363, 245-248, 1993.
- Staubes, R. and H. -W. Georgii, Biogenic sulfur compounds in seawater and atmosphere on the Antarctic region. *Tellus*, 45B, 127-137, 1993.

Stedman, D. H., M. Z. Creech, P. L. Cloke, S. E. Kesler, and M. Gardner, Formation of CS_2 and OCS from decomposition of metal sulfides. *Geophys. Res. Lett.*, **1**, 858-860, 1984.

Steudler, P. A., and B. J. Peterson, Contribution of gaseous sulphur from salt marshes to the global sulphur cycle. *Nature*, **311**, 455-457, 1984.

Stickel, R. E., Z. Zhao, and P. H. Wine, Branching ratios for hydrogen transfer in the reactions of OD radicals with CH_3SCH_3 and $\text{CH}_3\text{SC}_2\text{H}_5$. *Chem. Phys. Letters*, **212**, 312-318, 1993.

Supina, W. R., The Packed Column in Gas Chromatography, Supelco Inc, 1974.

Taubman, S. J., and J. F. Kasting, Carbonyl sulfide: no remedy for global warming. *Geophys. Res. Lett.*, **22**, 803-805, 1995.

Thompson, B., S. Bay, D. Greenstein, and J. Laughlin, Sublethal effects of hydrogen sulfide in sediments of the urchin *Lytechinus pictus*. *Mar. Environ. Res.*, **31**, 309-321, 1991.

Thompson, H. W., L. F. Kearton, and S. A. Lamb, The kinetics of the reaction between carbonyl sulfide and water, *J. Chem. Soc.*, 1033-1037, 1935.

Tolbert, M.A., M.J. Rossi and D.M. Golden, Heterogeneous interactions of chlorine nitrate, hydrogen chloride, and nitric acid with sulfuric acid surfaces at stratospheric temperatures. *Geophys. Res. Lett.*, **15**, 847-850, 1988

Torgerson, T., G. Mathieu, R. H. Hesslein and W. S. Broecker, Gas exchange dependency on diffusion coefficient: Direct ^{222}Rn and ^3He comparisons in a small lake. *J. Geophys. Res.*, **87**, 546-556, 1982.

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

Turco, R. P., P. Hamill, O. B. Toon, R. C. Whitten, and C. S. Kiang, A one-dimensional model describing aerosol formation and evolution in the stratosphere, I, Physical processes and mathematical analogs. *J. Atmos. Sci.*, **36**, 699-717, 1979.

Turco, R. P., R. C. Whitten, O. B. Toon, Stratospheric aerosols: observation and theory. *Rev. Geophys. Space Phys.*, **20**, 233-279, 1982.

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

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

Uher, G., and M. O. Andreae, The diurnal cycle of carbonyl sulfide in seawater: a simple empirical model. In *Eurotrac Symposium*, P. Borrell, Ed., Garmisch-Partenkirchen, ISS, 1994.

Ulshofer, V. S., O. R. Flock, G. Uher, and M. O. Andreae, Photochemical production and air-sea exchange of carbonyl sulfide in the Eastern Mediterranean Sea. Submitted to *Marine Chemistry*, 1994.

Ulshofer, V. S., G. Uher, and M. O. Andreae, Evidence for a winter sink of atmospheric carbonyl sulfide in the northeast Atlantic Ocean. Submitted to *Geophys. Res. Lett.*, 1995.

Valentine, R.L., and R.G. Zepp, Formation of carbon monoxide from the photodegradation of terrestrial dissolved organic carbon in natural waters. *Environ. Sci. Technol.*, 27, 409-412, 1993.

Wahner, A., and A. Ravishankara, The kinetics of the reaction of OH with COS. *J. Geophys. Res.*, 92, 2189-2194, 1987.

Wallington, T. J., T. Ellermann, O. J. Nielsen, Atmospheric chemistry of dimethyl sulfide: UV spectra and self-reaction kinetics of CH_3SCH_2 and $\text{CH}_3\text{SCH}_2\text{O}_2$ radicals and kinetics of the reactions $\text{CH}_3\text{SCH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{O}_2$ and $\text{CH}_3\text{SCH}_2\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{SCH}_2\text{O} + \text{NO}_2$. *J. Phys. Chem.*, 97, 8442-8449, 1993.

Wanninkhof, R., Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.*, 97, 7373-7382, 1992.

Warneck, P., Chemistry of the Natural Atmosphere, Academic Press, San Diego, CA., 1988

Weiss, R. F., and B. A. Price, Nitrous oxide solubility in water and seawater. *Marine Chemistry*, 8, 347-359, 1980.

Weiss P. S., S. A. Andrews, J. E. Johnson, and O. C. Zafiriou, Photoproduction of carbonyl sulfide in south pacific ocean waters as a function of irradiation wavelength. *Geophys. Res. Lett.*, 22, 215-218, 1995a.

Weiss P. S., J. E. Johnson, R. H. Gammon, and T. S. Bates, A reevaluation of the open ocean source of carbonyl sulfide to the atmosphere. In Press, *J. Geophys. Res.*, 1995b.

Williams, P. M., and E. R. Druffel, Radiocarbon in dissolved organic matter in the central North Pacific Ocean. *Nature*, 330, 246-248, 1987.

Wine, P. H., R. C. Shah, and A. R. Ravishankara, Rate of reaction of OH with CS₂, *J. Phys. Chem.*, 84, 2499-2503, 1980.

Wolfe, G. V., The cycling of climatically active dimethyl sulfide (DMS) in the marine euphotic zone: biological and chemical constraints on the flux to the atmosphere. Ph. D. Thesis, University of Washington, Seattle, 1992.

Zepp, R.G. and M.O. Andreae, Photosensitized Formation of Carbonyl Sulfide in Sea Water, In: Effects of Solar Ultraviolet Radiation on Biogeochemical Dynamics in Aquatic Environments, Blough and Zepp, eds., WHOI Technical Report 90-09, Woods Hole 1990.

Zepp, R. G. and M. O. Andreae, Factors affecting the photochemical production of carbonyl sulfide in seawater. *Geophys. Res. Lett.*, 21, 2813-2816, 1994.

Zepp, R. G., and D. M. Cline, Rates of direct photolysis in aquatic environment. *Environ. Sci. Technol.*, 11, 359-366, 1977.

Zurer, P. S., Ozone depletion's recurring surprises challenge atmospheric scientists. *C&EN*, 8-18, May 24, 1993.

Appendix

```

*****Program SEASBURD.BAS*****
'
'SEASBURD stands for seasonal burden--designed to calculate the seasonal
'cycle of a gas for both the northern and southern hemispheres. The
input
'functions are files containing average hemispheric fluxes to/from each
'sink/source, in summer and winter.

OPTION BASE 1
DIM nBt(0 TO 3000)      'Northern burden total
DIM sBt(0 TO 3000)      'Southern burden total
DIM nflxsum(3000)       'Northern summer flux
DIM sflxsum(3000)       'Southern summer flux
DIM nflxwin(3000)       'Northern winter flux
DIM sflxwin(3000)       'Southern winter flux
DIM nflx(3000)          'Northern total flux
DIM sflx(3000)          'Southern total flux
DIM Flns(3000)          'Flux between the Northern and Southern hemispheres

a$ = "###.#####, ###.#####, ###.#####, ###.#####, ###.#####"

OPEN "nhsumflx.csv" FOR INPUT AS #1
OPEN "nhwinflx.csv" FOR INPUT AS #2
OPEN "shsumflx.csv" FOR INPUT AS #3
OPEN "shwinflx.csv" FOR INPUT AS #4
OPEN "test.csv" FOR OUTPUT AS #5      'main output file
OPEN "test1.csv" FOR OUTPUT AS #6     'test output file

INPUT "Enter delta t in days: ", delt      'entering 1.825 gives 200
points/year
INPUT "If NHwin is larger than NHsum type 1, else type 0: ", NHcase
'provides logic for calculation of flux
INPUT "If SHsum is less than zero type 1 else type 0: ", SHcase
INPUT "Enter the hemispheric mixing time: ", tau 'years
INPUT "Enter the number of years you want the model to run: ", years

nburden = 2.3      'starting burdens, based on 4.6 global burden
sburden = 2.3

nBt(0) = nburden
sBt(0) = sburden
dt = 365 / (2 * delt) - 1      'dt=time-steps per season
i% = 1
j% = 1
pi = 3.14159

DO UNTIL EOF(1)                                'get input data
    INPUT #1, nso, nss, nsc, nsv, nsb, nsa, nsch, nsp
LOOP
DO UNTIL EOF(3)

```

```

INPUT #3, sso, sss, ssc, ssv, ssb, ssa, ssoh, ssp
LOOP
DO UNTIL EOF(2)
    INPUT #2, nwo, nws, nwc, nwv, nwb, nwa, nwoh, nwp
LOOP
DO UNTIL EOF(4)
    INPUT #4, swo, sws, swc, swv, swb, swa, swoh, swp
LOOP
FOR h% = 0 TO years      'i% is for Northern summer, j% is for
Northern winter
    t = 0
    FOR i% = j% TO j% + dt
        IF nso < 0 THEN 'different ways to calculate flux depending if
                        the ocean is a source or sink
            nflxsum(i%) = 1 / dt * ((nss + nsc) * nburden / nBt(i% -
                1) + nsv + nsb + nsa + nBt(i% - 1) / nburden *
                (nso + nsch + nsp))
        ELSE
            nflxsum(i%) = 1 / dt * ((nso + nss + nsc) * nburden /
                nBt(i% - 1) + nsv + nsb + nsa + nBt(i% - 1) /
                nburden * (nsch + nsp))
        END IF
        IF swo < 0 THEN
            sflxwin(i%) = 1 / dt * ((sws + swc) * sburden / sBt(i% -
                1) + swv + swb + swa + (sBt(i% - 1) / sburden) *
                (swo + swoh + swp))
        ELSE
            sflxwin(i%) = 1 / dt * ((swo + sws + swc) * sburden /
                sBt(i% - 1) + swv + swb + swa + sBt(i% - 1) /
                sburden * (swoh + swp))
        END IF
        IF nwo < 0 THEN
            nflxwin(i%) = 1 / dt * ((nws + nwc) * nburden / nBt(i% -
                1) + nwv + nwb + nwa + nBt(i% - 1) / nburden *
                (nwo + nwoh + nwp))
        ELSE
            nflxwin(i%) = 1 / dt * ((nwo + nws + nwc) * nburden /
                nBt(i% - 1) + nwv + nwb + nwa + nBt(i% - 1) /
                nburden * (nwoh + nwp))
        END IF
        IF sso < 0 THEN
            sflxsum(i%) = 1 / dt * ((sss + ssc) * sburden / sBt(i% -
                1) + ssv + ssb + ssa + sBt(i% - 1) / sburden *
                (sso + ssoh + ssp))
        ELSE
            sflxsum(i%) = 1 / dt * ((sso + sss + ssc) * sburden /
                sBt(i% - 1) + ssv + ssb + ssa + sBt(i% - 1) /
                sburden * (ssoh + ssp))
        END IF
    
```

'input fluxes are calculated given a burden of 2.3 Tg / hemisphere
'fluxes are dependent on the deltaC between the source/sink and the atmospheric reservoir.

```
temp = sBt(i% - 1) / sburden
PRINT #6, USING a$; i%; temp; nflxsum(i%); sflxwin(i%) 'test
      output

Anh = (ABS(nflxsum(i%)) + ABS(nflxwin(i%))) / 2 'used to
                                             generate a
Ash = (ABS(sflxsum(i%)) + ABS(sflxwin(i%))) / 2 'smoothly
                                             changing
Rnh = (ABS(nflxsum(i%)) - ABS(nflxwin(i%))) / 2 'flux between
                                             sum and win
Rsh = (ABS(sflxsum(i%)) - ABS(sflxwin(i%))) / 2

Flns(i%) = 1 / (2 * tau * dt) * (nBt(i% - 1) - sBt(i% - 1))

IF NHcase = 0 THEN
    nflxsum(i%) = Anh * COS(i% / (dt * 2) * pi * 2) + Rnh
ELSE
    nflxsum(i%) = Rnh * COS(i% / (dt * 2) * pi * 2) + Anh
END IF
```

'these lines generate the periodic flux, and the conditional if/then allows the
'proper calculation regardless of the input.

```
IF SHcase = 0 THEN
    sflxwin(i%) = -Ash * COS(i% / (dt * 2) * pi * 2) + Rsh
ELSE
    sflxwin(i%) = Rsh * COS(i% / (dt * 2) * pi * 2) - Ash
END IF

nflx(i%) = nflxsum(i%)
sflx(i%) = sflxwin(i%)
nBt(i%) = nBt(i% - 1) + nflxsum(i%) - Flns(i%)
sBt(i%) = sBt(i% - 1) + sflxwin(i%) + Flns(i%)
temp1 = -Ash * COS(i% / (dt * 2) * pi * 2)
PRINT #5, USING a$; nBt(i%); nflxsum(i%); sBt(i%); sflxwin(i%);
      i%; temp1; Rsh
PRINT USING a$; nBt(i%); sBt(i%); nflxsum(i%); sflxwin(i%); t
t = t + 1 'variable of periodicity
```

NEXT i%

t = 0

'Northern wintertime flux

FOR j% = i% TO i% + dt

IF nwo < 0 THEN

```
    nflxwin(j%) = 1 / dt * ((nws + nwc) * nburden / nBt(j% -
      1) + nwv + nwb + nwa + nBt(j% - 1) / nburden *
      (nwo + nwoh + nwp))
```

```

ELSE
    nflxwin(j%) = 1 / dt * ((nwo + nws + nwc) * nburden /
        nBt(j% - 1) + nwv + nwb + nwa + nBt(j% - 1) /
        nburden * (nwoh + nwp))
END IF
IF sso < 0 THEN
    sflxsum(j%) = 1 / dt * ((sss + ssc) * sburden / sBt(j% -
        1) + ssv + ssb + ssa + sBt(j% - 1) / sburden *
        (sso + ssch + ssp))
ELSE
    sflxsum(j%) = 1 / dt * ((sso + sss + ssc) * sburden /
        sBt(j% - 1) + ssv + ssb + ssa + sBt(j% - 1) /
        sburden * (ssch + ssp))
END IF
IF nso < 0 THEN
    nflxsum(j%) = 1 / dt * ((nss + nsc) * nburden / nBt(j% -
        1) + nsv + nsb + nsa + nBt(j% - 1) / nburden *
        (nso + nsch + nsp))
ELSE
    nflxsum(j%) = 1 / dt * ((nso + nss + nsc) * nburden /
        nBt(j% - 1) + nsv + nsb + nsa + nBt(j% - 1) /
        nburden * (nsch + nsp))
END IF
IF swo < 0 THEN
    sflxwin(j%) = 1 / dt * ((sws + swc) * sburden / sBt(j% -
        1) + swv + swb + swa + (sBt(j% - 1) / sburden) *
        (swo + swch + swp))
ELSE
    sflxwin(j%) = 1 / dt * ((swo + sws + swc) * sburden /
        sBt(j% - 1) + swv + swb + swa + sBt(j% - 1) /
        sburden * (swch + swp))
END IF
temp = sBt(j% - 1) / sburden
PRINT #6, USING a$; j%; temp; nflxwin(j%); sflxsum(j%)

Anh = (ABS(nflxsum(j%)) + ABS(nflxwin(j%))) / 2
Ash = (ABS(sflxsum(j%)) + ABS(sflxwin(j%))) / 2
Rnh = (ABS(nflxsum(j%)) - ABS(nflxwin(j%))) / 2
Rsh = (ABS(sflxsum(j%)) - ABS(sflxwin(j%))) / 2

IF NHcase = 0 THEN
    nflxwin(j%) = Anh * COS(j% / (dt * 2) * pi * 2) + Rnh
ELSE
    nflxwin(j%) = Rnh * COS(j% / (dt * 2) * pi * 2) + Anh
END IF

IF SHcase = 0 THEN
    sflxsum(j%) = -Ash * COS(j% / (dt * 2) * pi * 2) + Rsh
ELSE
    sflxsum(j%) = Rsh * COS(j% / (dt * 2) * pi * 2) - Ash
END IF

```

```

Flns(j%) = 1 / (2 * tau * dt) * (nBt(j% - 1) - sBt(j% - 1))
nflx(j%) = nflxwin(j%)
sflx(j%) = sflxsum(j%)
nBt(j%) = nBt(j% - 1) + nflxwin(j%) - Flns(j%)
sBt(j%) = sBt(j% - 1) + sflxsum(j%) + Flns(j%)
temp2 = -Ash * COS(j% / (dt * 2) * pi * 2)
PRINT #5, USING a$; nBt(j%); nflxwin(j%); sBt(j%); sflxsum(j%);
      j%; temp2; Rsh
PRINT USING a$; nBt(j%); sBt(j%); nflxwin(j%); sflxsum(j%); t
t = t + 1
NEXT j%
NEXT h%

```

'Now print the results to the screen

```

Xstart = 0
Xfin = j% - 1
CLS
SCREEN 12
WINDOW (Xstart, .9 * nBt(1))-(Xfin, 1.1 * nBt(1))
FOR k% = 1 TO j%
LINE (k%, nBt(k%))-(k% + 1, nBt(k% + 1))
LINE (k%, sBt(k%))-(k% + 1, sBt(k% + 1))
NEXT k%
DO
PRINT "Type Q to quit "
reply$ = UCASE$(INPUT$(1))
LOOP UNTIL reply$ = "Q"
CLS
WINDOW (Xstart, 1.05 * sflxwin(1))-(Xfin, 1.05 * nflxsum(1))
FOR l% = 1 TO j%
LINE (l%, nflx(l%))-(l% + 1, nflx(l% + 1))
LINE (l%, sflx(l%))-(l% + 1, sflx(l% + 1))
NEXT l%
DO
PRINT "Type Q to quit "
reply$ = UCASE$(INPUT$(1))
LOOP UNTIL reply$ = "Q"
CLOSE
END

```

VITAE

Peter Weiss was born July 17, 1967 in Los Gatos, California. He attended high school in Yreka, California until 1984, and college at Southern Oregon State in Ashland, Oregon for two more years. He received a B.S. in Chemistry from the University of California in Santa Cruz in June of 1988. He then worked as an analytical chemist for Toxscan Inc. in Watsonville, California until coming to the University of Washington in 1990 to pursue a Ph.D. in chemistry. Peter's other interests include music, sports, mountaineering, skiing, and teaching.