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Joël Radford-Knoery
Old Dominion University

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THE BIOGEOCHEMISTRY OF HYDROGEN SULFIDE IN THE OPEN OCEAN

by
Joël Radford-Knœry
B.S. June 1986, McPherson College

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Abstract

The Biogeochemistry of Hydrogen Sulfide in the Open Ocean

Joël Radford-Knœry

Old Dominion University

Director: G. A. Cutter

Hydrogen sulfide is a poorly quantified component of the global sulfur cycle. In seawater, its dissolved species (dissolved sulfide) can react with trace metals to form dissolved complexes and insoluble compounds. Therefore, the study of dissolved sulfide in the open ocean can yield a better understanding of the biogeochemical cycles of sulfur and trace metals.

The biogeochemical cycling of dissolved sulfide was examined using specially developed sampling and analytical methods. In the western North Atlantic and central Equatorial Pacific Oceans, total dissolved sulfide concentrations ranged from <2 to 550 pmol/L; they were highest in the mixed layer and decreased with depth. The depth distribution and the rate of carbonyl sulfide (OCS) hydrolysis to hydrogen sulfide under oceanographic condition were determined because of their importance for the cycling of dissolved sulfide. Depth profiles of OCS show near-surface enrichment up to 150 pmol/L, and depletion at depth. These profiles suggest *in situ* OCS production, perhaps by organic matter regeneration. A budget was constructed to quantify the sources and sinks of dissolved sulfide in the Sargasso Sea mixed layer. The rate of dissolved sulfide production was 5.43 pmol/L/h (OCS hydrolysis + air/sea exchange), and the removal rate was 115.2 pmol/L/h (oxidation + particulate sinking). Similarities in profiles of dissolved sulfide and chlorophyll *a* or *Synechococcus sp.*, and results from recent phytoplankton culture studies, also suggest its production by phytoplankton; this source is necessary to balance the dissolved sulfide budget.

The conditional formation constant of $Cu(HS)^+$ was determined under oceanographic conditions and is $10^{9.1\pm0.6}$. The speciation of dissolved sulfide was computed with this constant and literature thermodynamic data using a multiequilibrium model. The calculation predicts that 80% of dissolved sulfide is uncomplexed in the mixed layer, while over 90% is complexed by zinc and copper below the pycnocline.

Because dissolved sulfide is rapidly cycled and interacts with trace metals, future studies should continue to quantify, under oceanographic conditions, its the interactions with trace metals, and its rate of production by phytoplankton.

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Chapter 1

General Introduction

Recently, there has been increased concerns over the anthropogenic impact on the geochemical cycles of carbon and sulfur. While the global impact of increased CO_2 emissions is still uncertain (*e.g.,* the current controversy over the magnitude of global warming; Trenberth, 1990), anthropogenic sulfur emissions have measurable effects on continental scales both in the atmosphere and at ground level (Charlson *et al.*, 1991, Likens and Butler, 1981). With respect to the latter, acidic precipitation due to elevated sulfate concentration disrupts freshwater ecosystems by altering the composition of the watershed (Galloway *et al.*, 1983).

On a larger scale, sulfur compounds may have an influence on mechanisms regulating the global climate. The stratosphere contains a layer with latitudinally uniform aerosol concentration where sulfate aerosols represents a substantial portion of the submicron particle size class (Junge, 1963). These stratospheric particles absorb and backscatter incident solar radiation before it reaches and warms the troposphere. Sources of these sulfur particles include gaseous emissions of sulfur dioxide (Charlson *et al.*, 1991) and carbonyl sulfide (OCS; Turco *et al.*, 1980, Servant, 1986). Other trace sulfur gases such as carbon disulfide and hydrogen sulfide also contribute to the concentration of stratospheric sulfate aerosols (*e.g.,* Toon *et al*, 1987).

The relative contributions of natural and anthropogenic sources of sulfur to the atmosphere is subject to debate (Sze and Ko, 1979, Herrmann and Jaeschke, 1984, Guenther *et al.*, 1989, Aneja, 1990), although it is clear that human activities play a major role in the atmospheric sulfur cycle (Rodhe, 1981, Charlson *et al.*, 1991). Factors that contribute to the uncertainty in quantifying the different natural sulfur sources include episodic and remote volcanic sulfur fluxes, and the smaller fluxes occurring over large areas (*i.e.*, DMS; Bates *et al.*, 1987) or large fluxes from small areas (*i.e.*, OCS; Andreae and Ferek, 1992, Cutter and Radford-Knœry, 1993).

The estimated anthropogenic and oceanic sulfur fluxes are approximately equal (Andreae, 1986, 1990, Bates *et al.*, 1987), and thus natural sulfur emissions from coastal areas may have an impact on sulfur deposition on land. It was shown that dimethyl sulfide (DMS) emissions from coastal seas of western Europe can contribute significantly to the non sea-salt sulfur burden of Scandinavian precipitation during spring blooms of phytoplankton (Turner *et al.*, 1988, Fletcher, 1989). In the atmosphere, DMS undergoes a series of oxidation reactions which ultimately yield atmospheric sulfate. Estimates of the atmospheric residence time of DMS with respect to its oxidative removal to SO_2 and methane sulfonic acid vary between one day and one week (Andreae *et al.*, 1988, Hynes and Wine, 1989, Berresheim *et al.*, 1990). The biogenic nature of DMS, the importance of its flux and the potential impact on climate of one of its degradation product (sulfate aerosols) led Charlson *et al.* (1987) to propose that DMS is a biological feedback mechanism influencing the climate of Earth.

Our understanding of the marine biogeochemistry of another reduced sulfur compound, hydrogen sulfide, is rudimentary. The magnitude and direction of the air/sea flux of hydrogen sulfide (H_2S_g) is geographically variable in the western North Atlantic Ocean, although it is predominantly into the sea (Andreae *et al.*, 1991). In the marine boundary layer of the remote atmosphere, H_2S_g concentrations are between 5 and 15 pptv (parts per trillion volume/volume; Cooper and Saltzman, 1989). Because the atmospheric lifetime of H_2S_g is on the order of only two days (Sze and Ko, 1980, Toon *et al.*, 1987) this wide distribution suggests a marine source of H_2S. Recently, hydrogen sulfide dissolved in seawater was observed in surface waters of the western North Atlantic at concentrations up to 1.1 nmol/L (Cutter and Krahforst, 1988, Luther and Tsamakis, 1989). Since hydrogen sulfide dissolved in seawater is readily oxidized (*i.e.*, by oxygen), its presence in the ocean raises the question of its sources and sinks.

Beside atmospheric influx (Andreae *et al.*, 1991), possible sources of dissolved hydrogen sulfide include OCS hydrolysis (Elliott *et al.*, 1987) or dissimilatory sulfate reduction in microenvironments (Cutter and Krahforst, 1988). To help sustain the observed levels of dissolved hydrogen sulfide with OCS hydrolysis as its single source, Luther and Tsamakis (1989) proposed that the complexation of dissolved sulfide with trace metals could shield it from rapid oxidation. Indeed, dissolved hydrogen sulfide and trace metals form complexes in seawater (Dyrssen and Wedborg, 1989, Elliott *et al.* 1989a). This suggests that the biogeochemical cycles of dissolved sulfide and trace metals may be linked, although experimental evidence to evaluate this coupling is not yet available.

The purpose of this dissertation is to examine the processes that affect the distribution and the speciation of hydrogen sulfide in the open ocean. The possible sources of dissolved hydrogen sulfide to the ocean, and its interactions with trace metals were assessed quantitatively. Specific aspects of the marine biogeochemistry of hydrogen sulfide that were examined by this research included:

1. The development of sampling and shipboard determination procedures in order to examine the distribution and forms of dissolved hydrogen sulfide species (*i.e.,* particulate and dissolved sulfide). These procedures are described in Chapter 2 of this dissertation, the data are discussed in Chapter 3 and 4, and are tabulated in Appendix A, B, and D.
2. An assessement of the contribution of OCS hydrolysis to the marine biogeochemistry of hydrogen sulfide. The rate constant of OCS hydrolysis in seawater was determined and used to compute the rate of production of dissolved hydrogen sulfide, as shown in Chapter 3.
3. The calculation of the chemical speciation of dissolved hydrogen sulfide in the open ocean using the conditional formation constant of copper-sulfide determined under oceanographic conditions. The procedures used to obtain this constant and the calculation of the equilibrium speciation of dissolved sulfide are described in Chapter 4.
4. The construction of a budget for hydrogen sulfide in the open ocean. This budget is given in Chapter 3.

Chapters 2, 3 and 4 were written so as to be self-contained, and thus Chapter 5 synthesizes the previous chapters, as well as suggesting further work that will enhance our understanding of the biogeochemistry of dissolved hydrogen sulfide. The remainder of this chapter is devoted to briefly reviewing the general chemistry of sulfur, and the aquatic chemistry and biogeochemistry of dissolved sulfide and OCS that are directly relevant to the objectives outlined above.

1.1 General Sulfur Chemistry

Sulfur (atomic number 16, mean atomic mass of 32.06 AMU) is the second element in Group VI of the Periodic Table. This group also includes oxygen, selenium and polonium. Table 1.1 summarizes selected physical properties of the element sulfur.

Among the ten known isotopes, six are radioactive (Table 1.2) and among the four stable isotopes, S-32 and S-34 are the most abundant in nature (95.1

and 4.2%, respectively), while S-33 and S-36 are the least abundant (0.74 and 0.016%, respectively).

For biogeochemical studies, sulfur isotopes can be used as tracers of chemical pathways and rates of transformation of sulfur compounds, allowing the construction of mass balances (Goldhaber and Kaplan, 1974). Sulfur can exist as several metastable allotropes at room temperature, but the only stable form below 370 K is α−sulfur. This form of sulfur is an arrangement of octahedral and puckered rings in monoclinic crystalline form. The chemical formula for this form of sulfur, which is also called elemental sulfur, is S_8 (Heslop and Jones, 1976).

For this dissertation, the compound of interest is hydrogen sulfide which belongs to the family of sulfane (or polysulfide) compounds. Polysulfides are the sulfur analogs of normal alkanes and obey the same nomenclature. They are compounds with formulae of the form H_2S_n with $n \leq 10$ (Schmidt and Siebert, 1973). They do not usually branch and are stable in solution with liquid sulfur, but slowly dissociate in water (Meyer, 1977). In water, their acidity increases with the number of sulfur atoms in the molecule (pK_1 of H_2S is 6.5 and pK_1 of H_2S_8 is 2.9; Meyer, 1977). The simplest sulfane is H_2S. While oxygen and sulfur are in the same group of elements, H_2S displays

Table 1.1: Atomic Properties of Sulfur. (Heslop and Jones, 1976)

Atomic number	16
Electronic configuration	[Ne]$3s^2 3p^4$
Covalent radius (pm)	104
Tetrahedral ionic radius (-II), (pm)	184
Tetrahedral ionic radius (+VI), (pm)	12
I(1) (kJ/mol)	1070
Electron affinity (kJ/mol)	-353
Electronegativity (Allred-Rochow)	2.44
Oxidation states	6, 4, 3, 2, 0, -2

little of water's strong hydrogen bonding properties as suggested by its low boiling temperature (Table 1.3).

The concentration of sulfur in the lithosphere is 0.05%, which ranks sulfur 15th in abundance among all the elements. The geochemical inventory of sulfur shows that sedimentary rocks have a mean sulfur content 10 to 20 times that of igneous rocks (Garrels and Mackenzie, 1971, Hallberg, 1976). The reservoir of sedimentary sulfur is dominated by evaporites (gypsum and anhydrite are two common sulfur-containing evaporites), and shales rich in pyritic ores. In the biosphere, sulfur seems to be evenly distributed among fauna and flora, with $\approx 1\%$ dry weight sulfur (Goldhaber and Kaplan, 1974). Proteinaceous material is relatively enriched in sulfur because of the presence of sulfur-containing amino acids (cysteine and methionine; Meyer, 1977).

These paragraphs attempted to give a broad overview of the rich geochemistry of sulfur and the following section presents aspects of the marine biogeochemistry of hydrogen sulfide and OCS. Carbonyl sulfide is a sulfur compound relevant to this study because its hydrolysis in seawater has been predicted to be a major source of dissolved sulfide to the open ocean (Elliott *et al.*, 1987).

Table 1.2: Radioisotopes of Sulfur. (Heslop and Jones, 1976).

Isotope	Mass (AMU)	Half-life (s)	Decay Energy (MeV)
^{29}S	-	-	3.60, 3.86, 5.35, 5.59
^{30}S	29.9847	1.35 ± 0.1	4.30, 4.98
^{31}S	30.97960	2.6	3.87
^{35}S	34.96903	7.52×10^6	0.167
^{37}S	36.9710	306	1.6, 4.8
^{38}S	37.9712	1.034×10^4	1.1, 1.88

1.1.1 Carbonyl Sulfide

As a chemical compound, carbonyl sulfide (OCS) is one of the few known inorganic molecules containing carbon and sulfur atoms. Its molecular weight is 60.07 AMU and it is gaseous at room temperature (Table 1.4).

Carbonyl sulfide is a by-product of textile fiber synthesis (Elliott *et al.*, 1989), but it is also produced by the reduction of SO_2 to elemental sulfur on a hot coal bed (Meyer, 1977). While OCS is a commercially unimportant sulfur compound, it is an important atmospheric sulfur gas because its average atmospheric boundary layer concentration is greater than 500 pptv, the largest of any sulfur gas. This elevated concentration, coupled with a slow reactivity with respect to atmospheric oxidation, allows it to diffuse to the stratosphere where it is oxidized to sulfate. During periods of low global volcanic activity (*i.e.*, low sulfur dioxide injections to the upper troposphere), OCS may be an important sulfur source for stratospheric sulfate aerosols (Sze and Ko, 1979, Servant, 1986).

An early study of the geochemistry of OCS predicted that the ocean could be a sink for atmospheric OCS because it hydrolyzes in seawater (Johnson, 1981). Later determinations of the solubility and concentration of OCS in surface seawater demonstrated that OCS is supersaturated with respect to

Table 1.3: Physical properties of H_2S. (Schmidt and Siebert, 1973)

Melting point (°C)	-80.6
ΔH (kcal/mol)	0.5676
Boiling point (°C)	-60.8
Critical temperature (°C)	100.4
Heat of formation (kcal/mol)	4.80
Liquid density (g/cm^3)	0.993
Dielectric constant (Liquid)	$\approx$ 10
Dipole moment (Gas, μ)	1.1×10^{-18}

the atmosphere (Rasmussen *et al.*, 1982), which thus raised questions about the origin and fate of dissolved OCS.

In an attempt to gain better understanding of the processes affecting OCS concentrations in surface waters, studies examined the distribution of OCS in estuaries, in nearshore waters, and in the open ocean (*e.g.,* Ferek and Andreae, 1983, 1984, Johnson and Harrison, 1986, Mihalopoulos *et al.*, 1991, Andreae and Ferek, 1992). These studies found that the distribution of OCS is dependent on several factors, which include seawater temperature, atmospheric boundary layer OCS concentration, and latitude (Johnson and Harrison, 1986), although it appear that OCS concentrations are better correlated with primary production (Andreae and Ferek, 1992). Concentrations of OCS and DMS seem to be positively correlated over wide concentration ranges (Mihalopoulos *et al.*, 1991). On average, concentrations of OCS range from 13–110 pmol/L in oligotrophic and coastal waters, respectively (Andreae and Ferek, 1992), although diurnal and seasonal concentration variations do occur (Ferek and Andreae, 1983, Andreae and Ferek, 1992, Mihalopoulos *et al.*, 1992). Recently, there has been increased awareness of the importance of coastal regions to the global OCS sea/air flux (0.3–0.6 Tg S/yr). While the concentration of OCS ranges by a factor of 10 between different biogeographical regions, the supersaturation ratio of surface waters with respect to the atmosphere varies between 1.5–8.9 for oligotrophic and coastal waters,

Table 1.4: Physical properties of C–S compounds. (Meyer, 1977)

	C_3S_2	CS_2	H_2CS_3	OCS
Melting point (°C)	0.5	-111.6	-26.9	-138.2
Boiling point (°C)	90	46.3	-	-50.2
Density (g/cm^3)	1.274	1.263 (20°C)	1.476 (25°C)	1.24 (-87°C)

respectively (Andreae and Ferek, 1992). Using flux estimates in the different biogeographical regions of the world ocean, Andreae and Ferek (1992) computed that the flux of OCS from the coastal ocean represents 62% of the the global oceanic flux. Furthermore, recent work suggests that estuaries may be "hot spots" of sea/air OCS fluxes (Andreae and Ferek, 1992, Cutter and Radford-Knœry, 1993).

Some features of the geochemistry of dissolved carbonyl sulfide have not been fully elucidated, including the presence of elevated OCS levels in anoxic sediments (Cutter and Radford-Knœry, 1993). Indeed, photochemical production and pyrite oxidation are the only known OCS production mechanisms (Ferek and Andreae, 1983, Stedman *et al.*, 1984). The possibility for biologically mediated production has not yet been thoroughly investigated.

1.1.2 Hydrogen Sulfide

As a chemical compound, hydrogen sulfide is a weak diprotic acid with pK's of 6.5 and 17.1 (Millero, 1986, Millero *et al.*, 1989). Hydrogen sulfide is sometimes used as raw material for the production of sulfur dioxide and elemental sulfur from natural gas. Hydrogen sulfide is a poisonous, colorless gas with a characteristically pungent odor of rotten eggs. For humans, lethal concentrations fall between those of hydrogen cyanide and of the more toxic OCS. In air, the explosivity threshold of H_2S is 4.3% (v/v; Meyer, 1977). The very strong propensity for dissolved sulfide to form essentially insoluble metal sulfide compounds makes it a valuable tool in qualitative and quantitative chemistry (Schmidt and Siebert, 1973).

In the marine environment, dissolved hydrogen sulfide results from biologically-mediated dissimilatory reduction of sulfate (*e.g.*, in anoxic sediments and basins) or abiotic processes similar to those occurring in hydrothermal vents (*e.g.,* Von Damm, 1990). The rich and diverse aquatic chemistry of hydrogen sulfide has been extensively examined and reviewed (*e.g.,* Millero 1986, Morse *et al.*, 1987, Millero and Hershey, 1989).

Hydrogen sulfide is a soluble gas; in water, it behaves as a weak acid. In water and at infinite dilution, the equation of the first dissociation of hydrogen sulfide is:

$$\mathrm{H_2S} \rightleftharpoons \mathrm{H^+} + \mathrm{HS^-} \tag{1.1}$$

with

$$\mathrm{K}_1^* = \frac{[\mathrm{H^+}][\mathrm{HS^-}]}{[\mathrm{H_2S}]} \tag{1.2}$$

In high ionic strength solutions such as seawater activities are not unity, and thus the conditional first dissociation constant, K_1^*, is used following the convention:

$$\mathrm{K}_1 = \mathrm{K}_1^* \frac{\gamma_{\mathrm{H^+}}\gamma_{\mathrm{HS^-}}}{\gamma_{\mathrm{H_2S}}} \tag{1.3}$$

where γ_i is the activity coefficient of the species i, while square brackets indicate the molar concentration of i, and K_1 is the thermodynamic first dissociation constant for hydrogen sulfide. Literature values for the first ionization constant of hydrogen sulfide in seawater vary by less than 0.1 log unit (Morse *et al.*, 1987) indicating good agreement between researchers. An equation describing the variations of pK_1^* as a function of ionic strength and temperature using these values is given in Millero and Hershey (1989), and yields $\mathrm{pK}_1^*=6.52$ at 25°C and 35 psu. Because seawater $p\mathrm{H}$ varies between 8.2 and 7.5 (Broecker and Peng, 1982) over 90% of hydrogen sulfide is ionized to bisulfide ($\mathrm{HS^-}$). Estimates of pK_2 range between 12.44 and 18.9, although the higher value is probably more accurate (Millero and Hershey, 1989), indicating that its value is known with less precision than pK_1^*. Nevertheless, the proportion of $\mathrm{S^{2-}}$ is less than 10^{-2}–10^{-8}% of dissolved hydrogen sulfide species at the *p*H of most natural waters. For the purpose of clarity in the remainder of this dissertation, "dissolved sulfide" includes the different forms that hydrogen sulfide takes when it is dissolved in seawater.

In addition to exhibiting acid-base behavior in seawater, dissolved sulfide can also be involved in redox reactions. At thermodynamic equilibrium, the redox speciation of dissolved sulfide (and sulfur) can be predicted using an Eh–*p*H diagram similar to that presented in Figure 1.1. For seawater at *p*H∼8, assuming that Eh is controlled by the H_2O/O_2 redox couple (*i.e.*, Eh=0.75; Stumm and Morgan, 1981), this diagram indicates that sulfate concentrations should exceed those of dissolved sulfide by many tens of orders of magnitude because the reduction of sulfate involves the transfer of eight electrons to the sulfur atom. Observed concentrations of dissolved sulfide are "only" six orders of magnitude smaller than sulfate (pico– to nanomolar range *vs.* 28 mmol/L), and thus vastly out of equilibrium (Cutter and Krahforst, 1988). This lack of equilibrium with the H_2O/O_2 redox couple indicates that dissolved sulfide is unstable with respect to its oxidation by oxygen.

The rate of oxidation of dissolved sulfide by dissolved oxygen has been extensively examined (Ostlund and Alexander, 1963, Avrahami and Golding, 1968, Cline and Richards, 1969, Chen and Morris, 1972, Millero *et al.*, 1987). While the results vary by two orders of magnitude, recently determined rates converge toward a single value (Morse *et al.*, 1987). The half-time for the oxidation of dissolved sulfide by oxygen in air-saturated seawater is about one day (Millero and Hershey, 1989). A general equation for the oxidation of sulfide by oxygen is (Millero *et al.*, 1987):

$$\mathrm{aS}_t + \mathrm{bO}_2 \longrightarrow \text{products} \tag{1.4}$$

The overall rate equation is $-\mathrm{d}[\mathrm{S}]_t/\mathrm{d}t = \mathrm{k}_n[\mathrm{S}]_t^a[\mathrm{O}_2]^b$ where S_T is the concentra-

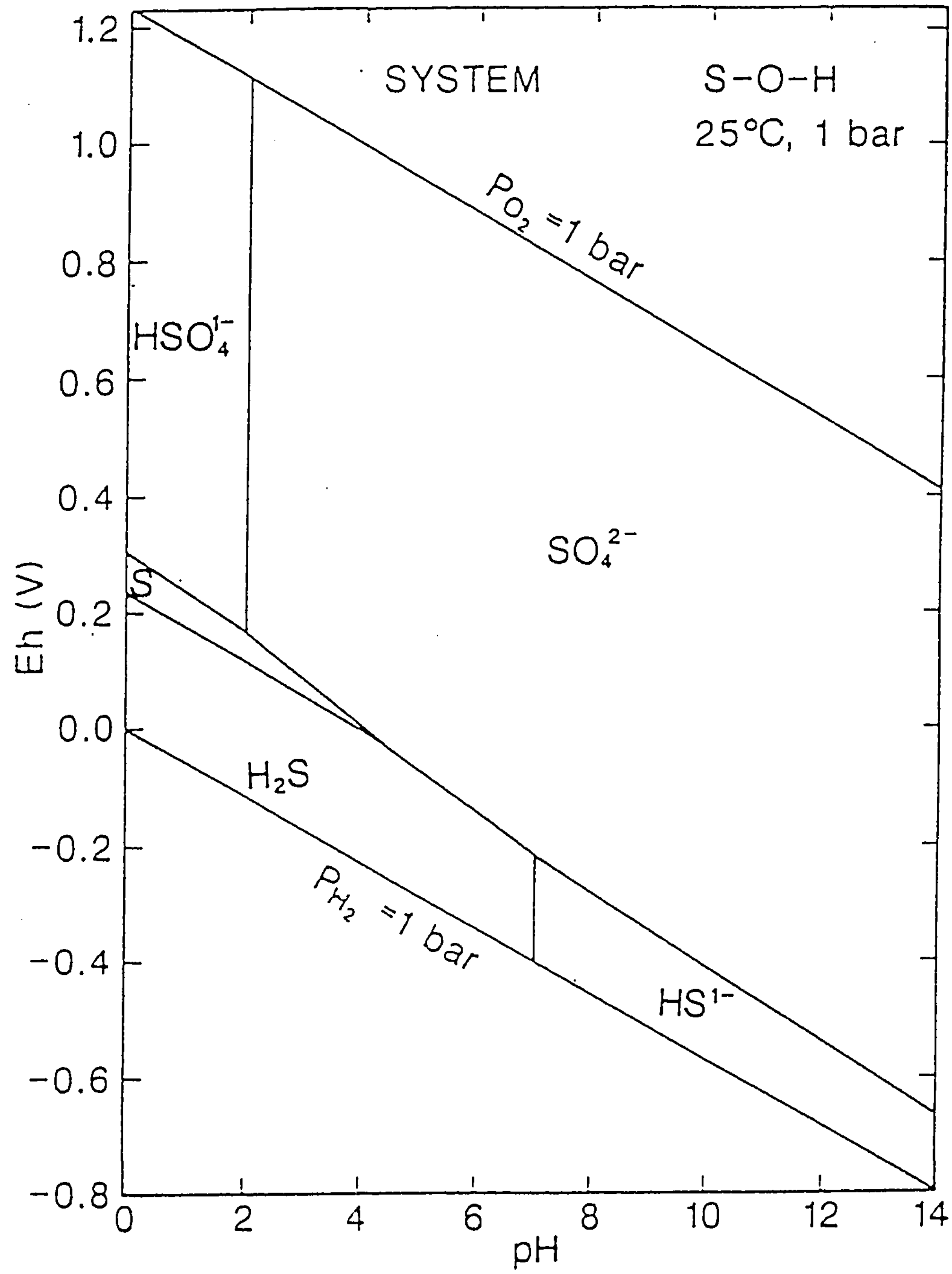

Figure 1.1: Eh-pH diagram of the sulfur-oxygen-hydrogen system. Activity of dissolved sulfur is 10^{-3} M, temperature is 25°C and pressure is 1 atmosphere (from Brookins, 1988).

tion of dissolved sulfide, k_n is the rate constant and n=a+b is the overall order of the reaction. When *p*H is constant and O_2 concentration is much greater than dissolved sulfide concentration, the rate expression can be simplified to $-d[S]_t/dt = k_1[S]_t$, where $k_1 = k_2[O_2]$, and where $[S]_t$ is the concentration of dissolved sulfide. This simplification assumes that a=b=1 (as shown experimentally by Millero *et al.*, 1987); k_1 becomes the pseudo-first order rate constant. The half-time of dissolved sulfide oxidation is then $T_{1/2} = \ln(2)/k_1$. Avrahami and Golding (1968) proposed that the rate limiting step for the oxidation of low levels of dissolved sulfide might be:

$$HS^- + \frac{3}{2}O_2 \longrightarrow SO_3^{2-} + H^+ \tag{1.5}$$

where sulfite is rapidly oxidized along the two following pathways:

$$SO_3^{2-} + \frac{1}{2}O_2 \longrightarrow SO_4^{2-} \tag{1.6}$$

and

$$SO_3^{2-} + HS^- + \frac{1}{2}O_2 \longrightarrow S_2O_3^{2-} + OH^- \text{ and } S_2O_3^{2-} + \frac{1}{2}O_2 \longrightarrow SO_4^{2-} + S^0 \tag{1.7}$$

According to Equation 1.5, the rate limiting step is dependent on the proportion of HS^-, and therefore on *p*H.

Chen and Morris (1972) and Millero *et al.*, (1987) studied the effects of *p*H on the oxidation rate of dissolved sulfide by oxygen. Conflicting results were obtained in alkaline medium (*p*H $\geq$ 8). While Chen and Morris (1972) found a complex relationship between the oxidation rate and *p*H, Millero *et al.* (1987) found that the dependence on *p*H was minimal. These differences were tentatively attributed to varying levels of trace metal contamination due to the use of several buffers to maintain the solutions at the *p*H of interest (Millero *et al.*, 1987).

Further exploring trace metal catalysis of the oxidation of dissolved sulfide by oxygen, Chen and Morris (1972) and Vazquez *et al.* (1989) found that the presence of trace metals (M^{2+}) shortened the induction period of the reaction as well as accelerated the rate of oxidation. They both suggested that the formation of free radicals activates autooxidation:

$$M(HS)^+ + O_2 \longrightarrow M^{2+} + S^0 + HO_2^- \tag{1.8}$$

and

$$HO_2^- + HS^- \longrightarrow 2OH^- + S^0 \tag{1.9}$$

Chen and Morris (1972) found that the trace metal-induced increase of the oxidation rate of dissolved sulfide follows the sequence $Ni^{2+} > Co^{2+} > Mn^{2+} > Cu^{2+} > Fe^{2+} > Ca^{2+} = Mg^{2+}$, while Vazquez *et al.*, (1989) found that catalysis increased along the sequence $Fe^{2+} > Cu^{2+} > Fe^{3+} > Ni^{2+} > Co^{2+} > Mn^{2+}$. The reasons for this discrepancy are not readily apparent, and may be due to differences in experimental conditions (*e.g.,* concentrations of dissolved sulfide).

Oxidants such as hydrogen peroxide (H_2O_2) and iodate (IO_3^-) also react with dissolved sulfide. The rate of dissolved sulfide oxidation by H_2O_2 exhibits *p*H dependence, which suggests that the oxidation of HS^- is faster than the oxidation of either H_2S and S^{2-} (Millero *et al.*, 1989). The rate of reaction is then highest at the *p*H of seawater due to the weak acid/base behavior of hydrogen sulfide. Nevertheless, at 25°C and at the H_2O_2 concentrations found in the surface ocean (*e.g.,* 0.1–0.2 μmol/L; Zika *et al.*, 1985), the half-life for the oxidation of dissolved sulfide by H_2O_2 is 2800 h (Millero *et al.*, 1989).

The rate of dissolved sulfide oxidation by IO_3^- was examined in seawater by Zhang and Whitfield (1986). Using stoichiometric measurements and the concentration of reaction end-products, these workers found that dissolved sulfide was oxidized to elemental sulfur and iodate reduced to molecular iodine according to the reaction:

$$5HS^- + 2IO_3^- + 7H^+ \rightleftharpoons I_2 + 5S^0 + 6H_2O \qquad (1.10)$$

In seawater at 25°C, Zhang and Whitfield observed that the reaction proceeded at a rate k' of 105–162 $mol^{-1/2}/min$ according to the equation:

$$\frac{d[S_T]}{dt} = k'[IO_3^-]^{0.5}[S_T] \qquad (1.11)$$

where S_T is the the concentration of dissolved sulfide. Thus, at the iodate concentrations found in the open ocean (0.2–0.5 μmol/L; Wong and Brewer, 1977, Jickells *et al.*, 1988), the pseudo-first order removal rate of dissolved sulfide by iodate is 5–6 h^{-1}. While this rapid rate of reaction may have been observed at elevated concentrations of dissolved sulfide, recent evidence suggests that this rate may not be directly applicable to the nanomolar levels observed in seawater. Indeed, experiments by Luther and Tsamakis (1989) indicate that the oxidation of dissolved sulfide by iodate may be inhibited by the formation of metal sulfide complexes. Therefore, the rate of dissolved sulfide oxidation by iodate may depend on its speciation. Dissolved sulfide may be either complexed by a metal (M^{+m}) to form $MS_s(SH)_h^{m-2s-h}$ (s and h are stoichiometric coefficients; Elliott *et al.*, 1989a), or found as free sulfide (the uncomplexed species H_2S_{aq}+HS^-+S^{2-}).

In anoxic marine environments, the interactions between metals and dissolved sulfide have been extensively studied (*e.g.,* Spencer and Brewer, 1971, Emerson *et al.*, 1979, Emerson *et al.*, 1983, Dyrssen 1985 and 1988, Jacobs *et al.*, 1985 and 1987, Landing and Lewis, 1991, Lewis and Landing, 1991). An approach commonly used by these researchers was to compare dissolved metal and sulfide concentration data with calculated ion activity products.

These calculations suggested that precipitation of trace metals with sulfide appears to be an important process, although it is not the only one controlling the concentration of trace metals in solution (Jacobs *et al.*, 1987). Their calculations were performed using solubility products for pure metal sulfide phases (*e.g.,* MS_s produced from the reaction between dissolved metal and sulfide), but other important species (both solids and dissolved complexes) may have been overlooked (Jacobs *et al.*, 1987). The frequent discrepancies between the predictions of metal distribution and the observed metal solubilities may have come from the omission of organic and polysulfide ligands from the calculations, and the uncertainties of thermodynamic data (Jacobs *et al.*, 1987). As an example, laboratory studies of the solubility of copper in sulfidic waters that included polysulfide complexes (Shea and Helz, 1988) could duplicate the observed concentrations of copper in solution with the solubility of CuS (covellite). More recently, comprehensive approaches for calculating the speciation of dissolved constituents in anoxic seawater, neglecting as few as possible complexation reactions, are used with increased success and can better approximate the observed speciation of metals (*e.g.,* Lewis and Landing, 1991, Landing and Lewis, 1991).

Until recently, the marine geochemistry of dissolved sulfide was thought to be limited to hydrothermal plumes or anoxic environments. However, the discovery of nanomolar levels of dissolved sulfide in the mixed layer of the western North Atlantic Ocean (Cutter and Oatts, 1987) showed that this was not the case, and opened a new field of investigations which has only begun to be explored (Cutter and Krahforst, 1988, Luther and Tsamakis, 1989). The available data on the distribution of dissolved sulfide indicate that concentrations are higher near the surface (0.4–2.5 nmol/L), and lower at depth (Cutter and Krahforst, 1988, Luther and Tsamakis, 1989). Concentrations of dissolved sulfide exhibit cross-shelf gradients, decreasing seaward (Cutter and Krahforst, 1988). Dissolved sulfide concentrations show diel variability; pre-dawn concentrations of dissolved sulfide are the highest, decrease throughout the daylight hours, and increase at night (Cutter and Krahforst, 1988). These variations suggest the influence of photochemical processes including photoproduction of oxidants (Cutter and Krahforst, 1988), and photolytic metal-sulfide bond breaking (Luther and Tsamakis, 1989).

Although other sources have been proposed, the only identified dissolved sulfide source to the surface of the open ocean is the hydrolysis of carbonyl sulfide (OCS; Elliott *et al.*, 1987). For the surface ocean, Elliott *et al.* (1987) predicted that dissolved sulfide could be present in the same concentration range as OCS, because its rate of hydrolysis and the rate of oxidation of dissolved sulfide by oxygen are similar. Elliott *et al.* (1989b) examined the hydrolysis of carbonyl sulfide under various conditions of pH and temperature, and concluded that the hydrolysis mechanisms are pH dependent. At low pH, the hydrolysis is unimolecular, following the pathway:

$$\mathrm{OCS} + \mathrm{H_2O} \rightleftharpoons \mathrm{OCS{\cdot}H_2O} \longrightarrow \mathrm{CO_2} + \mathrm{H_2S} \qquad (1.12)$$

and in alkaline medium, the reaction is:

$$\mathrm{OCS} + \mathrm{OH^-} \rightleftharpoons \mathrm{OCS{\cdot}OH^-} \longrightarrow \mathrm{CO_2} + \mathrm{SH^-} \qquad (1.13)$$

These researchers also proposed that the monothiocarbonate intermediates in Equations 1.12 and 1.13 might react in the following manner:

$$\mathrm{OCS{\cdot}H_2O} \rightleftharpoons \mathrm{OCS{\cdot}OH^-} \rightleftharpoons \mathrm{OCS{\cdot}O^{2-}} \qquad (1.14)$$

While the contribution of OCS hydrolysis to the budget of dissolved sulfide can be quantified, it is only one of the possible sources of dissolved sulfide to the open ocean.

Other sources of dissolved sulfide have been proposed (*i.e.*, dissimilatory sulfate reduction in microenvironments; Cutter and Krahforst, 1988), but they have not yet been quantified. Another source that has been proposed is the release of dissolved sulfide by phytoplankton (Andreae, 1986). Indeed, the biochemical pathways for assimilatory sulfate reduction are similar in plankton and terrestrial plants, and thus their mechanisms for regulating the concentration of intracellular reduced sulfur may be similar as well (Andreae, 1986). For terrestrial plants, the release of hydrogen sulfide shunts the intracellular sulfur cycle and helps to decrease excessive levels of reduced sulfur (see Rennenberg, 1991 for a recent review).

In the oxygenated water column, it is also important to quantify the interactions between trace metals and dissolved sulfide because they affect its oxidation rate, and thus these interactions may be significant for their cycling in surface waters. At present, experimental approaches to define the speciation of dissolved sulfide in relation to trace metals are limited to anoxic environments with elevated concentrations of dissolved sulfide because the higher concentrations of metal complexes and precipitates can be analytically determined. In contrast to this empirical approach, thermodynamic calculations have been used for surface waters in order to identify metal sulfide complexes, and hence the concentrations of free and complexed sulfide.

Dyrssen and Wedborg (1989) and Dyrssen (1988) used thermodynamic equilibrium calculations to investigate the speciation of 0.1–0.3 nmol/L dissolved sulfide in the presence of trace metals concentrations that are found in the ocean. The formation constants of metal sulfide complexes were taken from the critical compilation of Smith and Martell (1976), and from extrapolations using dithizone as a model ligand (Dyrssen, 1985). For copper levels greater than 0.1 nmol/L, these calculations show that the speciation of appears to be independent of the concentrations of dissolved sulfide because it is bound in CuS complexes. Below 0.1 nmol/L copper, complexes with zinc and mercury begin to play important roles for the speciation of dissolved sulfide (Dyrssen and Wedborg, 1989). Since seawater concentration of copper range between 0.5 and 6 nmol/L (Bruland, 1983), these calculations indicate that copper should play the dominant role in the speciation of dissolved sulfide in the open ocean. However, these calculations did not include the effects of copper and zinc complexation by organic ligands (*e.g.*, Coale and Bruland, 1988, Bruland, 1989). Organic complexation may decrease the availability of copper and zinc to their complexation by dissolved sulfide. In addition, more recent examinations of the complexation of metals by dissolved sulfide (*e.g.*, Elliott *et al.*, 1989a, Elliott and Rowland, 1990) suggested that the calculation of the formation constants for copper-sulfide and mercury-sulfide complexes may have been substantially overestimated. It is then highly desirable to obtain accurate values of the formation constants of metal sulfide complexes to be able to accurately predict the speciation of dissolved sulfide in the open ocean.

While the speciation of dissolved sulfide is subject to debate, the known mechanisms for the removal of dissolved sulfide from seawater include oxidation, precipitation, and adsorption onto sinking particles. Oxidation by iodate, oxygen and hydrogen peroxide is likely to represent an important term in the removal of dissolved sulfide. The rates of reaction between dissolved sulfide and these oxidants have been determined in seawater (see above). Luther and Tsamakis (1989) suggest that these rates of oxidation may be be affected by the speciation of dissolved sulfide at nanomolar levels. In contrast to these reactions which change the oxidation state of sulfide-sulfur, sinking of dissolved sulfide (after reaction with trace metals) associated with particles "physically" removes sulfide from the upper ocean. The magnitude of the flux of sinking particulate sulfide has not yet been quantified. If a substantial portion of sinking particulate sulfide comprises metal sulfide compounds, then this flux may also be important for the cycling of trace metals.

In summary, this brief review highlighted gaps in our understanding of the biogeochemistry of hydrogen sulfide that this dissertation aims at closing. The data that will be used in this dissertation were collected in the western North Atlantic and central Equatorial Pacific Oceans and cover a wide range of biogeographical regions. Furthermore, these data are augmented by results from laboratory experiments to determine the rate constant of OCS hydrolysis, and the interactions between copper and dissolved sulfide. A crucial aspect of these experiments is that they were performed under oceanographic conditions, in order to apply the results with a minimum of assumptions and obtain reliable results.

Chapter 2

Experimental Methods

It has become increasingly important to distinguish between natural and anthropogenic sources of sulfur to the atmosphere because these sources are of equal magnitude (Andreae, 1990), and because tropospheric sulfur has been proposed as a negative feedback to the global warming of Earth (Charlson *et al.*, 1987). The natural flux of sulfur gases into the atmosphere is dominated by oceanic emissions. Dimethyl sulfide and carbonyl sulfide (OCS) represent over 95% and 1% of this flux, respectively, while the flux of hydrogen sulfide (H_2S) is $\leq 1\%$ (Andreae, 1990, Andreae *et al.*, 1991). A direct link between the biogeochemical cycles of the latter two gases has been proposed since the hydrolysis of dissolved OCS yields hydrogen sulfide (Elliott *et al.*, 1987). Hydrogen sulfide is a weak diprotic acid that exists as H_2S_{aq}, HS^-, and S^{2-}; collectively, these three dissolved, uncomplexed species can be termed "free sulfide". However, both HS^- and S^{2-} can react with metals to form dissolved metal sulfide complexes and precipitates (*e.g.*, Dyrssen, 1988, Elliott *et al.*, 1989a), and thus may affect trace metal cycling. Therefore, hydrogen sulfide dissolved in natural waters can exist as "complexed sulfide" and "free sulfide" ($H_2S_{aq}+HS^-+S^{2-}$); "total dissolved sulfide" is the sum of free sulfide and complexed sulfide that are dissolved in water. For these reasons, the simultaneous determination of OCS and total dissolved sulfide in the aquatic environment is useful to the study of these important sulfur gases, as well as to the study of trace metals.

Because total dissolved sulfide and OCS are highly reactive and are found at pico- to nanomolar concentrations in oxygenated natural waters (Cutter and Oatts, 1987, Luther and Tsamakis, 1989, Johnson and Harrison, 1986, Leck and Bagander, 1988, Andreae and Ferek, 1992), determinations in the field are necessary. There are several methods for the shipboard determination of either total dissolved sulfide (Cutter and Oatts, 1987, Luther and Tsamakis, 1989) or OCS (Johnson and Harrison, 1986, Leck and Bagander, 1988) in oceanic waters. However, these methods do not afford the simultaneous determination of both compounds at the picomolar concentrations encountered in oligotrophic waters. In particular, the photoionization detector used by Cutter and Oatts (1987) is not sensitive to OCS, while other procedures do not use sample acidification that enables the quantitative recovery of total dissolved sulfide as H_2S_g.

Sampling procedures and analytical techniques for the simultaneous determination of total dissolved sulfide (*i.e.,* complexed sulfide plus free sulfide), and OCS in a variety of natural waters are described in this chapter. These procedures were used to collect the data that are discussed in Chapter 3 and 4. Sampling procedures are specially designed to minimize contamination and loss; they are followed by the gas stripping of an acidified sample, cryogenic trapping, gas chromatography, and quantification of the evolved H_2S_g and OCS_g using a flame photometric detector (FPD). Low detection limits allow the use of small samples while maintaining good precision. In addition, these procedures have been applied to the determination of total inorganic sulfide in suspended particles, and extended to the determination of headspace hydrogen sulfide (H_2S_g). This determination allows the concentration of free sulfide that is in equilibrium with H_2S_g to be calculated. Complexed sulfide can then be estimated from the difference between total dissolved sulfide and free sulfide.

2.1 Experimental Section

2.1.1 Sampling Apparatus

Water column samples are acquired using Teflon-coated Go-Flo sampling bottles (General Oceanics) modified to allow their pressurization by filtered (0.2 μm) nitrogen gas. The air bleed and sampling valves are replaced by a nylon connector (# NY-600-1-OR, Swagelok) and by a 3/8" Teflon plug valve (Berghoff America), respectively. Samples are transferred from the Go-Flo's into 4-L polyethylene Cubitainers (Cole-Parmer) whose caps are modified to accommodate two ports. One port is fitted with 3/8" I.D. Tygon tubing that can be closed by a Mohr clamp. The second port has 1/8" O.D. Teflon tubing extending 25 cm into the Cubitainer, while the other end of the tubing is fitted with a 2-way polycarbonate stopcock (Cole-Parmer). The first port is used for sample transfer, and the second one permits the complete expulsion of air bubbles.

Porewater samples are obtained using a pressurized core barrel assembly described by Jahnke (1988). For each sampling port on the core barrel, a porous polyethylene rod (40×2 mm, 120 mesh; Porex) is used to prefilter the sample into a gas-tight syringe (10 mL; Hamilton). These syringes are fitted with a 3-way stopcock to allow rinsing and removal of air from the syringe barrel, while isolating the sample from the atmosphere.

The sampling gear is cleaned using detergent wash (Micro), distilled, deionized water rinsing, acetone rinsing (for Cubitainers and syringes only), one day soak in 0.5 M HCl, and 3 deionized water rinses.

2.1.2 Analytical Apparatus.

The analytical system consists of two main components that are represented in Figure 2.1. The stripping/trapping component is largely adapted from the apparatus used for total dissolved sulfide (Cutter and Oatts, 1987) and metalloid determinations (Cutter *et al.*, 1991). The internal volume (300 mL) of the stripping vessel is gravimetrically calibrated by filling with deionized water until overflow (Figure 2.1). The gas dispersion tube is made of Goretex microporous tubing (Cutter and Oatts, 1987). The sample and drain ports have Teflon stopcocks, while the reagent injection port is a Teflon fitting (Swagelok) housing a Teflon-backed, silicone rubber septum. For samples where OCS and total dissolved sulfide concentrations exceed 100 pmol/L, a 50 mL stripper can be used. A chemical scrubber that retains H_2S_g is used for the determination of OCS concentrations in samples with ≥ 2 μmol/L total dissolved sulfide (*e.g.*, sediment porewaters). The scrubber is placed between the stripper and water trap, and consists of a 5 cm length of 1/4" O.D. Teflon tubing housing a strip of Whatman AF/41 filter paper (10×2.5 cm) tightly wound in a roll. The filter paper is impregnated with a 2% (w/v) solution of silver nitrate. The water vapor trap is a borosilicate glass U-tube (36 cm long, 14 mm I.D.; Cutter *et al.*, 1991) immersed in 2-propanol held at −50°C by a cryogenic probe (Neslab). a cryogenic trap made of U-shaped borosilicate glass tubing (1/4" O.D.) loosely packed with silanized glass wool (Supelco; Cutter *et al.*, 1991) collects H_2S_g and OCS_g that are stripped from the sample. A simpler trap consisting of 40 cm of 1/8" Teflon tubing that is loosely packed with silanized glass wool may be used with 50 mL stripping vessels. The cryogenic trap is connected to a 6-way stainless steel valve (Teflon-filled rotor; Valco). With the valve in the *strip/trap* position, helium stripping gas passes through the cryogenic trap before being vented to the

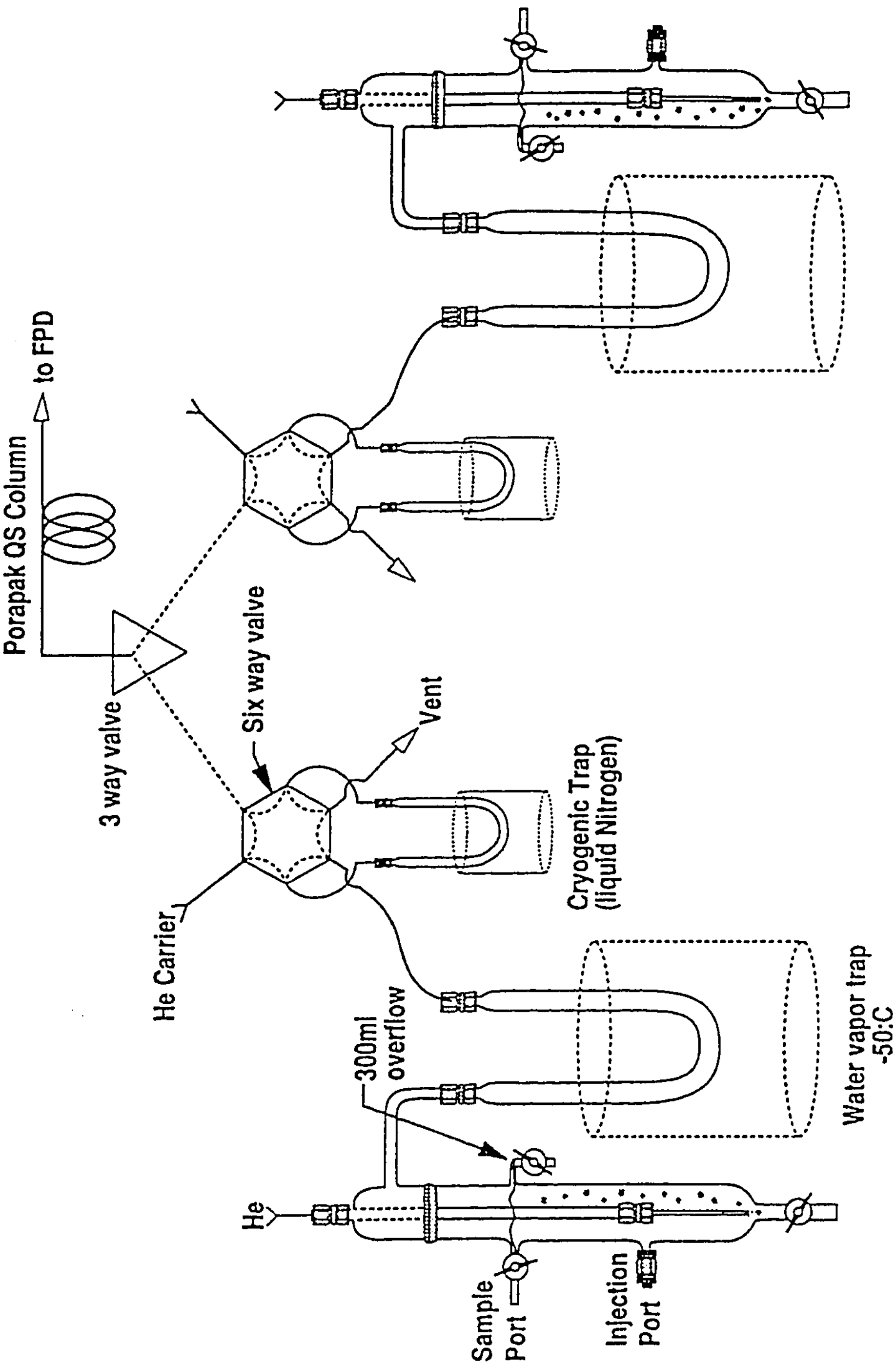

Figure 2.1: Schematic of the analytical system for the simultaneous determination of total dissolved sulfide and OCS.

atmosphere, and the carrier gas flows directly to the chromatographic column. In the *inject* position, the carrier gas passes through the cryogenic trap while the stripping gas is directly vented to the atmosphere. All connections are made with Teflon Swagelok fittings and Teflon tubing. To minimize adsorption, all internal glass surfaces are treated with dimethyldichlorosilane. To process two samples simultaneously, two identical stripping and trapping apparati are interfaced to a single gas chromatograph by a 3-way stainless steel valve (Teflon-filled rotor; Valco).

The quantification component of the apparatus includes a chromatographic column held at 40°C in a gas chromatograph (Hewlett Packard Model 5890 II) that is equipped with a FPD maintained at 170°C (HP Model 19258A). The column is Teflon tubing (0.16 mm I.D. × 180 cm) packed with acetone-washed, 50/80 mesh Porapak QS (de Souza *et al.*, 1975). The analog output signal from the detector is processed using a Hewlett-Packard 3396A plotter/integrator. Hydrogen (75 mL/min) and air (100 mL/min) are used for the FPD flame, while helium (zero grade) is used as the stripping gas (120 mL/min) and the carrier gas (30 mL/min). To purify the stripping gas, a 1-m coil of copper tubing (1/4" O.D.) is packed with Carbosieve SIII (60/80 mesh; Supelco) and held in liquid nitrogen. The response of the FPD is optimized by doping the hydrogen gas with carbonyl sulfide from a permeation device (62 ng OCS/min.; Metronics) held at 40°C in a thermostatted water bath.

2.1.3 Reagents and Standards

Two certified H_2S and OCS permeation devices (Metronics) are maintained at 40°C in a thermostatted water bath. These devices are used to calibrate the instrument for H_2S and OCS, and are weighed at 3-month intervals to monitor their permeation rates (7.02 pmol H_2S/sec and 4.05 pmol OCS/sec). Pure, compressed H_2S and OCS are obtained from Matheson, and anhydrous sodium sulfide (Na_2S) is obtained from Alfa. Metal solutions are atomic absorption spectroscopy standards (Baker).

Distilled, deionized (DDI) water with a specific resistance of 18 MΩ-cm is used in all experiments. All acids are reagent grade (Baker) and phosphoric acid is diluted with DDI water to a concentration of 1.5 mol/L, while HCl is diluted to 4.0 mol/L. A chromium (II) solution is prepared by passing 1 mol/L chromium chloride (dissolved in 1 mol/L HCl) through a Jones reductor column (Kolthoff and Belcher, 1957). Immediately after preparation, this reagent is sealed under nitrogen atmosphere to prevent its oxidation.

2.1.4 Procedures

Determination of Total Dissolved Sulfide and OCS in Water

Immediately after the sample is acquired using a Go-Flo sampling bottle, the bottle is pressurized (7 kPa) with filtered nitrogen, the sample is passed through a polycarbonate filter (0.4 μm pore size, 142 mm diameter; Nuclepore) held in a Teflon filter holder, and hermetically transferred into a Cubitainer. The Cubitainer should be rinsed with the sample 3 times, and while being filled, air bubbles are rapidly and completely expelled through the Teflon tubing and 2-way valve. In addition, exposure to light should be minimized by covering the Cubitainer while it is being filled. The filtered sample is analyzed immediately for total dissolved sulfide and OCS, or it can be refrigerated (4°C) in the dark until analysis ($\leq$ 2 hours).

For analysis, a 300 mL sample is hermetically transferred from a Cubitainer into the stripper with rinsing, while the stripping gas flow is stopped and the 6-way valve is set on *strip/trap*. The cryogenic trap is then immersed in liquid nitrogen and stripping gas flow started. Twelve milliliters of 1.5 mol/L phosphoric acid are immediately injected into the stripper and the timing of stripping/trapping begun. After 20 minutes of stripping, the 6-way valve is set on *inject* (ensure that the 3-way valve is set to interface the proper strip/trap apparatus) and the trap removed from the liquid nitrogen; the integrator is started at this time. After 60 seconds, return the 6-way valve to the *strip/trap* position. The stripper is drained and is ready for the next analysis. Using conditions given above, retention times are approximately 4.3 minutes for H_2S and 6.8 minutes for OCS. Elevated total dissolved sulfide and OCS concentrations in coastal and estuarine waters allow a 50 mL stripper and an all-Teflon cryogenic trap to be used. The amount of acid injected is reduced to 2 mL and the stripping/trapping time decreased to 15 minutes.

Determination of Total Dissolved Sulfide and OCS in Porewaters

Sediment cores in the special core barrel are pressurized with nitrogen to 250 kPa, and sediment porewater samples are hermetically extracted from the sediments into 10 mL gas-tight syringes fitted with 3-way stopcocks. With the stopcocks closed to isolate the samples from the atmosphere, the syringes can be refrigerated (4°C) in the dark until analysis ($\leq$ 2 hours), although immediate analysis is preferred.

A 50 mL stripper is filled with 25 mL of deionized water and 2 mL of 1.5 mol/L phosphoric acid. With the trap in liquid nitrogen and using a gas-tight syringe, a sample aliquot (0.1–5 mL) is filtered (0.4 μm pore size, polycarbonate membrane; Nuclepore) and injected through the reagent port of the stripper using a platinum needle. The sample is analyzed for total dissolved sulfide and OCS as described above. Multiple determinations can be performed without draining the stripper until 25 mL of porewaters have been analyzed. For porewaters with total dissolved sulfide concentrations ≥ 2 μmol/L, H_2S_g can interfere with the quantification of OCS. In this case, a sulfide scrubber is inserted in the gas stream between the stripper and the water trap, and no acid is added to the sample.

Determination of Acid Volatile and Chromium-Reducible Sulfur in Suspended Particulate Matter

Using nitrogen overpressure (7 kPa), a known volume of water (5 to 30 L) from a Go-Flo sampling bottle is passed directly through a polycarbonate filter (0.4 μm poresize, 142 mm diameter; Nuclepore) placed in an all-Teflon filter holder. The filter is folded, placed in a polyethylene vial and immediately frozen until analysis. The analytical procedure of Cutter and Oatts (1987) is modified for the sequential analyses of acid volatile and chromium reducible sulfide. A filter is placed in a 50 mL stripper with 10 mL of deionized water. After a 2-minute purge with helium stripping gas, the cryogenic trap is immersed in liquid nitrogen and 10 mL of 1 mol/L HCl is added. After 15 minutes of stripping and trapping, the 6-way valve is set to *inject*, and the procedure for total dissolved sulfide described above is followed; this yields the concentration of particulate acid volatile sulfide (pAVS). After 2 minutes, the cryogenic trap is immersed in liquid nitrogen, and 4 mL of concentrated HCl and 10 mL of Cr(II) solution are introduced in the stripper. After 20 minutes of stripping/trapping, H_2S_g retained on the cryogenic trap is determined as above, yielding the concentration of particulate chromium-reducible sulfur (pCRS).

Determination of H_2S_g in the Headspace of a Sample.

In a Cubitainer containing 3 L of sample, 400 mL of high purity helium gas are introduced through one of the ports on the cap. The Cubitainer is shaken for 30 seconds to equilibrate gas and liquid phases. The stripping gas tubing and the tubing leading to the cryogenic trap are connected by a Teflon tee, thus bypassing the stripper/U-tube assembly. The third arm of the tee is connected to an all Teflon injection port similar to that on the stripping vessel. The gas flow rate through the tee (*i.e.,* stripping gas) is reduced to 30 mL/min. The trap is immersed in liquid nitrogen, and 10–100 mL of headspace are then injected into the tee at a rate of 90 mL/min using a gas tight syringe fitted with a platinum needle. Two minutes after completing the injection, the determination of H_2S_g follows the procedure given above for total dissolved sulfide. Along with the measurement of sample pH, temperature and salinity, this procedure is used to determine the concentration of free sulfide in equilibrium with the concentration of H_2S_g (*i.e.,* $H_2S_{aq}+HS^-+S^{2-}$).

Calibration

Calibration is carried out using H_2S_g and OCS_g from two permeation devices diluted in a stream of helium (120 mL/min). To calibrate the system, the 6-way valve is set on *inject* and the effluent from the permeation devices passes through the cryogenic trap *via* the 6-way valve. While the cryogenic trap is immersed in liquid nitrogen, the valve is switched to the *trap* position for known periods of time (typically 5, 10, 15, 20, and 25 seconds) and then back to *inject*. When the trap is removed from liquid nitrogen, H_2S and OCS are swept into the chromatographic column. A linear, least squares fit of peak areas *vs.* amounts of H_2S_g and OCS retained on the trap is used as a calibration curve.

2.2 Results and Discussion

2.2.1 Sample Acquisition

The elimination of sampling artifacts is essential for the accurate determination of dissolved sulfur gases at picomolar concentrations. As an example, dissolved sulfide species readily form insoluble compounds with transition and "B" type metals (Stumm and Morgan, 1981) that may affect the recovery of total dissolved sulfide. In addition, contamination from the atmosphere or emissions from fossil fuel combustion must be avoided. Several procedures are used to overcome these potential problems, including the use of Go-Flo bottles that are cleaned following trace metal-clean procedures (Bruland *et al.*, 1979). For identical reasons, the filters for particulate sulfide speciation are also collected using trace metal-clean procedures and apparatus.

Previous work has shown that Go-Flo bottles can contaminate water samples for OCS (Johnson and Harrison, 1986). Therefore, cleaned sampling bottles are checked for contamination by the following procedure. Aliquots of deionized water with a known OCS concentration are analyzed as described above after 2, 4, 6 and 24 hours of being placed in the Go-Flo. An increase in OCS concentration with time warrants another cleaning and testing. A similar check is performed at the first sampling station by comparing the concentrations of OCS in water samples taken from the same depth using different Go-Flo's. Only bottles that show no contamination using these two procedures are used. It has been our experience that new Go-Flo's and Go-Flo's which have been repaired with PVC cement are severely contaminating.

To overcome the problem of atmospheric contamination, the Go-Flo's are pressurized with filtered nitrogen, ensuring that air does not enter the bottle and contaminate the sample while it is being withdrawn. Potential contamination by the pressurizing gas is assessed in the blanking procedure described above. To eliminate gas exchange between the sample and the atmosphere, hermetic transfer steps are used throughout the procedure. For manipulating large samples, Cubitainers can expand or collapse without introducing air bubbles. Gas tight syringes function similarly for smaller samples (*i.e.*, $\leq$ 50 mL). When samples cannot be analyzed immediately, they are refrigerated in the dark to prevent the production of carbonyl sulfide *via* photolysis (Ferek and Andreae, 1984) and to slow the oxidation of dissolved sulfide (Millero *et al.*, 1987).

Due to 10^2–10^4 fold supersaturation of OCS in sediment porewaters, loss of OCS from discrete core sections can be significant. Therefore, a hermetically sealed, pressurized core barrel (Jahnke, 1988) is used; additional advantages include ease of operation and rapidity of porewater sampling. This apparatus was checked for contamination by filling the core barrel with deionized water having a known OCS concentration, and treating it as a sample; no contamination was apparent.

2.2.2 Apparatus for the Determination of Total Dissolved Sulfide and OCS

Gas stripping and cryogenic trapping is commonly used for the determination of volatile sulfur compounds (Cutter and Oatts, 1987, Johnson and Harrison, 1986, Andreae and Barnard, 1983). A drawback of this general method is that the stream of stripping gas becomes laden with water vapor which can clog the cryogenic trap. This problem has been circumvented using different approaches, including chemical water traps (Andreae and Barnard, 1983), Nafion dryers (Johnson and Harrison, 1986), and progressive immersion of the cryogenic trap in liquid nitrogen using a motorized laboratory jack (Leck and Bagander, 1988). Cooled U-tubes have also been used to remove water vapor (Cutter and Oatts, 1987, Andreae and Barnard, 1983). A silanized glass U-tube was chosen for this work because the reactivity of H_2S_g precludes the use of chemical scrubbers with oxidative or acid-base properties such as magnesium perchlorate or potassium carbonate.

Different trapping schemes have been used for the gas chromatographic determination of gaseous sulfur compounds, including preconcentration onto solid adsorbents (Andreae and Barnard, 1983, Braman *et al.*, 1978) and cryogenic trapping (Leck and Bagander, 1988, Andreae and Barnard, 1983). For optimum recovery and simplicity, liquid nitrogen-cooled trapping was chosen. The construction of cryogenic traps vary, but usually comprise silanized glass beads or silanized glass wool packed in U-shaped glass tubing that can be heated to quickly volatilize the sulfur compounds (Andreae and Barnard, 1983). The low boiling points of hydrogen sulfide and carbonyl sulfide do not require heating of the cryogenic trap to quantitatively desorb them, and thus 1/8" O.D. Teflon tubing (loosely packed with silanized glass wool) can also be used. This all-Teflon cryogenic trap is simpler to prepare than glass traps because it does not require silanization or glass-Teflon connectors. For the determination of total dissolved sulfide and OCS in a large seawater sample (*i.e.*, 300 mL), glass U-tube traps are used because the amount of CO_2 stripped from an acidified 300-mL sample can clog the smaller bore, all-Teflon cryogenic trap. Carry-over of H_2S_g or OCS_g from one sample to the next was not observed using either type of cryogenic trap.

Packings used for the chromatographic separation of gaseous sulfur compounds include Chromosil 310 and 330, and Porapak QS. The latter is a silanized Porapak Q, and can resolve the large CO_2 peak (evolved from acidified seawater) from the much smaller and neighboring H_2S and OCS peaks. In addition, Porapak QS held at 40°C retains non-polar compounds such as dimethyl sulfide. This is useful when analyzing samples over long periods of time because there is no need for more than a daily 30-minute column bake-out at 110°C to elute high boiling compounds. An example chromatogram of a 300 mL seawater sample shows that OCS and H_2S are well separated from each other and the negative CO_2 peak (Figure 2.2).

In sediment porewaters where total dissolved sulfide concentrations reach millimolar levels, nanomolar concentrations of OCS cannot be accurately quantified due to chromatographic interference. However, OCS can be determined by removing H_2S_g from the stripping gas using a silver nitrate scrubber. Filter paper moistened with silver nitrate has been shown to quantitatively retain H_2S_g while retaining less than 1% of the OCS (Cooper and Saltzman, 1987, Farwell *et al.*, 1987). For the apparatus used here, repeated injections of 424 pmol OCS into the strip/trap apparatus show that 97.8±2.2% (n=8) of OCS passes through the H_2S_g scrubber. With a single scrubber, over 100 mL of porewater samples can be analyzed without H_2S_g interference.

The use of flame photometric detectors for the quantification of sulfur compounds has been the choice of many investigators because of their selectivity and sensitivity. In the reducing flame of the detector, the dissociation of S-S dimers formed during combustion of sulfur compounds radiates at 393 nm. The non-linear response of the detector's photomultiplier tube to the concentration of sulfur in the flame has been described by d'Ottavio *et al.* (1981), who showed that doping the flame with a background sulfur concentration linearizes and increases the sensitivity of the detector. The detector used here is doped with 62 ng OCS/min., increasing the sensitivity of the

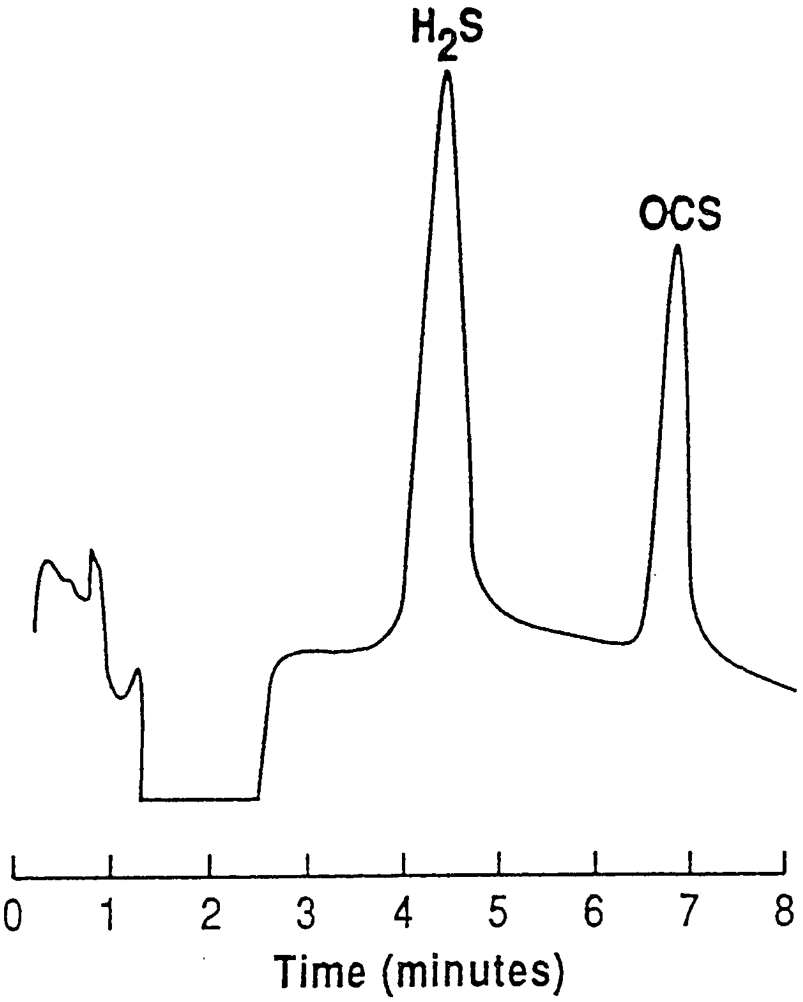

Figure 2.2: A chromatogram showing the separation of CO_2 (0.1 mmol/L, negative peak) from H_2S (48.5 pmol/L) and OCS (79.2 pmol/L) in a 300 mL sample.

FPD by a factor of 20 (at the 20 pmol S level) while maintaining a wide working range (0–140 pmol S).

In their method for the determination of nanomolar levels of total dissolved sulfide, Cutter and Oatts (1987) used a standard solution of Na_2S that was prepared daily for calibration. However, such solutions cannot be accurately prepared in the field. Moreover, the calibration for OCS requires a gas standard. The calibration of the FPD for H_2S was examined in the laboratory using a liquid standard (*i.e.,* Na_2S dissolved in water) added to the stripper and treated as a sample, and a gas standard from a permeation device that was trapped as described above. A comparison between the calibrations obtained using the H_2S permeation device and the liquid standard is shown in Figure 2.3. This comparison demonstrates that the two calibration methods are equivalent. Furthermore, the calibration using permeation devices is linear from 0 to 140 pmol S, with correlation coefficients being >0.998.

2.2.3 Conditions for the Determination of Total Dissolved Sulfide and OCS

With the chromatographic parameters established, the recoveries of total dissolved sulfide and OCS were examined as a function of the stripping/trapping time. Additionally, the effects of two different acids and various trace metals on the recovery of total dissolved sulfide were investigated. With respect to the latter, dissolved metals readily form insoluble compounds and soluble complexes with free sulfide (Elliott *et al.*, 1989, Dyrssen, 1988, Stumm and Morgan, 1981) that may not be determined using the experimental conditions given here.

The effect of stripping and trapping time was investigated in two exper-

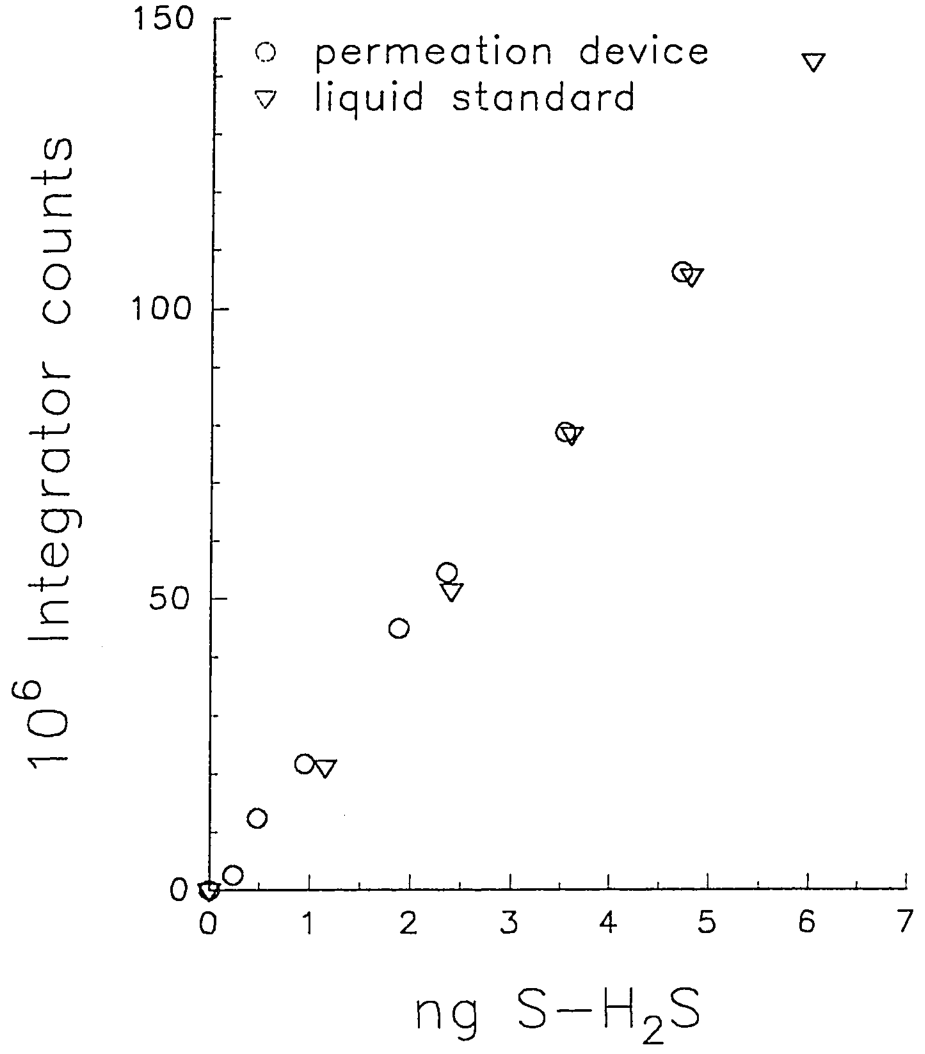

Figure 2.3: Comparison of FPD calibrations for H_2S using a liquid standard run through the entire analytical procedure (triangles) and by direct trapping of H_2S from a permeation device (circles).

iments. Dissolved sulfide (added as Na_2S) or OCS (added as gaseous OCS; both at 160–200 pmol/L) in deionized water were stripped at 120 mL/min for different lengths of time. The results presented in Figure 2.4 show that quantitative recovery for both gases is achieved in less than 15 minutes for 50 mL samples, and in less than 20 minutes for 300 mL samples. However, 15 and 20-minute stripping times are used so that the determination is relatively time independent.

In a second series of experiments, the effect of acid concentration and type on the recovery of total dissolved sulfide and OCS was investigated. Aliquots of DDI water or Sargasso Sea water containing total dissolved sulfide and OCS (at the 0.2 nmol/L level) were analyzed using varying acid concentrations. Total dissolved sulfide was quantitatively recovered using 2 mL of 1.5 mol/L phosphoric acid in a 50 mL sample (final *p*H: 1.7); the recovery of OCS was unaffected by this acid concentration. Hydrochloric acid (4 mol/L) was also tested in stripping/trapping experiments. Quantitative recovery of total dissolved sulfide was achieved in deionized water and Sargasso Sea water with 0.4 mL of 4 mol/L HCl. For Sargasso Sea water, the recovery of total dissolved sulfide decreased rapidly with increasing amounts of HCl added; this effect was not observed with DDI water. The reasons for the loss of total dissolved sulfide in Sargasso Sea water are unclear, but similar to the observation of Cutter *et al.* (1991), we speculate that free chlorine present in the HCl reacts with hydrogen sulfide when HCl is introduced to seawater. Because of this problem, acidification with phosphoric acid is used for all samples.

A third series of experiments were designed to examine the effects of trace metals on the recovery of total dissolved sulfide. Distilled, deionized water was placed into a Cubitainer, purged with nitrogen for one hour at

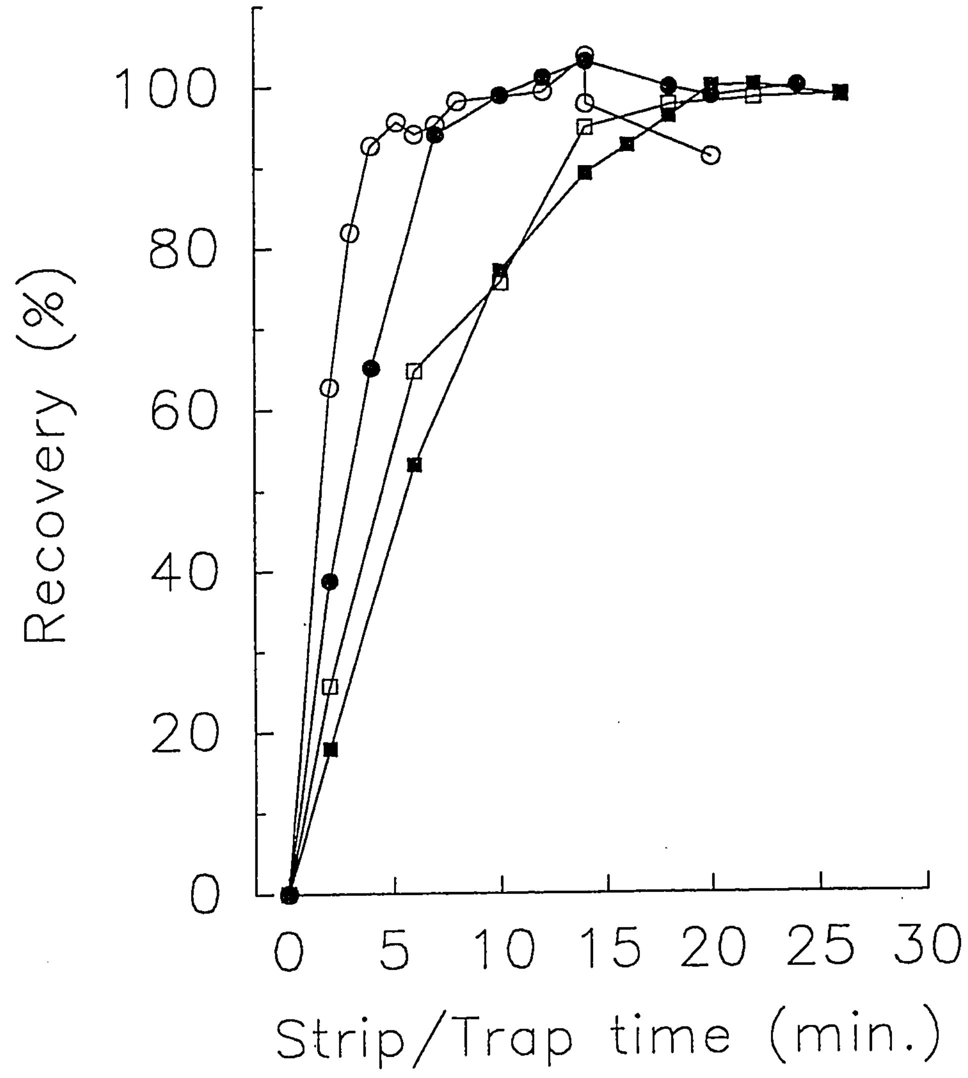

Figure 2.4: Recoveries of total dissolved sulfide and OCS as a function of stripping and trapping time. For the 300 mL stripper hollow squares represent total dissolved sulfide, while filled squares are OCS. For the 50 mL stripper, hollow circles are total dissolved sulfide and filled circles are OCS. Recoveries are calculated from the concentrations determined using gas calibrations.

300 mL/min to remove dissolved oxygen; the solution was then amended with a trace metal. Added trace metals were copper (5–56 nmol Cu(II)/L), zinc (53 nmol/L), mercury (10.4 nmol/L), iron (16–46 nmol Fe(II)/L), silver (9–39 nmol/L), and chromium (50 nmol Cr(VI)/L). To minimize contamination, trace metal additions to the Cubitainers were performed in a class 100 clean room using trace metal-clean plasticware. In every case, H_2S_g was then introduced in the Cubitainer to achieve a final dissolved concentration of 50 nmol/L. Total dissolved sulfide was then determined in triplicate using the method described above. From these experiments, it appears that copper-, mercury-, and silver-sulfide complexes are not completely acid-labile at high concentrations (Figure 2.5), while zinc-, iron-, and chromium-sulfide complexes are acid-labile and total dissolved sulfide can be quantitatively recovered. The slight decrease in recovery with Fe(III) is likely due to sulfide oxidation, since the same behavior is not observed with Fe(II). The recovery of total dissolved sulfide in the presence of copper did not improve by increasing the final acid concentration to 12 mol H_3PO_4/L, or to 10 mol HCl/L. Total dissolved sulfide in copper-sulfide complexes can be recovered using an acidic chromium (II) solution (refer to next section), however this procedure is rather cumbersome for large water samples. However, the concentrations of metals and total dissolved sulfide examined in this experiment are much greater than those found in seawater, and thus the results may not be directly applicable.

The degree of metal interference on the determination of total dissolved sulfide in seawater (*i.e.*, the formation of non acid-labile metal-sulfide complexes) was evaluated using typical concentrations found in natural waters. Trace metals were added individually to Cubitainers containing deoxygenated Sargasso Sea water that had been amended immediately beforehand with

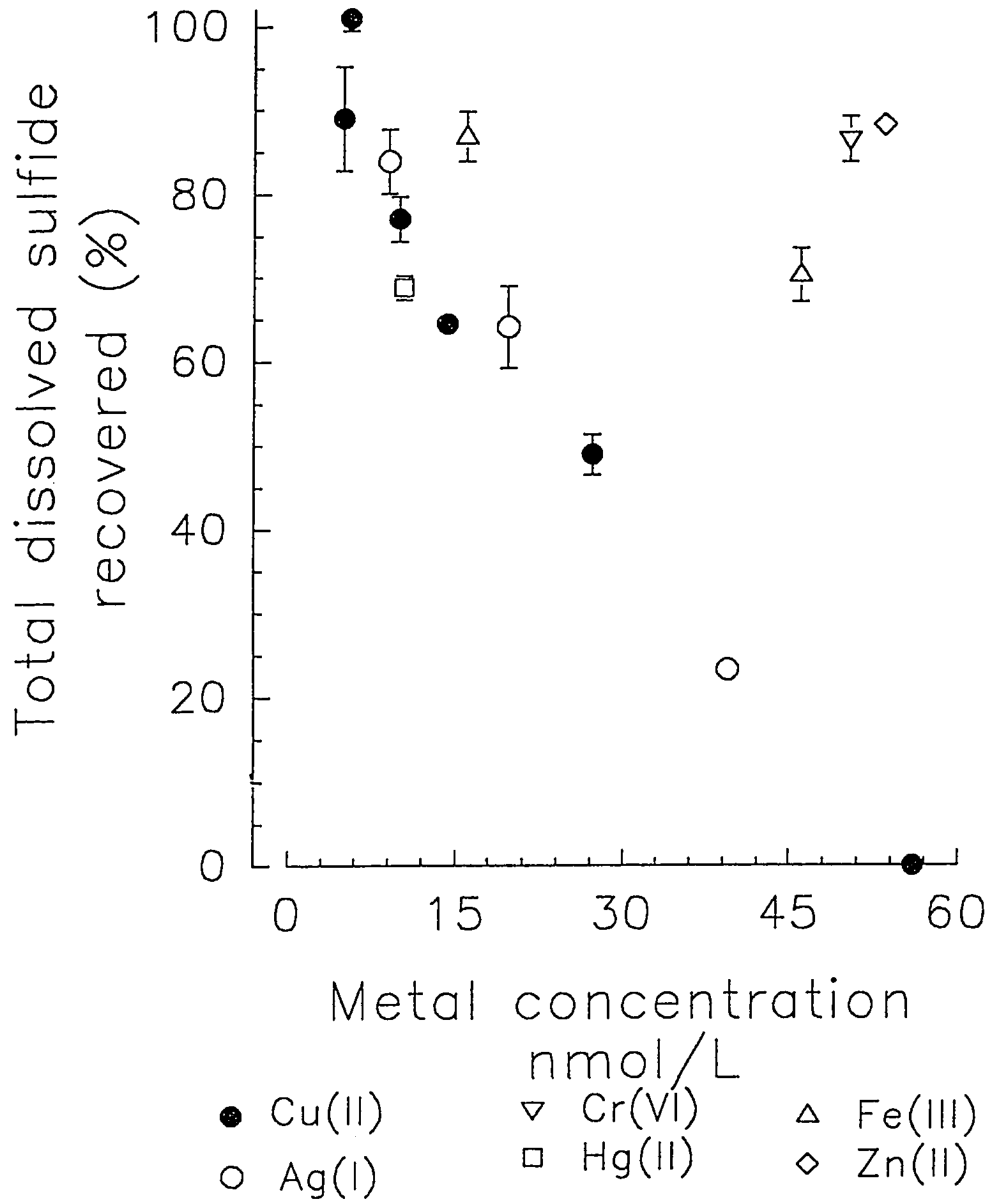

Figure 2.5: Recovery of 50 nmol/L total dissolved sulfide as a function of the concentration of six individual trace metals. Error bars are ± one standard deviation (n=3).

H_2S_g to give a total dissolved sulfide concentration of 1 nmol/L. Trace metals were added so that their concentrations matched the maximum of these ions found in seawater; (Bruland, 1983; Cu(II), 6 nmol/L; Cd(II), 1.1 nmol/L; Ni(II), 12 nmol/L; Pb(II), 0.15 nmol/L; Zn(II), 9 nmol/L). These metals were chosen because they form strong metal-sulfide complexes (Dyrssen and Wedborg, 1988, Elliott, 1988) and because their concentrations are sufficiently elevated in the upper ocean to warrant their consideration. The results in Fig. 2.5 indicate that Ag and Hg sulfides may not be recoverable. However, with maximum seawater concentrations of 15 pmol/L (Bruland, 1983) and 10 pmol/L (Bruland, 1983) for Ag and Hg respectively, these metals should not cause significant interference. Analysis of the resulting solutions for total dissolved sulfide showed full recovery within experimental error for all cases except Cu(II). At a Cu(II) concentration of 6 nmol/L, none of the 1 nmol/L total dissolved sulfide was recovered. Thus, total dissolved sulfide is operationally-defined since it does not include sulfide in dissolved copper-sulfide complexes. However, the procedure for total dissolved sulfide includes all the other significant metal-sulfide complexes likely to be encountered in most natural waters.

2.2.4 Determination of Particulate Acid Volatile Sulfide and Chromium-Reducible Sulfur

Free sulfide can react with trace metals to form insoluble metal sulfides in the water column. The method to determine the concentration of these inorganic compounds on suspended particles was adapted from Cutter and Oatts (1987). In their sediment work, they showed that sulfide bound in iron monosulfide is quantitatively released as H_2S using 0.4 mol/L HCl, while Cr(II)/HCl reagent must be used to release H_2S_g from pyrite (FeS_2). It should be noted that while the Cr(II)/HCl reagent reduces elemental sulfur to H_2S, it does not cleave C–S bonds in organic sulfur compounds (Cutter and Oatts, 1987), and thus the chromium reducible fraction only includes inorganic sulfur compounds.

To evaluate the applicability of these methods to the determination of other metal sulfide compounds, known (0.5 mg, ground to a fine powder) amounts of a metal sulfide compound (Cu_2S, CuS, and ZnS) were subjected to the 0.5 mol/L HCl and Cr(II)/HCl treatments. The Cu_2S and CuS were obtained from Alfa, and ZnS was filtered from a solution of zinc acetate and sodium sulfide, then dried and ground to a fine powder. Consistent with Cutter and Oatts (1987), the 0.5 mol/L HCl treatment quantitatively released H_2S_g from zinc sulfide (98.4±2.6%, n=4). However, the more rigorous Cr(II)/HCl treatment was necessary to recover H_2S_g from copper sulfide compounds (H_2S recovery: 101.4±3.8%, n=3). Considering the dissolved metal experiments discussed previously, particulate acid volatile sulfide includes compounds such as ZnS and FeS. After these compounds are removed, particulate chromium reducible sulfur includes copper-sulfide compounds, as well as pyrite.

2.2.5 Determination of H_2S_g

For this determination, conditions for the cryogenic trapping of gas-phase H_2S (H_2S_g) are similar to those for total dissolved sulfide and OCS. The injection tee is made of Teflon to minimize loss of H_2S_g, and the cumulative gas flow rate (headspace + stripping) through the cryogenic trap is maintained at 120 mL/min. to prevent sample break through. To collect all H_2S_g from the tee, the trap is kept in liquid nitrogen for two minutes after completing the injection. The determination of H_2S_g can be used to calculate the concentration of free sulfide (*i.e.*, H_2S_{aq}+HS^-+S^{2-}) in a sample at *in situ* conditions of temperature, salinity and *p*H. Along with the determination of total dissolved sulfide (as described above), the concentration of dissolved sulfide species complexed with metals in acid-labile complexes can then be estimated by difference between free and total dissolved sulfide concentrations.

The method used to calculate the concentration of free sulfide is based on the coupled equilibria shown in the following equation:

$$S^{2-} + 2H^+ \overset{K_2^*}{\rightleftharpoons} HS^- + H^+ \overset{K_1^*}{\rightleftharpoons} H_2S_{aq} \overset{K_d^*}{\rightleftharpoons} H_2S_g \qquad (2.1)$$

where K_1^* and K_2^* are the conditional dissociation constants (*i.e.*, corrected for temperature and salinity using the equations in Millero, 1986), and K_d^* is the conditional distribution coefficient (*i.e.*, corrected for temperature and salinity using the solubility table in Douabul and Riley, 1979). The fraction of free sulfide with concentration C that exists as H_2S_{aq} is (Stumm and Morgan, 1981):

$$\alpha = \left(1 + \frac{K_1^*}{[H^+]} + \frac{K_1^* \times K_2^*}{[H^+]^2}\right)^{-1} \qquad (2.2)$$

and thus,

$$H_2S_{aq} = \alpha C \qquad (2.3)$$

If a pure nitrogen headspace of volume V_g is introduced over a sample of volume V_l and allowed to equilibrate, then

$$\alpha C_0 V_l = [H_2S_{aq}]V_l + [H_2S_g]V_g \qquad (2.4)$$

where C_0 is the original concentration of uncomplexed, dissolved hydrogen sulfide. Since $[H_2S_{aq}] = K_d^*[H_2S_g]$, Equation 2.4 can be rewritten as

$$C_0 = \frac{H_2S_g}{\alpha} \times (K_d^* + \frac{V_g}{V_l}) \qquad (2.5)$$

Thus, the determination of H_2S_g, *p*H, temperature, and salinity of a sample (the latter two are necessary to adjust the conditional dissociation and distribution constants), allow the calculation of the concentration of free sulfide. At a given concentration of $[H_2S_{aq}+HS^-+S^{2-}]$, the quotient H_2S_g/α presents the largest uncertainty for C_0. In particular, when the pH is greater than pK_1^*, α changes by a factor of 10 for each variation of one pH unit. Thus, an accurate determination of pH using a pH scale appropriate for the ionic strength of the water considered (*e.g.*, Culberson, 1981) is necessary to reduce systematic error.

To evaluate this headspace method in DDI water, a Cubitainer containing 3.00 L of trace metal-clean, water at 24°C, with a pH of 8.52 (adjusted with NaOH) and deoxygenated using a stream of helium (one hour at 300 mL/min.) was amended with H_2S_g to give a concentration of 6.6 nmol/L. Using the procedure described above, the headspace concentration of H_2S_g was determined to be 85.1±19.6 pmol/L (n=6). Applying Equation 2.5, the concentration of free sulfide was 7.3±1.7 nmol/L, in good agreement with the actual concentration of 6.6 nmol/L. To evaluate this method in seawater, a Cubitainer containing 3.00 L of Sargasso Sea water at 23°C, with a *p*H of 8.29 and deoxygenated as above, was amended with H_2S_g to a final concentration of total dissolved sulfide of 51 nmol/L. This elevated concentration was chosen to minimize the impact of sulfide complexation by dissolved metals in the sample on the inventory of free sulfide. The concentration of H_2S_g determined in the headspace after equilibration was 311±15 pmol/L (n=5), which yields a concentration of free sulfide of 47.0±2.3 nmol/L (92±5% recovery). Thus, the headspace method also appears to be reliable in a more complex matrix.

2.2.6 Analytical Figures of Merit

The detection limit for total dissolved sulfide and OCS in water samples was evaluated using five determinations of a blank consisting of deionized water (300 mL) degassed in the stripper with helium. The absolute detection limits (3 σ of a blank) are 0.06 pmol H_2S and 0.4 pmol OCS. For a 300 mL sample, the relative detection limits are then 0.2 pmol/L for total dissolved sulfide and 1.3 pmol/L for OCS. Similarly, for a 1 mL sediment porewater aliquot, the relative detection limits are 60 pmol/L H_2S and 400 pmol/L OCS. The absolute detection limits for particulate acid volatile sulfide and chromium reducible sulfur were evaluated using five determinations of blank (unused) filters. The detection limits are 0.2 pmol S as acid volatile sulfide, and 2 pmol S as chromium-reducible sulfur. For a 30 L sample, this corresponds to relative detection limits of 0.007 pmol/L for particulate acid volatile sulfide, and 0.07 pmol/L for particulate chromium-reducible sulfur.

Using 0.06 pmol H_2S as the absolute detection limit and a 100 mL headspace sample, the relative detection limit for H_2S_g is 0.6 pmol/L. At pH 8, a salinity of 35 psu (practical salinity units), and 25°C, this corresponds to a relative detection limit of 52 pmol/L for free sulfide. In freshwater at pH 7 and at 25°C, the relative detection limit for free sulfide is 3.5 pmol/L. It should be noted that the detection limit for free sulfide can be improved by a factor of 10 for each *p*H unit decrease until pK_1^* is reached. At concentrations of 20 pmol/L of total dissolved sulfide or OCS, precision is 5% relative standard deviation for both sulfur compounds (n=5), and 4% relative standard deviation (n=5) at concentrations $\geq$ 5 nmol/L. By varying the volume analyzed (1 to 300 mL), samples with total dissolved sulfide and OCS concentrations ranging from 0.2 pmol/L to 100 nmol/L can been analyzed.

2.2.7 Application to Field Samples

Using the methods described above, samples from a variety of environments have been analyzed for total dissolved sulfide and carbonyl sulfide; some of the resulting data are presented in Table 2.1. For total dissolved sulfide and OCS in the water column, concentrations generally increase with proximity to land masses. Additionally, concentration depth profiles exhibit surface and subsurface maxima, suggesting a link between total sulfide, OCS and biological activity. Elevated OCS concentration in marine sediments is evidence for OCS production by diagenetic processes. Detectable concentrations of particulate acid volatile sulfide and particulate chromium reducible sulfur in the remote Pacific Ocean strongly suggest that these compounds may be formed in the oxic water column. To illustrate how the methods presented above can be used to examine the interactions between metals and sulfide, an experiment was performed using 3.00 L of seawater (pH 8.27, 24°C, 34.1 psu, collected at 8°59'N, 147°24'W). The water was amended with H_2S_g to a final concentration of 2.12 nmol/L. After a 10 minute equilibration period and using the method described above, the concentration of H_2S_g in the headspace was 7.37±1.0 pmol/L (n=3), which corresponds to 1.0±0.13 nmol/L of free sulfide using Equation 2.5; total dissolved sulfide was 1.23 ±0.01 nmol/L (n=3). With these concentrations, the fraction of the amended H_2S_g which remained free is 47% (1.0/2.12), and the fraction of the added H_2S_g which reacted with metals such as copper is 42% ((2.12–1.23)/2.12). The remainder of the H_2S_g amendement (11%) is complexed with metals such as zinc, cadmium, and nickel. Thus, the headspace method allows an unobtrusive examination of the interactions between dissolved sulfide species and these metals at near-*in situ* conditions. Moreover, in natural waters where total dissolved sulfide concentrations are > 300 pmol/L, the headspace method

Table 2.1: Total Dissolved Sulfide and OCS in Natural Waters.

Sample type and location		Concentration	
Water column	Depth (m)	Total dissolved sulfide (pmol/L)	OCS (pmol/L)
Pacific Ocean, 08/1991	5	46.0±2.7	10.0±0.4
8°59'N, 147°24'W	150	39.1±1.5	22.3±1.1
Pettaquamscutt River, RI	0.25	615±27	636±14
8/1990	3.85	1220±40	415±13
Sediment porewaters	Depth interval (cm)	Total dissolved sulfide (nmol/L)	OCS (nmol/L)
Atlantic Ocean, 06/1990	0-2.5	34.9	37.4
38°20'N, 74°45'W			
Chesapeake Bay, 10/1991	interface	^{a}N.A.	14.0±0.9
38°57'N, 76°45'W	1-2	N.A.	24.7±2.0
	4-6	N.A.	36.2±2.1
Lake 5.0, FL, 06/1990	5	69.2±3.5	53.2±5.7
Suspended part. matter	Depth (m)	pAVS (pmol/L)	pCRS (pmol/L)
Pacific Ocean, 08/1991	65	3.38	18.3
8°59'N 147°24'W	150	4.43	67.3

Triplicate determinations were performed on water column samples.
Duplicate determinations were performed on sediment porewaters.
Particulate sample concentrations were determined by single analysis.
^{a} N.A. is not analyzed.

can be used directly to evaluate sulfide-metal complexation. Overall, the results in Table 2.1 confirm that the methods described above are applicable to a variety of environments, while maintaining good precision for a wide range of concentrations. Furthermore, picomolar concentrations of total dissolved sulfide and OCS found in the open ocean demonstrate the need for contamination-free sampling and analytical methods.

Chapter 3

Biogeochemistry of Dissolved Hydrogen Sulfide Species and Carbonyl Sulfide in the Western North Atlantic Ocean

3.1 Introduction

Non-sea salt sulfate aerosols can be produced in the atmosphere by the oxidation of sulfur gases such as carbonyl sulfide (OCS), dimethyl sulfide (DMS) and sulfur dioxide (Fitzgerald, 1991). In the stratosphere, sulfate aerosols backscatter incident solar radiation, and thus have a bearing on the global radiation budget (Twomey, 1991). In the troposphere, sulfate aerosols can increase the number density of cloud condensation nuclei and thereby affect cloud albedo (Twomey *et al.*, 1984). Therefore, anthropogenic and natural emissions of these sulfur gases can impact the radiation budget of Earth (Charlson *et al.*, 1991, Charlson *et al.*, 1987). Considerable effort has been devoted to the study of the biogeochemistry of DMS and OCS, and it appears that the oceans play a crucial role in the cycling of these naturally-emitted sulfur gases. Results from numerous investigations indicate that DMS is the biogenic gas that dominates oceanic concentrations and atmospheric fluxes (Andreae, 1986, 1990, Bates *et al.*, 1987). In comparison, the biogeochemistry of hydrogen sulfide (H_2S) has received comparatively little attention. Dissolved in seawater, H_2S can dissociate to bisulfide (HS^-) and sulfide (S^{2-}) ions. These ions can in turn react with trace metals to form metal sulfide complexes. This situation necessitates the nomenclature introduced in Chapter 2, where free sulfide is the concentration of uncomplexed H_2S_{aq}+HS^-+S^{2-}, and where complexed sulfide is the concentration of dissolved sulfide bound in metal sulfide complexes. Total dissolved sulfide is the sum of free and complexed sulfide.

The paucity of data on dissolved sulfide in the open ocean is partly due to the sampling and analytical difficulties that arise from its low (*i.e.*, picomolar) concentrations and from its reactivity with metals and oxidants. The existing dissolved sulfide data focuses on its distribution in the western North Atlantic Ocean and the Mediterranean Sea; mixed layer concentrations of dissolved sulfide range from <0.1 to 2 nmol/L (Cutter and Krahforst, 1988, Luther and Tsamakis, 1989). Concentrations of total dissolved sulfide decrease with depth, and maxima coincident with chlorophyll *a* concentration have been found (Cutter and Krahforst, 1988, Luther and Tsamakis, 1989). On an horizontal scale, dissolved sulfide concentrations decrease from the coastal to the open ocean (Cutter and Krahforst, 1988, Andreae *et al.* 1991). Temporally, concentrations of total dissolved sulfide in surface waters show diel variability, reaching maximum concentrations in the late night and minimum concentrations in the late afternoon (Cutter and Krahforst, 1988). Reasons for this behavior are unclear, but the involvement of photochemical reactions in the cycling of dissolved sulfide has been suggested (Cutter and Krahforst, 1988, Luther and Tsamakis, 1989). Proposed sources of dissolved sulfide include OCS hydrolysis (Elliott *et al.*, 1987), *in situ* dissimilatory sulfate reduction (Cutter and Krahforst, 1988), and assimilatory sulfate reduction (Andreae, 1986). Also, a recent study of the western North Atlantic Ocean indicates that the atmosphere can act as a source of hydrogen sulfide to surface waters (Andreae *et al.*, 1991). These preliminary findings indicate the potential complexity of the cycle of dissolved sulfide in the surface ocean.

Elliott *et al.* (1987) first proposed that OCS hydrolysis is a source of dissolved sulfide in oxic seawater and that it can reach pico- to nanomolar levels in the surface ocean. While these concentrations have been found, the apparent lack of coupling between the temporal and spatial behaviors of dissolved sulfide and OCS suggest that other sources must be present (Cutter and Krahforst, 1988). Dissimilatory sulfate reduction in ubiquitous marine snow could be a source of dissolved sulfide to the ocean (Cutter and Krahforst, 1988). This hypothesis is based on results from Karl and Knauer (1984), who found indirect evidence of anaerobic respiration in particles intercepted by sediment traps (*i.e.,* marine snow). Marked oxygen depletion in marine snow particles (Alldredge and Cohen, 1987) helps to support the notion of dissimilatory sulfate reduction in particles. In addition to these sources, Andreae (1986) hypothesized that the release of dissolved sulfide by marine algae could occur. Emissions of hydrogen sulfide have been observed in higher plants as a means to regulate the intracellular concentration of reduced sulfur (see Rennenberg, 1991, for a review).

While little is known about the relative importance of the sources of dissolved sulfide, several sinks in the open ocean have been clearly identified, including removal due to oxidation by oxygen, hydrogen peroxide (H_2O_2), and iodate (IO_3^-). The rates of reaction between dissolved sulfide and these oxidants have been determined in water and natural seawater under a range of oceanographic conditions of *p*H and temperature. Beside loss to the atmosphere, another sink of dissolved sulfide is the formation of insoluble metal sulfide compounds that may be associated with sinking particles (Cutter and Krahforst, 1988, Cutter and Radford-Knœry, 1991). This process may be very important because a substantial fraction of dissolved sulfide appears to be complexed with trace metals (Luther and Tsamakis, 1989). The overall balance between these numerous sources and sinks ultimately determines the horizontal, vertical, and temporal distribution of dissolved sulfide. Processes that control this balance, however, remain to be elucidated.

This chapter presents data collected in the western North Atlantic Ocean that are used to quantitatively examine the processes affecting the concentration of dissolved sulfide in the open ocean. Because of the widely recognized importance of OCS as a potential source of dissolved sulfide (Elliott *et al.*, 1987, Cutter and Krahforst, 1988, Luther and Tsamakis, 1989), the coupling between OCS and dissolved sulfide is assessed using a newly determined rate of OCS hydrolysis in seawater, as well as using the first open ocean OCS depth profiles. The relative importance of known sources and sinks of dissolved sulfide is then evaluated, and its budget for the Sargasso Sea is constructed.

3.2 Methods

3.2.1 Field Sampling

The R/V Cape Hatteras was used to sample the western North Atlantic Ocean from 12 to 29 April 1989, and from 24 October to 9 November 1989 at Stations 8, 12 and 15 that are shown in Figure 3.1. Station 12 is at the location of the Bermuda Atlantic Time Series (BATS) station of the U.S. Joint Global Ocean Flux Study (JGOFS). Samples for total dissolved sulfide and OCS were collected using 5-L Go-Flo bottles deployed on a CTD/rosette system, or using 30-L Go-Flo bottles hung on a Kevlar hydrowire. Sample

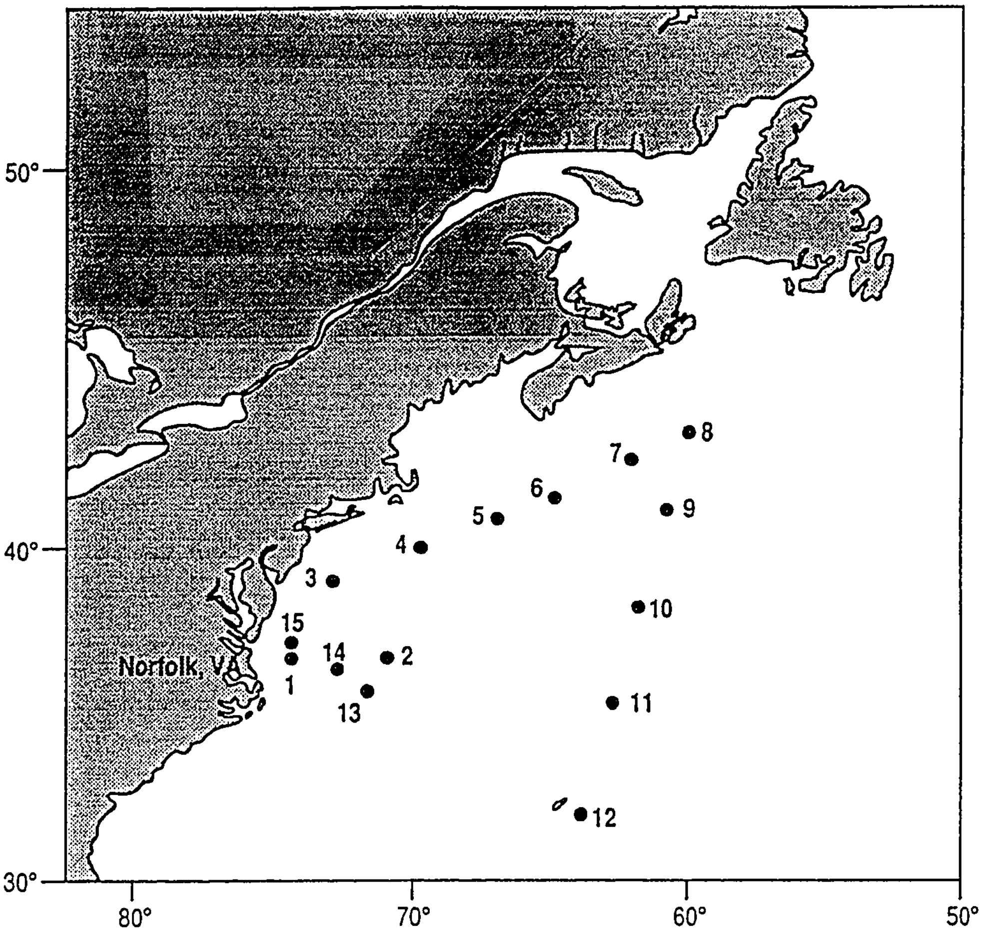

Figure 3.1: Station map for the April and November 1989 expeditions. Station 15 was sampled in April, Station 8 was sampled in November, and Station 12 was sampled at both times. Station 12 also corresponds to the JGOFS Bermuda Atlantic Time Series station.

collection and handling followed trace metal-clean procedures. Samples were hermetically transferred into 4-L polyethylene Cubitainers for analysis in the shipboard laboratory (Chapter 2).

3.2.2 Analytical Methods

Two methods were used for the determinations of total dissolved sulfide. The first method for the "direct" determination of total dissolved sulfide and OCS is based on hermetically dispensing a sample in a glass stripping vessel, acidifying it (*p*H 1.6), stripping the dissolved gases for 20 minutes, and cryogenically trapping them (Chapter 2). Upon warming of the trap, the trapped OCS and H_2S are volatilized and separated by gas chromatography (GC) and quantified using a flame photometric detector (FPD). Analytical precision was better than 10% (RSD) at the 50 pmol/L level of dissolved sulfide and OCS. The detection limits were 0.5 pmol/L for total dissolved sulfide using the "direct" method, and 20 pmol/L for OCS. The concentration of total dissolved sulfide was also determined using an "indirect" method, where a 300-mL sample is reacted with zinc acetate to precipitate total dissolved sulfide as zinc-sulfide (Cutter and Oatts, 1987). The treated sample is immediately filtered (0.4 μm polycarbonate membrane) in a nitrogen atmosphere, and the filter is frozen until analysis (<2 days). For analysis, the filter is placed in a glass stripping vessel with deionized water and acidified with HCl to 0.5 mol/L, quantitatively releasing sulfide from the precipitate as H_2S. Using the GC/FPD system, total dissolved sulfide is then quantified as described above. The "direct" and "indirect" methods give comparable results (Fig. 3.2 and Cutter and Krahforst, 1988). The "direct" determination is the preferred method of analysis because of better precision, but an important advantage of the "indirect" method is that numerous samples can

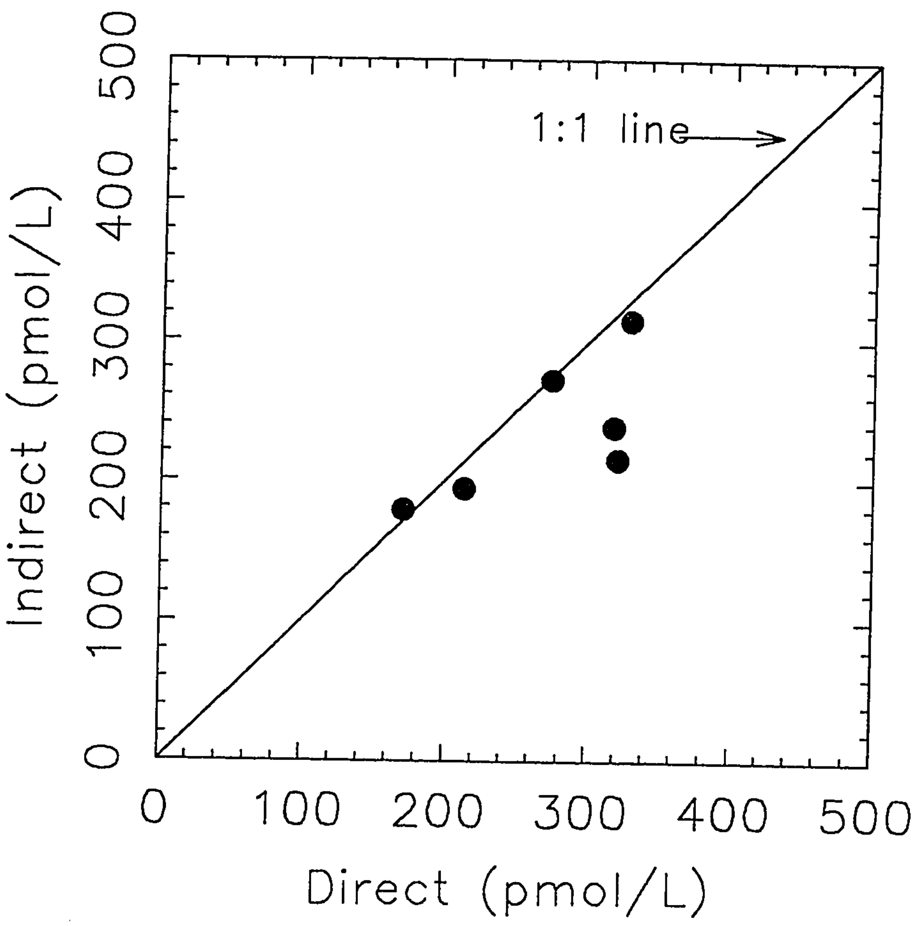

Figure 3.2: Correlation between results obtained using the "direct" and "indirect" method; r=0.701, y=0.55x+85.5 (n=6). Refer to the text for analytical details.

be processed at once and preserved for later analysis. The detection limit of the indirect method was 5 pmol/L. However, dissolved sulfide bound in complexes that are not acid-labile (*e.g.*, copper-sulfide; Chapter 2) are not detected by the "direct" method.

To determine only free sulfide, a 300 mL sample was introduced in a glass stripping vessel and purged with helium for 20 minutes *without acidification*. Since metal sulfide complexes are kinetically stable (Luther and Tsamakis, 1989), free sulfide is stripped from the sample and quantified as described above. The detection limit for free sulfide was 15 pmol/L and the precision was 10% (RSD). The degree of sulfide association with particles was obtained from the concentration difference between unfiltered and filtered samples analyzed for total dissolved sulfide. To obtain filtered samples, an acid-cleaned cartridge filter (0.4 μm pore size) was placed between the nitrogen-pressurized Go-Flo bottle and the Cubitainer. Chlorophyll *a* was either determined on discrete samples using the method of Strickland and Parsons (1972), or estimated using the fluorometer mounted on the CTD. Temperature was obtained from the CTD, while salinity (Minisal salinometer) and dissolved oxygen concentrations (Carpenter, 1965) were determined on discrete samples. Nutrient concentrations were determined using the methods of Strickland and Parsons (1972), as modified for an Alpkem Rapid Flow Analyzer.

3.2.3 Determination of the OCS Hydrolysis Rate

The rate of OCS hydrolysis was determined under oceanographic conditions using Sargasso Sea water that had been collected following trace metal-clean procedures from 15 m depth at Station 12 (Fig. 3.1). The Sargasso Sea water was passed directly through a filter cartridge (0.4 μm) and stored in

20-L Cubitainers that were kept in the dark until use. At the shore laboratory, all sample manipulations were carried out in a Class 100 clean room (< 100 particles/m^3). Water was distilled before deionization to a specific conductance of 18 MΩcm. All the plastic-ware and sampling gear were acid cleaned.

To determine the rate of hydrolysis, two 3-L aliquots of deionized water and Sargasso Sea water were placed in Cubitainers. The Cubitainers were then placed in a dark incubator that was held at either 3, 6, 13, 17.8, or 23°C, where they could equilibrate for two days before being amended with a gas mixture of OCS (99.9%, Matheson) and helium. For all experiments, the initial concentrations of OCS in the Cubitainers that was determined at the first time point ranged between 16.3–88.6 nmol/L. The concentration of OCS was then determined over 2–7 days, depending on the temperature (*e.g.*, 2 days at 23°C and 7 days at 3°C) using the analytical methods described above. The relation between OCS concentrations and elapsed time was used to determine the hydrolysis rate.

The effects of trace metals on the rate of hydrolysis were examined in three additional experiments with Sargasso Sea water at a temperature of 18°C. These experiments exactly duplicated the ones described above (3-day time period), except for the addition of either Cu^{2+}, Zn^{2+}, or Hg^{2+} to a final concentration of 53 nmol/L prior to the amendment with OCS.

3.3 Results and Discussion

3.3.1 Laboratory Studies of OCS Hydrolysis

The hydrolysis rate of OCS at millimolar levels has been determined in water as a function of *p*H (2–12), temperature (−30–40°C), and ionic strength (up to 6.5 mol/L, for a review, see Elliott *et al.*, 1989b). Since OCS hydrolysis is possibly the most important source of dissolved sulfide to the open ocean, it is essential to establish the kinetics of this reaction under oceanographic conditions. Therefore, the rate of hydrolysis of OCS was redetermined at nanomolar levels using Sargasso Sea water, and following trace metal-clean procedures.

The results in Fig. 3.3 show the expected decrease of OCS concentrations over time. The hydrolysis reaction follows first order kinetics (Elliott *et al.*, 1989), and thus the curves in Fig. 3.3 are non-linear, least-squares fits of the data to the exponential decay equation

$$C_t = C_0 e^{-k_{hyd} t} \tag{3.1}$$

where C_t is the concentration of OCS at time t, C_0 is the initial concentration, and k_{hyd} is the observed hydrolysis rate constant (Gardiner, 1969). The remaining data from the hydrolysis experiments in Sargasso Sea water and deionized water were fitted in the same manner, yielding the hydrolysis rate constant at each of the five temperatures in water and seawater. The rates are summarized in Table 3.1

The rate constant of the reaction at any temperature can be calculated using the Arrhenius Expression (Gardiner, 1969):

$$\ln(k_{hyd}) = \ln(A) - \frac{E_a}{RT} \tag{3.2}$$

if the values for the activation energy (E_a) and the preexponential factor (A) of the reaction are known (R is the ideal gas constant, and T is the temperature in °K). The kinetic data in Table 3.1 must be interpreted with care, because the reaction of OCS hydrolysis proceeds simultaneously along acidic (*p*H independent) and alkaline (*p*H dependent) pathways. Although both pathways involve the hydration of OCS to a monothiocarbonate, and then very rapid conversion to H_2S and CO_2, each pathway has a different

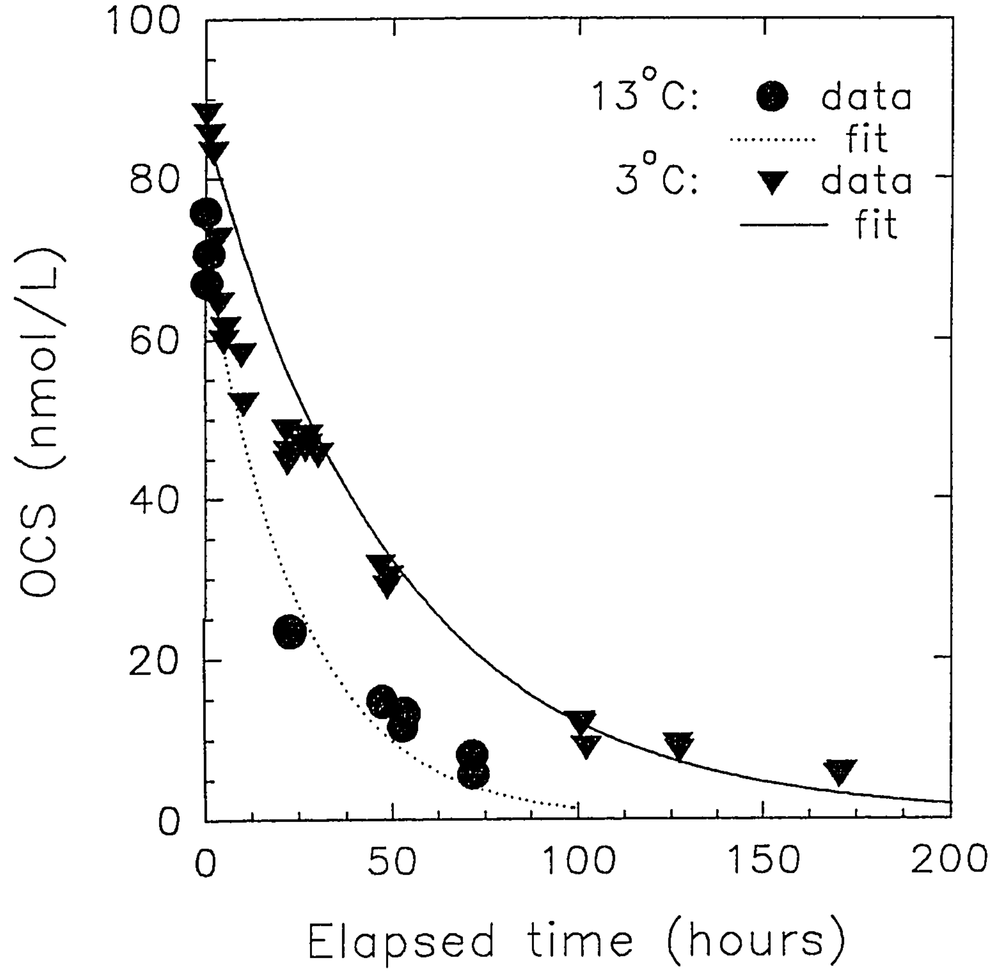

Figure 3.3: Example of kinetic data obtained for the determination of OCS hydrolysis rate in Sargasso Sea water. Each symbol represents a single determination of OCS concentration. The lines are the least-squares fit of the data used to obtain the rate of hydrolysis at that temperature.

Table 3.1: Observed OCS hydrolysis rate constants.

	Deionized water:		Sargasso Sea water[a]:	
Temperature (°C)	Observed rate (in $10^{-6}s^{-1}$)	Std. Dev.	Observed rate (in $10^{-6}s^{-1}$)	St. Dev.
3	2.52	0.71	5.52	0.44
6	4.91	0.29	4.25	0.19
13	5.83	0.47	11.0	0.86
17.8	11.9	0.56	21.9	1.41
17.8[b]	N.D.	N.A.	23.9	1.13
17.8[c]	12.9	0.58	21.4	1.83
17.8[d]	N.D.	0.76	29.1	1.06
23	11.6	0.66	32.4	0.91
23	N.D.	N.A.	28.1	0.91

[a] Sargasso Sea water *p*H is 8.285. Sargasso Sea water amended with 53 nmol/L of zinc[b], mercury[c] and, copper[d]. Copper amended water was not fitted to the Arrhenius Expression. Std. Dev. is the error of the exponential fit, N.D. is not determined, N.A. is not applicable.

temperature dependency (Elliott *et al.*, 1989b). The observed hydrolysis rate constant is then the sum of the rate constant along each pathway (Elliott *et al.*, 1989b):

$$k_{hyd} = k_{acidic} + k_{alkaline} \times 10^{pOH} \tag{3.3}$$

Below *p*H 7 (*e.g.*, in deionized water), k_{acidic} is equal to the observed rate of hydrolysis (k_{hyd}) because the contribution of the alkaline pathway to the observed rate constant is negligible (*e.g.*, $k_{alkaline} \times 10^{pOH} \ll k_{acidic}$; Elliott *et al.*, 1989b). Therefore, to obtain E_a and ln(A) for the reaction of OCS hydrolysis in deionized water (*e.g.*, Reaction 1.12, Chapter 1), the natural logarithms of the reaction rates determined at five temperatures presented in Table 3.1 were plotted against 1/T. The linear, least-squares fit of the resulting plot yielded a line whose Y-intercept was ln(A) and whose slope was E_a/R (Gardiner, 1969). The values of E_a/R and A determined in this manner were obtained using all the kinetic data from the deionized water hydrolysis experiment (Table 3.1). The obtained values of E_a/R and ln(A) given in Table 3.2 are 38% and 56% smaller, respectively, than those reported

Table 3.2: Comparison of hydrolysis rate parameters.

	Acidic pathway:		**Alkaline pathway:**	
Parameter	This work	Elliott *et al.* (1989b)	This work	Elliott *et al.* (1989b)
Ln(A)	10.7 ± 3.9^{a}	24.3	44.9 ± 0.32	22.8
$-E_a/R$	6459 ± 1230	10450	12630 ± 3316	6040

[a] Standard deviation of the parameter for each fit. Acidic pathway: r=-0.9344 (n=6), and alkaline pathway r=-0.8411 (n=8). Note: the observed hydrolysis rate is equal to $k_{acidic} + 10^{pOH} \times k_{alkaline}$.

in Elliott *et al.* (1989b) for the acidic pathway.

Because the rates of the alkaline and acidic pathways are nearly equal at the *p*H of seawater (Elliott *et al.*, 1989; here *p*H=8.285), the alkaline rate constant cannot be obtained directly from the observed hydrolysis rate. Thus, at each temperature the acidic rate constant (calculated from the data in the left hand columns of Table 3.2) was subtracted from the observed rate in Sargasso Sea water to determine the rate along the alkaline pathway. The rate along the alkaline pathway was then divided by the concentration of OH^- obtained from *p*H measurements (yielding $k_{alkaline}$), and fitted to Equation 3.2 as described above. The resulting values of E_a/R and ln(A) for the reaction along the alkaline pathway (*i.e.,* Reaction 1.13) in Sargasso Sea water are reported in Table 3.2, and utilize all the kinetic data acquired at five temperatures. Compared to calculations based on the results of Elliott *et al.* (1989b) presented in Table 3.2, the observed rate of hydrolysis ($k_{acidic} + k_{alkaline}$) in Sargasso Sea water at *p*H 8.285 is 36% slower at 5°C, and 10% slower at 25°C.

The laboratory experiments also examined the possibility of trace metal catalysis or inhibition on the hydrolysis of OCS that was proposed by Elliott *et al.* (1989b). To do so, the effects of 53 nmol/L concentrations of copper, zinc or mercury on the rate of reaction at 18°C were examined. This temperature was selected to speed up the experiment, and the metals were chosen because of their role in catalyzing or inhibiting the oxidation of dissolved sulfide with oxygen (Vazquez *et al.*, 1989). The concentration of trace metals was selected on the premise that, if the trace metals tested have a catalytic effect at their concentrations in seawater, this effect will be more easily detected at greater concentrations. However, the metal concentrations that were used are not unrealistically elevated. An increase in the rate of hydrolysis was observed in seawater spiked with copper, but not in seawater spiked with zinc or mercury (Table 3.1). In contrast with zinc and mercury, the rate obtained in copper-amended seawater was 32% greater than in unamended seawater (Table 3.1). This effect was observed at copper levels of 53 nmol/L, which are 10–500 times higher than concentrations found in the open ocean (Bruland, 1983), and thus the catalytic effects of copper for the hydrolysis of OCS may only be a factor in coastal waters.

3.3.2 Distribution of OCS in the Sargasso Sea

Previous attempts to sample OCS below the surface ocean were often unsuccessful because of contamination by the sampling bottles (Johnson and Harrison, 1986). Using sampling procedures that alleviate this problem (Chapter 2), and an accurate hydrolysis rate constant, the biogeochemistry of OCS in the ocean was re-examined in the Sargasso Sea. Depth profiles of OCS obtained at Station 12 in April and November 1989 are shown in Fig. 3.4a and 3.4b. A prominent and distinct maximum at 550 m was observed in April (Fig. 3.4a). The November depth profile shows maxima at the surface and at 100 m, as well as a distinct maximum at 550 m (Fig. 3.4b).

The only known sources of OCS in marine waters are the photolysis of dissolved organic sulfur compounds (Andreae and Ferek, 1992) and the input

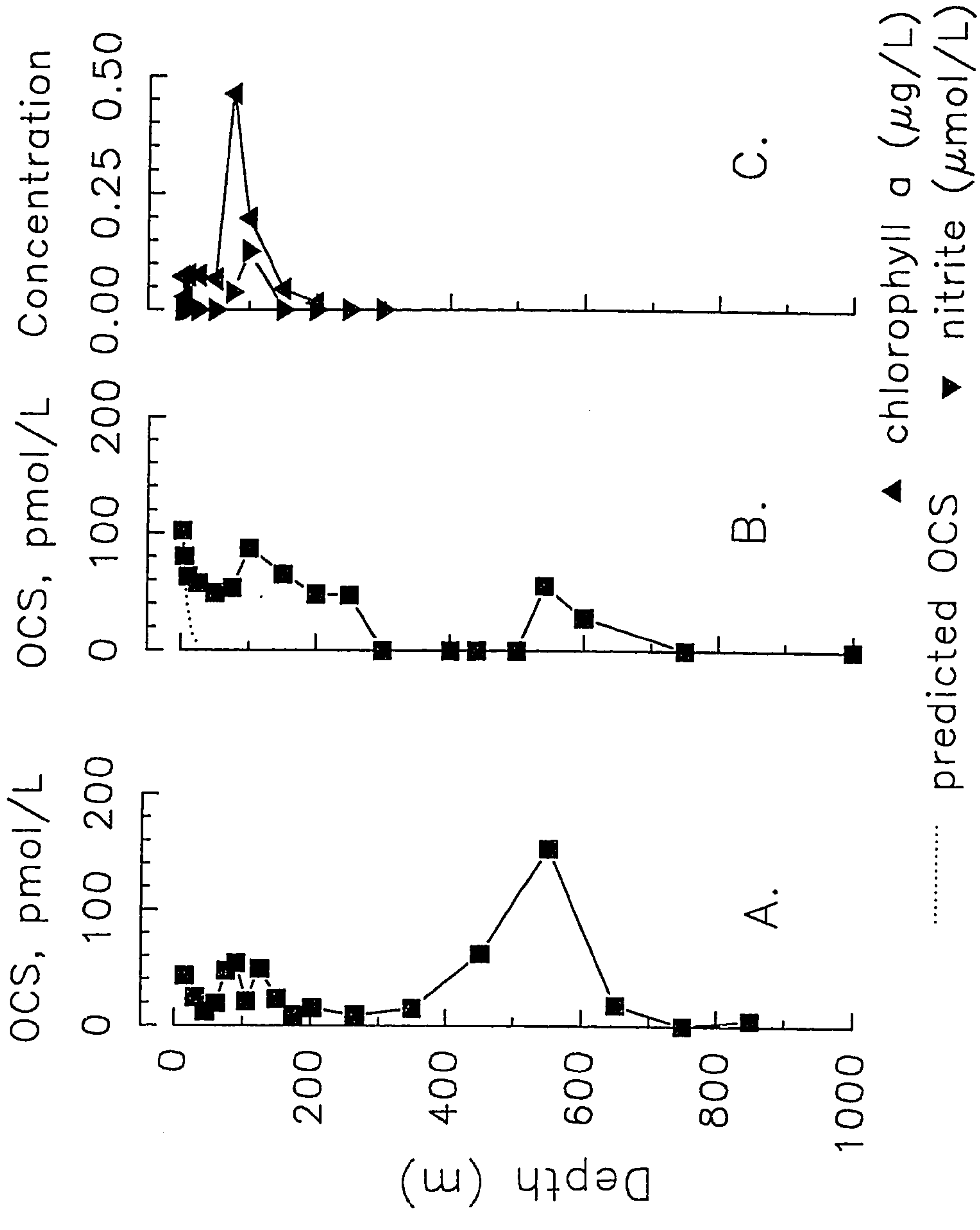

Figure 3.4: Station 12 depth profiles of: (A) OCS concentration in April 1989; the profile shown has been corrected for a blank of 39 pmol/L discovered at the shore laboratory, (B) OCS concentration in November 1989; the dotted line is OCS concentration predicted using Equation 3.4, and (C) nitrite and chlorophyll *a* concentrations observed in November 1989.

of OCS from estuarine sediments (Cutter and Radford-Knœry, 1993). The following scaling calculation can be used to examine the OCS depth profile in view of these known production mechanisms. Photochemical production of OCS is primarily induced by the U.V.-B (280–320 nm) portion of the solar spectrum (Zepp and Andreae, 1989); at these wavelengths, light has a $1/e$ penetration depth of 7 m in the open ocean (Smith and Baker, 1979). This depth limits the direct photochemical production of OCS to the upper 20 m of the open ocean water column, and less in coastal waters. Because the hydrolysis rate of OCS in seawater proceeds on the order of hours, the effects of advection and horizontal concentration gradients are negligible. Indeed, the horizontal OCS concentration gradient (ΔOCS/Δy) is on the order of 1 pmol/L/100 km in the Sargasso Sea (Andreae *et al.*, 1991), and the horizontal velocity (Δy/Δt) is less than 5 km/h (Stommel *et al.*, 1978). The product of this gradient and of the advective velocity yields a rate (*e.g.*, $\Delta\mathrm{OCS}/\Delta\mathrm{t} = 0.05$ pmol $\mathrm{L^{-1}h^{-1}}$) that is much smaller than the product of the hydrolysis rate (*i.e.*, $11\times10^{-6}\ s^{-1}$; Table 3.1) and the observed OCS concentration (102 pmol/L). The magnitude of these rates indicates that the effects of horizontal advection are negligible in comparison with OCS hydrolysis. Based on these arguments, the predicted OCS depth profile shows a concentration maximum at or near the surface, and an exponentially decrease due to hydrolysis and downward diffusion (*e.g.*, Johnson, 1981):

$$\mathrm{C_z} = \mathrm{C_0} e^{-z\left(\frac{k_{hyd}}{K_z}\right)^{1/2}} \tag{3.4}$$

where $\mathrm{C_z}$ is the concentration of OCS at depth z ($\mathrm{C_0}$ is the concentration of OCS at the base of the photochemical production layer), depth is positive downward, and $\mathrm{K_z}$ is the vertical eddy diffusion coefficient. To compare OCS concentration predicted using Equation 3.4 with the observations at

Station 12, a value of 102 pmol OCS/L for C_0 at 7 m, $3.13\times10^{-5}s^{-1}$ for k_{hyd} (*p*H 8.2 and T 297.6°K; Table 3.2) and 20 cm^2s^{-1} for K_z (Johnson, 1981) were used. The eddy diffusion coefficient used here corresponds to that determined in the mixed layer of the trade wind belt (Peng *et al.*, 1979) and is applicable to the upper water column of the Sargasso Sea (Landing *et al.*, manuscript in preparation). Using these parameters, the predicted profile is shown by the dotted line in Fig. 3.4b. It should be noted that under these conditions, the half-time of OCS with respect to hydrolysis is 6.2 h and the $1/e$ penetration depth of OCS is 7.2 m. The vertical attenuation of the concentration is relatively insensitive to variations of K_z because the penetration of OCS increases only by a factor of 3.2 when K_z increases by an order of magnitude (*e.g.,* if K_z increases to 200 cm^2s^{-1} determined in the stormy North Pacific (Peng *et al.*, 1979), the $1/e$ penetration depth of OCS becomes 23 m). This simple scaling calculation shows that vertical depth profiles of OCS that are observed are not significantly influenced by horizontal advection, and that hydrolysis attenuates features on the 7.2 m depth scale. Thus, the maxima in OCS depth profile that are observed are due to processes occurring at the depths sampled, rather than being due to advection/diffusion of OCS-rich water.

At Station 12, the positive difference between the concentrations observed and the concentration calculated using Equation 3.4 (Fig. 3.4b) is evidence for additional inputs of OCS to the water column. In particular, the OCS concentration maximum (87 pmol/L) observed at 100 m in November (Fig. 3.4b) cannot be explained by the simple vertical diffusion model presented above. If this feature is due to the isolation of OCS-rich water by seasonal stratification, then the rate of hydrolysis calculated from the data in Table 3.2 for 20°C seawater ($0.07\ h^{-1}$) can be used to predict the original OCS concentration. The water column stratifies in April-May at Station 12 (Jenkins and Goldman, 1985), and thus OCS concentrations of the mixed layer would have to be 10^{111} times greater than actually observed in April. Since this is not the case, the maximum at 100 m is probably due to *in situ* processes. Significantly, nitrite at 100 m depth also shows a concentration maximum (Fig 3.4c). The nitrite maximum observed at 100 m can result from the release of ammonium followed by its oxidation in well oxygenated seawater (Codispoti and Christensen, 1985). Such a primary nitrite maximum is indicative of active regeneration of organic matter in the water column. Thus, the co-occurrence of nitrite and OCS maxima suggest that OCS production may be associated with recycling of organic matter in the water column.

Figure 3.4a and 3.4b also show OCS maxima at 550 m that cannot be explained by the downmixing of surface production, nor by the ventilation of this isopycnal (σ_θ=26.6) which occurs on the scale of many months (Jenkins, 1980, 1982). Thus, an *in situ* source of OCS must exist, and speculation on its nature is presented here. The likelihood of a sampling artifact is decreased because the 550 m maximum was observed in April and November 1989. In April 1989 elevated concentrations of particulate and dissolved iron and aluminum were observed at a depth coincident with the OCS maximum (Lewis and Landing, 1990, 1991); trace metal samples were not collected in November 1989. Elevated iron and aluminum concentrations suggest that the composition of water near 550 m was affected by sedimentary matter in suspension, in a manner similar to that described by Landing and Bruland (1987). Significantly, OCS concentrations up to 0.5 μmol/L have been reported in anoxic and oxic sediments (Cutter and Radford-Knœry, 1993). The shape of the maximum rules out vertical diffusion from the seafloor, 3.98 km below the 550 m maximum. Along the 26.6σ_θ isopycnal surface, the distance between Station 12 and the sea floor is either 50 km (Bermuda platform) or 860 km (Mid-Atlantic Bight). Based on the times necessary to travel these distances (weeks to months, Stommel *et al.*, 1978) and the rate of hydrolysis of OCS at that depth and temperature (0.04 h^{-1} at 15°C), the maximum probably does not result from a flux of OCS from the sea-floor; indeed, initial concentrations of OCS would have to be absurdly elevated. Due to the rapid hydrolysis rate of OCS, the elevated OCS levels observed at 550 m cannot originate from very far. Thus, the OCS maximum would have to be produced *in situ*, perhaps from the degradation of sedimentary organic matter transported with elevated Al and Fe along the 26.6-σ_θ isopycnal. The decrease of the size of the OCS concentration peak observed over six months (Fig. 3.4a and 3.4b) indicates that the 550 m OCS maximum is a transient feature. While the OCS maximum found at 550 m could be due to organic matter remineralization, this proposed OCS production mechanism needs to be examined further.

3.3.3 Dissolved Sulfide and Carbonyl Sulfide in the Western North Atlantic Ocean

It is important to evaluate the coupling between dissolved sulfide and OCS since the hydrolysis of OCS was the first recognized source of dissolved sulfide to the open ocean (Elliott *et al.*, 1987). Because the processes controlling their concentrations can be segregated both temporally and vertically, their coupling can be assessed using time series and depth profiles. The temporal variation of total dissolved sulfide and OCS concentrations was examined using two series of depth profiles from Station 15 (April 1989; fig. 3.5) and Station 8 (November 1989; fig. 3.6). At these stations, total dissolved sulfide concentrations increased during the night and decreased in the early morning.

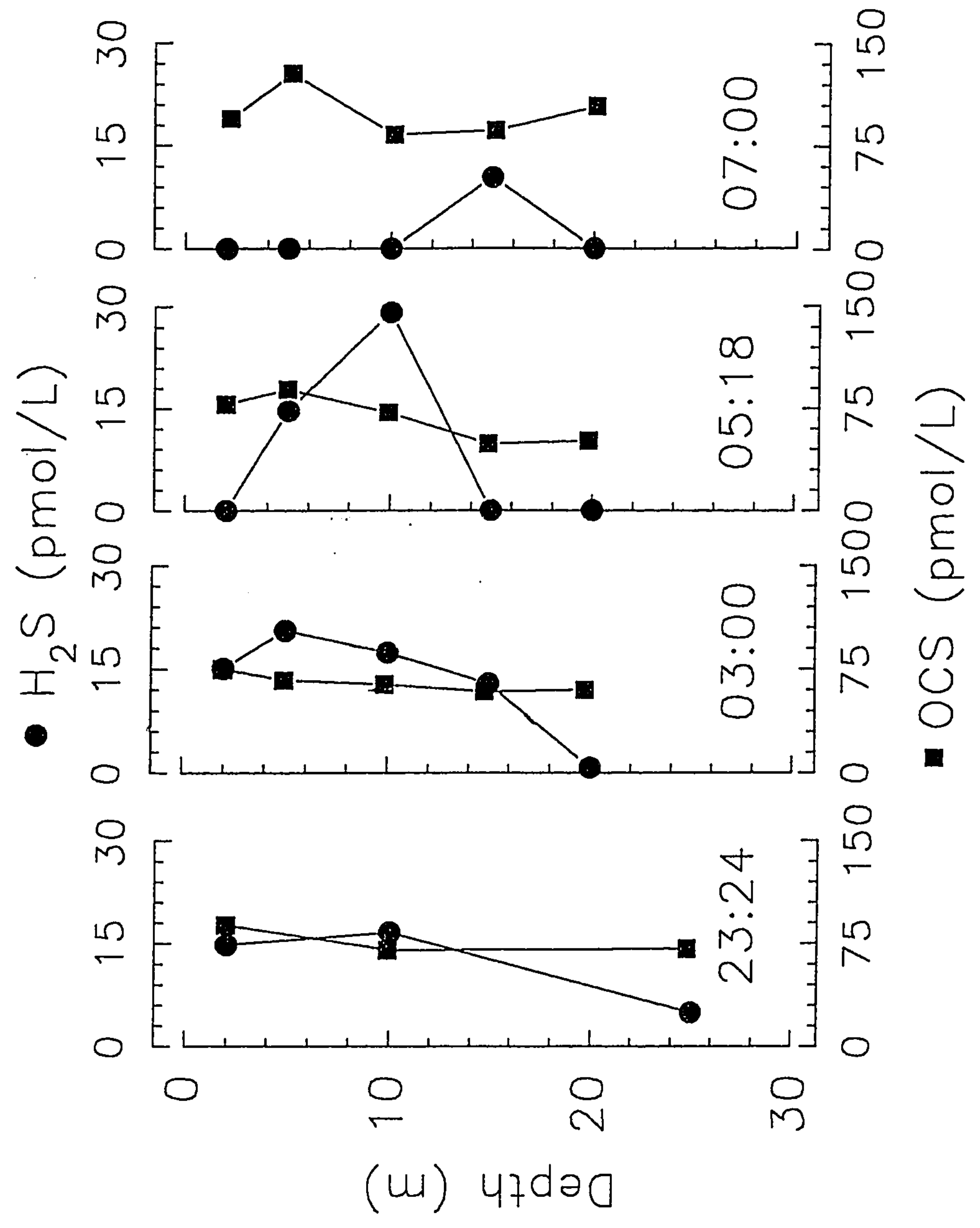

Figure 3.5: Time series for depth profiles obtained during the night and early morning at Station 15 (Fig 3.1) in April 1989. Local times are indicated.

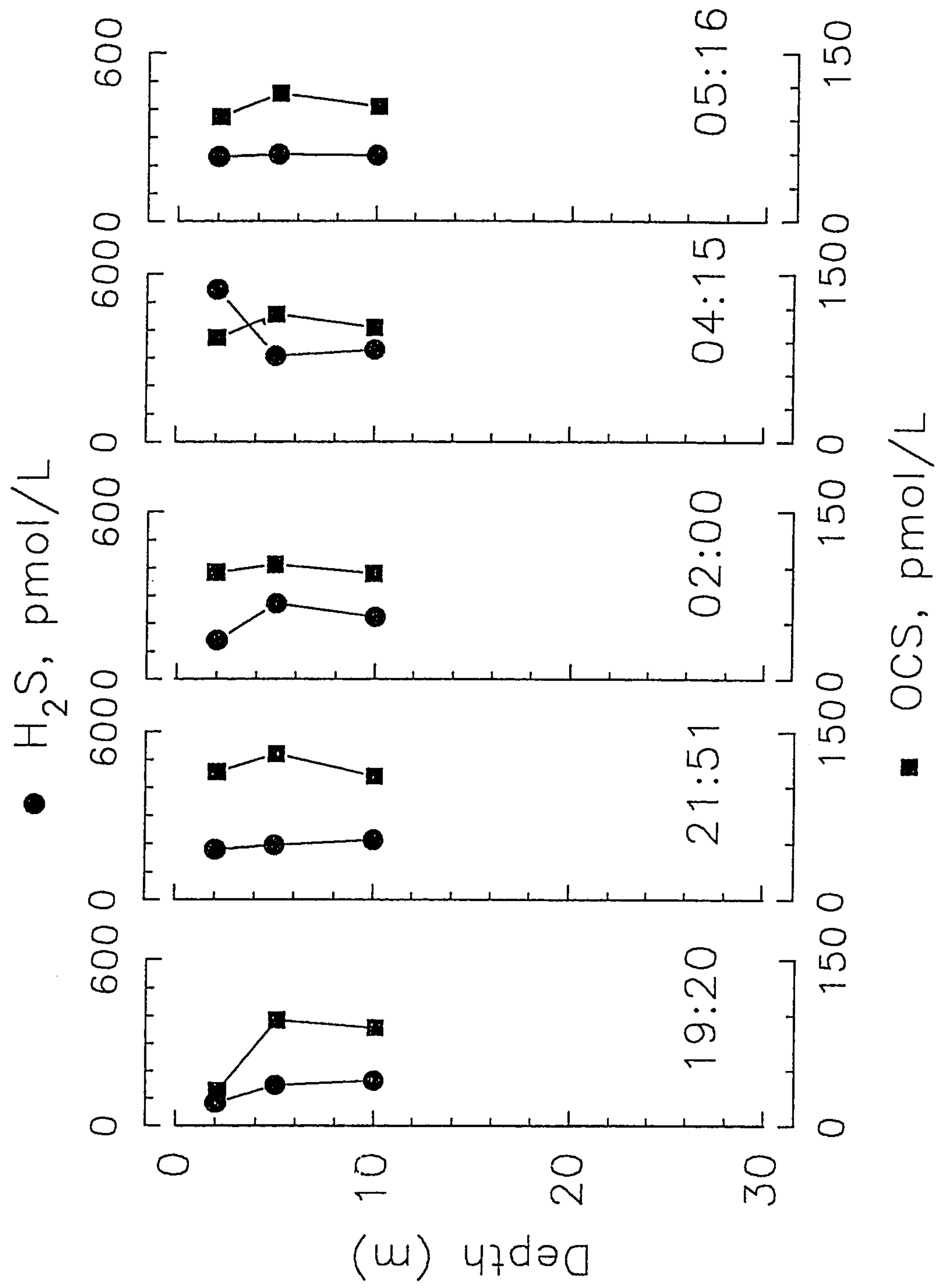

Figure 3.6: Time series of depth profiles obtained during the night and early morning at Station 8 (Fig 3.1) in November 1989. Local times are indicated.

In contrast, concentration depth profiles of OCS were nearly constant through the night at Station 8 (93± 14 pmol/L) and Station 15 (76±14 pmol/L). The nocturnal behaviors of total dissolved sulfide and OCS described here are identical to those observed previously (Cutter and Krahforst, 1988, Andreae and Ferek, 1992). If dissolved sulfide is produced by OCS hydrolysis and removed *via* oxidation by oxygen as proposed by Elliott *et al.* (1987), then the observed concentrations of total dissolved sulfide and OCS should co-vary. Since this is not the case, the time series presented above confirm the existence of source(s) of dissolved sulfide in addition to that by OCS hydrolysis (Cutter and Krahforst, 1988).

The coupling between OCS and dissolved sulfide was also examined using depth profiles. In the profiles collected at Station 8 (Fig 3.7a and 3.7b), concentrations of total dissolved sulfide dropped rapidly in the first 25 m, and then more gradually below 75 m (Fig. 3.7). The profile of OCS at Station 8 showed concentrations of 75 pmol/L throughout the mixed layer, and decreased with depth. At Station 12, concentrations of total dissolved sulfide showed a maximum (175 pmol/L) at 75 m, and below 200 m total dissolved sulfide concentrations were uniform at 62 pmol/L (Fig. 3.8). Concentrations of free sulfide ranged from <15 to 28 pmol/L in the upper 150 m at Station 12 (Fig. 3.8). At this station, the depth profile of OCS exhibited prominent subsurface maxima at 100 and 550 m (Fig. 3.4b), as described above.

The rate of dissolved sulfide production from OCS hydrolysis (*i.e.,* the OCS hydrolysis rate) is the product of the hydrolysis rate constant and the concentration of OCS. While a more quantitative treatment of the data is described below, it is sufficient to realize that OCS hydrolysis rate and concentration profiles are roughly parallel for the qualitative discussion presented here. The depth profiles of OCS and total dissolved sulfide both show ele-

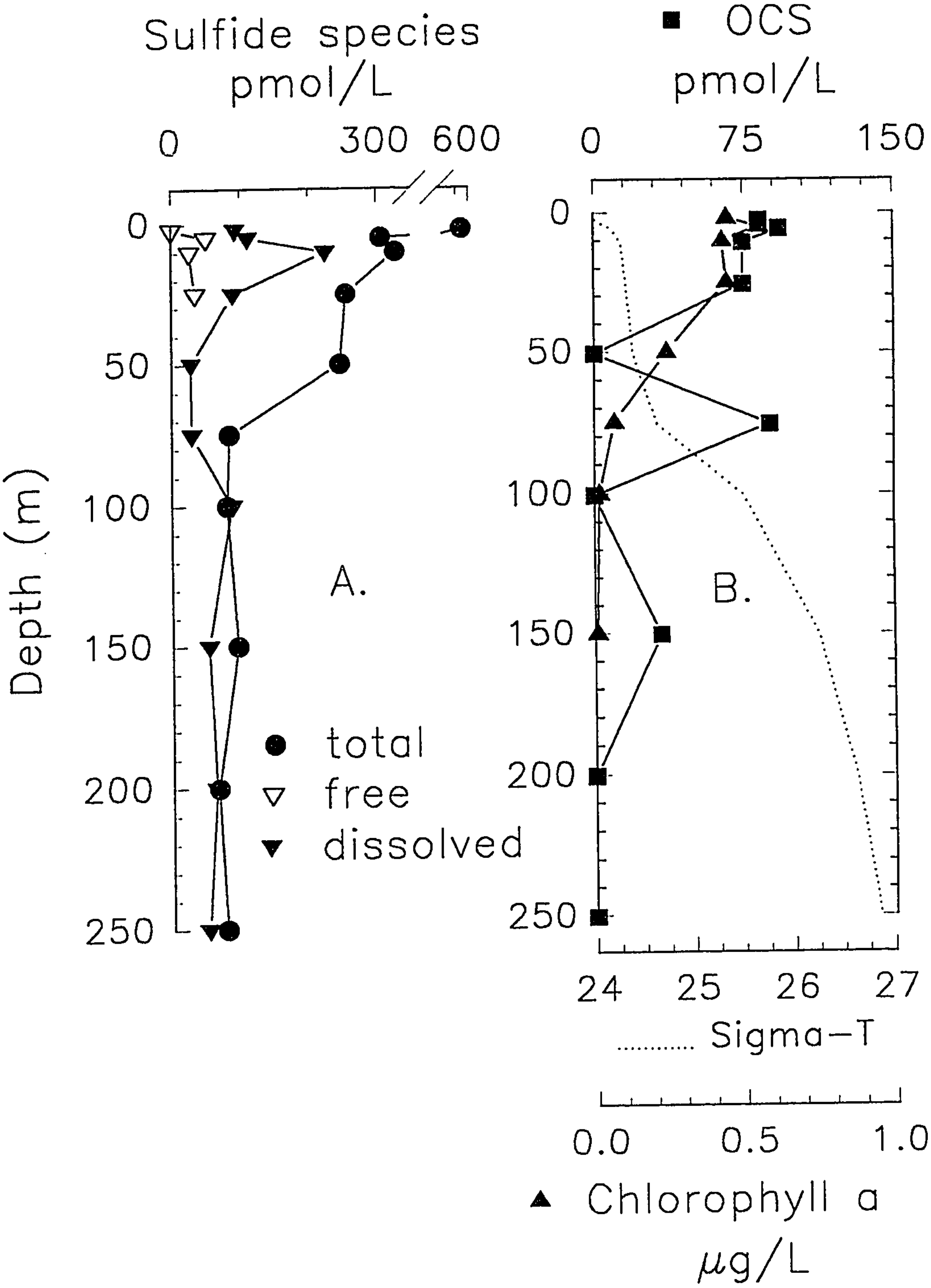

Figure 3.7: Depth profiles of (A) the different forms of total dissolved sulfide, and (B) ancillary parameters at Station 8.

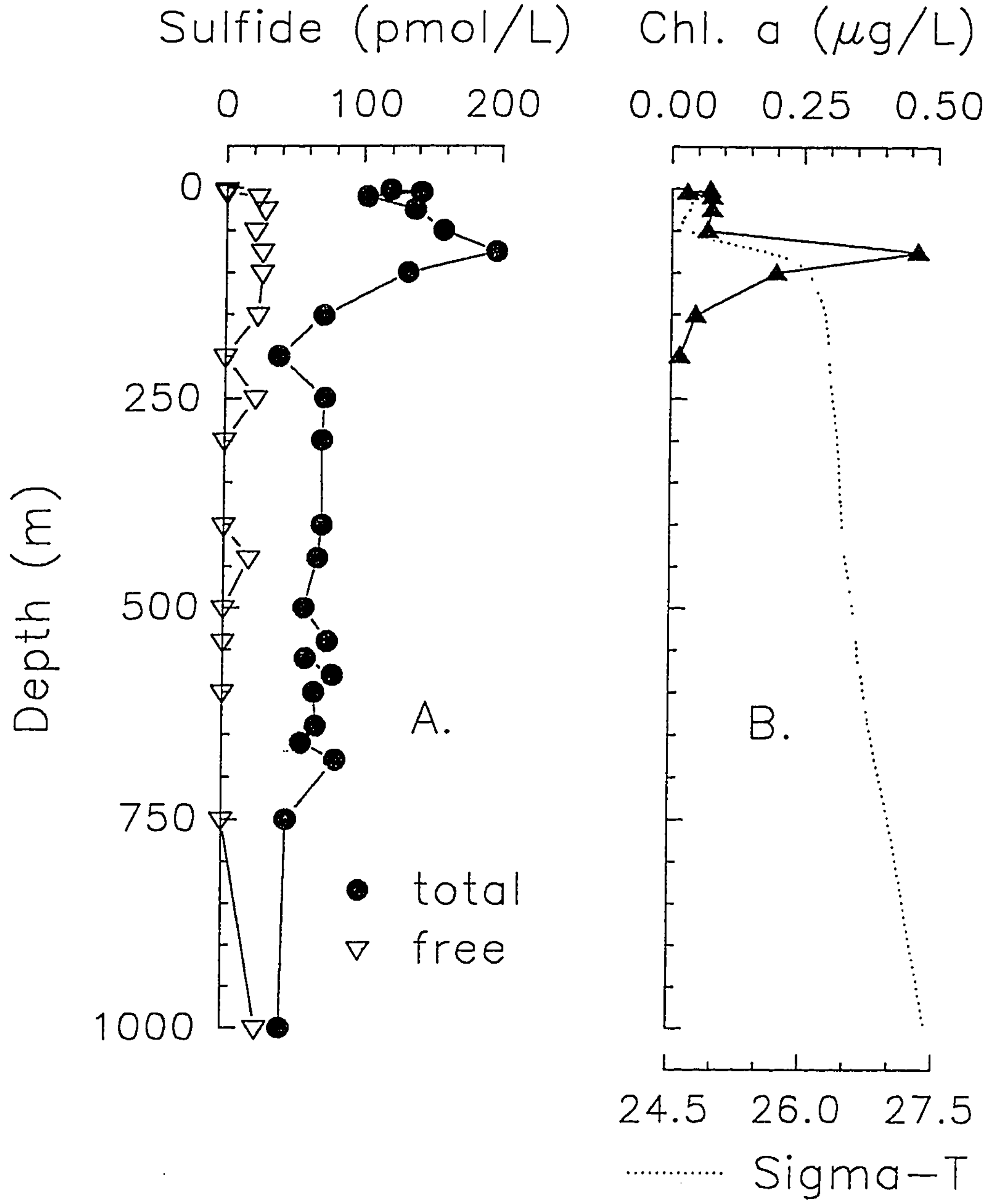

Figure 3.8: Station 12 (Fig 3.1) depth profiles of (A) total dissolved sulfide and free sulfide, and (B) chlorophyll *a* and density in November 1989.

vated values in the mixed layers of Station 8 and 12, suggesting that the presence of total dissolved sulfide may be due to OCS hydrolysis. However, at Station 12 the concentrations of total dissolved sulfide do not vary below 200 m, while OCS concentrations show a distinct maximum at 550 m (Fig. 3.4 and 3.8). The lack of a maximum of total dissolved sulfide near 550 m indicates that it is removed much faster than it is produced from the hydrolysis of OCS. Considering this observation and the qualitative examination of the time series, it appears that the coupling between OCS and total dissolved sulfide is obscured by other sources and sinks of dissolved sulfide. A more quantitative treatment of the coupling between OCS and total dissolved sulfide is presented in a section below.

Existing data on total sulfide (dissolved and particulate) in the open ocean reports only unfiltered or filtered concentrations (*e.g.,* Cutter and Krahforst, 1988, Luther and Tsamakis, 1989), and little information on the different forms (particulate, uncomplexed) of total sulfide is available. It is important to distinguish between its different forms, because air/sea exchange depends on the concentration of uncomplexed H_2S_{aq} (Andreae *et al.*, 1991). Moreover, the rate of oxidation of total dissolved sulfide by IO_3^- depends on the proportion of free sulfide (Luther and Tsamakis, 1989). To obtain data on the different forms of total sulfide, filtered and unfiltered depth profiles for total sulfide, and free sulfide were obtained at Stations 8 and 12 in November 1989.

Depth profiles of this gross speciation of total sulfide are presented in Fig. 3.7 (Station 8) and Fig. 3.8 (Station 12). The concentration of particulate sulfide was obtained from the difference between filtered and unfiltered samples. At Station 8, concentrations of total dissolved sulfide range between 30 and 50 pmol/L, except for a maximum (210 pmol/L) at 10 m (Fig. 3.7).

The concentration of particulate sulfide (*i.e.,* difference between total and dissolved sulfide in Fig. 3.7) drops rapidly below the surface and reaches near constant levels at the base of the pycnocline. In the mixed layer of Station 8, free sulfide concentrations ranged between <15 and 51 pmol/L (Fig. 3.7).

A preliminary assessment of the gross speciation of dissolved sulfide was obtained from these depth profiles. In the mixed layer, most total sulfide (68%) is associated with particles, which is then a potentially important loss for total dissolved sulfide *via* sinking (Cutter and Krahforst, 1988). Furthermore, the decrease in particulate sulfide concentrations below the pycnocline of Station 8 indicates that depth-dependent processes are also important for the cycling of particulate sulfide including larger particles sinking out of the mixed layer. Because rapidly sinking particles are undersampled by conventional bottles (*e.g.,* McCave, 1975), the depth profile needs to be complimented with particle flux data to quantitatively evaluate this loss; the next section presents a discussion of sediment trap data for Station 12.

Thermodynamic calculations of inorganic equilibria indicate that nearly ≥99% of dissolved sulfide (at the concentrations observed in the open ocean) should be complexed by trace metals (Dyrssen, 1988, Elliott *et al.*, 1990). In contrast to these calculations, free sulfide comprises 10–13% of total dissolved sulfide in the upper 25 m at Station 8 (Fig. 3.7a). In the upper 125 m of Station 12, the fraction of free sulfide was 19% of total dissolved sulfide (Fig. 3.8a). The discrepancy between the observations and thermodynamic predictions could arise if the analytically determined fraction of free sulfide includes a portion of the complexed sulfide fraction. However, experimental evidence suggests that such complexes are not broken by gas stripping (Luther and Tsamakis, 1989). The discrepancy between the observed and calculated gross speciation of sulfide may also arise from inaccuracies in thermodynamic equilibrium constants of metal sulfide complexes. Few equilibrium constants for metal-sulfide complexes have been actually determined, requiring the use of estimates that are the subject of considerable debate over their accuracy (*e.g.,* Dyrssen, 1985, Elliott, 1988, Dyrssen, 1988, Elliott and Rowland, 1990).

3.3.4 Sources and Sinks of Dissolved Sulfide in the western North Atlantic Ocean

To obtain a quantitative understanding of the cycling of dissolved sulfide in the surface ocean, its input and output fluxes must be known. Proposed sources of dissolved sulfide in the surface ocean include atmospheric input, OCS hydrolysis and dissimilatory sulfate reduction within marine snow (Elliott *et al.*, 1987, Cutter and Krahforst, 1988). Sinks of dissolved sulfide include oxidation, sinking with particles, and sea/air exchange. To assess these sources and sinks quantitatively, the November 1989 results for the upper 150 m of Station 12 will be used because of the amount of dissolved sulfide data available (Fig. 3.4 and 3.8), and because of the ancillary data available from the JGOFS program and other studies at this location. A schematic representation of the sources and sinks of dissolved sulfide is presented in Fig. 3.9. Observed OCS concentrations and the rate constants calculated from Table 3.2 were utilized to accurately determine the production of dissolved sulfide from OCS hydrolysis. After correction for temperature and *p*H effects, the hydrolysis rate of OCS at each of the eight depths within the upper 150 m water column varied between 11.5 pmol L^{-1} h^{-1} at the surface and 3.97 pmol L^{-1} h^{-1} at 150 m. Because of the small depth range considered here, the effects of pressure on the rate of OCS hydrolysis were not

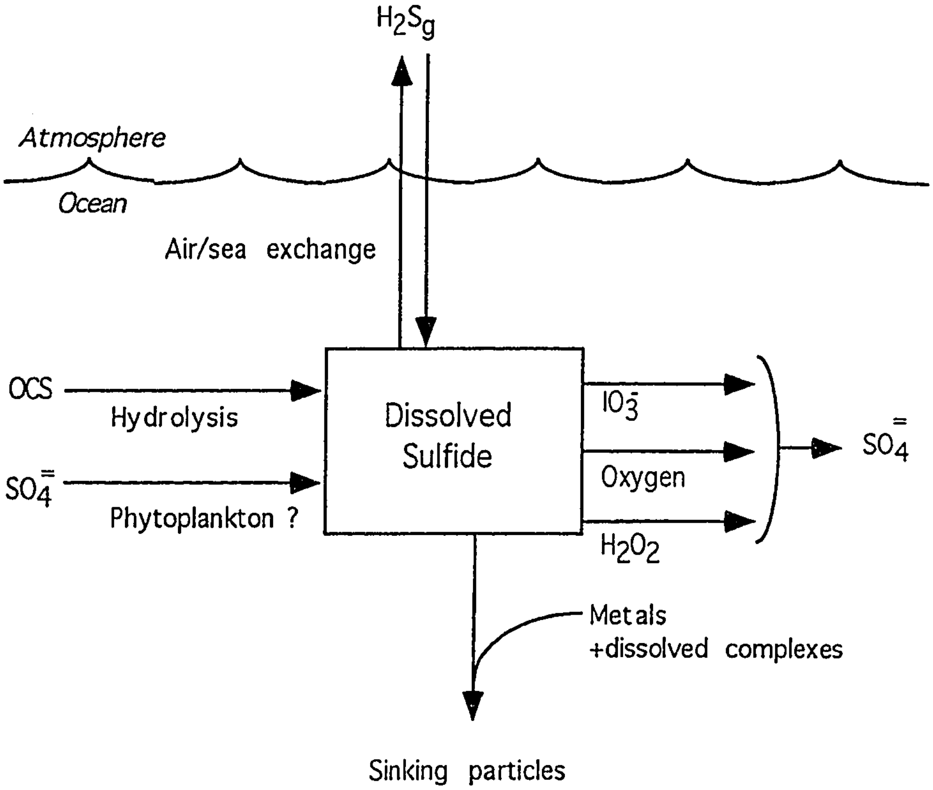

Figure 3.9: A diagram of processes affecting the distribution of dissolved sulfide in the upper 150 m of the Sargasso Sea.

Table 3.3: Sources and sinks of dissolved sulfide in the upper 150 m of the Sargasso Sea.

	Ranges of species Concentration	Depth-averaged sulfide fluxes (over 150 pmol L^{-1} h^{-1}) [a]	Uncertainty (%)[b]
Sources:			
Atmospheric input		000.03	
OCS hydrolysis	49–102 pmol/L OCS	005.35	±21
	Total sources:	*005.38*	±21
Sinks:			
Sulfide oxidation	0–0.14 μmol/L H_2O_2	000.02	±25
	212–219 μmol/L O_2	003.07	±18
	0.33–0.38 μmol/L IO_3^-	112.00	±30
Particle sinking		000.18	
	Total sinks:	*115.27*	±30
	Source needed to balance: (Phytoplankton production ?)	109.89	±30

[a] Range of values encountered are given in the text

[b] Uncertainty calculated from propagation of errors in the concentration and reaction rate between the appropriate species.

taken into account. The depth integrated average for the production rate of dissolved sulfide due to OCS hydrolysis is 5.35 pmol L^{-1} h^{-1} (Table 3.3).

Dissimilatory sulfate reduction within micro-environments was not specifically investigated during either of the sampling cruises. However, the possible importance of this source of dissolved sulfide for the water column can be gauged from the composition of marine snow particles. Marine snow is enriched in trace metals (Hebel *et al.*, 1986), which favors both the catalysis of dissolved sulfide oxidation by oxygen (Vazquez *et al.*, 1989), and the precipitation with metals (Stumm and Morgan, 1981). Thus, the combined effects of trace metals may decrease the diffusive flux of dissolved sulfide from marine snow particles. In addition, the steepness of oxygen concentration gradients near the particle/water interface in marine aggregates depends on the ability of oxygen to diffuse into the particle (Alldredge and Cohen, 1987). Thus, if the influx of oxygen is hampered, so is the diffusion of dissolved sulfide out of marine particles. Overall, chemical and physical barriers likely prevent dissolved sulfide from leaving such particles, and limit the importance of marine aggregates for dissolved sulfide concentrations observed in the bulk water column.

Simultaneous determinations of free sulfide and H_2S_g in and over the western North Atlantic Ocean showed that the flux of this gas varied between 19 and 8 nmol m^{-2} h^{-1} (Andreae *et al.*, 1991). The direction and magnitude of this flux depend on the concentration difference between free sulfide at the sea surface and atmospheric boundary layer concentration of H_2S_g. At Station 12, the flux of sulfide was directed into the sea and had a value of 4.2 nmol m^{-2} h^{-1}, which is close to the average value determined for the western North Atlantic Ocean (3.5 nmol m^{-2} h^{-1}, Andreae *et al.*, 1991). Averaged over the 150 m water column, the atmospheric flux of H_2S_g amounts to 0.03 pmol L^{-1} h^{-1} (Table 3.3).

Removal of dissolved sulfide occurs by association with sinking detritus and by oxidation. Sediment traps are necessary to quantify the flux of particulate sulfide because the particle mass flux is dominated by large and rapidly sinking particles that are infrequently sampled by conventional water bottles (McCave, 1975). Marine particles are a potentially important removal term because they are enriched in trace metals (Hebel *et al.*, 1986, Fowler, 1977), which could scavenge dissolved sulfide *via* complexation/precipitation as they sink through the water column.

The vertical flux of particulate sulfide was estimated using sediment trap measurements. Since these data are not available for the November occupation of Station 12, they were estimated from the molar ratio of particulate sulfide (pS) to particulate organic carbon (POC, 4.0×10^{-7}; Cutter and

Radford-Knœry, 1991) in April, and from the November POC flux at 150 m from the JGOFS Bermuda Atlantic Times Series (1.94×10^{-3} mol C m^{-2} d^{-1}; Knap *et al.*, 1992). Using these data, the calculated November flux of pS at 150 m is 32.3 pmol m^{-2} h^{-1}. This calculation assumes that the ratio of pS:POC is the same for suspended and sinking particulate matter, and that this ratio does not vary seasonally. While many assumptions are necessary to make this calculation possible, it allows an order of magnitude estimate of the flux of particulate sulfide at 150 m. Particulate data from the central Equatorial Pacific Ocean indicate that concentrations of suspended pS are 21 times smaller than suspended particulate chromium reducible sulfur (pCRS; Cutter and Radford-Knœry, in preparation). Chromium reducible sulfur includes sulfide bound in refractory compounds such as copper-sulfide, which are not detected as particulate sulfide (Chapter 2). Using the ratio of pCRS:POC would increase the calculated flux to 0.67 nmol m^{-2} h^{-1}. For the sake of consistency with the rest of this calculation, the flux of pS is used; over 150 m, the depth averaged flux is then 0.03 pmol L^{-1} h^{-1}.

Removal by oxidation is a potentially large sink of dissolved sulfide. In seawater the rates of removal of dissolved sulfide by oxygen, H_2O_2 and IO_3^- are well known (Millero and Hershey, 1989, Zhang and Whitfield, 1986). The oxidation of dissolved sulfide by oxygen proceeds at a rate proportional to the concentration of dissolved oxygen because its concentration is five orders of magnitude greater than that of dissolved sulfide (Millero *et al.*, 1987). In the upper 150 m of Station 12, oxygen concentrations were in the range of 202–320 μmol/L, while temperature varied between 19 and 24.4°C. Applying the rate laws presented by Millero *et al.* (1987), the rate of sulfide oxidation by oxygen ranged between 1.17 and 4.18 pmol L^{-1} h^{-1}, and the depth averaged oxidation rate was then 3.07 pmol L^{-1} $h-1$ (Table 3.3).

Another oxidant for dissolved sulfide in surface waters is H_2O_2 (Millero *et al.*, 1989). The rate of dissolved sulfide oxidation is proportional to the concentration of H_2O_2. This rate has been determined as a function of *p*H, temperature and salinity (Millero *et al.*, 1989). Although H_2O_2 concentrations were not determined in November 1989 at Station 12, the concentrations can be estimated from H_2O_2 profiles taken at 15:00h at this site in June 1987 (Palenik and Morel, 1988). Because H_2O_2 is produced photochemically (Zika *et al.*, 1985), the June profile is likely to represent a maximum for the month of November. Using the June concentration data, the rate of dissolved sulfide oxidation by H_2O_2 varied between 0 (at 100 and 150 m where no H_2O_2 was detected by Palenik and Morel, 1988), and 0.067 pmol L^{-1} h^{-1} at the surface where H_2O_2 concentrations are maximum. The depth integrated removal of dissolved sulfide due to H_2O_2 oxidation is 0.02 pmol L^{-1} h^{-1}.

The third oxidant of dissolved sulfide that should be considered is iodate (IO_3^-). Unlike H_2O_2 and oxygen, the rate of dissolved sulfide removal by IO_3^- is proportional to the square root of oxidant concentration and first order with respect to the concentration of dissolved sulfide (Zhang and Whitfield, 1986). In natural seawater, the rate constant for dissolved sulfide oxidation by IO_3^- was found to vary between 102 and 165 $mol^{-1/2}$ min^{-1} at 25°C, but the effects of temperature and ionic strength on that rate are unclear (Zhang and Whitfield, 1986). Furthermore, Luther and Tsamakis (1989) indicate that iodate reacts only with free sulfide, presumably because the kinetic stability of metal sulfide complexes that inhibits oxidation. In this budget, only free sulfide concentrations are used to compute the rate of sulfide oxidation by IO_3^-.

While IO_3^- concentrations were not determined in November, they can be obtained from salinity measurements, and from the relationship between salinity and IO_3^- for the Sargasso Sea (Jickells *et al.*, 1988). At these sites the ratio of iodate to salinity (as nmol iodate L^{-1} psu^{-1}) ranged between 9.1±0.9 at the surface and 10.4±0.3 at 150 m. To calculate the rate of dissolved sulfide removal due to IO_3^- oxidation at each of the eight depths in the 150 m-thick surface layer, the square root of the calculated IO_3^- concentration was multiplied by the free sulfide concentration (Fig. 3.8), and by the average rate constant for the reaction (2.2 $mol^{-1/2}$ h^{-1}). In view of the uncertainty on the rate constant itself, potential temperature and pressure effects were ignored. In the upper 150 m at Station 12, the rate of removal of dissolved sulfide by iodate varied between 0 (where no free sulfide was detected) and 125 pmol $L^{-1}h^{-1}$. The depth-integrated rate of the oxidation of dissolved sulfide by IO_3^- is 112 pmol L^{-1} h−1 (Table 3.3), which dominates the other oxidative removal pathways.

Examination of the depth averaged values for the sources and sinks in Table 3.3 shows a substantial imbalance in the production and removal fluxes of dissolved sulfide. In the strict sense, a steady state (*i.e.,* dC/dt = 0) for dissolved sulfide concentrations is never reached because of diel variations in total sulfide concentrations (Fig. 3.5 and 3.6; Cutter and Krahforst, 1988). Because sampling at Station 12 was completed in 8 hours, the budget obtained reflects the balance of processes occurring on that time scale. The possibility that the imbalance would be attributable to an overestimate of the oxidation rate of dissolved sulfide by iodate can be evaluated as follows. If this rate were much lower, then the hydrolysis of OCS would become a proportionately more important source term, and the depth profiles of total dissolved sulfide and OCS would then be better correlated. However, the spatial and temporal behaviors of total dissolved sulfide and OCS were not found to co-vary in the western North Atlantic Ocean (*i.e.,* Fig. 3.4b–3.6, 3.8). An additional source term of dissolved sulfide must then be invoked to balance the budget, and speculation on its nature follows.

Previous studies of dissolved sulfide in the coastal ocean noted that the maximum concentrations were often coincident with the maximum chlorophyll *a* concentration (Cutter and Krahforst, 1988, Luther and Tsamakis, 1989). This correspondence between total dissolved sulfide and chlorophyll *a* was also observed in more oceanic waters of the western North Atlantic Ocean at Stations 8 and 12, where their respective maxima are found at the same depth (Fig. 3.4c, 3.7, 3.8). Least-squares linear regression fits to the total dissolved sulfide concentration (in pmol/L) and chlorophyll *a* (in μg/L) data yield a correlation coefficient of $r^2=0.657$ (n=8) at Station 8 (dissolved sulfide= 580 × chlorophyll a + 82), and a correlation coefficient of $r^2=0.458$ (n=9) at Station 12 (dissolved sulfide = 226 × chlorophyll a + 96). The Y–intercepts are different from zero at both stations, which is consistent with the presence of other sources of dissolved sulfide (*i.e.,* OCS hydrolysis). From the observed correspondence between chlorophyll *a* and total dissolved sulfide, a substantial fraction of total dissolved sulfide that was observed in the Sargasso Sea may have been released by phytoplankton.

The release of hydrogen sulfide by terrestrial plants has been well documented (see Rennenberg, 1991 for a review), and is thought to play a regulatory role in assimilatory sulfate reduction (*i.e.,* production of cysteine, a sulfur amino-acid). Cysteine is produced from the reaction between O-acetyl serine and a sulfide-carrier molecule (Rennenberg, 1991). Based on results of substrate limitation and enrichment experiments performed on cucurbit cells, Rennenberg *et al.* (1982) proposed that the availability of O-acetyl serine is a rate limiting step in cysteine synthesis. He suggested that when the supply of carrier-sulfide exceeds the rate of synthesis of O-acetyl serine, hydrogen sulfide is released as a means to regulate the intracellular concentration of carrier-sulfide. With respect to marine phytoplankton, the biochemical reactions that produce cysteine in the alga *Chlorella* (Andreae, 1986) are identical to those mentioned above for cucurbit cells, and thus the results obtained by Rennenberg *et al.* (1982) may be applicable to phytoplankton. Indeed, recent work in this laboratory with axenic cultures of actively growing oceanic phytoplankton unequivocally shows the production of dissolved and particulate sulfide (Walsh *et al.*, submitted).

If a portion of dissolved sulfide is produced in the water column by phytoplankton as hypothesized above, chlorophyll *a* and total dissolved sulfide concentrations need not be perfectly correlated, because other processes are also involved in cycling of dissolved sulfide (*e.g.*, OCS hydrolysis), and also because the possible production of dissolved sulfide may depend on the species of phytoplankton present. With respect to the latter, dimethyl sulfide concentrations are better correlated with the abundance of certain phytoplankton species than chlorophyll *a* concentrations (Keller *et al.*, 1989, Holligan *et al.*, 1989). The balance of dissolved sulfide production and removal terms given in Table 3.3 suggests that phytoplankton may contribute up to 110 pmol sulfide L^{-1} h^{-1} to the Sargasso Sea. This preliminary estimate of the production rate of dissolved sulfide by phytoplankton needs to be confirmed by additional laboratory and field experiments.

3.4 Conclusions

This study presented depth profiles of the different forms of dissolved sulfide; the concentrations varied in the range $\leq$ 1–550 pmol/L. The depth profiles presented above confirm the presence of dissolved sulfide beyond the coastal and shelf environment, indicating the global importance of this sulfur species.

The concentrations of total dissolved sulfide were in the range of values previously reported in the coastal region of the western North Atlantic Ocean. Furthermore, significant OCS concentrations were found below the mixed layer. From these results, the following concluding remarks on biogeochemistry of dissolved sulfide and OCS can be drawn.

1) In addition to direct photochemical production, other sources of OCS must be present, as shown by the OCS depth profiles. A likely source is organic matter remineralization.

2) In the mixed layer of the Sargasso Sea, dissolved sulfide is produced by OCS hydrolysis, and perhaps by phytoplankton.

3) The removal of dissolved sulfide is due to its oxidation by IO_3^-, oxygen and H_2O_2, and its sinking with particles. The rate and mechanisms of the most important removal processes for dissolved sulfide, oxidation, suggest that the observed diel variations of total dissolved sulfide are likely due to diel variations in its production rate.

4) In the upper ocean, up to 23% of total dissolved sulfide is free sulfide, which is not predicted by thermodynamic equilibrium calculations.

In addition to the cycling of sulfur, pico– to nanomolar concentrations of dissolved sulfide in the open ocean may have ramifications for biogeochemical cycling of certain trace metals. Although calculations of the equilibria of dissolved sulfide in seawater indicate strong interactions with trace metals such as copper, zinc and nickel (*e.g.*, Dyrssen and Wedborg, 1989), observations of the different forms of dissolved sulfide presented above support the notion that these interactions may not be as strong as calculated. Therefore, further examination of the relationship between dissolved sulfide and trace metals is needed to resolve the discrepancy between the observed and the calculated speciation of this important sulfur species.

Chapter 4

Processes Affecting Hydrogen Sulfide Species in the Central Equatorial Pacific Ocean

4.1 Introduction

Hydrogen sulfide dissolved in seawater (H_2S_{aq}) is in equilibrium with its conjugate bases bisulfide (HS^-) and sulfide (S^{2-}). In addition to exhibiting this weak acid–base behavior, S^{2-} and HS^- can interact with metals present in seawater to form soluble complexes and insoluble compounds. Thus, to describe the different forms of hydrogen sulfide dissolved in seawater, the terminology introduced in Chapter 2 is also used in this chapter. "Free sulfide" is the hydrogen sulfide species that are uncomplexed (*i.e.*, free sulfide = $H_2S_{aq}+HS^-+S^{2-}$), while "complexed sulfide" is the hydrogen sulfide species that are complexed with metals. The sum of the two fractions is then "total dissolved sulfide".

Recent measurements of pico- to nanomolar levels of total dissolved sulfide and free sulfide in the open ocean (Cutter and Krahforst, 1988, Luther and Tsamakis, 1989, Andreae *et al.*, 1991, Chapter 3) verified the prediction of Elliott *et al.* (1987) that the hydrolysis of carbonyl sulfide (OCS) dissolved in seawater could sustain pico- to nanomolar levels of total dissolved sulfide in the ocean. Because free sulfide forms strong complexes with transition and "B-type" metals (Stumm and Morgan, 1981), these measurements prompted assessments of the equilibrium complexation of free sulfide with trace metals in the upper ocean (Dyrssen, 1988, Dyrssen and Wedborg, 1989, Elliott *et al.*, 1989). The interactions between free sulfide and trace metals were examined using thermodynamic equilibrium models and available values of the formation constants of metal sulfide complexes (Dyrssen, 1988, Dyrssen and Wedborg, 1989, Elliott *et al.*, 1989). These theoretical studies suggest that >99% of total dissolved sulfide is complexed at the concentrations of dissolved metals and sulfide that are found in the open ocean. However, the determination of up to 73 pmol/L of free sulfide (Andreae *et al.*, 1991) in surface waters of the western North Atlantic Ocean conflicts with the results of these thermodynamic calculations. The formation constants used in these complexation models were based on extrapolations from the formation constants of metal-dithizone complexes (Dyrssen, 1985), and from linear free-energy techniques (Elliott, 1988). The uncertainty associated with these constants is substantial (Elliott and Rowland, 1990), and therefore, the calculation of the equilibrium speciation of total dissolved sulfide may be inaccurate. This may help explain the discrepancy between the predicted and observed speciation of total dissolved sulfide. A more accurate assessment of the interactions between metals and free sulfide in seawater could reconcile observations with calculations.

Existing data on the distribution of dissolved sulfide in the open ocean were acquired in the western North Atlantic Ocean and the eastern Mediterranean Sea. In the mixed layer of the western North Atlantic Ocean, concentrations of total dissolved sulfide range from <5 pmol/L to 2 nmol/L, and decrease with depth (Cutter and Krahforst, 1988, Luther and Tsamakis, 1989, Chapter 3). In the upper 150 m of the Sargasso Sea, the average concentration of total dissolved sulfide was 124 pmol/L (Chapter 3). Sources of total dissolved sulfide include OCS hydrolysis (Elliott *et al.*, 1987), air/sea exchange, and perhaps phytoplankton emissions (Andreae, 1986). Such biotic production of total dissolved sulfide is supported by results from axenic cultures of four oceanic phytoplankton species that release dissolved and particulate sulfide during log phase growth (Walsh *et al.*, submitted). In the open ocean, known sinks of total dissolved sulfide include oxidation by iodate and oxygen, sea-air exchange, and removal *via* association with sinking of particulate sulfide (Chapter 3). The rate of removal of total dissolved sulfide *via* sinking particulate matter can be obtained empirically using sediment traps, but the rate of oxidation of total dissolved sulfide by iodate must be calculated from kinetic and concentration data. Luther and Tsamakis (1989) suggest that only free sulfide reacts with iodate in an oxidation reaction which is the dominant removal pathway for total dissolved sulfide; it is then crucial to accurately know the speciation of total dissolved sulfide in order to estimate its removal rate (Chapter 3).

This chapter examines the biogeochemistry of dissolved sulfide under the contrasting oceanographic regimes of the central Equatorial Pacific Ocean. These sites allowed *in situ* processes (because of the remote location of the sampling sites) affecting the distribution of total dissolved sulfide in oligotrophic and upwelling regimes to be revealed. This is in contrast to the western North Atlantic Ocean where hydrogen sulfide inputs from continental air masses were found (Andreae *et al.*, 1991). In addition, the conditional formation constant of copper-sulfide was determined at near-*in situ* conditions. This conditional formation constant was then used to predict the speciation of dissolved sulfide at thermodynamic equilibrium in the central

Equatorial Pacific Ocean.

4.1.1 Methods

Sampling Sites

The R/V Moana Wave was used to obtain samples from the central Equatorial Pacific from 29 July to 31 August, 1991. The cruise track roughly followed a "concave southwest" arc between 20°S, 135°W and 15°N, 150°W, that crossed the Equator at 140°W (Figure 4.1). Station locations are given in Table 4.1.

The description of the circulation in the central Equatorial Pacific Ocean by Wyrtki and Kilonsky (1984) can place these stations in their hydrographic context. Between 9°S and 4°N, surface circulation is to the West, while subsurface flows are to the East. Near the Equator, the flow of surface water diverges due to the Northeast and Southeast trade winds; this divergence induces upwelling of nutrient-rich water into the mixed layer (Wyrtki and Kilonsky, 1984). Because of the divergence, a band of nutrient-rich surface water can extend between 11°S and 4-5 °N, where it supports elevated total primary production relative to the oligotrophic gyres that border it to the North and South (Chavez and Barber, 1987).

Because of these circulation patterns, surface nitrate concentrations observed during the cruise varied between <0.1 μmol/L and 6.1 μmol/L. In the following discussion, stations are placed in two categories based on the nitrate concentration in their mixed layer: "divergence" stations were between 9°S and 5°N and had mixed layer nitrate concentrations >4 μmol/L (Stations 4, 5, and 6), and "gyre" stations had lower nitrate levels and were outside the 9°S–5°N latitudinal band (Stations 1–3, 7–10).

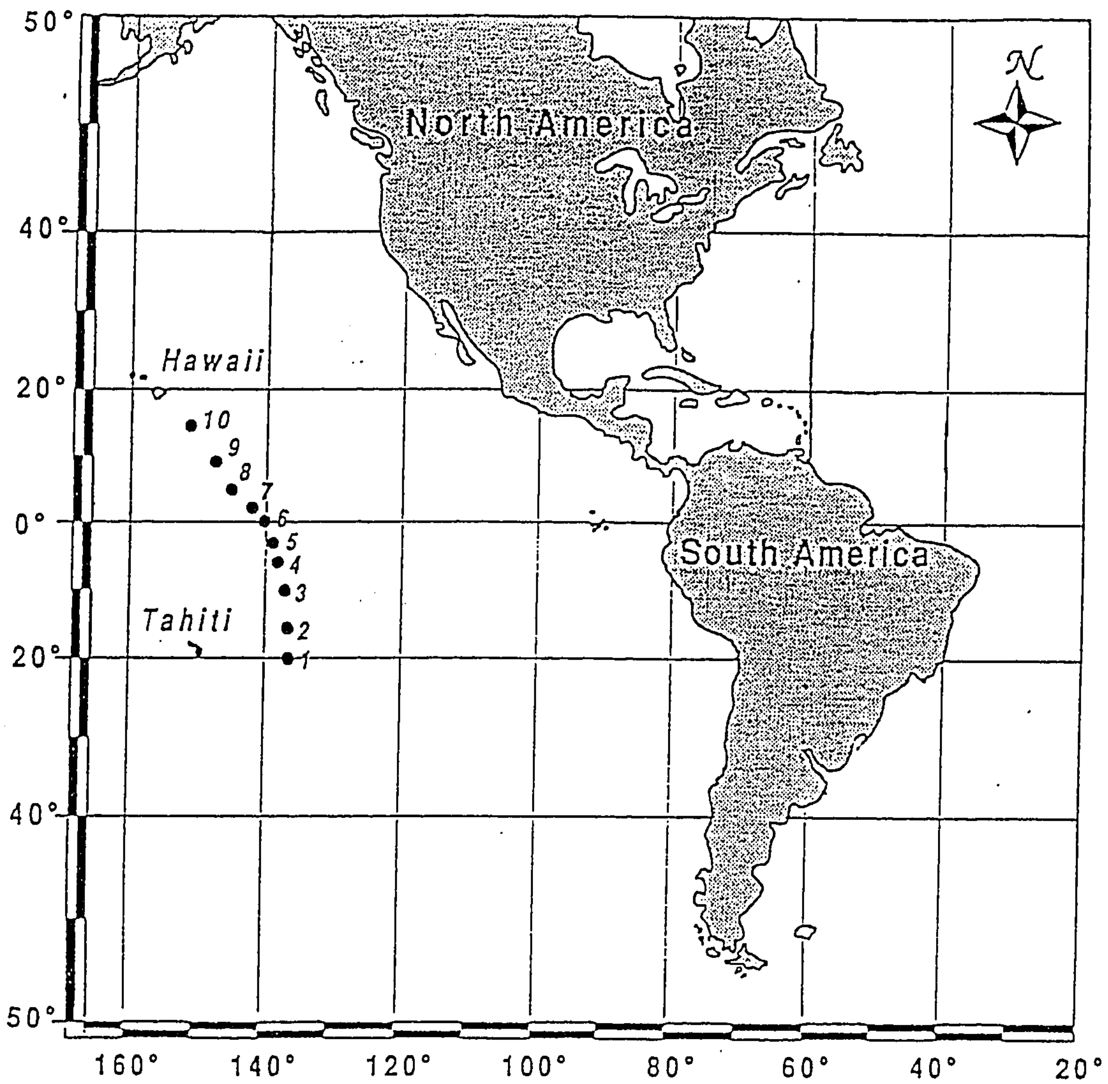

Figure 4.1: Stations occupied in August 1991 using the R/V Moana Wave.

Table 4.1: Station coordinates.

Station number	Latitude	Longitude
1	19°59.6′South	135°00.1′West
2	14°59.8′South	134°59.6′West
3	9°19.8′South	136°45.5′West
4	4°57.5′South	138°19.6′West
5	1°58.9′South	139°19.6′West
6 (Equator)	0°00.5′North	139°59.2′West
7	1°59.9′North	141°38.6′West
8	5°00.7′North	144°05.3′West
9	8°59.2′North	147°24.1′West
10	15°00.3′North	152°30.9′West

Sample Collection

Unfiltered water samples were obtained using 5- and 30-L Teflon-coated Go-Flo bottles hung on Kevlar hydrowire. Upon arriving on deck, samples were transferred from the sampling bottles to polyethylene Cubitainers that were then brought into the ship's laboratory for immediate (<2 h) analysis. Sample collection and handling followed trace metal-clean and hermetic procedures that minimized contamination with metals and exchange with the atmosphere (Chapter 2). For the the determination of the conditional formation constant of copper-sulfide complex(es), a seawater sample was collected using a single 30-L Go-Flo bottle to ensure sample homogeneity, and then split into nine 2.50-L aliquots held in Cubitainers.

Determination of Total Dissolved Sulfide and OCS. Concentrations of total dissolved sulfide and OCS in seawater were determined in triplicate using the methods described in Chapter 2. A sample aliquot (50–300 mL) was hermetically transferred from a Cubitainer to a glass stripper and acidified to *p*H 1.6 using 1.5 mol/L phosphoric acid. A stream of helium stripped

H_2S and OCS from the sample, and these gases were collected in a liquid nitrogen-cooled trap. The cryogenically trapped gases were revolatilized by removing the trap from liquid nitrogen, and were swept into the chromatographic column (1.8 m Porapak QS, acetone washed; de Souza *et al.*, 1975). The sulfur gases were then quantified using a linearized flame photometric detector (Hewlett Packard) interfaced to a digital plotter/integrator. Trace metal-clean and unreactive materials (Teflon, polyethylene, silanized glass) were used throughout the sampling and analytical systems to minimize loss of H_2S and OCS. Detection limits are 0.2 and 1.3 pmol/L for total dissolved sulfide and OCS, respectively, and precision is 5% (RSD) at the 20 pmol/L level for both gases. The analytical apparatus is calibrated using certified permeation devices (Metronics) held in a constant temperature water bath. It is important to note that copper-sulfide is not detected by the analytical method used here for total dissolved sulfide (Chapter 2).

Determination of the Conditional Copper-Sulfide Formation Constant

The following procedures were used to determine the conditional formation constant of copper-sulfide. One hour after spiking a 2.5 L seawater aliquot held in a Cubitainer with copper (II), 400 mL of high-purity helium was added to the Cubitainer. Then, 1–3 mL of a gaseous mixture (high purity helium and pure hydrogen sulfide; 99.9%, Matheson) that was prepared in a silanized glass bulb was added to the 400 mL of headspace. The Cubitainer was shaken to partition the added hydrogen sulfide between the seawater and the headspace. After a 15 min. equilibration period, the concentration of H_2S_g was determined by injection of a 50–100 mL aliquot of headspace into the helium stripping gas line as described in Chapter 2. To calculate the concentration of uncomplexed sulfide in equilibrium with the headspace (*i.e.*, free sulfide), the following equation was used (Chapter 2):

$$[\text{free sulfide}] = \frac{[\mathrm{H_2S_g}]}{\alpha_0}(\mathrm{K_d^*} + \frac{\mathrm{V_g}}{\mathrm{V_l}}) \qquad (4.1)$$

where the conditional distribution coefficient of H_2S_g (K_d^*) was calculated from sample temperature and salinity according to the equations in Douabul and Riley (1979). The percentage of undissociated free sulfide (α_0; Stumm and Morgan, 1981) was obtained from sample *p*H (Ross liquid junction electrode calibrated with N.I.S.T. buffers), pK_1', and pK_2. While pK_1' was calculated from sample temperature and salinity using the equations in Millero *et al.* (1986), the recently determined value of pK_2 was set at 18.94 (Schoonen and Barnes, 1988). Known volumes of headspace and seawater sample were V_g and V_l, respectively. Free sulfide concentrations and H_2S_g have the same units (*i.e.*, pmol/L).

To quantify the interactions between dissolved sulfide and copper under oceanographic conditions, two types of experiments were performed using the above procedures. With a series of Cubitainers, the first type of experiments reacted a constant level of added copper with increasing additions of hydrogen sulfide. With another series of Cubitainers, the second type of experiments reacted constant levels of added hydrogen sulfide with increasing additions of copper. The determination of free sulfide and total dissolved sulfide yielded individual points along titration curves (Fig. 4.12). These data were then used to calculate the conditional formation constant of copper-sulfide.

At the low concentrations of added metal and hydrogen sulfide (<12 nmol/L for both) at which the titrations were performed, mass action dictates that mononuclear complexes predominate (Elliott *et al.*, 1989a), and the precipitation of solids is probably very minor (Dyrssen and Wedborg, 1989). Furthermore, bisulfide (HS^-) is the dominant form of dissolved sulfide species (>95%) at the pH of seawater. Thus, the interactions between copper and dissolved sulfide can be treated by considering only dissolved HS^- and copper in a manner analogous to that described in Bruland (1989) for the interactions between zinc and a single ligand class.

For the titrations, the added hydrogen sulfide dissociates to bisulfide which acts as a ligand that can react with the added copper to form a copper-sulfide complex according to the reaction:

$$Cu^{2+} + HS^- = Cu(HS)^+ \tag{4.2}$$

This reaction can be generalized to:

$$M' + L' = ML \tag{4.3}$$

where M′ is copper not complexed by bisulfide, and L′ is free bisulfide. The conditional formation constant of the ML complex is:

$$K'_{cond} = \frac{\{ML\}}{\{M'\}\{L'\}} \tag{4.4}$$

The following mass balances can then be written, omitting for simplicity the curly brackets that indicate the activity of species:

$$L_T = ML + L' \tag{4.5}$$

$$M_T = ML + M' \tag{4.6}$$

Because ML is a copper-sulfide complex that is not detected by the analytical method used (Chapter 2), Equation 4.5 can be rearranged to obtain ML as a function of the known L_T and L'.

$$ML = L_T - L' \tag{4.7}$$

It follows from Equation 4.6 and Equation 4.7 that

$$M' = M_T - L_T + L' \tag{4.8}$$

Substituting Equation 4.8 and 4.7 into the expression of K'_{cond} yields:

$$K'_{\text{cond}} = \frac{L_T - L'}{L'(M_T - L_T + L')} \tag{4.9}$$

where the terms in the right hand side of the equation are either experimentally determined (*i.e.*, L' is obtained for each titration point from triplicate determinations of free sulfide.) or are known (*i.e.*, L_T, and M_T). A slightly different approach can also be used to derive K'_{cond}. By rearranging the mass balance equations given above, the following equation which is analogous to that given by Ruzic (1982) can be written:

$$\frac{L'}{L_T - L'} = \frac{L'}{M_T} + \frac{1}{K'_{\text{cond}} M_T} \tag{4.10}$$

This equation indicates that a linear fit of the plot of $L'/(L_T - L')$ *vs.* L' yields a line whose slope is $1/M_T$ and Y-intercept is $1/(M_T K'_{\text{cond}})$. Using Equations 4.9 or 4.10, K'_{cond} can be calculated for each titration point for the titration of known concentrations of copper and dissolved sulfide. This procedure is analogous to the one used by Bruland (1989) to obtain the conditional stability constant of a single class of zinc ligands.

Ancillary parameters. Nutrient and chlorophyll *a* concentrations were determined on board ship using the procedures of Strickland and Parsons (1972). *Synechococcus sp.* were enumerated using flow cytometry (FACScan), and the data kindly provided by M. Durand and J. Duesenberry of Woods Hole Oceanographic Institution. Water column temperature and salinity were determined using a CTD instrument.

4.2 Results and Discussion

4.2.1 Distribution of Total Dissolved Sulfide and OCS

The surface water distribution of total dissolved sulfide is given in Fig. 4.2. The concentrations vary between 4 and 95 pmol/L in the region sampled; they are lowest at the Equator, increase to maxima (59 pmol/L) at 15°S and at 5°N (95 pmol/L), and decrease into the gyres. The surface water distribution of OCS is also given in Fig. 4.2. Surface concentrations decrease slightly, from 20°S and then increase to a pronounced maximum (418 pmol/L) at 5°S. Concentrations then decrease rapidly to 10 pmol/L at the Equator. In the Northern Hemisphere, concentrations range from 10–50 pmol/L. The surface OCS concentrations reported here are in the range 10–418 pmol/L, while Johnson and Harrison (1986) found surface concentrations ranging from 5 to 150 pmol/L in two extensive surveys of the Pacific Ocean. To check for possible contamination, each GoFlo bottle was verified using the procedure described in Chapter 2; no contamination was apparent on the samplers that were used. Furthermore, high and low concentrations samples were collected from the same GoFlo, thus decreasing the likelyhood of systematic contamination. Seasonal effects may help explain the more elevated OCS concentrations reported here. The samples for the study presented here were acquired during the month of August, while Johnson and Harrison (1986) examined the distribution of OCS periods ranging from March to May. The seasonal variations of surface OCS concentration in the surface waters was examined at Amsterdam Island in the Southern Indian Ocean (Mihalopoulos *et al.*, 1992) where OCS concentrations were highest in the summer months. This behavior may then explain the greater concentrations found in this study.

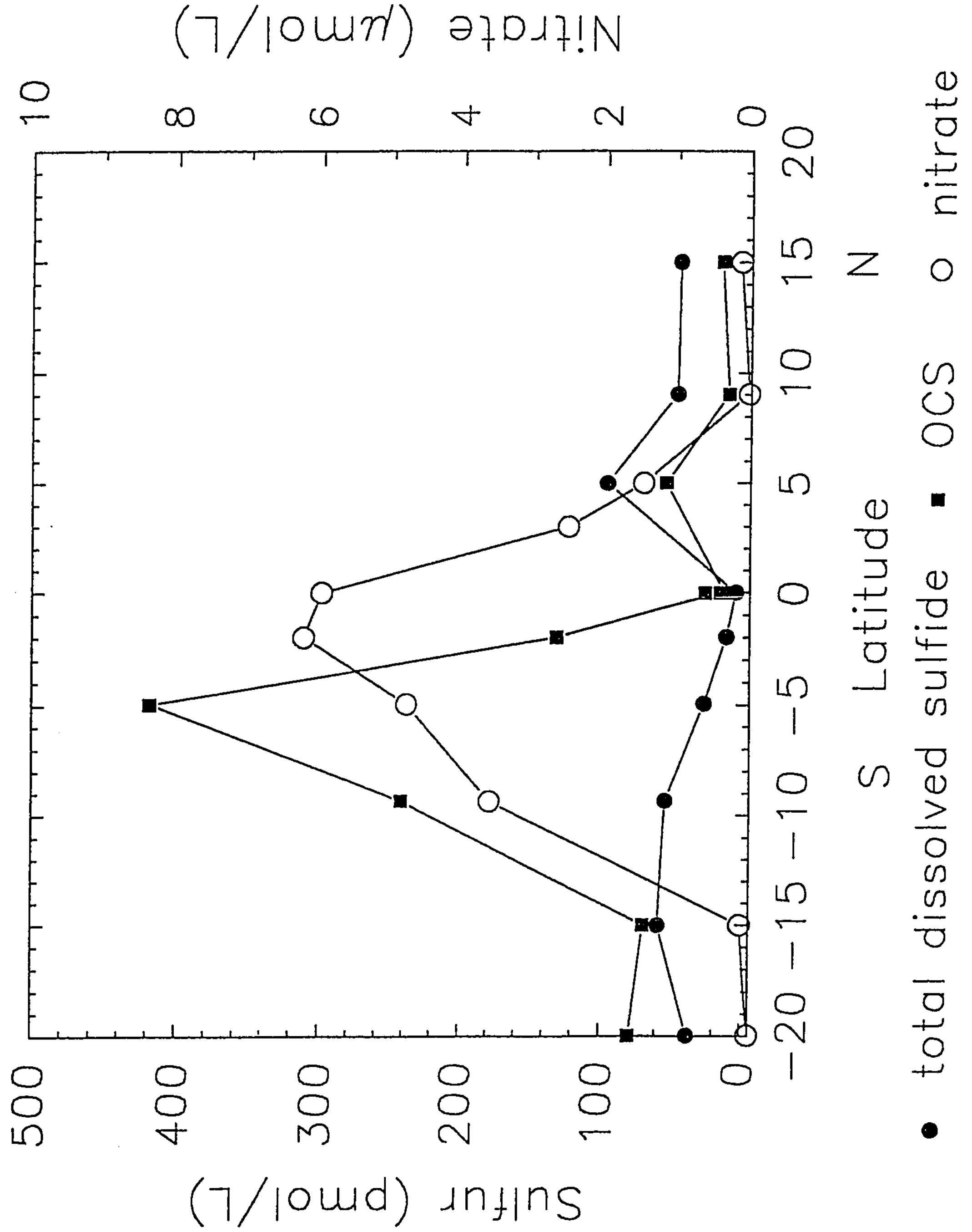

Figure 4.2: Surface water transect of total dissolved sulfide, carbonyl sulfide (OCS) and nitrate in the central Equatorial Pacific Ocean (See Fig. 4.1 for station locations)

Surface OCS concentrations vary substantially with latitude, and exhibit a prominent maximum at 5°S. This maximum may be associated with upwelling near the Equator. Indeed, surface nitrate concentrations (Fig. 4.2) shows that the OCS maximum is in the southern portion of the divergence. Similar increases of OCS concentrations were also observed near the Equator, albeit less clearly, by Johnson and Harrison (1986). In surface water, OCS is produced from the photolysis of dissolved organic matter, most probably by the oxidation of sulfhydryl groups in proteinaceous material (Andreae and Ferek, 1992). Although no measurement of such compounds were made on the cruise, surface water DOC data obtained six months later show a minima at the Equator, and concentrations rising in the North and South Pacific gyres (Peltzer, 1992). Although speculative, this suggests that the dissolved precursors of OCS have latitudinal variations that may explain the observed distribution of OCS.

Depth profiles of total dissolved sulfide obtained at Stations 1, 8, 9, and 10 (Fig. 4.1) show near surface (0-10 m) maxima in the range 82–91 pmol/L (Fig. 4.3–4.9). Pronounced secondary maxima in total dissolved sulfide are also observed in the upper pycnocline at Stations 4, 8, 9, and 10 (Fig. 4.3–4.9). Below these maxima, concentrations of total dissolved sulfide decrease to lower levels at 250 m (~19 pmol/L on average). While total dissolved sulfide concentrations in the Pacific Ocean (Fig. 4.3–4.9) are generally lower than in the western North Atlantic Ocean, the shapes of the depth profiles are similar (Chapter 3). In both oceans, the highest concentrations are found in the mixed layer, and the presence of secondary maxima in the pycnocline are also observed. These similarities indicate that similar oceanographic processes are affecting the distribution of total dissolved sulfide in the two oceans assuming that horizontal inputs are minimal (*i.e.*, with a residence

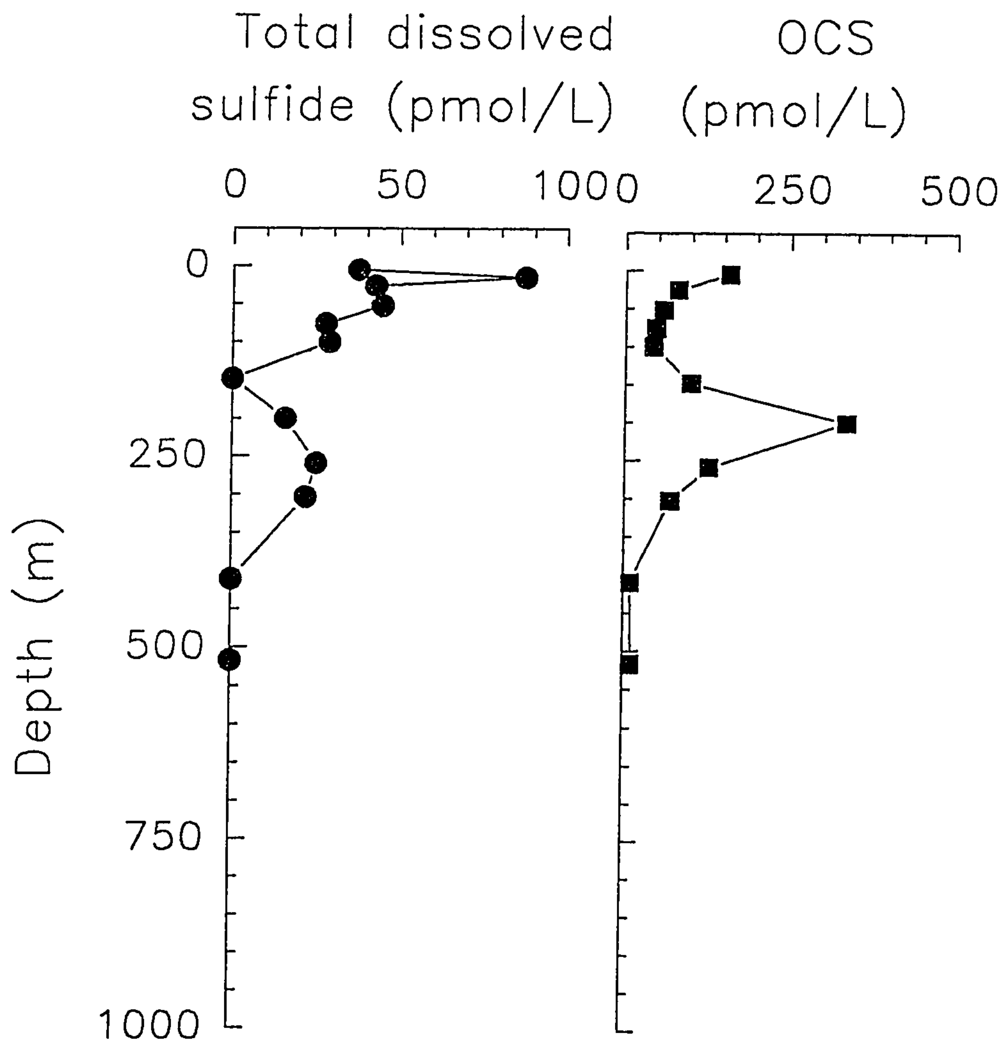

Figure 4.3: Depth profiles of total dissolved sulfide and OCS at Station 1 in the central Equatorial Pacific Ocean.

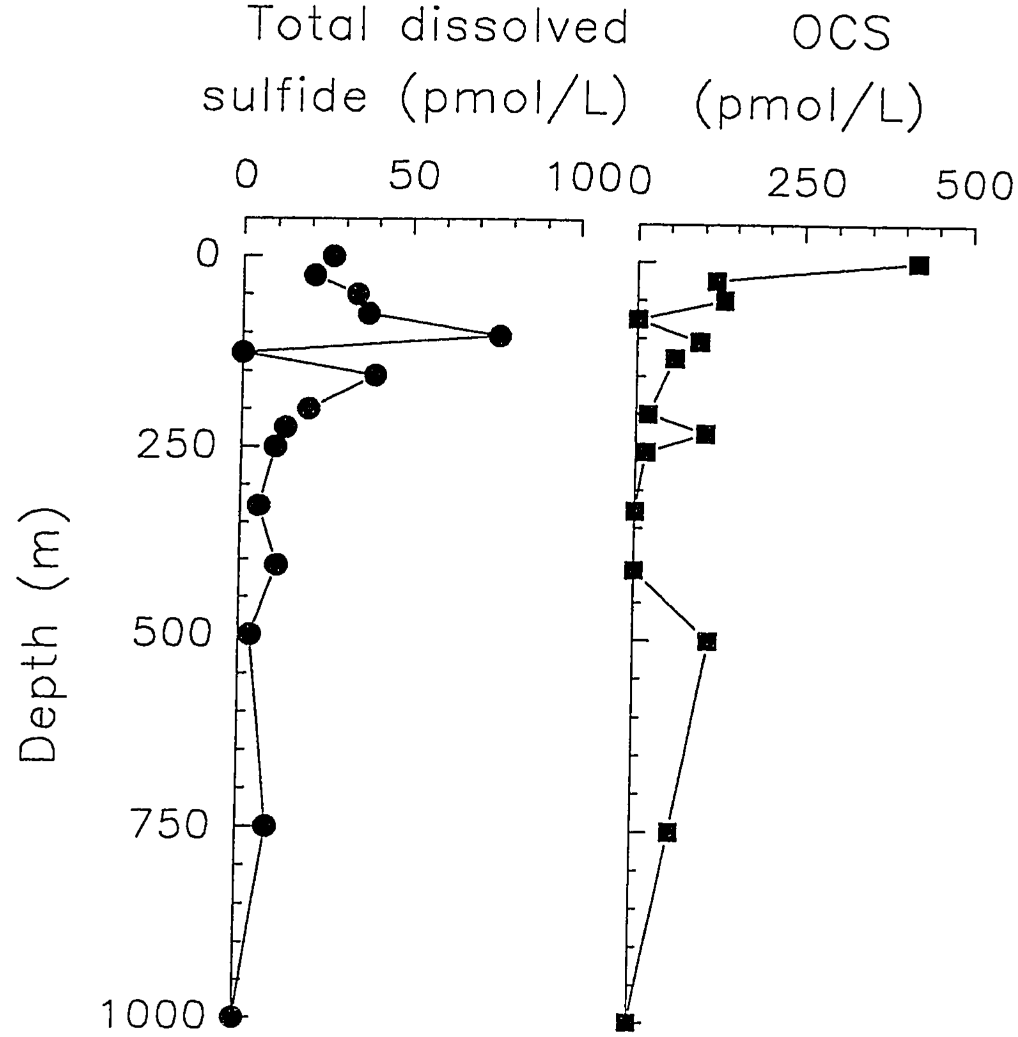

Figure 4.4: Depth profiles of total dissolved sulfide and OCS at Station 4 in the central Equatorial Pacific Ocean.

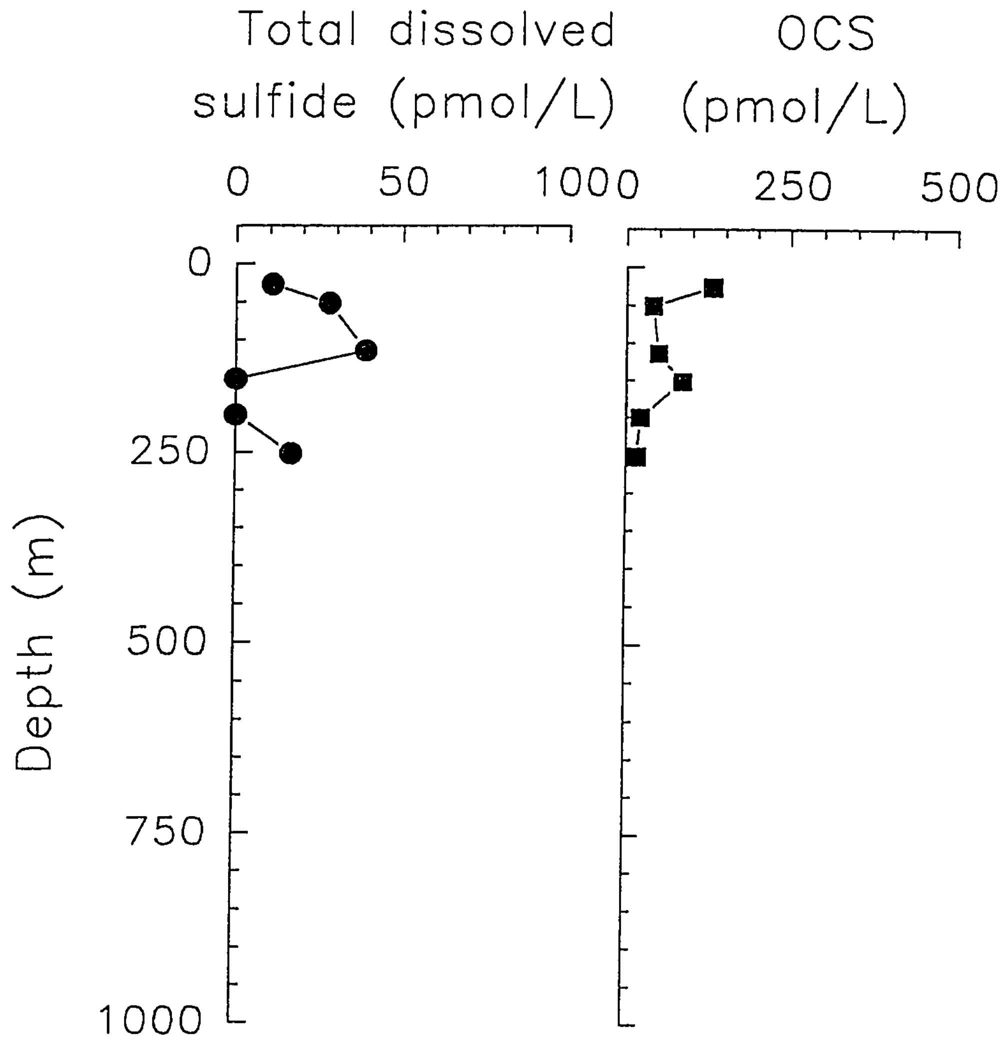

Figure 4.5: Depth profiles of total dissolved sulfide and OCS at Station 5 in the central Equatorial Pacific Ocean.

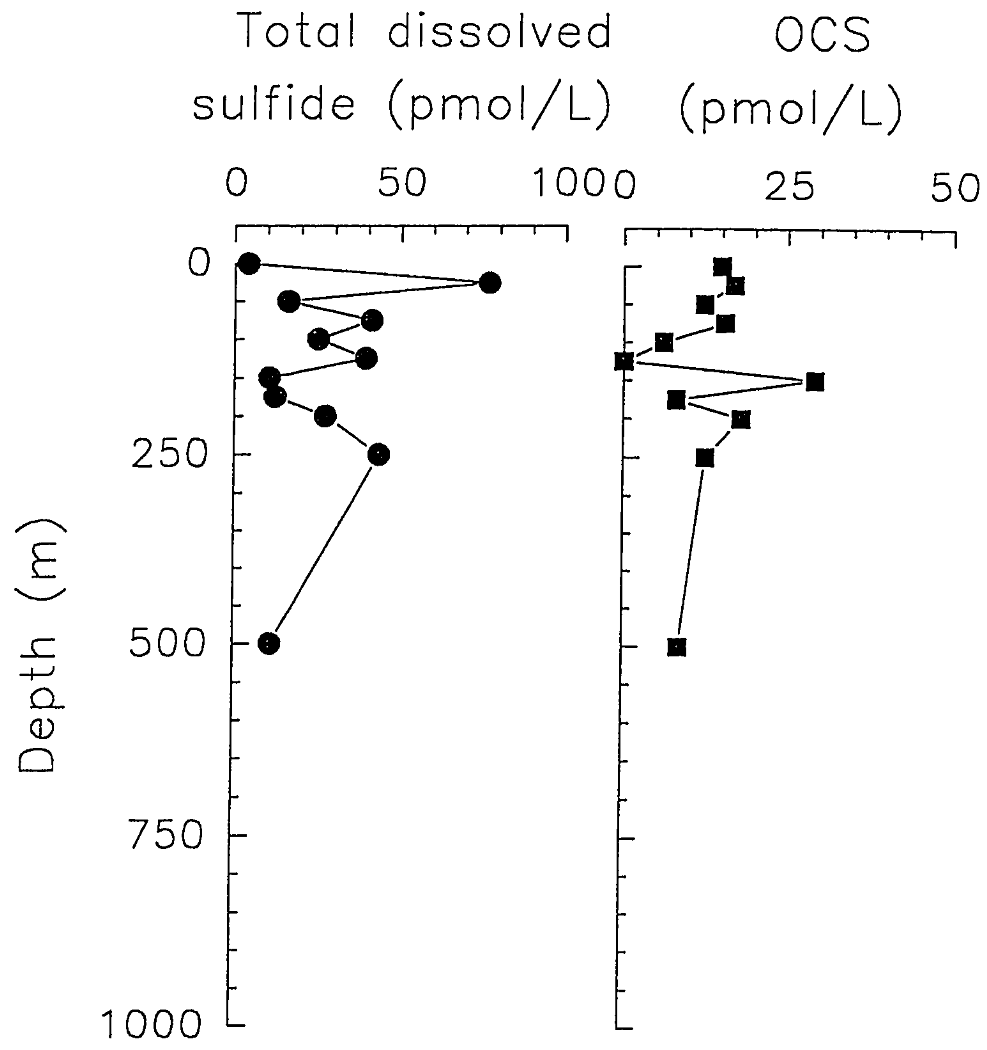

Figure 4.6: Depth profiles of total dissolved sulfide and OCS at Station 6 (Equator) in the central Equatorial Pacific Ocean.

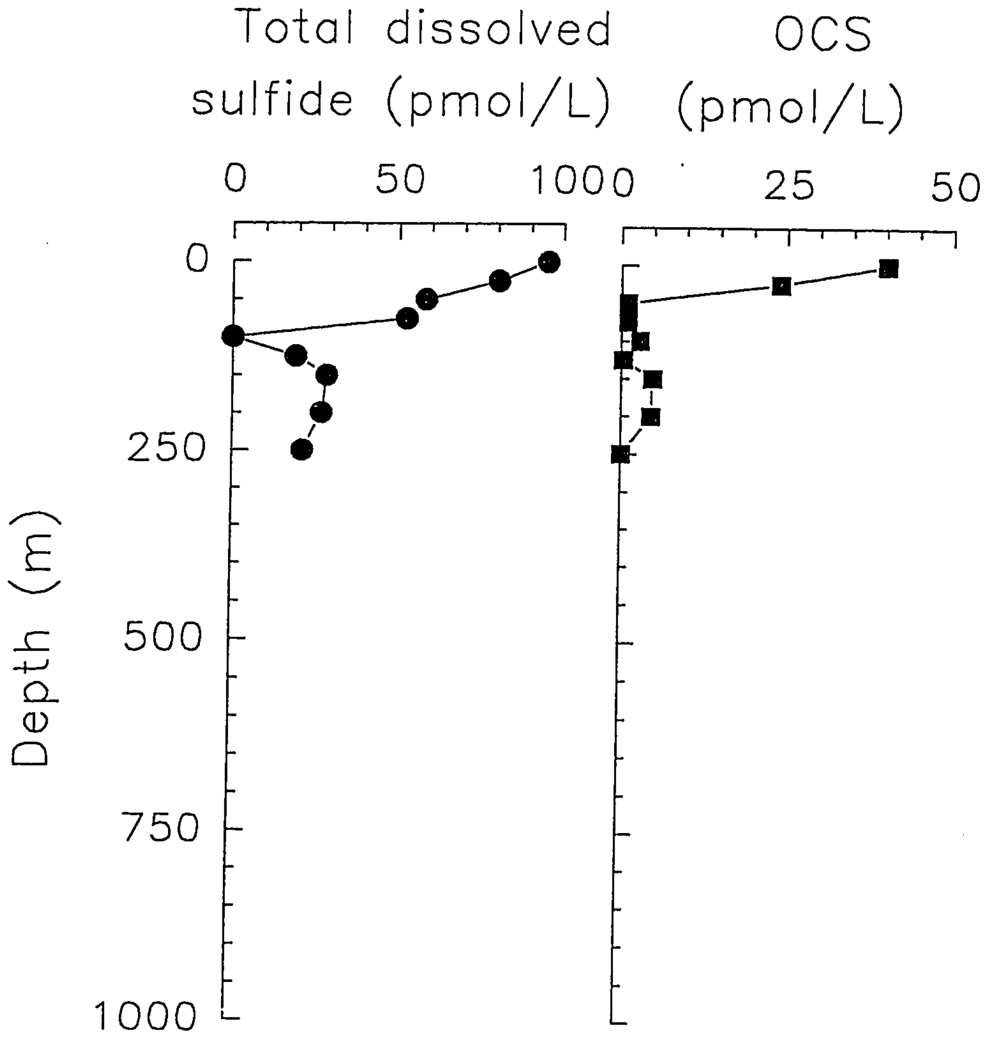

Figure 4.7: Depth profiles of total dissolved sulfide and OCS at Station 8 in the central Equatorial Pacific Ocean.

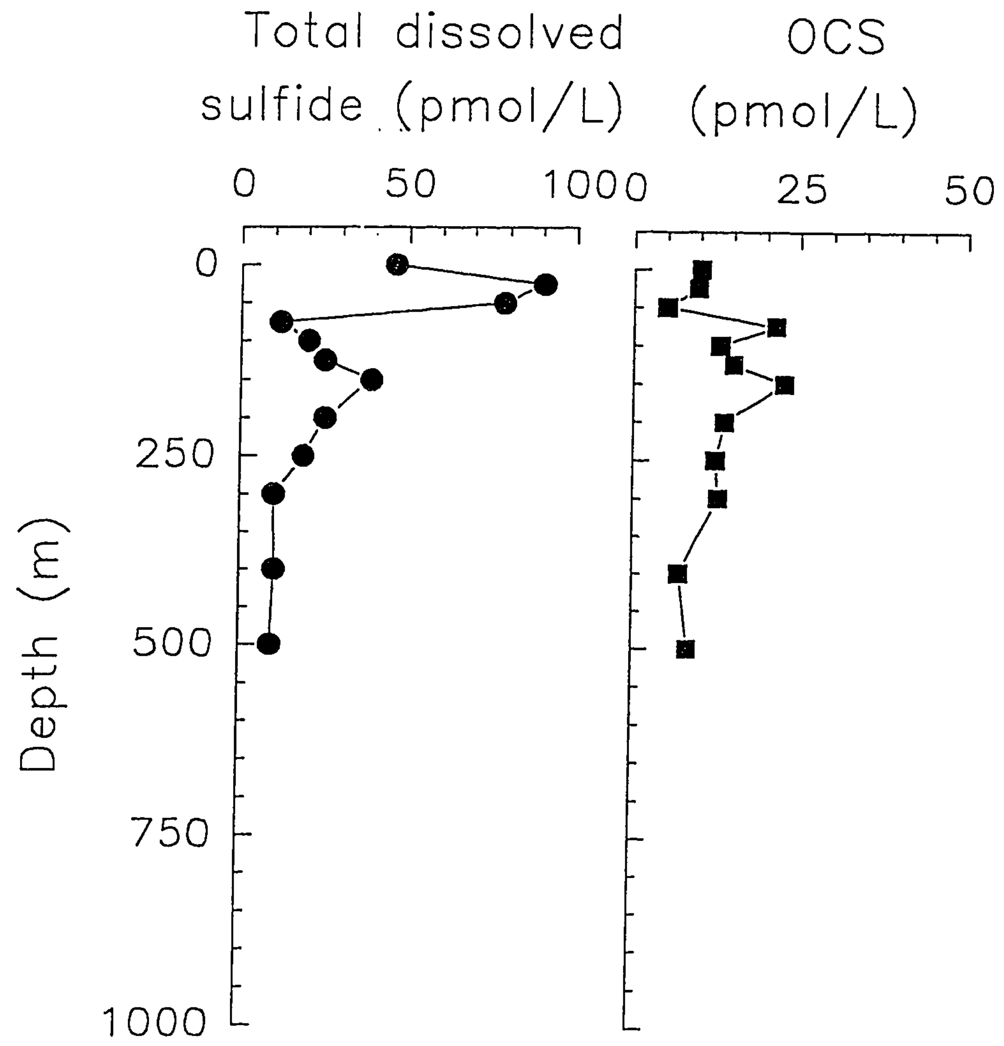

Figure 4.8: Depth profiles of total dissolved sulfide and OCS at Station 9 in the central Equatorial Pacific Ocean.

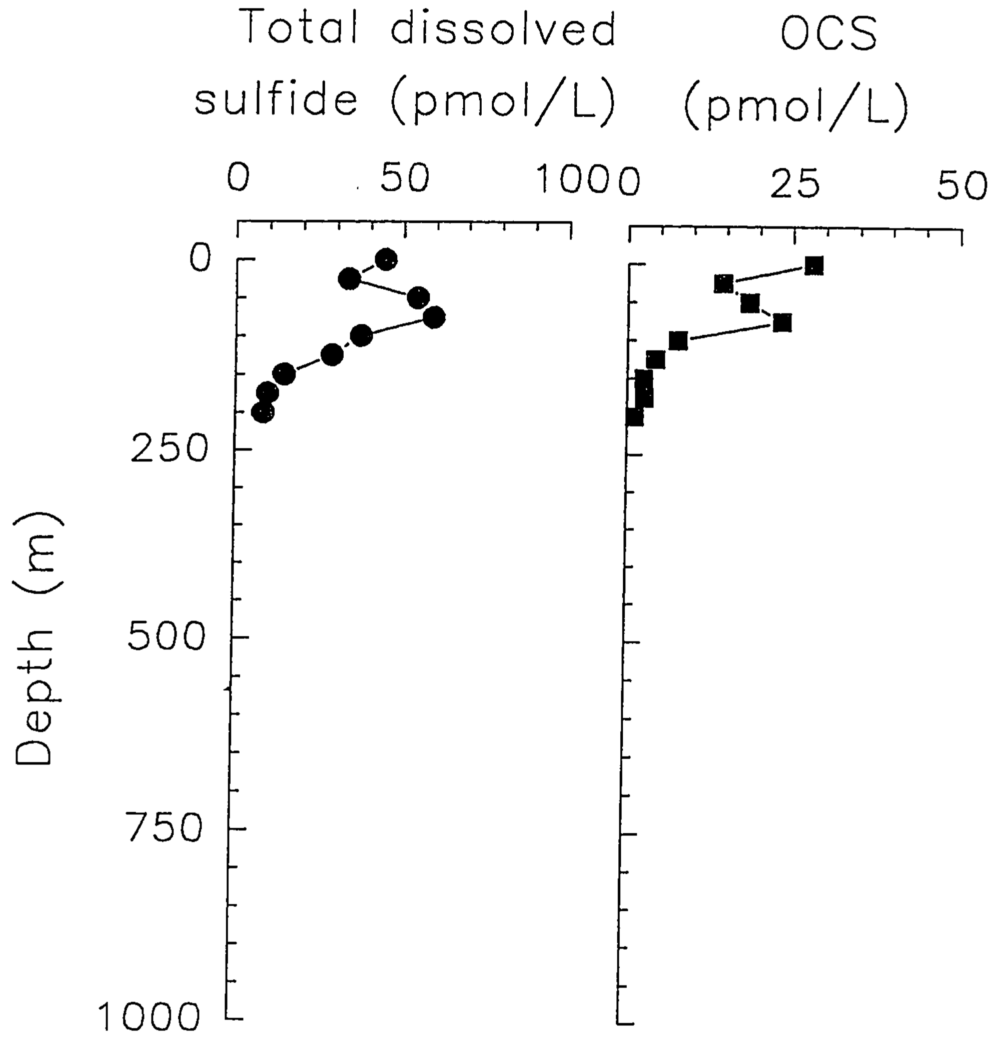

Figure 4.9: Depth profiles of total dissolved sulfide and OCS at Station 10 in the central Equatorial Pacific Ocean.

time of 1 day, Chapter 3, the effects of horizontal transport are minimized). These processes are examined next.

The production of dissolved sulfide from OCS hydrolysis can be assessed using OCS depth profiles. Like OCS depth profiles from the western North Atlantic Ocean (Chapter 3), profiles in the Pacific Ocean (Fig. 4.3–4.9) show near surface and secondary concentration maxima. The near-surface maxima are consistent with a photolytic production of OCS, and the secondary maximum suggest an *in situ* (dark) source. Photochemically mediated production is relatively well known (Andreae and Ferek, 1992), while evidence for dark reactions that produce OCS has only begun to be uncovered (Chapter 3, Cutter and Radford-Knoery, 1993). In Chapter 3, it was proposed that the remineralization of organic matter could release OCS. The sparse nitrite data set for the Pacific cruise does not allow a further comparison between the two oceans.

In seawater, OCS hydrolyzes to H_2S and HS^- (Elliott *et al.*, 1987), and these dissolved sulfide species are then complexed by metals or oxidized. In the surface ocean, these processes occur on time scales shorter than a day (Chapter 3), and thus features such as maxima and minima of OCS and total dissolved sulfide should coincide. Indeed, depth profiles of OCS and total dissolved sulfide correspond very well at Stations 8 and 10 (Fig. 4.7 and 4.9). However, OCS and total dissolved sulfide do not correspond very well at the other stations (Fig. 4.3– 4.6, and 4.8), suggesting that the coupling between OCS and total dissolved sulfide is obscured by other production and removal processes. An analogous situation has already been observed in the Sargasso Sea, where it was found that OCS hydrolysis was a small fraction of the production needed to balance consumption of total dissolved sulfide (Chapter 3).

Besides OCS hydrolysis, release from phytoplankton has been proposed as an important source of dissolved sulfide to the western North Atlantic Ocean, based on similar distributions for chlorophyll *a* and total dissolved sulfide (Chapter 3). However, some uncertainty on this relationship remained because of the greater flux of atmospheric H_2S into the ocean near the coast (Andreae *et al.*, 1991), where concentrations of total dissolved sulfide and chlorophyll *a* both increase. For this Pacific cruise, the influx of from air masses with a continental origin is small because atmospheric H_2S is a short lived species ($\sim$ 2 days; Toon *et al.*, 1987) and because the stations were located in the remote ocean. Thus, the relationship between phytoplankton and total dissolved sulfide concentrations can be assessed without a potentially large atmospheric contribution. The latitudinal distribution of total dissolved sulfide (Fig. 4.2) in surface waters and those of chlorophyll *a* (Appendix D) are uncorrelated, indicating that chlorophyll *a* is a poor predictor of total dissolved sulfide. Even though this suggests that total dissolved sulfide may not be produced by phytoplankton, the situation may be analogous to that of dimethyl sulfide (DMS), another biogenic sulfur gas. DMS is better correlated to the abundance of a single phytoplankton species like *Phaeocystis sp*, than to the bulk concentration of chlorophyll *a* (*e.g.*, Holligan *et al.*, 1987, Turner *et al.*, 1988).

For total dissolved sulfide, results from laboratory cultures (Walsh *et al.*, submitted) show that dissolved and particulate sulfide are produced by phytoplankton, and that *Synechococcus sp.* dominates this biotic source of dissolved sulfide. The oceanic species examined in the study of Walsh *et al.* (submitted) were the cyanobacterium *Synechococcus sp.*, the coccolithophore *Emiliania huxleyi*, the prasinophyte *Pyramimonas obovata* and the diatom *Thalassosira oceania*. Each culture produced dissolved and particulate sulfide during their log phase growth, but it is interesting to note that *Synechococcus sp.*, produced the most total dissolved sulfide per unit of cellular volume (Walsh *et al.*, submitted). The depth profiles of *Synechococcus sp.* cell abundance and total dissolved sulfide at Stations 9 and 10 exhibit concentration maxima at the same depths (*i.e.,* Fig. 4.10 and Fig. 4.11). This correspondence suggests that *Synechococcus sp.* may be a dominant source of total dissolved sulfide at these stations. At other stations where total dissolved sulfide is found, but the abundance of *Synechococcus* is low, total dissolved sulfide can be released by other phytoplankton species (Walsh *et al.*, submitted), as well as by OCS hydrolysis.

4.2.2 Metal-Sulfide Interactions

Because iodate is an important removal pathway for dissolved sulfide, but reacts only with free sulfide (Luther and Tsamakis, 1989), the chemical speciation of dissolved sulfide is crucial to quantifying its cycling in the ocean. Moreover, the complexation of trace metals by free sulfide can affect their cycling. Previous theoretical studies of the speciation of dissolved sulfide (Dyrssen, 1988, Dyrssen and Wedborg, 1989, Elliott *et al.*, 1989a) indicate that it is largely (>98%) complexed by copper. However, these theoretical results may not be directly applicable to the conditions of concentration and salinity encountered in the surface ocean because of the methods that were used to estimate the thermodynamic constants. To begin a re-examination of the interactions between copper and dissolved sulfide, the formation constant of copper-sulfide was determined under oceanographic conditions of salinity, *p*H, and metal concentrations.

For this work, titrations of free sulfide by copper (and vice versa) at the nanomolar level were performed on selected samples from the upper 1000 m

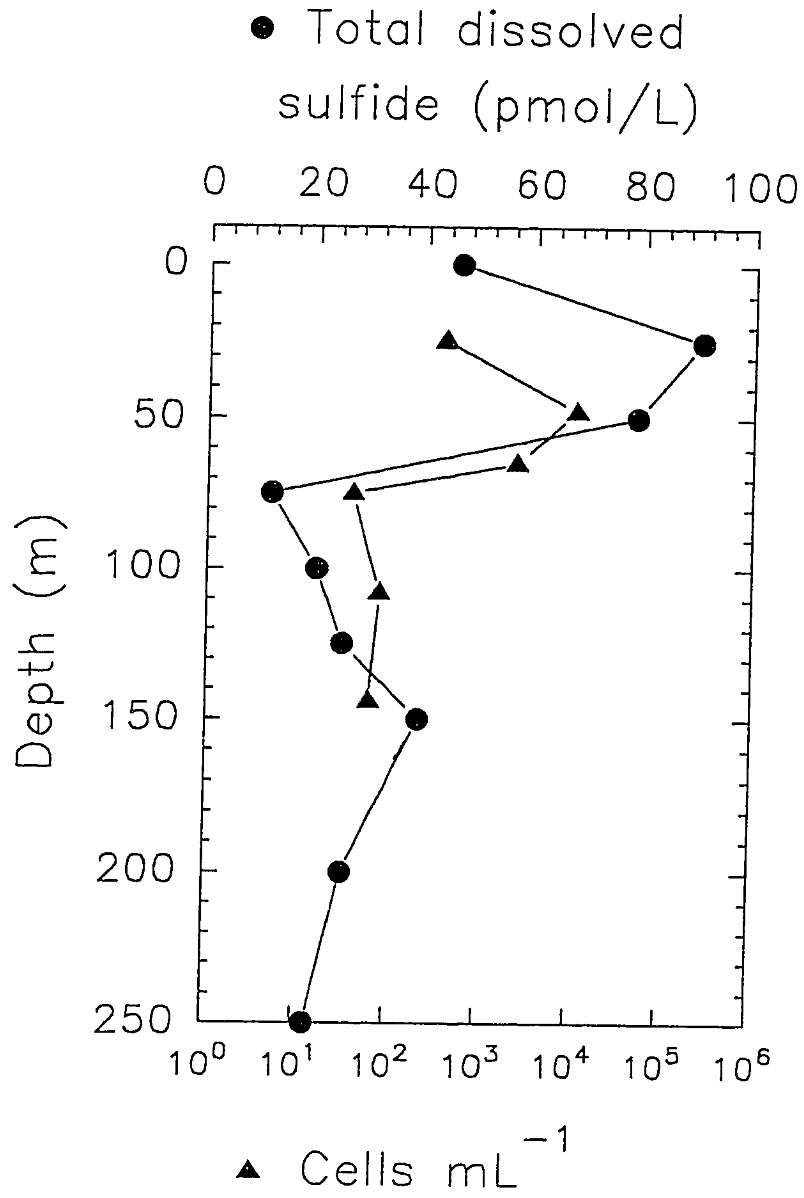

Figure 4.10: Depth profiles of *Synechococcus sp.* cell number (semi-logarithmic) and total dissolved sulfide at Station 9.

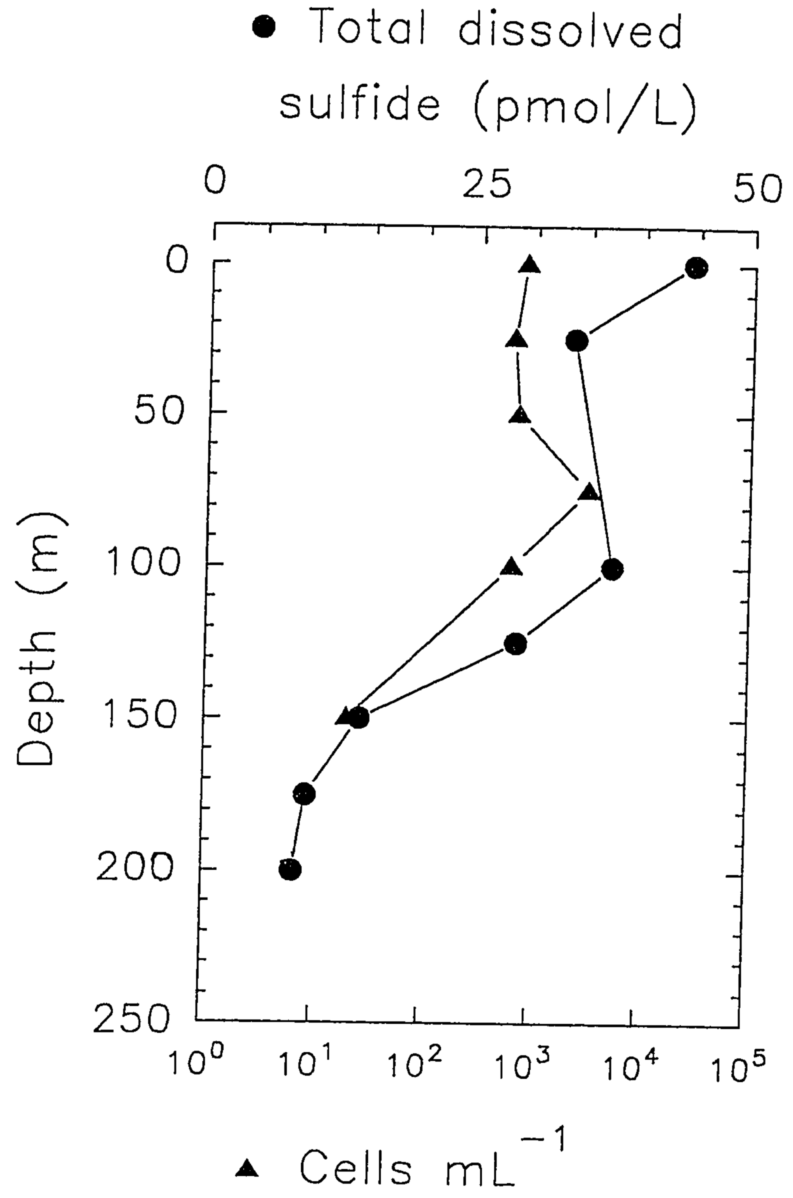

Figure 4.11: Depth profiles of *Synechococcus sp.* cell number (semi-logarithmic) and total dissolved sulfide at Station 10.

of Stations 6, 8 and 9. An example of a titration of a seawater sample with a fixed hydrogen sulfide concentration by increasing additions of copper is shown in Fig. 4.12. The experimentally determined values of $\log(K'_{cond})$ were obtained using Equation 4.9 and are included in Appendix E.

The following precautions were taken to minimize kinetic effects that may affect the accuracy of the determination of $\log(K'_{cond})$. Firstly, the Cubitainers were allowed to equilibrate in the dark for 1 h after their amendement with copper, and 15 minutes after the addition of hydrogen sulfide. Coale and Bruland (1988) indicate that copper-organic ligand complexation (which dominates copper speciation in surface waters) is reached within 5 minutes. Furthermore, experiments indicate that the equilibration time between nanomolar levels of copper and dissolved sulfide is less than 15 minutes. Thus, the determination of free sulfide performed on the samples held in the Cubitainers should reflect equilibrium conditions. Second, the removal of dissolved sulfide due to oxidation was minimized by completing the experiments as rapidly as possible (<2.5 h). To ensure that the titration curves were not biased, the Cubitainers were analyzed in the following order: highest addition, lowest addition, second highest addition, etc... (see Fig. 4.12).

Values of $\log(K'_{cond})$ averaged 9.1±0.6 (n=17) and ranged from 8.2 to 9.6; no obvious trend with depth was observed. It should be emphasized that this value of $\log(K'_{cond})$ is an expression for *all* the interactions between dissolved sulfide and copper at the experimental conditions described in the Methods Section. Thus, this value of $\log(K'_{cond})$ can be used to quantify all the interactions between copper and dissolved sulfide (*i.e.*, the amount of dissolved sulfide that is complexed by copper), but it cannot be used to distinguish between the different copper-sulfide complexes that may be formed. For the following discussion and keeping this important limitation

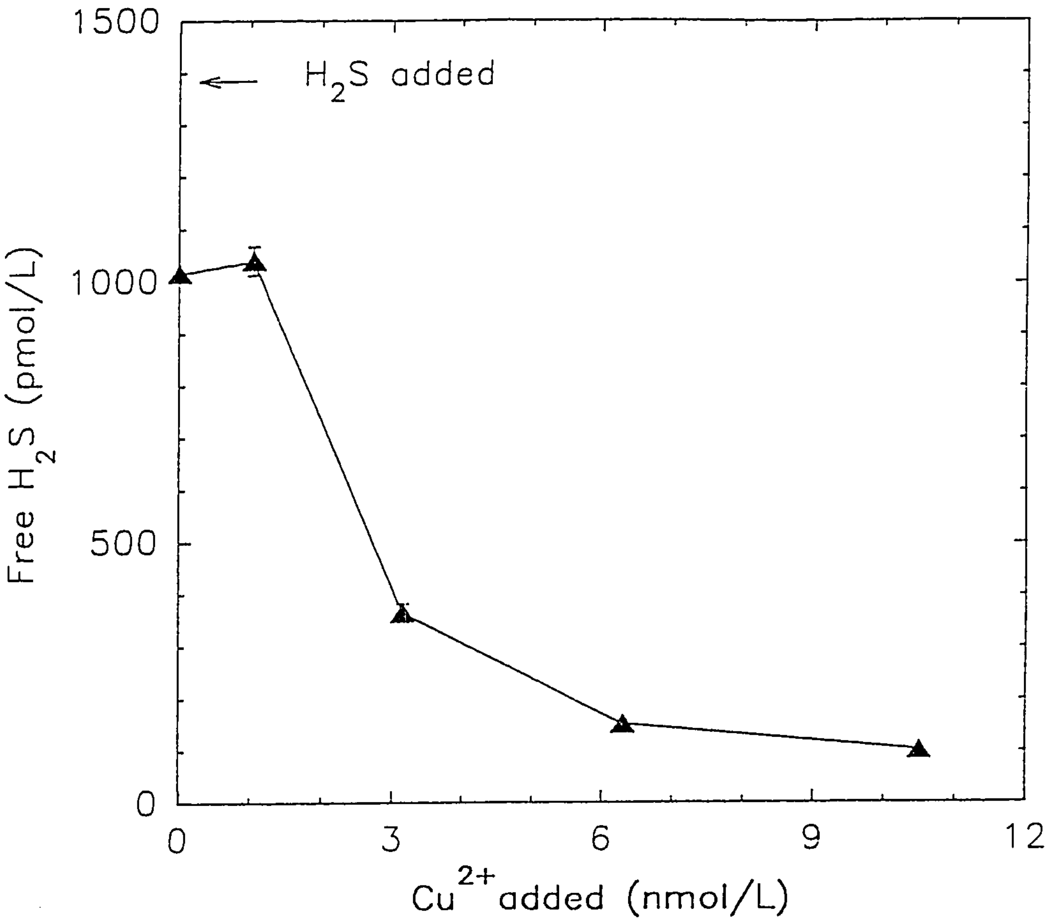

Figure 4.12: A titration using a fixed concentration of copper and additions of gaseous H_2S used to obtain K'_{cond} for the formation of copper-sulfide complex(es) at Station 8, 500 m depth.

in mind, the interactions between copper and dissolved sulfide were then amalgamated into the formation of the complex $Cu(HS)^+$ from Cu^{2+} and HS^- with a $\log(K'_{cond})$ of 9.1 (*e.g.,* Reaction 4.2).

The value of $\log(K'_{cond})$ obtained in this work (9.1±0.6) is substantially lower than previous estimates reported by Dyrssen and Wedborg (1989), 14.1, but it is at the lower end of the range of likely values for $\log(K'_{cond})$ of $Cu(HS)^+$ proposed by other researchers (*e.g.,* 10; Elliott and Rowland, 1990). However, this value of $\log(K'_{cond})$ is conditional (*i.e.,* under oceanographic conditions) and thus it is not directly comparable to literature values. Nevertheless, this value of $\log(K'_{cond})$ can be used directly to predict the equilibria between copper and dissolved sulfide at nanomolar levels in seawater. Indeed, this constant was determined in seawater at near *in situ* conditions and concentrations of dissolved sulfide and copper. Interestingly, Luther *et al.* (1989) also suggest that the conditional formation constant for copper-sulfide complexes at *in situ* conditions in the Black Sea is lower than that suggested by Dyrssen and Wedborg (1989), and may be about $10^{10.3}$.

Calculation of the speciation of dissolved sulfide in the Pacific Ocean. To predict the equilibrium speciation of dissolved sulfide with respect to trace metal complexation at Station 9, the speciation of total sulfide was calculated using the computer program MINEQL (V. 2.0, Westall *et al.*, 1976). Inputs to the program were the concentrations of total dissolved sulfide determined at this station, the concentrations of major ions in seawater, observed *p*H values, and trace metal concentrations. Because copper, zinc, nickel and cadmium data for this station were not available, concentrations from another station in the North Pacific Ocean (32°N, 144°W; Bruland, 1980) were used. The depth distributions for chromium and lead for the northern Pacific Ocean were taken from Bruland (1983), while the depth distributions for iron and manganese were those of Landing and Bruland (1987). Mercury concentrations for the North Pacific Ocean were taken from Gill and Fitzgerald (1988). The data base of thermodynamic equilibrium constants relating all the dissolved species mentioned above was taken from Landing and Lewis (1991), except for copper–sulfide interactions which were amalgamated into the single constant relating Cu^{2+}, H^+, $S^=$ and $Cu(HS)^+$ (species #4004 of the MINEQL data base). The $Cu(HS)^+$ complex was chosen to represent all the interactions between nanomolar levels of copper and total dissolved sulfide in seawater because HS^- is the dominant form of hydrogen sulfide at the pH of seawater, and because mass action dictates that mononuclear complexes predominate at low concentrations (Elliott *et al.*, 1989a). The formation of organic complexes with copper and zinc that was observed in the oligotrophic North Pacific Ocean (Coale and Bruland, 1988, Bruland, 1989) was included in the calculation using the interactive feature of MINEQL. Corrections of the thermodynamic constants for temperature less than 25°C were not made, because the inorganic speciation of metals in seawater shifts by about 10% toward free metal concentrations as temperature decreases from 25 to 5°C (Byrne *et al.*, 1988), while the uncertainties on the formation constants of copper-sulfide (and other metal sulfide complexes; *i.e.*, Elliott and Rowland, 1990) are certainly much larger than 10%. Since the software corrects the equilibrium constants for ion pairing and shielding effects using the Davies equation (Stumm and Morgan, 1981), the constants that were added to the data base (*e.g.*, constants of copper-sulfide and organic ligand–metal complexes) were adjusted so that they regained their observed values after the ionic strength correction (*i.e.*, $\log(K'_{cond}(Cu(HS)^+))_{I=0.7}$ was 9.1).

According to the computed results, the metals that are the most important to the speciation of dissolved sulfide are mercury, cadmium, nickel, lead and zinc, and copper (Fig. 4.13). These results are contrast with those obtained by Dyrssen (1988) who predicts that the speciation of dissolved sulfide is dominated by copper. His calculations were performed without ionic strength adjustments or taking into account the organic complexation of copper and zinc, and used dissolved sulfide concentrations of 0.1 and 0.3 nmol/L, which are higher than those at Station 9 (Fig. 4.8) used in the calculation presented here. However, the results of the calculations presented here are similar to those given by Elliott and Rowland (1990) for the predicted speciation of dissolved sulfide in the absence of copper. For the Pacific calculations, the speciation of zinc and copper that were calculated (along with that of dissolved sulfide) are consistent with those observed by Bruland (1989) and Coale and Bruland (1988). Indeed, copper and zinc are almost fully (>99%) complexed by organic ligands in surface waters (<50 m depth), while the inorganically complexed fraction of these metals increases below the mixed layer. It should be noted that for all calculations, mercury was quantitatively complexed into HgS complexes, and thus mercury and sulfide cycles may be interdependent. Having established that the thermodynamic calculations duplicate the observed speciation of zinc and copper, the predicted speciation of dissolved sulfide at Station 9 can be examined.

At Station 9, free sulfide was 80% of total dissolved sulfide in the mixed layer, and decreased with depth (Fig. 4.13). Because copper, zinc and cadmium are depleted in surface waters of the central North Pacific Ocean (Bruland, 1980), the concentrations of nickel are sufficient to complex with 20% of the total dissolved sulfide in the upper 100 m of the water column. Below 100 m, the decrease in the fraction of free sulfide is matched by a corresponding increase of zinc, copper, and cadmium complexes (Fig. 4.13). Although

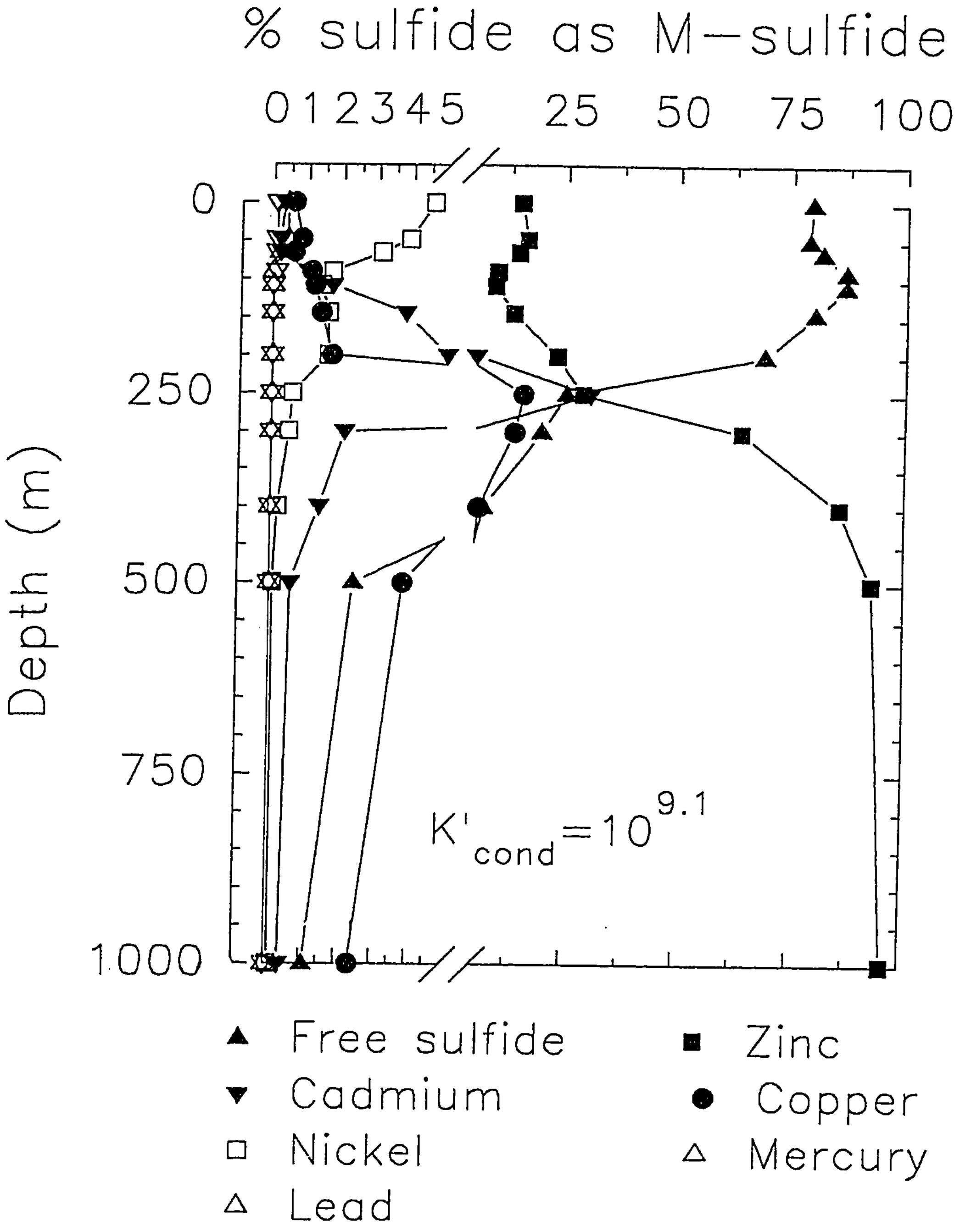

Figure 4.13: Predicted speciation of dissolved sulfide at Station 9 with $\log(K'_{cond})=9.1$.

zinc clearly dominates the speciation of dissolved sulfide below 250 m at Station 9 (Fig. 4.13), it is interesting to note the effects of the increasing concentration of cadmium and copper. The fractions of total dissolved sulfide as cadmium-sulfide and copper-sulfide are maximal at 250 m, and decrease below this depth. This behavior is due to the rapid increases of the concentrations of these metals to 250 m, without a concomitant increase in zinc. However below 250 m, zinc outcompetes cadmium and copper for dissolved sulfide, resulting in greater fraction of zinc-sulfide complexes (Fig. 4.13).

The calculations presented here predict that in the open ocean at thermodynamic equilibrium, a substantial fraction of total dissolved sulfide is uncomplexed in surface waters, or complexed with zinc rather than with copper. These results are more consistent with determinations of free sulfide and total dissolved sulfide in the surface ocean (Chapter 3, Cutter and Krahforst, 1988) than with previous theoretical examinations of this problem (*e.g.*, Dyrssen and Wedborg, 1989, Elliott *et al.*, 1989a). However, these predictions of the speciation of dissolved sulfide are still inconsistent with our current understanding of the rates and pathways for its cycling because iodate reacts only with free sulfide (Luther and Tsamakis, 1989). The rapid oxidation of a such a large fraction of total dissolved sulfide would in turn necessitate very rapid production of dissolved sulfide to maintain the observed concentrations. While this possibility cannot be ruled out, it conflicts with known dissolved sulfide production rates (*i.e.*, OCS hydrolysis, phytoplankton emissions).

The predicted speciation of total dissolved sulfide at thermodynamic equilibrium was recomputed in order to assess its sensitivity to the value of $\log K'_{\mathrm{cond}}(\mathrm{Cu(HS)}^{+})$. These calculations were performed using values of $\log K'_{cond}$'s that are one standard deviation away from the mean $\log K'_{cond}$

(*e.g.*, 8.5 and 9.7). While the general patterns of the speciation of dissolved sulfide are only slightly affected by the choice of log K_{cond} (Fig. 4.14–4.15), the fraction of copper-sulfide at 250 m increases from 4.8 to 43% of dissolved sulfide when log K_{cond} increases from 8.5 to 9.7. The increase in the fraction of copper-sulfide is balanced by a decrease in the fractions of zinc-sulfide and free sulfide. It is then apparent that the accuracy of the predicted speciation strongly depends on the values of the metal sulfide formation constants used in the calculation. However, this sensitivity study indicates that the the overwhelming dominance of the speciation of total dissolved sulfide by copper is unlikely, in contrast to previous studies (*e.g.*, Dyrssen, 1988).

4.3 Summary and Conclusions

In the Pacific Ocean, depth profiles of total dissolved sulfide show enrichment in the mixed layer (82 to 93 pmol/L), and usually show a secondary concentration maximum in the upper pycnocline. While total dissolved sulfide concentrations in the Pacific Ocean are lower than in the western North Atlantic Ocean, the shapes of the depth profiles are similar. These observations suggest that processes controlling the concentrations of total dissolved sulfide are similar between the two oceans, but that the production of dissolved sulfide may be slower in the Pacific Ocean. In this respect, the depth of maxima in total dissolved sulfide and *Synechococcus sp.* concentrations frequently correspond, suggesting that the production of dissolved sulfide by phytoplankton may be dominated by this species.

To begin an examination of the thermodynamic equilibrium speciation of dissolved sulfide in the open ocean, its interactions with copper were experimentally quantified. The conditional formation constant of copper-sulfide was determined under oceanographic conditions, and was found to have a

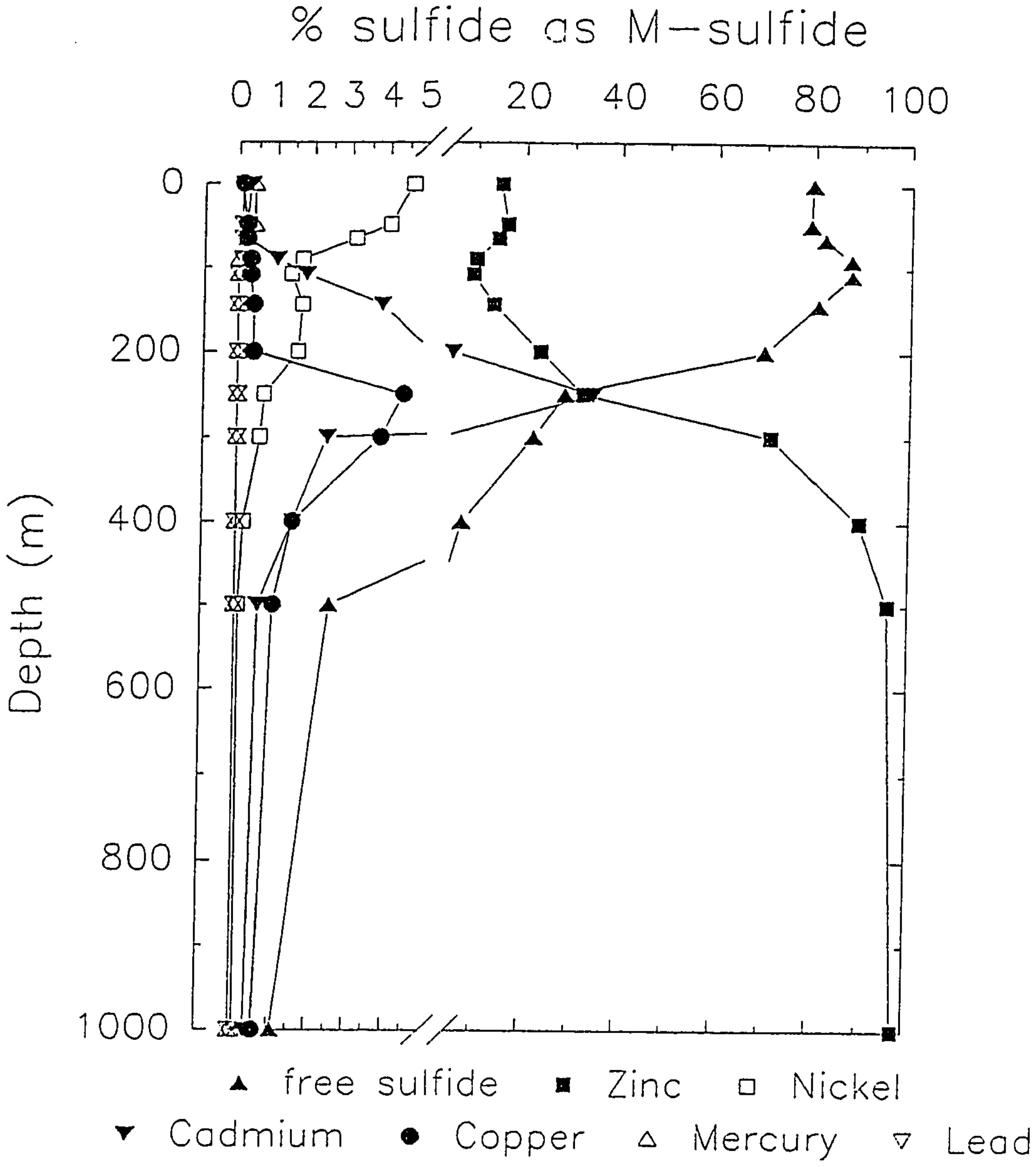

Figure 4.14: Predicted speciation of dissolved dissolved sulfide at Station 9 with $\log(K'_{cond})=8.5$.

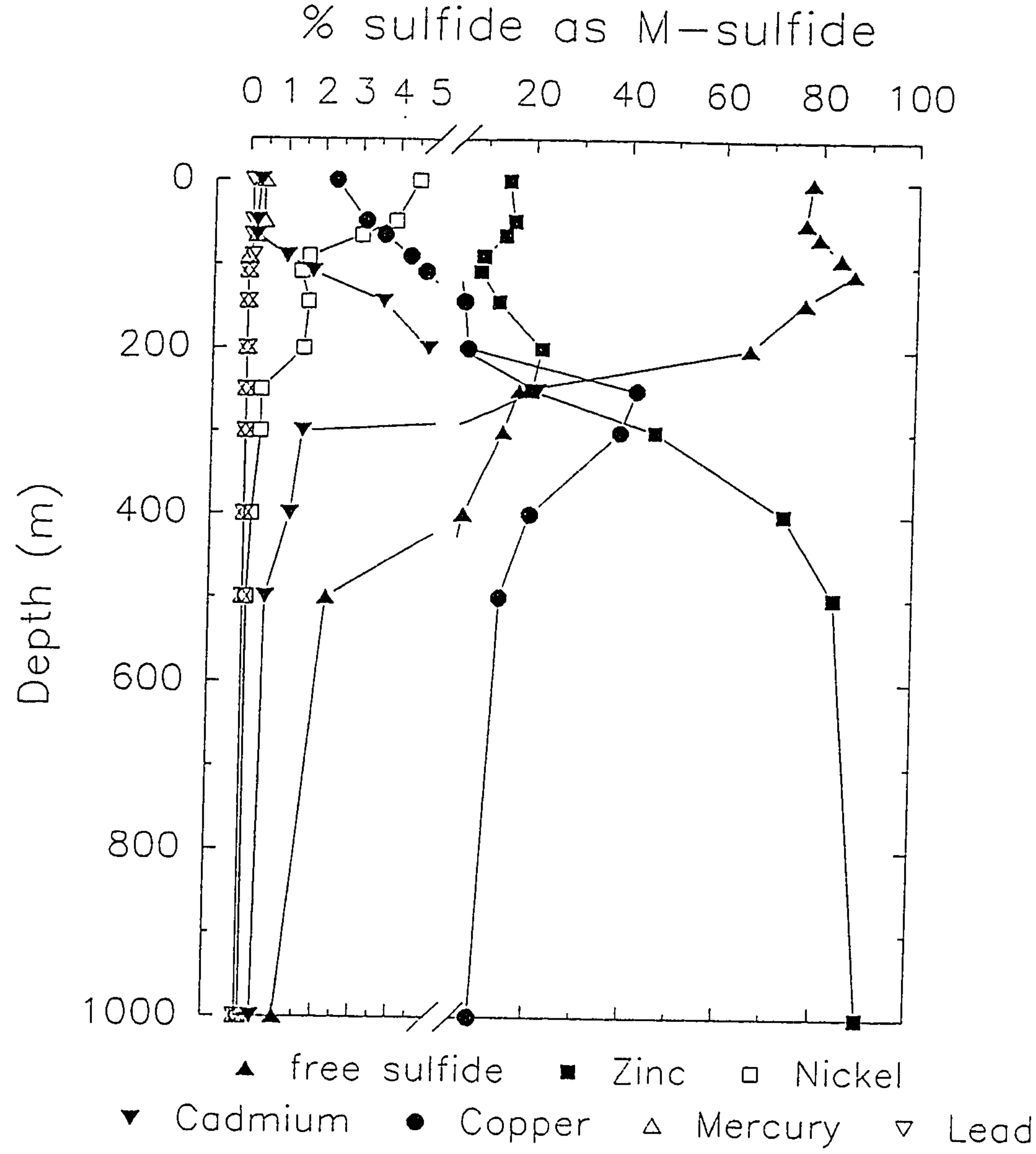

Figure 4.15: Predicted speciation of dissolved sulfide at Station 9 with $\log(K'_{cond})=9.7$.

log value of 9.1±0.6. Using this experimentally determined conditional formation constant, the predicted speciation of dissolved sulfide in seawater at thermodynamic equilibrium was calculated. Results from these calculations indicate that 80% of dissolved sulfide is uncomplexed in the mixed layer, and that this fraction decreases below the mixed layer due to increased concentrations of trace metals. These results also suggest that the speciation is dominated by free sulfide and by complexes with zinc, cadmium, copper, and nickel.

To gain a better (*i.e.,* more reliable) understanding of the thermodynamic equilibrium speciation of total dissolved sulfide, the formation constants for metal sulfide complexes other than copper-sulfide need to be redetermined under oceanographic conditions. Trace metals such as zinc, cadmium, nickel interact strongly with total dissolved sulfide, and thus are logical starting points. The results of this speciation study can in turn be used in the construction of more accurate budgets of the cycling of dissolved sulfide, since the cycling rate and speciation are interdependent.

Chapter 5

Conclusions and Directions for Future Research

To accomplish the original objectives of this study, it was necessary to develop sampling and analytical protocols sensitive and reliable enough for shipboard determinations of hydrogen sulfide species and carbonyl sulfide at the picomolar level. The following conclusions about the biogeochemical behavior of total dissolved sulfide in the ocean can be drawn from the results generated during field studies in the western North Atlantic Ocean and in the central Equatorial Pacific Ocean:

- The distribution and gross speciation of total sulfide in the open ocean were examined (Chapters 3 and 4). Total dissolved sulfide is enriched in the mixed layer of the water column, and decreases with depth. Secondary maxima are generally observed in the upper pycnocline. Concentrations of total dissolved sulfide are in the range <5–580 pmol/L in the western North Atlantic Ocean (Chapter 3), and <0.5–90 pmol/L in the central Equatorial Pacific Ocean (Chapter 4). The fraction of sulfide associated with particles is greatest in the mixed layer and decreases with depth. Observed concentrations of uncomplexed sulfide (*i.e.*, free sulfide; <15–30 pmol/L) in the western North Atlantic Ocean suggest that literature equilibrium speciation of sulfide which predict nearly 100% complexation with copper may not be accurate.

- The contribution of carbonyl sulfide (OCS) hydrolysis to the dissolved sulfide budget was quantified. Using the rate of OCS hydrolysis determined under oceanographic conditions and depth profiles of OCS in the open ocean, the rate was calculated to be 5 pmol/L/h in the upper 150 m of the Sargasso Sea. However, this production rate is too slow to balance the calculated removal rate of sulfide in the Sargasso Sea, indicating that other sources of dissolved sulfide may exist. Recent evidence suggests that phytoplankton emissions may account for a substantial fraction of dissolved sulfide production in the open ocean.

- The chemical speciation of dissolved sulfide was examined in the Atlantic and Pacific Oceans. The interactions between copper and sulfide were examined under oceanographic conditions and the formation constant of $Cu(HS)^+$ was determined. This formation constant was in turn used to predict the equilibrium speciation of dissolved sulfide in the upper ocean. Similar to observations, the predictions indicate that a significant (80%) fraction of dissolved sulfide is uncomplexed in surface waters, although this fraction declines rapidly with depth when the concentrations of metals such as zinc, nickel and cadmium begin to increase.

- To synthesize the observations in the North Atlantic, a mass balance of dissolved sulfide in the Sargasso Sea was constructed. From this budget, it appears that the cycling rate of sulfide is very rapid (hours). Iodate oxidation of free sulfide dominates the other dissolved sulfide removal pathways. However, the quantification of this rate is difficult because it depends on the chemical speciation of sulfide which is beginning to be better understood

From the above observations, it appears that the biogeochemistry of sulfide is considerably more complex than the original model proposed by Elliott *et al.* (1987). Indeed, the cycle of hydrogen sulfide species is affected by many additional factors which are not yet clearly understood. These factors include the release of dissolved and particulate sulfide by phytoplankton, the chemical speciation of total dissolved sulfide, and free sulfide oxidation by iodate. Thus, in order to further our understanding of hydrogen sulfide biogeochemistry, the following questions should be examined with appropriate laboratory and field experiments:

- What are the phytoplankton species that release the most total sulfide in the ocean and under what conditions? The study of Walsh *et al.* (submitted) demonstrates that phytoplankton production of sulfide appears to be species-dependent. Based on their results, phytoplankton species that have a large biomass should be examined in priority because total sulfide production is more closely related to cellular volume than to cell number. Moreover, the rates of production by these phytoplankton species need to be measured.
- What is the characteristic time scale for the complexation of free sulfide with trace metals? If the complexation reactions are slow relative to production/removal of free sulfide, then the speciation of total dissolved sulfide may be dominated by kinetic processes (*e.g.,* production and/or consumption) rather than by equilibrium processes (*e.g.,* complexation). Calculation of the speciation of total dissolved sulfide would then need to take this situation into consideration.
- What are the conditional formation constants of metal-sulfide complexes? To refine the calculations of total dissolved sulfide speciation in the open ocean, accurate constants are sorely needed. In this respect, the literature formation constants need to be re-examined at *in situ* conditions to obtain conditional constants that are directly applicable to this oceano-

graphic problem. Metals that could be tested initially include zinc, nickel and cadmium because of their importance for total dissolved sulfide speciation. Furthermore, equilibrium calculations indicate that all mercury should be complexed with free sulfide, and thus examination of the interaction between mercury and free sulfide would certainly be beneficial to the understanding of mercury biogeochemistry.

- To better understand total dissolved sulfide removal processes and rates, its oxidation by iodate needs to be re-evaluated. Specifically, the temperature dependence of the reaction, as well as the influence of total dissolved sulfide speciation on the removal rate should be re-determined. Finally, the vertical flux of particulate sulfide needs to be determined directly to verify the magnitude of the value estimated in Chapter 3.

Answers to the questions posed above can be used to construct a more elaborate model of the biogeochemistry of dissolved sulfide in the open ocean. This model should incorporate both kinetic and equilibrium processes affecting dissolved sulfide, and quantify the impact of ocean dynamics on these processes. Only then will the effects of the interactions between kinetic and equilibrium processes on the biogeochemical cycling of dissolved sulfide be fully understood.

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Appendices

Appendix A

Sulfide Experiment Cruise 1 Complete Data Report: Dissolved Sulfide, Carbonyl Sulfide, and Ancillary Parameters

Station Information

Station	GMT Date	GMT Time	Depth (m)	Location	Samples
1	04/13/89	0207	17	37o44.0'W 75o14.7'N	N,S
3	04/13/89	0442	26	37o39.1'W 75o03.5'N	N,S
4	04/13/89	0726	26	37o36.7'W 74o57.7'N	N,S
5	04/13/89	0944	32	37o34.1'W 74o52.5'N	N,S
1A	04/13/89	1444	15	37o43.9'W 75o14.5'N	N,S
3A	04/13/89	1824	27	37o39.0'W 75o03.0'N	N,S
5A	04/13/89	2104	32	37o34.0'W 74o52.4'N	N,S
6	04/14-15/89	0340- 1627	215	37o22.3'W 74o28.1'N	N,S
8	04/18-23/89	2114- 1740	4490	31o48.2'W 64o10.2'N	N,S,ST
7.5	04/25/89	1416	5040	34o01.3'W 71o01.3'N	N
7	04/26-27/89	1404- 1914	2760	34o53.1'W 75o01.2'N to 35o05.6'W 74o00.6'N	N,S
6A	04/28/89	0424- 1158	210	37o22.8'W 74o28.4'N	N,S

N = Nutrients S = Sulfur species ST = Sediment traps

Ancillary Data
(* = Trace Metal Go-Flo, ND = Non-Detectable)

Stn.	Temp.	Sal.	Oxy.	PO4	SiO2	NO3	NO2	Chl. a
ID	°C	psu	<-----------		umol/l	--------->		ug/L
1 Date: 4/13/89 Time: 02:07 Lat:37o44.16'N Long:75o14.58'W								
2m	7.91	32.3207		0.267	3.55	0.02	ND	
13m	7.78	32.3466		0.272	5.26	0.01	ND	
1A Date: 4/13/89 Time: 14:44 Lat:37o43.98'N Long:75o14.57'W								
2m	7.96	32.3535						
11m	7.78	32.3766						
3 Date: 4/13/89 Time: 04:42 Lat:37o39.02'N Long:75o03.58'W								
2m		32.8125		0.313	ND	ND	ND	
20m		32.8717		0.317	ND	ND	ND	
3A Date: 4/13/89 Time: 18:24 Lat:37o39.02'N Long:75o03.06'W								
2m	8.17	32.8175		0.309	ND	ND	ND	
20m	7.57	32.8191		0.303	ND	ND	ND	
4 Date: 4/13/89 Time: 07:25 Lat:37o36.73'N Long:74o57.72'W								
2m				0.288	ND	0.01	ND	
20m		32.9232		0.267	ND	ND	ND	
5 Date: 4/13/89 Time: 09:44 Lat:37o34.06'N Long:74o52.51'W								
2m	8.18	33.1355		0.309	ND	0.03	ND	
26m	7.80	33.2283		0.363	ND	0.24	ND	
5A Date: 4/13/89 Time: 21:04 Lat:37o34.05'N Long:74o52.49'W								
2m	8.74	33.0537		0.287	ND	ND	ND	
26m	7.56	33.1712		0.454	ND	0.77	ND	
6A								
10m	9.64	33.8719		0.378	ND	0.84	ND	
40m	10.5	34.2659		0.418	ND	1.79	ND	
130m	11.6	35.2302		0.977	4.75	10.35	ND	
6I Date: 4/15/89 Time: 07:22 Lat:37o22.52'N Long:74o28.17'W								
2m	10.0	33.7134		0.349	ND	0.02	ND	2.241
200m	9.94							
6J Date: 4/15/89 Time: 09:14 Lat:37o23.38'N Long:74o27.46'W								
2m	10.4	33.8129		0.334	ND	ND	ND	2.149
30m	10.1							1.087
6K Date: 4/15/89 Time: 11:19 Lat:37o22.35'N Long:74o28.32'W								
2m	10.2	33.8432		0.320	ND	ND	ND	2.809
20m	10.7							2.165
6L Date: 4/15/89 Time: 13:14 Lat:37o22.59'N Long:74o27.48'W								
2m	10.1	33.8058		0.327	ND	0.03	ND	2.492
10m	9.29							3.445

Stn. ID	Temp. °C	Sal. psu	Oxy.	PO4	SiO2	NO3	NO2	Chl. a ug/L
			<----------- umol/l --------->					
6M Date: 4/15/89 Time: 15:21 Lat:37o22.06'N Long:74o28.11'W								
2m	9.61	33.7138		0.341	ND	0.04	ND	3.401
10m	9.30							2.801
6AA Date: 4/28/89 Time: 04:11 Lat:37o22.77'N Long:74o28.14'W								
2m	18.3	36.1889		0.100	ND	0.21	0.070	
10m	16.4	35.8261		0.094	ND	0.08	0.041	
25m	14.8	35.2159		0.117	ND	0.12	0.071	
35m		35.2766		0.128	ND	ND	ND	
40m	12.9	35.2759		0.426	0.29	2.45	0.077	
65m	11.4	34.8489		0.691	1.99	6.79	0.243	
80m	11.7	34.9395		0.715	2.38	7.41	0.072	
110m	11.8	35.2524		0.764	3.06	8.20	0.027	
140m	11.7	35.3471		0.849	4.78	9.74	0.006	
155m	11.6	35.2842		1.002	6.12	12.12	0.015	
170m	11.7	35.5091		1.082	6.37	13.52	2.171	
185m	10.9	35.5084		1.327	9.43	15.93	0.592	
6AB Date: 4/28/89 Time: 08:00 Lat:37o22.44'N Long:74o28.09'W								
2m	17.6	36.0221		0.115	ND	ND	0.016	0.271
5m	17.5	35.5865		0.094	ND	ND	ND	0.254
10m	16.9	35.5214		0.086	ND	ND	0.015	0.247
15m	16.4	36.4522		0.107	ND	ND	0.070	0.334
20m	16.7	35.6007		0.118	ND	ND	0.143	0.604
25m	16.3			0.093	ND	ND	0.022	0.571
6AC Date: 4/28/89 Time: 10:18 Lat:37o22.32'N Long:74o28.18'W								
2m	13.9	34.9714		0.216	ND	ND	0.068	0.436
5m	13.3	34.6044		0.230	ND	ND	0.040	0.454
10m	14.8	35.1552		0.226	ND	ND	0.087	0.402
15m	15.0	35.5344		0.129	ND	ND	0.065	0.550
20m	14.4	34.9025		0.171	ND	ND	0.111	0.630
6AD Date: 4/28/89 Time: 11:58 Lat:37o22.41'N Long:74o28.22'W								
2m	10.4	34.0396		0.367	ND	ND	0.086	0.410
5m	10.5	33.9000		0.351	ND	ND	0.076	0.495
10m	10.6	36.6548		0.364	ND	ND	0.099	0.537
15m	11.0	34.0252		0.334	ND	ND	0.057	0.563
20m	11.9	34.3734		0.305	ND	ND	0.075	0.530
25m	12.8	34.3029		0.266	ND	ND	ND	0.500
7 Date: 4/26/89 Time: 14:04 Lat:34o53.11'N Long:75o01.74'W								
15m		36.4000		ND	ND	ND	ND	
*		36.4030		ND	ND	ND	ND	
30m		ND		ND	ND	ND	ND	
*		36.4046		ND	ND	ND	ND	
45m		36.4054		ND	ND	ND	0.167	
*		36.4085		0.079	ND	ND	ND	
60m		36.5467		ND	ND	ND	ND	
*		36.4332		ND	ND	ND	ND	
75m		36.6449		ND	ND	ND	ND	
*		36.4642		ND	ND	ND	ND	
90m		36.5864		ND	ND	ND	0.117	
*		36.6042		ND	ND	ND	0.097	

Stn. ID	Temp. °C	Sal. psu	Oxy.	PO4	SiO2	NO3	NO2	Chl. a ug/L
			<-----------		umol/l		---------->	
105m		36.7552		ND	ND	ND	0.046	
*		36.6706		ND	ND	ND	0.057	
125m		36.7774		ND	ND	ND	ND	
*		36.7184		ND	ND	ND	ND	
150m		36.7905		ND	ND	ND	ND	
*		36.6877		ND	ND	ND	ND	
198m		36.9933		0.330	0.59	5.38	ND	
*		36.7914		0.315	0.54	5.30	ND	
248m		36.6698		0.637	1.92	9.90	ND	
7B Date: 4/26/89 Time: 18:00 Lat:34o59.49'N Long:74o54.38'W								
25m	24.4	36.3977		ND	ND	ND	ND	
125m	22.7	36.7474		ND	ND	ND	0.056	
7C Date: 4/26/89 Time: 20:22 Lat:35o03.33'N Long:74o50.15'W								
25m	24.4	36.3946		ND	ND	ND	ND	0.091
125m	22.5	36.6471		ND	ND	0.01	ND	0.152
7D Date: 4/26/89 Time: 23:52 Lat:35o11.58'N Long:74o44.55'W								
2m	24.5							0.090
25m	24.4	36.4457		ND	0.50	0.02	ND	0.084
125m	22.5	36.9185		ND	0.08	ND	ND	0.143
7E Date: 4/27/89 Time: 00:30 Lat:35o10.88'N Long:74o44.34'W								
2m	24.5	36.4067		ND	0.44	ND	ND	0.092
25m	24.4	36.5723		ND	0.40	ND	ND	0.100
80m	23.8							0.121
125m	22.5	36.6653		ND	0.01	0.44	ND	0.113
7F Date: 4/27/89 Time: 02:13 Lat:35o18.13'N Long:74o36.77'W								
2m	24.5			ND	0.35	0.02	ND	0.085
25m	24.4			ND	0.32	ND	ND	0.084
108m	22.9	36.6730		ND	0.12	0.66	ND	0.081
125m	22.6	36.6776		ND	ND	0.63	ND	0.092
7G Date: 4/27/89 Time: 04:16 Lat:35o21.60'N Long:74o33.86'W								
2m	24.5	36.3904		ND	0.26	ND	ND	0.073
25m	24.5	36.3873		ND	0.28	ND	ND	0.039
125m	22.6	36.9376		ND	ND	0.75	ND	0.048
135m	22.6	37.1778		ND	ND	0.87	ND	0.067
7H Date: 4/27/89 Time: 06:16 Lat:35o26.86'N Long:74o29.44'W								
2m	24.5	36.4392		ND	0.18	0.05	ND	0.074
25m	24.5	36.3801		ND	0.16	0.10	ND	0.067
75m	23.9	36.7490		ND	0.07	0.07	ND	0.157
125m	22.6	36.7029		ND	ND	0.92	ND	0.052
7I Date: 4/27/89 Time: 08:15 Lat:35o30.44'N Long:74o26.51'W								
2m	24.5	36.4066		ND	0.09	ND	ND	0.073
25m	24.5	36.5926		ND	0.05	ND	ND	0.078
55m	24.1	36.4252		ND	0.04	ND	ND	
75m	23.9	36.5647		ND	ND	ND	ND	

Stn.	Temp.	Sal.	Oxy.	PO4	SiO2	NO3	NO2	Chl. a
ID	°C	psu	<-----------		umol/l		--------->	ug/L
7J Date: 4/27/89 Time: 10:15 Lat:35o37.78'N Long:74o21.19'W								
2m	24.8	36.3596		ND	0.07	0.01	ND	
25m	24.5	36.3903		ND	ND	0.03	ND	
7H1 Date: 4/27/89 Time: 19:14 Lat:36o05.63'N Long:74o00.55'W								
15m	25.3		201.3	ND	0.07	0.02	ND	0.070
30m	24.6	36.3601	199.9	ND	0.13	0.05	ND	0.097
45m	24.4	36.6390	201.6	ND	ND	ND	ND	0.150
60m	23.9	36.8735	203.8	ND	ND	ND	ND	0.150
75m	23.8	36.4922	205.5	ND	ND	ND	ND	0.184
90m	23.0	36.5774	209.1	ND	ND	0.03	ND	0.150
105m	22.7	37.0962	204.2	ND	ND	0.23	0.029	0.130
125m	21.9	36.8204	199.5	ND	ND	0.58	ND	0.097
150m	21.1	36.8177	203.4	ND	ND	0.59	ND	0.070
200m	20.0	36.9986	159.0	0.264	0.48	5.24	ND	0.044
250m	17.8	36.4265	149.6	0.555	2.34	9.76	ND	0.064
7.5 Date: 4/25/89 Time: 14:16 Lat:34o01.36'N Long:71o01.27'W								
15m	19.2	36.5186		ND	ND	0.10	0.016	
65m	19.2	36.8135		ND	ND	0.06	ND	
8 Date: 4/19/89 Time: 23:01 Lat:31o43.06'N Long:64o10.27'W								
15m		36.5993		ND	ND	ND	ND	
*		36.6036		ND	ND	0.13	ND	
30m		36.5929		ND	ND	0.04	ND	
*		36.6009		ND	ND	0.11	0.008	
45m		36.6071		ND	ND	0.03	0.028	
*		36.6160		ND	ND	0.16	ND	
60m		36.6152		ND	ND	0.07	0.044	
*		36.6112		ND	ND	0.08	0.046	
75m		36.6104		ND	ND	0.08	0.036	
*		36.6146		ND	ND	0.10	0.006	
90m		36.7352		0.007	ND	0.75	ND	
*		36.6182		0.003	ND	0.67	0.044	
105m		36.6052		ND	ND	0.33	0.028	
*		36.6124		ND	ND	0.23	ND	
125m		36.6006		0.021	ND	1.21	ND	
*		36.6033		0.025	0.49	1.04	0.017	
150m		36.5739		0.200	ND	1.52	0.010	
*		36.5937		0.045	ND	1.56	0.007	
175m		36.6980		0.067	ND	1.81	ND	
*		36.5750		0.066	ND	2.11	ND	
203m		36.5604		0.081	ND	2.20	ND	
*		36.5736		0.064	ND	1.90	ND	
265m		36.5315		0.124	ND	2.98	ND	
255m*		36.5398		0.119	ND	2.81	ND	
340m		36.4536		0.253	0.30	4.79	ND	
350m*		36.4416		0.273	0.41	4.99	ND	
440m		36.5322		0.371	0.87	6.41	ND	
450m*		36.4631		0.420	1.19	6.92	ND	
550m		35.9840		0.812	3.56	12.45	ND	
*		36.0004		0.754	3.52	12.54	0.005	
650m				1.159	6.71	16.67	ND	
*		35.5694		1.232	7.42	18.24	ND	
750m		35.3132		1.542	12.08	23.84	ND	

Stn.	Temp.	Sal.	Oxy.	PO4	SiO2	NO3	NO2	Chl. a
ID	°C	psu	<-----------		umol/l		--------->	ug/L
*		35.2298		1.576	12.72	23.57	ND	
850m		35.1338		1.577	13.01	23.57	ND	
*		35.1095		1.562	12.67	23.26	ND	
1000m		35.0586		1.379	12.31	19.67	ND	
*		35.0596		1.392	11.28	19.70	ND	
1480m		34.9870		1.237	10.62	17.18	0.038	
1490m*		34.9827		1.252	10.69	17.15	0.020	
1958m		34.9839		1.283	13.97	17.46	0.020	
1968m*		34.9862		1.284	14.02	17.52	0.038	
2984m		35.0142		1.285	10.57	18.05	0.017	
2994m*		35.0752		1.302	10.62	18.03	0.026	
3995m		34.8917		1.428	32.24	19.00	0.005	
4005m*		34.9040		1.427	32.47	18.92	0.020	
8A Date: 4/18/89 Time: 21:15 Lat:31o48.18'N Long:64o10.21'W								
2m	21.2	36.6025		0.028	ND	ND	ND	0.052
8B Date: 4/18/89 Time: 23:16 Lat:31o47.80'N Long:64o12.31'W								
2m	21.2	36.5930		0.018	ND	ND	0.038	0.051
8C Date: 4/19/89 Time: 01:13 Lat:31o49.57'N Long:64o11.88'W								
2m	21.2	36.8849		0.016	ND	ND	0.026	0.045
8D Date: 4/19/89 Time: 03:17 Lat:31o49.38'N Long:64o10.88'W								
2m	21.2	36.6031		0.010	ND	ND	0.021	0.045
8E Date: 4/19/89 Time: 05:17 Lat:31o48.72'N Long:64o10.35'W								
2m	21.1	36.6145		0.012	ND	ND	0.029	0.049
8F Date: 4/19/89 Time: 07:15 Lat:31o46.61'N Long:64o09.57'W								
2m	21.0	36.5819		0.016	ND	ND	0.038	0.056
8G Date: 4/19/89 Time: 09:22 Lat:31o46.31'N Long:64o08.64'W								
2m	20.9	36.5800		0.011	ND	ND	0.009	0.055
8H Date: 4/19/89 Time: 11:18 Lat:31o46.36'N Long:64o10.26'W								
2m	20.9	36.6018		0.010	ND	ND	0.022	0.060
8I Date: 4/19/89 Time: 13:14 Lat:31o45.40'N Long:64o10.55'W								
2m	20.9	36.5782		0.021	ND	ND	0.031	0.061
8J Date: 4/19/89 Time: 15:12 Lat:31o44.98'N Long:64o11.14'W								
2m	21.0	36.5905		0.016	ND	ND	0.074	0.051
8K Date: 4/19/89 Time: 17:11 Lat:31o44.44'N Long:64o12.02'W								
2m	21.1	36.6048		0.012	ND	ND	0.086	0.043
8L Date: 4/19/89 Time: 19:10 Lat:31o45.15'N Long:64o12.18'W								
2m	21.6	36.6099		0.015	ND	ND	0.084	0.042
8M Date: 4/19/89 Time: 21:10 Lat:31o45.49'N Long:64o12.36'W								
2m	21.6			0.020	ND	ND	0.154	0.044
8O Date: 4/20/89 Time: 01:15 Lat:31o43.06'N Long:64o10.27'W								
2m	21.3	36.6129		0.014	ND	ND	0.104	

Stn.	Temp.	Sal.	Oxy.	PO4	SiO2	NO3	NO2	Chl. a
ID	°C	psu	<-----------		umol/l		--------->	ug/L
8P Date: 4/20/89 Time: 05:16 Lat:31o42.73'N Long:64o09.45'W								
2m	21.0	36.5958		0.020	ND	ND	0.121	0.051
8Q Date: 4/20/89 Time: 09:15 Lat:31o42.05'N Long:64o10.61'W								
2m	20.9	36.5913		0.019	ND	ND	0.116	0.054
8R Date: 4/20/89 Time: 13:14 Lat:31o40.77'N Long:64o08.93'W								
2m	21.0	36.5997		0.039	ND	ND	0.160	0.055
8S Date: 4/20/89 Time: 17:56 Lat:31o42.05'N Long:64o10.88'W								
2m	21.3	32.9350		0.012	ND	ND	ND	0.047
8T Date: 4/20/89 Time: 21:13 Lat:31o42.18'N Long:64o11.59'W								
2m	21.4	36.6070		0.002	ND	ND	ND	0.047
8U Date: 4/21/89 Time: 01:17 Lat:31o42.06'N Long:64o11.63'W								
2m	21.3	36.6010		0.017	ND	ND	ND	0.049
8V Date: 4/21/89 Time: 05:15 Lat:31o41.46'N Long:64o09.45'W								
2m	21.1	36.5835		ND	ND	ND	ND	0.048
8W Date: 4/21/89 Time: 09:10 Lat:31o40.18'N Long:64o08.77'W								
2m	21.0			ND	ND	ND	ND	0.047
30m	21.0	36.6964	224.4	ND	ND	ND	ND	
8H1 Date: 4/20/89 Time: 16:42 Lat:31o42.28'N Long:64o11.72'W								
15m		36.6998	242.2	0.010	ND	ND	ND	0.032
45m	20.6	36.6210	224.4	0.001	ND	ND	ND	0.066
60m	19.8	36.6184	224.6	ND	ND	ND	ND	0.107
75m	19.6	36.6111	224.6	0.003	ND	ND	ND	0.174
90m	19.5	36.6143	222.0	ND	ND	0.00	ND	0.378
105m	19.4	36.6714	214.9	0.025	ND	0.62	0.046	0.283
125m	19.3		221.1	0.043	ND	0.87	ND	0.120
150m	19.1	36.5943	213.3	0.059	ND	1.24	ND	0.039
175m	18.9	36.5790	207.6	0.068	ND	1.38	0.027	0.039
200m	18.7	36.5568	198.2	0.094	ND	2.17	ND	0.032
300m	18.1	36.4986	197.3	0.200	ND	4.29	0.016	0.025
8H2 Date: 4/21/89 Time: 20:43 Lat:31o39.65'N Long:64o11.05'W								
400m	17.4	36.4102	192.6	0.316	0.62	5.19	ND	0.025
500m	16.1	36.1815	176.6	0.572	2.02	8.98	ND	0.025
550m	15.2	36.0878	175.9	0.669	2.65	10.76	ND	
650m	12.9	35.6989	165.2	1.099	6.52	20.47	0.010	
750m	10.4	35.6875	158.7	1.113	6.49	16.11	0.025	
850m	8.21	35.290	157.5	1.597	13.50	24.18	ND	
1000m	6.03	35.1252	205.0	1.466	12.41	20.41	0.068	
1500m	4.31	35.0282	255.8	1.275	11.17	17.03	0.035	
2000m	3.71	34.9978	259.3	1.290	13.43	17.33	ND	
2500m	3.13	34.9628	262.9	1.266	18.07	17.57	ND	
3000m	2.63	34.9302	264.5	1.333	21.27	17.32	ND	
3500m	2.30	34.9072	261.4	1.383	27.26	17.66	0.026	
4000m	2.21	34.9591	264.7	1.381	26.72	17.74	ND	
4440m	2.23	34.8960	260.4	1.451	33.59	19.05	ND	

Stn. ID	Temp. °C	Sal. psu	Oxy.	PO4	SiO2	NO3	NO2	Chl. a ug/L
			<------------		umol/l		---------->	
8H3 Date: 4/23/89	Time: 07:07	Lat:31o34.83'N	Long:64o04.42'W					
425m	17.2	36.3651		0.427	1.13	5.00	ND	
475m	16.5	36.2863		0.522	1.45	6.40	ND	
500m	16.1	36.5981		0.608	2.04	7.97	0.033	
550m	15.2	36.0209		0.779	3.03	10.58	ND	
575m	14.6	35.9290		0.868	3.71	12.23	ND	
8H4 Date: 4/23/89	Time: 17:40	Lat:31o36.25'N	Long:64o04.34'W					
410m	17.3	36.5409		0.166		1.60	0.024	
430m	17.1	36.5147		0.419	0.88	5.30	0.023	
440m	16.9	36.3280		0.472	1.23	5.89	0.013	
450m	16.9	36.4186		0.482	1.28	6.20	0.010	
460m	16.7	36.4317		0.499	1.24	6.47	0.020	
470m	16.6	36.2626		0.533	1.47	7.00	0.014	
480m	16.4	36.2417		0.570	1.64	7.32	0.083	
490m	16.2	36.2720		0.597	1.84	7.79	0.075	
500m	16.0	36.1767		0.624	1.92	8.30	ND	
510m	15.8	36.1414		0.675	2.22	8.94	0.072	
520m	15.6	36.1030		0.711	2.39	9.34	0.069	
Sediment Traps								
Cod End								
1		36.6492		2.89	3.67	0.80	ND	
2		36.6158		4.70	2.45	0.52	0.051	
Inner A				24.98	33.66	3.30	ND	
Inner B				16.30	24.77	3.28	ND	
T-inner				23.66	21.83	3.45	5.095	

Sulfide Experiment Cruise 1
Particulate Data

Stn. ID	Depth	<--------Total	--------	-------->	
		Carbon	Nitrogen	Sulfur	Org. C
		<----------	ug/L	---------->	
1	2m	484.4	53.11	13.65	
	13m	207.7	21.00	17.42	
1a	2m	135.0	3.24	1.186	135.0
	11m	108.8	10.60	18.61	108.8
3	2m	76.86	11.72	4.973	
	20m	65.05	7.867	9.077	
3a	2m	68.11	5.997	3.032	68.11
	20m	50.41	7.202	0	43.09
4	2m	158.2	16.21	4.851	158.2
	20m	65.5	10.25	4.783	
5	2m	58.45	7.867	1.800	
	26m	53.16	7.5	0	46.60

		<------------Total------------>			
Stn. ID	Depth	Carbon	Nitrogen	Sulfur	Org. C
		<------------ug/L------------>			
5a	2m	75.76	9.855	0	35.89
	26m	51.31	5.671	0	
7H1	15m	31.10	2.320	0.981	
	30m	37.85	2.799	0	23.00
	45m	30.07	2.862	16.11	
	60m	33.88	2.377	0	
	75m	29.57	1.866	0	
	90m	25.60	1.543	1.025	15.71
	105m	24.33	0.872	0.772	
	125m	25.44	0.748	0.766	
	150m	15.70	1.204	1.844	5.631
	200m	15.00	0	0	0
	250m	14.61	1.340	0.930	
8w	30m	20.86	1.584	0	16.73
	400m	12.66	1.275	3.179	
	500m	13.44	0	1.195	
8H1	15m	30.70	2.183	4.173	1.92
	45m	27.94	0.948	0	
	60m	24.52	1.651	3.535	
	75m	27.47	2.634	1.431	25.31
	90m	32.41	2.694	1.210	11.98
	105m	21.05	1.201	0	
	125m	24.27	1.929	6.944	
	150m	13.78	0.673	1.880	
	175m	16.95	0.481	4.781	16.95
	200m	14.72	1.007	4.661	4.24
	300m	16.05	0.385	2.973	9.54
8H2	850m	4.566	0.545	2.289	
	1000m	27.28	0.839	2.192	
	1500m	7.84	0.44	4.323	0
	2000m	4.12	0.466	0	
	2500m	3.04	0.655	4.274	
	3000m	7.12	0	0.756	0
	3500m	10.46	0.062	3.771	
	4000m	11.27	0.509	3.793	
	4440m	13.15	0.643	3.039	5.464

Sulfide Experiment Cruise 1
Dissolved Sulfide Data

	Stn. ID	ZnS* nmol/L	OCS pmol/L	H2S pmol/L
1	2m	0.482	146	ND
	13m	0.769	216	ND
1a	2m		142	ND
	11m		144	ND
3	2m	0.728	119	ND
	20m	0.560	138	ND
3a	2m		229	ND
	20m		89	ND
4	2m	0.481	91	ND
	20m	0.682	71	ND
5	2m	0.455	96	ND
	26m	0.472	74	ND
5a	2m	0.637	276	ND
	26m	0.709	80	ND
6a	2m		169	ND
6c	2m		168	ND
	50m		67	ND
6d	2m		168	ND
	100m		59	ND
6e	2m		165	ND
	50m		63	ND
6f	2m		161	3.55
	50m		40	ND
6g	2m		190	2.80
	50m		45	ND
6h	2m		165	4.60
	50m		30	ND
6i	2m	0.692	160	ND
	200m	0.932	ND	ND
6j	2m	1.185	115	1.24
	30m	0.938	65	ND
6k	2m	0.988	115	0.09
	20m		60	ND
	Stn. ID	ZnS* nmol/L	OCS pmol/L	H2S pmol/L

61	2m	1.432	106	2.81
	10m		83	ND
6m	2m	1.026	80	ND
	10m		47	ND
6aa	2m	0.963	88	14.84
	10m	1.171	70	16.53
	25m	0.752	71	4.90
	40m		162	ND
	65m		60	
	80m		56	2.23
	110m		ND	
	140m		148	ND
	155m		49	ND
	170m		50	
	185m		292	ND
6ab	2m	1.414	75	15.1
	5m	0.688	67	20.6
	10m	1.028	64	17.4
	15m	0.181	59	12.9
	20m	0.959	60	0.7
6ac	2m	1.194	78	ND
	5m	1.074	89	14.6
	10m	0.020	72	29.2
	15m	0.643	49	ND
	20m		51	ND
6ad	2m		96	ND
	5m	0.942	129	ND
	10m	0.821	84	ND
	15m	0.977	87	10.32
	20m		105	ND
7	15m	1.465	65	ND
	30m		50	ND
	45m	1.060	51	ND
	60m	1.286		
	75m	0.923		
	90m	0.613		
	105m	2.138		
	125m	0.913		
	150m	1.696		
	198m	1.074		
	248m	0.998		
7b	25m		54	ND
	125m		54	ND
7c	25m		55	ND
	125m		49	ND

	Stn. ID	ZnS* nmol/L	OCS pmol/L	H2S pmol/L
7d	2m		51	ND
	25m		58	ND
	125m		53	ND
7e	2m		57	ND
	25m		66	ND
	80m		60	ND
	125m		79	ND
7f	2m		51	ND
	25m		58	ND
	108m		52	ND
	125m		86	ND
7g	2m		35	ND
	25m		52	ND
	125m		38	ND
	135m		36	ND
7h	2m		35	ND
	25m		39	ND
	75m		49	ND
	125m		43	ND
7i	2m		37	ND
	25m		76	ND
	55m		ND	ND
7j	2m		ND	ND
	25m		32	ND
8	15m	1.721	77	ND
	30m	1.646	58	ND
	45m	2.019	46	ND
	60m	1.531	53	ND
	75m	0.757	81	ND
	90m	0.530	68	ND
	105m	0.759	55	ND
	125m	0.481	83	ND
	150m	0.447	57	ND
	175m	0.570	43	ND
	203m	0.690	49	ND
	265m	0.579	43	ND
	350m	0.664	49	ND
	450m	0.318	96	ND
	550m	0.773	187	ND
	650m	0.648	52	ND
	750m	0.554	34	ND
	850m	0.591	39	ND
	1000m	0.550	83	ND
	1490m	0.707	44	ND
	1968m	0.738	39	ND
	2994m	0.513	41	ND
	4005m	0.976	46	ND

	Stn. ID	ZnS* nmol/L	OCS pmol/L	H2S pmol/L
8a	2m		87	ND
	90m		99	ND
8b	2m		68	0.37
	90m		58	ND
8c	2m		62	0.36
	100m		44	ND
8c	2m		58	ND
	85m		38	ND
8e	2m		56	ND
	90m		72	ND
8f	2m		42	ND
	92m		46	ND
8g	2m		56	ND
	50m		40	ND
8h	2m		51	ND
	90m		51	ND
8i	2m		58	ND
	90m		50	ND
8j	2m		54	ND
	85m		35	ND
8k	2m		56	ND
	85m		46	ND
8l	2m		61	ND
	85m		33	ND
8m	2m		84	ND
	85m		ND	ND
8o	2m		158	ND
	91m		75	ND
8p	2m		72	ND
	91m		58	ND
8q	2m	0.985	52	ND
	91m		ND	ND
8r	2m	1.207	69	ND
	88m		68	ND
8s	2m	0.559	77	ND
	85m		70	ND
8t	2m	0.721	63	ND
	95m		57	ND

	Stn. ID	ZnS* nmol/L	OCS pmol/L	H2S pmol/L
8u	2m	0.485	71	ND
	90m		59	ND
8v	2m	0.784	45	ND
	82m		ND	
8w	2m	0.721	61	ND
	80m		ND	ND
8h3	425m		98	ND
	475m		133	ND
	500m	0.873	572	37.8
	550m		ND	ND
	575m		ND	ND
8h4	410m	0.809	127	ND
	430m	0.159	389	ND
	440m	0.605	1030	27.2
	450m	0.367	96	ND
	460m	0.490	72	
	470m	0.549	76	ND
	480m	0.696	63	
	490m	0.922	621	2.0
	500m	0.282	57	
	510m	0.486	55	
	520m		101	

* ZnS is the concentration of total dissolved sulfide preserved by the addition of zinc acetate (which forms ZnS)

Appendix B

Sulfide Experiment Cruise 2 Complete Data Report for Dissolved Sulfide and Ancillary Parameters

Station Information

Station	GMT Date	GMT Time	Depth (m)	Location	Samples
1	10/25/89	0111	37	37o15.3'W 74o55.3'N	N,S
2	10/26-27/89	2128- 0158	340	36o24.9'W 70o52.5'N	N,S
3	10/27-28/89	2218- 0642	273	39o01.1'W 72o47.4'N	S
4	10/28/89	2036	380	39o58.9'W 70o18.1'N	N,S
5	10/29/89	1213	560	40o20.9'W 67o31.9'N	N,S
6	10/30/89	0621	3100	41o21.7'W 65o01.8'N	N,S
7	10/31/89	0016	2700	42o13.1'W 62o25.8'N	N,S
8	10/31 - 11/01/89	1014- 0800	2340	43o00.0'W 60o00.0'N	N,S
9	11/02/89	1655	5000	39o50.8'W 61o18.7'N	N,S
10	11/03/89	0926	5040	37o41.1'W 62o10.6'N	N,S
11	11/04/89	0847	4860	34o43.0'W 63o13.0'N	N,S
12	11/05/89	0355	4530	31o50.2'W 64o10.6'N	N,S
13	11/07-08/89	1825- 0248	4080	35o43.4'W 72o10.5'N	N,S
14	11/08/89	0610	3840	36o00.0'W 72o38.7'N	N
15	11/08-08/89	1949- 0518	180	37o20.8'W 74o29.0'N	N,S

N = Nutrients S = Sulfur species

All times and dates are GMT
(ND - Not Detectable)

Stn. ID	Temp. oC	Sal. ppt	Oxy. umol/L	Sulfide pmol/L	Free sulf. pmol/L	OCS pmol/L
2C 10/27/89 Time: 01:58 Lat:36o28.83'N Long:70o46.33'W						
5m	25.03	36.4133	188.3	86.7	---	61
75m	22.50	36.5210	236.3	82.2	---	ND
248m	19.37	36.5260	210.7	20.9	---	ND
397m	17.79	36.3888	198.7	47.2	---	ND
499m	16.74	36.1893	--	54.4	---	88
526m	16.33	36.1112	--	44.8	---	55
550m	15.81	36.0249	123.6	183.5	---	77
600m	14.93	35.9039	189.0	59.0	---	63
3B 10/27/89 Time: 23:05 Lat:39o01.10'N Long:72o47.36'W						
3m	17.24	34.1280	274.1	184.3	---	110
26m	16.87	34.1921	237.0	180.1	---	ND
48m	15.04	35.4503	152.0	52.7	---	ND
76m	14.88	35.9000	77.1	83.8	---	67
100m	13.33	35.7674	165.4	32.5	---	ND
150m	12.31	35.6121	165.7	52.2	---	--
200m	11.97	35.5914	158.1	37.3	---	ND
250m	10.64	35.3833	160.5	81.9	---	60
270m	10.32	35.4032	148.7	----	---	ND
4B 10/28/89 Time: 21:27 Lat:39o58.94'N Long:70o18.09'W						
2m	21.49	32.9387	244.6	269.2	---	72
5m	21.50	35.2208	242.3	163.8	---	105
10m	21.46	35.2116	242.3	142.2	---	ND
30m	20.61	35.2735	228.4	84.5	---	111
76m	15.41	35.7085	180.8	100.3	---	ND
100m	15.37	35.9576	154.7	56.9	---	59
125m	13.28	35.5374	192.2	78.9	---	75
375m	8.13	35.1488	172.4	48.9	---	ND
5B 10/29/89 Time: 13:05 Lat:40o20.96'N Long:67o32.15'W						
2m	13.86	35.5127	292.1	924.9	---	73
6m	13.86	35.6935	309.3	661.3	---	66
11m	13.86	35.6409	302.4	771.6	---	71
27m	12.31	35.3969	258.7	627.4	---	ND
75m	14.39	35.2082	164.0	399.8	---	ND
100m	13.61	32.6751	133.9	409.3	---	ND
125m	12.74	32.6727	110.2	548.0	---	ND
150m	11.96	32.6396	149.7	614.7	---	ND
6B 10/30/89 Time: 07:20 Lat:41o21.67'N Long:65o01.80'W						
2m	17.02	34.1108	263.6	465.8	---	82
10m	17.47	34.2680	267.2	470.4	---	79
25m	18.25	34.6401	261.3	416.6	---	76
75m	12.12	34.8989	220.0	255.3	---	ND
100m	12.40	35.2003	212.7	215.9	---	ND
126m	12.22	35.3447	209.3	272.5	---	81
150m	12.05	35.3408	198.7	234.8	---	ND
7B 10/31/89 Time: 01:28 Lat:42o12.97'N Long:62o25.34'W						
3m	14.70	33.2817	281.7	33.3	---	132

Stn. ID	Temp. oC	Sal. ppt	Oxy. umol/L	Total Sulf. pmol/L	Free sulf. pmol/L	OCS pmol/L
7B cont.						
5m	14.66	33.3125	280.8	9.24	---	116
10m	14.65	33.3213	279.6	5.20	---	92
33m	15.46	34.2769	258.6	9.31	---	88
72m	13.78	35.3864	209.6	9.92	---	68
90m	13.63	35.5084	205.8	9.23	---	102
150m	12.65	35.5117	193.5	ND	---	73
400m	7.08	35.0320	186.8	7.39	---	72
8A :10/31/89 Time: 10:14 Lat:43o00.00'N Long:59o59.98'W						
2m	13.80			458.8	ND	83
5m	13.77			306.9	51	93
10m	13.84			373.9	27	75
8B :10/31/89 Time: 12:30 Lat:42o59.57'N Long:59o59.94'W						
2m	13.70	32.1313	289.3	108.8	ND	83
5m	13.80	33.1952	283.6	121.2	51	93
10m	13.88	32.3867	285.3	209.7	27	75
25m	14.15	32.6251	277.7	98.9	35	75
50m	8.42	33.1978	315.6	38.6	ND	ND
75m	4.61	33.3933	319.7	36.8	ND	88
100m	5.46	33.9169	279.7	69.2	ND	ND
150m	7.09	34.5957	227.8	53.1	ND	33
200m	7.80	34.8873	191.2	70.9	ND	ND
250m	6.18	34.8573	210.2	50.9	ND	ND
300m	5.74	34.8495	217.3	60.9	ND	ND
400m	5.06	34.8380	245.2	88.1	ND	ND
500m	4.92	34.7222	257.6	64.7	ND	ND
750m	4.18	34.8680	284.9	67.2	ND	ND
1000m	4.12	34.8428	292.3	61.9	ND	64
8H 11/01/89 Time: 01:20 Lat:42o59.93'N Long: 60o01.51'W						
2m		32.1930		68.1	32.0	32
5m		32.1841		137.6	36	96
10m		32.2863		148.9	33	89
8K 11/01/89 Time: 03:51 Lat:42o59.97'N Long:60o01.25'W						
2m	13.88	32.0523		227.5	34.0	114
5m	13.85	32.0094		204.3	47	130
10m	13.79	31.8453		250.4	ND	110
8L 11/01/89 Time: 08:00 Lat:43o00.77'N Long:60o01.18'W						
2m	13.87			180.6	18.0	96
5m	13.87			239.1	37	103
10m	13.72			193.7	24	95
8M 11/01/89 Time: 10:16 Lat:43o01.79'N Long:60o02.66'W						
2m	13.86	32.0532		270.9	73.0	93
5m	13.86	32.0545		314.7	38	114
10m	13.83	36.3037		214.8	138	102

Stn. ID	Temp. oC	Sal. ppt	Oxy. umol/L	Total Sulf. pmol/L	Free sulf. pmol/L	OCS pmol/L
9B : 11/02/89		Time: 16:55		Lat:39o51.72'N	Long:61o17.34'W	
4m	25.25	36.3631	214.5	85.66	---	72
75m	24.71	36.3217	216.5	74.6	---	59
150m	21.44	36.6706	214.9	42.5	---	ND
301m	18.73	36.5361	207.0	78.9	---	--
399m	17.80	36.4239	201.2	55.2	---	ND
480m	17.00	36.3413	201.2	52.3	---	30
539m	15.90	36.1811	185.9	58.1	---	28
601m	14.37	35.8456	148.3	43.3	---	ND
10B 11/03/89		Time: 10:22		Lat:37o40.37'N	Long:62o10.48'W	
4m	24.21	36.4047	219.3	71.8	---	67
125m	23.25	36.6119	209.1	78.	---	36
300m	18.92	35.5919	216.6	54.1	---	ND
448m	18.20	36.4752	219.8	45.6	---	ND
499m	17.85	36.4354	209.8	40.3	---	ND
601m	16.99	36.3035	202.4	31.4	---	33
651m	16.43	36.2004	193.9	35.6	---	ND
11B 11/04/89		Time: 09:20		Lat:34o42.81'N	Long:63o12.70'W	
5m	23.81	36.3956	224.6	62.3	---	83
120m	21.38	36.6559	209.8	39.2	---	83
300m	18.71	36.5369	212.4	40.5	---	62
421m	18.07	36.4578	210.2	39.9	---	54
501m	17.55	36.4022	208.1	28.1	---	51
552m	17.04	36.3082	199.2	55.2	---	--
609m	16.15	36.1970	185.6	29.6	---	61
651m	15.34	36.0035	184.9	28.3	---	73
12B 11/05/89		Time: 05:30		Lat:31o49.62'N	Long:64o10.07'W	
2m	24.43	36.5565	214.3	131.7	ND	102
5m	24.44	36.5559	217.2	141.3	ND	80
10m	24.44	36.5538	219.0	101.8	23	63
25m	24.45	36.5571	218.1	136.6	28	57
50m	24.45	36.5661	215.8	140.1	21	49
75m	21.25	36.6834	217.4	195.6	26	53
101m	20.06	36.6485	216.6	132.4	26	87
150m	19.12	36.6075	211.6	70.9	23	65
200m	18.75	36.6003	214.4	38.3	ND	48
250m	18.47	36.5614	216.9	72.4	22	47
300m	18.22	36.5441	204.0	70.7	ND	ND
400m	17.64	36.4505	204.6	71.1	ND	ND
500m	16.78	36.3022	197.5	82.7	18	ND
540m	16.26	36.2233		75.2	ND	28
600m	15.19	36.0399	186.8	90.3	ND	28
700m	13.52	35.7780	184.0		ND	ND
750m	12.28	35.6117	166.7	128.6	19	ND
1000m	7.38	35.1185	185.8	39.2	25	ND
13B 11/07/89		Time: 19:20		Lat:35o43.50'N	Long:72o10.65'W	
3m	23.73	36.5857	209.9	314.3	9.0	63
5m	23.73	36.5568	212.7	308.0	ND	46
10m	23.74	36.5720	208.5	290.6	ND	51
25m	23.74	36.5917	213.1	324.7	ND	56
50m	23.74	36.6307	211.8	275.2	ND	54

Stn. ID	Temp. oC	Sal. ppt	Oxy. umol/L	Total Sulf. pmol/L	Free sulf. pmol/L	OCS pmol/L
75m	23.72	36.6181	211.2	334.6	19	69
100m	23.03	36.7146	202.4	203.2	15	41
150m	20.22	36.6392	213.0	228.9	8	39
200m	19.34	36.6139	206.4	207.2	ND	43
401m	18.11	36.5253	196.4	205.4	ND	28
501m	17.43	36.4496	193.0	162.9	ND	ND
599m	16.18	36.2094	185.8	192.6	ND	50
701m	14.33	35.9086	174.5	200.2	ND	ND
801m	12.34	35.5962	144.1	153.0	ND	ND
901m	10.23	35.3296	146.9	96.3	ND	ND
1000m	8.53	35.1866	164.6	92.6	ND	ND
15B 11/08/89		Time: 19:49		Lat:37o21.00'N	Long:74o28.87'W	
2m	16.93	34.1239	255.6	154.0	ND	ND
5m	16.76	34.0676	257.4	100.2	ND	ND
9m	16.89	34.1445	260.0	100.1	ND	ND
25m	18.61	34.9912	234.1	181.1	11	ND
49m	16.52	35.3738	197.4	70.2	13	26
75m	14.29	35.6542	163.8	207.9	31	98
101m	13.77	35.7063	157.5	229.9	37	102
126m	12.86	35.5883	159.7	106.9	29	59
151m	12.70	35.6050	158.2	123.8	30	67
175m	12.51	35.5848	158.6	99.1	31	72
15F :11/08/89		Time: 23:48		Lat:37o20.79'N	Long:74o29.04'W	
2m	16.26	33.7939		221.2	34.0	91
25m	18.81	35.0303		116.5	34	60
15J 11/09/89		Time: 03:56		Lat:37o20.22'N	Long:74o28.77'W	
5m	15.92	33.6431		148.1	30	75
19m	17.75	34.6466		127.2	36	ND
52m	12.76	34.1175		155.8	ND	ND
75m	14.90	35.6551		137.0	ND	ND
100m	13.76	35.7475		112.7	22	ND
125m	12.99	35.6035		71.7	21	ND
15K 11/09/89		Time: 05:18		Lat:37o20.22'N	Long:74o28.77'W	
6m	16.03	33.6838		165.2	29	60
18m	17.01	34.7127		106.8	28	ND
49m	12.98	34.2451		70.2	23	ND
75m	14.92	35.8041		89.1	28	ND
100m	14.44	35.8840		112.9	21	ND
125m	13.29	35.7385		155.1	24	ND

Suspended Particulate Data

All times and dates are GMT
(ND - Not Detectable)

Stn. ID	<-----Total Carbon ug/L	----- Nitrogen ug/L	----- Sulfur ug/L	-----> Organic C. ug/L
1B 10/25/89	Time: 01:42	Lat:37o15.45'N	Long:74o55.09'W	
2m	74.92	8.52	8.59	
16m	82.9	8.56	6.42	82.9
32m	232.2	19.01	44.37	118.1
2C : 10/27/89	Time: 01:58	Lat:36o28.83'N	Long:70o46.33'W	
5m	36.27	2.261	1.27	18.53
75m	36.64	3.013	0.89	32.89
150m	16.19	0.701	ND	13.10
250m	40.59	ND	2.53	
400m	45.42	4.289	16.71	27.53
550m	29.66	ND	ND	17.65
600m	40.88	ND	ND	
3B 10/27/89	Time: 23:05	Lat:39o01.10'N	Long:72o47.36'W	
3m	69.82	6.282	18.29	64.07
25m	52.00	3.372	ND	
49m	48.27	2.250	4.81	49.44
74m	36.79	2.198	16.26	17.09
100m	36.80	2.380	0.77	25.09
151m	22.40	0.420	1.70	16.92
198m	51.11	7.845	ND	24.12
251m	37.16	2.230	1.34	
272m	53.68	2.059	7.46	47.33
4B 10/28/89	Time: 21:27	Lat:39o58.94'N	Long:70o18.09'W	
2m	12.11	0.171	ND	
4m	31.68	1.893	1.33	
10m	37.66	3.329	5.29	37.66
31m	55.77	5.941	0.73	
75m	12.11	0.593	8.45	
101m	27.03	1.411	9.41	18.13
126m	33.76	1.873	4.29	20.51
377m	20.87	1.296	9.26	12.00
5B 10/29/89	Time: 13:05	Lat:40o20.96'N	Long:67o32.15'W	
2m	87.52	8.966	1.34	87.52
5m	85.87	10.08	5.83	85.87
10m	85.74	9.133	1.27	7.20
27m	95.43	14.13	ND	95.43
75m	20.79	0.847	ND	14.05
100m	25.01	0.658	4.19	
125m	23.50	1.174	2.51	15.45
150m	15.86	0.388	ND	15.86

Stn. ID	<----------------Total---------------> Carbon ug/L	Nitrogen ug/L	Sulfur ug/L	Organic C. ug/L
6B 10/30/89 Time: 07:20 Lat:41o21.67'N Long:65o01.80'W				
2m	77.20	11.15	4.84	51.28
10m	47.91	5.355	6.04	47.91
25m	40.09	4.128	1.56	40.09
75m	15.18	0.347	5.78	12.20
100m	12.11	0.171	ND	5.97
125m	15.87	ND	0.95	
150m	15.39	0.345	6.37	
200m	19.57	0.184	8.61	
7B : 10/31/89 Time: 01:28 Lat:42o12.97'N Long:62o25.34'W				
3m	69.35	6.432	0.53	
5m	68.86	6.072	2.36	68.86
10m	112.0	9.013	8.18	95.50
33m	51.15	4.862	3.04	51.15
71m	19.91	1.049	11.11	18.93
90m	22.10	1.575	2.25	22.27
150m	17.35	ND	3.02	12.57
400m	17.50	ND	0.23	17.55
8B 10/31/89 Time: 12:30 Lat:42o59.57'N Long:59o59.94'W				
3m	97.46	9.962	6.02	19.16
5m	66.32	8.287	ND	52.66
10m	54.94	7.369	5.98	42.98
25m	45.80	2.380	1.47	
50m	33.04	2.39	1.25	28.84
75m	29.45	1.323	1.00	26.50
101m	21.44	1.609	4.21	21.63
150m	19.70	0.475	2.37	15.41
8G 10/31/89 Time: 20:50 Lat:42o59.84'N Long:60o01.07'W				
200m	12.30	0.927	ND	12.53
250m	15.52	ND	1.43	15.94
300m	27.22	1.626	3.92	12.34
500m	2.43	ND	5.97	
750m	6.41	ND	2.31	
9B 11/02/89 Time: 16:55 Lat:39o51.72'N Long:61o17.34'W				
4m	25.73	1.651	2.10	24.34
75m	24.54	1.373	1.15	16.16
151m	19.43	2.027	8.18	14.02
301m	13.89	1.295	ND	9.92
401m	12.23	ND	ND	9.13
480m	10.29	ND	ND	8.83
539m	16.11	ND	ND	6.99
600m	13.38	0.391	ND	9.50
10B 11/03/89 Time: 10:22 Lat:37o40.37'N Long:62o10.48'W				
4m	23.15	1.866	1.20	23.10
125m	17.72	1.444	4.12	16.47
301m	17.10	0.160	2.17	
499m	10.58	0.077	6.99	10.25
600m				10.51
650m	9.27	ND	ND	

	<----------------Total--------------->			
Stn. ID	Carbon ug/L	Nitrogen ug/L	Sulfur ug/L	Organic C. ug/L
11B 11/04/89 Time: 09:20 Lat:34o42.81'N Long:63o12.70'W				
5m	18.98	1.243	ND	18.83
120m	14.58	0.782	16.74	9.11
300m	8.29	ND	1.31	8.20
420m	11.66	ND	3.71	5.15
499m	7.62	ND	ND	5.83
550m	17.79	0.710	9.08	
611m	19.16	ND	1.09	7.23
651m	13.47	ND	8.78	11.25
12B 11/05/89 Time: 05:30 Lat:31o49.62'N Long:64o10.07'W				
2m	20.89	0.236	ND	20.37
5m	22.88	1.195	1.37	18.68
10m	21.10	1.544	9.64	12.49
25m	24.98	1.708	4.69	20.39
50m	17.79	0.856	1.77	17.25
75m	33.69	2.996	ND	31.37
100m	17.61	1.175	1.19	16.64
12H 11/05/89 Time: 11:00 Lat:31o47.72'N Long:64o11.88'W				
200m	7.23	ND	3.40	
250m	10.67	ND	ND	5.63
300m	14.71	0.587	3.91	4.38
400m	9.98	0.581	2.87	3.89
500m	14.76	ND	1.63	5.52
600m	4.37	ND	1.69	
700m	10.92	0.360	1.54	6.03
750m	6.23	ND	2.38	2.29
1000m	12.24	ND	ND	7.48
12J 11/05/89 Time: 01:43 Lat:31o46.48'N Long:64o13.40'W				
150m	20.19	ND	5.56	16.11
13B 11/07/89 Time: 19:20 Lat:35o43.50'N Long:72o10.65'W				
3m	27.82	1.101	1.41	26.18
6m	26.46	1.533	7.71	26.68
10m	30.26	1.160	12.97	30.34
25m	23.90	1.236	4.09	23.08
50m	22.60	1.459	ND	18.39
75m	17.69	1.307	4.43	16.78
100m	19.54	1.604	ND	18.63
150m	15.34	0.583	2.624	11.64
13D 11/07/89 Time: 21:14 Lat:35o43.41'N Long:72o10.68'W				
200m	8.57	6.558	ND	8.12
300m	10.50	ND	7.56	7.09
399m	9.58	0.396	ND	7.73
500m	9.87	ND	4.98	9.30
599m	8.23	ND	2.11	8.07
700m	7.85	0.049	3.14	7.60
800m	12.83	ND	9.53	11.04
899m	13.97	ND	4.35	13.20
1000m	15.66	ND	6.75	15.75

	<----------------Total-------------->			
Stn. ID	Carbon ug/L	Nitrogen ug/L	Sulfur ug/L	Organic C. ug/L
15C	11/08/89	Time: 20:23	Lat:37o21.00'N	Long:74o28.87'W
2m	74.57	7.646	4.10	
5m	105.1	11.30	5.39	105.4
10m	109.6	13.19	6.48	109.5
25m	55.95	6.454	9.10	51.37
75m	21.60	1.231	6.14	20.66
100m	12.84	0.849	4.23	12.15
125m	11.24	0.883	5.19	11.91
15E	11/08/89	Time: 22:48	Lat:37o21.03'N	Long:74o28.72'W
50m	20.88	1.838	6.71	20.57
151m	15.84	0.239	ND	9.81
175m	18.03	ND		
188m	11.53	0.503	3.33	10.08

Ancillary Data

All times and dates are GMT
(ND = Non-Detectable)

Stn. ID	Temp. °C	Sal. psu	Oxy.	PO4	SiO4	NO3	NO2	NH4
			<---------------	---------------umol/L	--------------	--------------	-------------->	
1B	10/25/89	Time: 01:42		Lat:37o15.45'N		Long:74o55.09'W		
2m	16.31	32.1676		1.939	0.488	ND	0.050	2.769
16m	16.49	32.1622		1.438	0.471	0.069	0.078	1.873
32m	15.78	32.5479		1.354	2.107	ND	0.017	2.192
1C	10/25/89	Time: 04:10		Lat:37o15.21'N		Long:74o55.34'W		
8m		32.2050		3.693	ND	ND	ND	ND
2A	10/26/89	Time: 21:28		Lat:36o24.88'N		Long:70o52.48'W		
5m	24.63	36.4447		3.747	ND	ND	0.018	1.761
75m	23.13	36.5256		3.739	ND	0.062	0.039	1.726
397m	17.73	36.3924		3.732	0.335	6.036	0.038	1.491
499m	16.74	36.1893		3.724	1.413	8.856	0.040	2.771
526m	16.33	36.1112		3.716	1.714	10.27	0.006	2.912
548m	15.96	36.0504		3.709	2.071	11.11	ND	2.434
600m	15.11	36.0518		3.701	2.113	11.07	ND	2.288
2C	10/27/89	Time: 01:58		Lat:36o28.83'N		Long:70o46.33'W		
5m	25.03	36.4133	188.3	ND	ND	ND	0.060	2.356
75m	22.50	36.5210	236.3	ND	ND	ND	0.057	2.135
150m	19.39	36.5043		ND	ND	0.798	0.069	
250m	19.37	36.5260	210.7	0.280	ND	3.150	0.055	2.634
250m	18.62	36.4938		0.228	ND	3.081	0.032	2.225
400m	17.79	36.3888	198.7	0.484	0.274	5.813	0.038	1.500
550m	15.81	36.0249	123.6	1.146	2.177	11.24	0.016	1.996
600m	14.93	35.9039	189.0	2.080	2.990	12.90	0.020	2.501

Stn.	Temp.	Sal.	Oxy.	PO4	SiO4	NO3	NO2	NH4
ID	°C	psu	<---------------umol/L-------------->					
3B	10/27/89	Time: 23:05		Lat:39o01.10'N		Long:72o47.36'W		
3m	17.24	34.1280	274.1	0.203	ND	ND	0.025	ND
25m	16.87	34.1921	237.0	0.270	0.210	0.557	0.051	ND
49m	15.04	35.4503	152.0	1.098	2.767	15.53	0.092	ND
74m	14.88	35.9000	-----	1.393	3.867	12.95	0.103	0.64
100m	13.33	35.7674	165.4	0.498	6.833	17.51	0.117	0.68
151m	12.31	35.6121	165.7	2.308	8.776	19.43	0.055	0.56
198m	11.97	35.5914	158.1	2.456	9.182	20.79	0.025	0.47
251m	10.64	35.3833	160.5	2.764	11.39	23.90	0.012	2.93
272m	10.32	35.4032	148.7	2.715	11.87	24.77	ND	2.45
3D	10/28/89	Time: 03:12		Lat:39o00.85'N		Long:72o47.28'W		
10m		34.0014		1.620	ND	ND	0.031	ND
180m		35.1251		1.474	5.902	23.22	0.093	ND
3E	10/28/89	Time: 06:42		Lat:39o01.06'N		Long:72o47.25'W		
3m	16.67	33.8998		0.270	0.225	ND	0.026	ND
5m	16.67	33.9383		0.223	0.148	ND	ND	ND
10m	16.69	33.9145		0.254	0.173	ND	0.075	ND
15m	16.68	34.0156		0.258	0.255	ND	0.043	ND
75m	14.5	35.8153		0.275	4.198	22.98	0.059	ND
4A	10/28/89	Time: 20:36		Lat:39o58.95'N		Long:70o18.09'W		
2m	21.70			0.031	ND	0.020	0.032	ND
5m	21.70	35.2285		0.058	ND	0.037	0.079	ND
10m	21.65	35.2074		0.040	ND	ND	0.047	ND
30m	20.52	35.2353		0.128	ND	0.453	0.153	ND
76m	15.39	35.1831		0.861	3.066	----	0.130	ND
100m	15.13	35.9249		2.204	4.822	----	0.035	ND
125m	13.67	35.6604		1.515	4.948	----	----	ND
375m	8.16	35.1092		2.734	13.41	----	----	ND
4B	10/28/89	Time: 21:27		Lat:39o58.94'N		Long:70o18.09'W		
2m	21.49	32.9387	244.6	0.013	ND	ND	0.136	ND
4m	21.50	35.2208	242.3	0.026	ND	0.012	ND	ND
10m	21.46	35.2116	242.3	0.007	ND	ND	ND	ND
31m	20.61	35.2735	228.4	0.108	ND	0.892	0.039	ND
75m	15.41	35.7085	180.8	1.131	3.057	----	0.123	ND
101m	15.37	35.9576	154.7	1.159	4.986	----	ND	ND
126m	13.28	35.5374	192.2	1.329	4.609	16.99	ND	0.89
377m	8.13	35.1488	172.4	2.539	13.56	28.91	ND	.099
5A	10/29/89	Time: 12:13		Lat:40o20.89'N		Long:67o31.93'W		
2m	13.86	32.6451		0.339	ND	ND	ND	2.20
6m	13.87	33.0852		0.334	ND	ND	ND	2.94
11m	13.87	33.1551		0.374	ND	ND	ND	2.52
27m	12.55	33.1777		0.456	0.311	0.18	ND	2.61
75m	14.06	35.8128		1.069	3.593	12.49	ND	1.61
100m	13.72	35.5959		1.397	4.617	16.50	ND	1.34
125m	13.04	35.6574		1.603	5.615	19.19	ND	1.19
150m	12.5	35.9098		1.721	6.819	21.40	ND	0.74

Stn. ID	Temp. °C	Sal. psu	Oxy.	PO4	SiO4	NO3	NO2	NH4
			<----------------umol/L--------------->					
5B	10/29/89	Time: 13:05		Lat:40o20.96'N		Long:67o32.15'W		
2m	13.86	32.6396	292.1	0.381	ND	ND		1.25
5m	13.86	32.6727	309.3	0.367	ND	ND	ND	1.19
10m	13.86	32.6751	302.4	0.386	ND	ND	ND	1.06
27m	12.31	35.2082	258.7	0.605	0.849	1.65	ND	1.00
75m	14.39	35.3969	164.0	1.094	3.859	13.2	ND	0.91
100m	13.61	32.6409	133.9	1.400	4.682	16.7	0.081	0.88
125m	12.74	32.6935	110.2	1.703	6.163	20.2	0.111	0.72
150m	11.96	32.5127	149.7	1.927	7.668	23.1	ND	1.68
5D	10/29/89	Time: 14:15		Lat:40o20.86'N		Long:67o32.21'W		
10m		35.9951		0.376	ND	ND	ND	1.168
6A	10/30/89	Time: 06:21		Lat:41o21.68'N		Long:65o01.80'W		
2m	16.86	34.1096		0.249	ND	ND	ND	ND
10m	16.88	34.0213		0.200	ND	0.08	ND	ND
25m	17.3	34.3030		1.287	0.255	0.19	ND	ND
75m	12.84	34.7253		0.963	2.587	8.77	0.143	ND
100m	12.53	35.1394		1.211	3.649	12.9	ND	ND
126m	12.45	35.3147		1.395	4.151	14.44	0.032	ND
150m	12.18	35.3558		1.385	4.761	16.20	ND	ND
6B	10/30/89	Time: 07:20		Lat:41o21.67'N		Long:65o01.80'W		
2m	17.02	34.1108	263.6	0.388	ND	ND	ND	ND
10m	17.47	34.2680	267.2	0.361	ND	ND	ND	ND
25m	18.25	34.6401	261.3	0.343	ND	ND	ND	ND
75m	12.12	34.8989	220.0	1.262	3.234	9.39	ND	ND
100m	12.40	35.2003	212.7	1.266	3.799	11.3	ND	ND
125m	12.22	35.3447	209.3	1.320	4.563	13.1	ND	ND
150m	12.05	35.3408	198.7	1.532	5.417	14.7	ND	ND
200m	10.85	35.2823	162.9	1.994	8.904	19.7	ND	ND
7A	10/31/89	Time: 00:16		Lat:42o13.14'N		Long:62o25.78'W		
2m	14.71	33.2863		ND	5.53	ND	0.272	1.19
5m	14.82	33.2803		ND	5.67	ND	ND	ND
10m	14.65	33.3021		ND	5.97	ND	ND	ND
33m	15.29	34.2302		2.360	7.02	0.12	0.036	ND
72m	13.58	35.4188		1.372	9.90	9.17	ND	ND
90m	13.26	35.4746		1.324	3.27	10.7	ND	ND
400m	6.85	35.0191		2.509	13.2	23.2	ND	ND
7B	10/31/89	Time: 01:28		Lat:42o12.97'N		Long:62o25.34'W		
3m	14.70	33.2817	281.7	0.146	ND	ND	ND	ND
5m	14.66	33.3125	280.8	0.118	ND	ND	0.126	ND
10m	14.65	33.3213	279.6	0.087	ND	ND	ND	ND
33m	15.46	34.2769	258.6	0.176	0.358	0.333	ND	ND
71m	13.78	35.3864	209.6	0.820	2.798	8.532	ND	ND
90m	13.63	35.5084	205.8	0.881	3.097	10.04	ND	ND
150m	12.65	35.5117	193.5	1.218	8.435	14.36	ND	---
400m	7.08	35.0320	186.8	2.024	19.15	21.57	ND	0.24

Stn. ID	Temp. °C	Sal. psu	Oxy.	PO4	SiO4	NO3	NO2	NH4
			<-------------	-------------	umol/L	-------------	-------------	------------->
8B 10/31/89 Time: 12:30 Lat:42o59.57'N Long:59o59.94'W								
3m	13.70	32.1313	289.3	0.343	ND	ND	ND	0.058
5m	13.80	33.1952	283.6	0.319	ND	ND	0.010	0.337
10m	13.88	32.3867	285.3	0.309	ND	ND	0.037	0.187
25m	14.15	32.6251	277.7	0.316	ND	ND	0.062	0.053
50m	8.42	33.1978	315.6	1.080	0.348	2.36	0.065	ND
75m	4.61	33.3933	319.7	0.572	2.757	8.07	0.115	ND
101m	5.46	33.9169	279.7	2.208	4.939	12.9	ND	ND
150m	7.09	34.5957	227.8	2.724	8.272	19.5	ND	ND
8E 10/31/89 Time: 17:11 Lat:42o59.90'N Long:60o00.32'W								
2m	13.96	32.1723		0.355	ND	ND	ND	ND
5m	13.83	32.1853		0.333	0.161	ND	ND	ND
10m	13.76	32.1657		0.322	ND	ND	ND	ND
25m	13.90	32.3297		0.357	ND	ND	ND	ND
50m	6.47	33.1983		1.238	0.843	2.99	ND	ND
75m	4.65	33.3482		1.711	2.270	6.31	ND	ND
100m	5.36	33.7818		2.126	4.509	11.5	ND	ND
150m	7.93	34.6978		2.915	9.048	22.1	ND	ND
8G 10/31/89 Time: 20:50 Lat:42o59.84'N Long:60o01.07'W								
200m	7.80	34.8873	191.2	2.901	10.33	21.95	ND	ND
250m	6.18	34.8573	210.2	3.163	11.57	24.68	ND	ND
300m	5.74	34.8496	217.3	3.304	12.04	24.91	ND	ND
400m	5.06	34.8380	245.2	3.441	12.700	26.23	ND	ND
500m	4.92	34.7222	257.6	3.464	12.470	26.21	ND	0.111
750m	4.18	34.8680	284.9	3.593	12.140	27.65	ND	0.129
8H 10/31/89 Time: 23:20 Lat:42o59.93'N Long:60o01.51'W								
2m		32.1930		0.364	ND	ND	ND	0.160
5m		32.1841		0.315	ND	ND	ND	0.124
10m		32.2863		0.364	ND	0.044	ND	0.158
8J 11/01/89 Time: 01:00 Lat:42o59.63'N Long:60o01.77'W								
200m	7.96	34.9191		----	---	---	ND	ND
250m	6.06	34.8201		----	---	---	ND	ND
300m	5.62	34.7067		----	---	---	ND	ND
400m	5.30	34.7589		----	---	---	ND	ND
500m	4.74	34.8313		----	---	---	ND	ND
750m	4.20	34.8876		----	---	---	ND	ND
1000m	4.12	34.8428	292.3	3.040	10.98	---	ND	ND
8K 11/01/89 Time: 03:51 Lat:42o59.97'N Long:60o01.25'W								
2m	13.88	32.052		0.345	ND	ND	ND	ND
5m	13.85	32.0094		0.327	ND	ND	ND	ND
10m	13.79	31.8453		0.381	ND	ND	ND	ND
8M 11/01/89 Time: 10:16 Lat:43o01.79'N Long:60o02.66'W								
2m	13.86	32.0532		0.367	0.096	0.037	ND	ND
5m	13.86	32.0545		0.367	0.027	ND	ND	ND
10m	13.83	36.3037		0.386	ND	ND	ND	ND

Stn. ID	Temp. °C	Sal. psu	Oxy.	PO4	SiO4	NO3	NO2	NH1
			<--------	--------	umol/L	--------	--------	-------->
9B	11/02/89	Time:	17:25	Lat:39o51.72'N		Long:61o17.34'W		
4m	25.25	36.3631	214.5	ND	0.480	0.117	ND	ND
75m	24.71	36.3217	216.5	ND	0.540	0.129	ND	ND
151m	21.44	36.6706	214.9	ND	0.248	1.04	ND	ND
301m	18.73	36.5361	207.0	0.190	0.857	5.01	ND	ND
401m	17.80	36.4239	201.2	0.584	1.559	7.89	ND	ND
480m	17.00	36.3413	201.2	0.712	2.205	10.59	ND	ND
539m	15.90	36.1811	185.9	1.219	3.667	13.81	ND	ND
600m	14.37	35.8456	148.3	2.476	7.661	23.60	0.062	ND
10A	11/03/89	Time:	09:26	Lat:37o41.14'N		Long:62o10.56'W		
5m	24.2	36.4316		ND	0.68	ND	ND	ND
125m	23.49	36.5684		ND	0.66	0.13	ND	ND
300m	18.94	36.5930		0.093	0.73	1.76	ND	ND
448m	18.18	36.4911		0.231	1.20	3.41	ND	ND
499m	17.82	36.4525		0.526	1.872	7.11	ND	ND
600m	17.08	36.3170		0.817	2.554	8.66	ND	ND
601m	17.08	36.2919		0.768	2.471	8.46	ND	ND
651m	16.35	36.2004		1.226	3.423	13.8	ND	ND
10B	11/03/89	Time:	10:22	Lat:37o40.37'N		Long:62o10.48'W		
4m	24.21	36.4047	219.3	ND	0.71	ND	ND	ND
125m	23.25	36.6119	209.1	0.010	0.66	0.71	ND	ND
301m	18.92	35.5919	216.6	0.079	0.74	1.45	ND	ND
450m	18.20	36.4752	219.8	0.231	1.11	3.23	ND	ND
499m	17.85	36.4354	209.8	0.273	1.42	4.03	ND	ND
600m	16.99	36.3035	202.4	0.493	2.29	7.05	ND	0.056
650m	16.43	36.2004	193.9	0.616	2.96	5.65	ND	ND
11A	11/04/89	Time:	08:47	Lat:34o42.96'N		Long:63o13.01'W		
4m	23.81	36.3820		ND	0.61	ND	ND	ND
120m	21.36	36.6518		0.001	0.47	0.86	ND	ND
299m	18.68	36.5317		0.122	0.90	2.71	ND	ND
421m	18.03	36.4968		0.277	1.43	4.78	ND	ND
501m	17.49	36.4261		0.359	1.70	4.87	ND	ND
552m	17.00	36.3400		0.493	2.47	6.03	ND	ND
609m	16.04	36.1681		0.846	3.52	9.74	ND	ND
651m	15.36	36.0561		0.954	4.32	9.61	ND	ND
11B	11/04/89	Time:	09:20	Lat:34o42.81'N		Long:63o12.70'W		
5m	23.81	36.3956	224.6	ND	ND	ND	0.023	ND
120m	21.38	36.6559	209.8	0.031	ND	0.57	0.047	ND
300m	18.71	36.5369	212.4	0.108	0.81	2.56	ND	ND
420m	18.07	36.4578	210.2	0.293	1.21	4.56	ND	ND
499m	17.55	36.4022	208.1	0.354	1.60	4.88	ND	ND
550m	17.04	36.3082	199.2	0.550	2.19	7.50	ND	ND
611m	16.15	36.1970	185.6	0.837	3.03	10.16	ND	ND
651m	15.34	36.0035	184.9	1.019	4.22	12.17	ND	ND

Stn. ID	Temp. °C	Sal. psu	Oxy.	PO4	SiO4	NO3	NO2	NH4
			<---------------	umol/L	------------->			
12A	11/05/89	Time: 03:55		Lat:31o50.21'N		Long:64o10.57'W		
2m	24.44	36.5641		ND	ND	ND	0.211	ND
5m	24.45	36.5653		ND	ND	ND	ND	ND
10m	24.45	36.5576		ND	ND	ND	ND	ND
25m	24.45	36.5670		ND	ND	ND	ND	ND
51m	24.43	36.5595		ND	ND	ND	ND	ND
75m	21.38	36.6828		ND	ND	ND	0.018	ND
75m	21.38	36.6770		ND	ND	ND	0.050	ND
100m	20.23	36.6488		ND	ND	ND	0.127	ND
12B	11/05/89	Time: 05:30		Lat:31o49.62'N		Long:64o10.07'W		
2m	24.43	36.5565	214.3	ND	ND	ND	ND	ND
5m	24.44	36.5559	217.2	ND	ND	ND	ND	ND
10m	24.44	36.5538	219.0	ND	ND	ND	ND	ND
25m	24.45	36.5571	218.1	ND	ND	ND	ND	ND
50m	24.45	36.5661	215.8	ND	ND	ND	ND	ND
75m	21.25	36.6834	217.4	ND	ND	ND	ND	ND
100m	20.06	36.6485	216.6	ND	ND	ND	ND	ND
12G	11/05/89	Time: 10:30		Lat:31o48.1'N		Long:64o11.6'W		
151m	19.11	36.6078		0.023	ND	0.517	ND	ND
200m	18.74	36.6026		0.018	ND	0.506	ND	ND
249m	18.50	36.5698		ND	0.050	3.443	ND	ND
299m	18.25	36.5319		0.197	0.130	2.414	ND	ND
401m	17.70	36.4617		0.310	0.504	3.060	ND	ND
499m	16.82	36.2984		0.575	1.39	6.108	ND	ND
750m	12.21	35.582		1.72	7.65	15.96	ND	ND
12H	11/05/89	Time: 11:00		Lat:31o47.72'N		Long:64o11.88'W		
200m	18.75	36.6003	214.4	0.171	ND	1.59	ND	ND
250m	18.47	36.5614	216.9	0.229	0.09	2.28	ND	ND
300m	18.22	36.5441	204.0	0.280	0.22	3.00	ND	ND
400m	17.64	36.4505	204.6	0.485	0.78	4.06	ND	ND
500m	16.78	36.3022	197.5	0.786	1.60	6.76	ND	ND
600m	15.19	36.0399	186.8	1.491	3.18	10.35	ND	ND
700m	13.52	35.7780	184.0	1.706	5.02	13.25	ND	ND
750m	12.28	35.6117	166.7	2.053	7.52	16.43	ND	ND
1000m	7.38	35.1185	185.8	2.345	13.99	20.76	ND	0.084
12J	11/05/89	Time: 01:43		Lat:31o46.48'N		Long:64o13.40'W		
150m	19.12	36.6075	211.6	ND	ND	2.13	ND	ND
1000m	7.35	35.1286		-----	13.12	----	ND	ND
12K	11/05/89	Time: 04:41		Lat:31o51.12'N		Long:64o11.35'W		
540m	16.26	36.2233		0.875	2.15	7.94	ND	ND
580m	15.53	36.1029		1.093	2.87	7.66	ND	ND
620m	14.87	35.9835		1.340	3.60	11.23	ND	ND
640m	14.50	35.9187		1.443	4.24	12.30	ND	ND
660m	14.04	35.8947		1.587	4.98	13.17	ND	ND
680m	13.67	35.8228		1.739	5.45	14.16	ND	ND
12M	11/05/89	Time: 19:27		Lat:31o51.74'N		Long:64o10.79'W		
440m	17.78	36.4558		0.414	0.99	4.74	ND	ND
560m	15.99	36.1831		0.938	2.44	8.83	ND	ND

```
                <---------------Total-------------->
Stn. ID   Carbon     Nitrogen  Sulfur   Organic C.
           ug/L       ug/L      ug/L      ug/L

13B  11/07/89  Time: 19:20  Lat:35o43.50'N  Long:72o10.65'W
   3m    23.73   36.5857   209.9    ND        ND  0.082  ND     ND
   6m    23.73   36.5568   212.7    ND        ND   ND   0.095   ND
  10m    23.74   36.5720   208.5   0.005      ND   ND    ND     ND
  25m    23.74   36.5917   213.1    ND        ND   ND    ND     ND
  50m    23.74   36.6307   211.8    ND        ND   ND    ND     ND
  75m    23.72   36.6181   211.2    ND        ND   ND    ND     ND
 100m    23.03   36.7146   202.4    ND        ND 0.108   ND     ND
 150m    20.22   36.6392   213.0   0.027      ND 0.219   ND     ND

13D  Date: 11/07/89  Time: 21:14  Lat:35o43.41'N  Long:72o10.68'W
200m     19.34   36.6139   206.4    ND        ND     1.26  ND     ND
300m     18.62   36.5736   205.8   0.008      ND     2.88  ND     ND
399m     18.11   36.5253   196.4   0.218    0.362    4.51  ND     ND
500m     17.43   36.4496   193.0   0.225    1.034    6.25  ND     ND
599m     16.18   36.2094   185.8   0.425    2.251    8.99  ND     ND
700m     14.33   35.9086   174.5   0.740    4.480   13.17  ND     ND
800m     12.34   35.5962   144.1   1.237    8.960   19.61  ND     ND
899m     10.23   35.3296   146.9   1.447    12.24   22.71  ND     ND
1000m     8.53   35.1866   164.6   1.490    13.38   22.69  ND     ND

14A Date: 11/08/89  Time: 06:10  Lat:36o00.06'N  Long:72o38.72'W
   5m    25.03   36.2815             ND       ND      ND    ND      ND

15B Date: 11/08/89  Time: 19:49  Lat:37o20.81'N  Long:74o29.01'W
   2m    17.69   34.4512           0.245    0.783    ND    ND     ND
   5m    17.69   34.4683           0.241    0.667    ND    ND     ND
   9m    18.29   34.8295           0.127    0.128    ND    ND     ND
  25m    18.35   34.8569           0.632    0.062    ND  0.056    ND
  49m    16.91   35.3378           0.637    1.672  3.86  0.037    ND
  75m    14.47   35.6524           1.329    5.103 12.51   ND      ND
 101m    13.62   35.6548           1.540    6.311 14.31   ND      ND

15C Date: 11/08/89  Time: 20:23  Lat:37o21.00'N  Long:74o28.87'W
   2m    16.93   34.1239   255.6   0.283    1.477     ND  ND     ND
   5m    16.76   34.0676   257.4   0.298    1.582     ND  ND     ND
  10m    16.89   34.1445   260.0   0.314    1.846     ND  ND     ND
  25m    18.61   34.9912   234.1   0.119    0.098     ND  ND     ND
  75m    14.29   35.6542   163.8   1.343    5.577  10.88  ND     ND
 100m    13.77   35.7063   157.5   1.541    6.194  14.30  ND     ND
 125m    12.86   35.5883   159.7   1.715    7.247  15.79  ND     ND

15E Date: 11/08/89  Time: 22:48  Lat:37o21.03'N  Long:74o28.72'W
 50m     16.52   35.3738   197.4   0.723    2.107    4.93  ND     ND
126m     12.90   35.6265           1.695    7.260   15.60  ND     ND
150m     12.70   35.6050   158.2   1.780    7.559   16.89  ND     ND
151m     12.70   35.6043           1.825    7.587   17.39  ND     ND
174m     12.51   35.5848   158.6   1.800    7.969   16.82  ND     ND
175m     12.53   35.5954           1.847    8.037   17.35  ND     ND
188m     12.26   35.5632   150.8   1.904    8.448   17.44  ND     ND

15I Date: 11/09/89  Time: 02:33  Lat:37o20.99'N  Long:74o28.98'W
170m     11.87   35.5195           2.073    9.282   19.35  ND     ND
```

Stn. ID	Temp. °C	Sal. psu	Oxy.	PO4	SiO4	NO3	NO2	NH4
			<-------	-------	umol/L	-------	-------	------->
15J Date: 11/09/89 Time: 03:56 Lat:37o20.89'N Long:74o28.98'W								
5m	15.92	33.6431		0.403	1.558	ND	ND	ND
19m	17.75	34.6466		0.273	0.835	ND	ND	0.668
52m	12.76	34.1175		1.528	8.357	8.41	ND	ND
75m	14.90	35.6551		1.263	4.703	11.1	ND	ND
100m	13.76	35.7475		1.600	6.49	15.4	ND	ND
125m	12.99	35.6035		1.684	7.265	16.68	ND	ND
15K Date: 11/09/89 Time: 05:18 Lat:37o20.22'N Long:74o28.77'W								
6m	16.03	33.6838		ND	1.723	ND	0.085	ND
18m	17.01	34.7127		0.235	0.742	ND	ND	ND
49m	12.98	34.2451		1.545	8.123	8.32	ND	ND
75m	14.92	35.8041		1.507	4.717	13.7	ND	ND
100m	14.44	35.8840		1.858	6.114	17.0	ND	ND
125m	13.29	35.7385		2.119	7.280	19.1	ND	ND

Stn . ID	Temp. °C	Sal. psu	Chl. a	Pheo
			<----	ug/L---->
3B 10/27/89 Time: 23:05 Lat:39o01.10'N Long:72o47.36'W				
3m	17.24	34.1280	0.424	0.272
25m	16.87	34.1921	0.763	0.678
49m	15.04	35.4503	0.165	0.194
74m	14.88	35.9000	0.042	0.073
100m	13.33	35.7674	0.026	0.044
151m	12.31	35.6121	0.022	0.060
198m	11.97	35.5914	0.019	0.057
251m	10.64	35.3833	0.012	0.047
272m	10.32	35.4032	0.012	0.046
4B 10/28/89 Time: 21:27 Lat:39o58.94'N Long:70o18.09'W				
2m	21.49	32.9387	0.369	0.166
4m	21.50	35.2208	0.424	0.157
10m	21.46	35.2116	0.419	0.210
31m	20.61	35.2735	0.855	0.644
75m	15.41	35.7085	0.146	0.204
101m	15.37	35.9576	0.030	0.057
126m	13.28	35.5374	ND	0.888
377m	8.13	35.1488	ND	0.991
5B Date: 10/29/89 Time: 13:05 Lat:40o20.96'N Long:67o32.15'W				
2m	13.86	32.6396	0.675	0.269
5m	13.86	32.6727	0.624	0.328
10m	13.86	32.6751	0.677	0.325
27m	12.31	35.2082	1.920	0.792
75m	14.39	35.3969	0.086	0.148
100m	13.61	32.6409	0.034	0.072
125m	12.74	32.6935	0.017	0.058
150m	11.96	32.5127	0.021	0.068

Stn .	Temp.	Sal.	Chl. a	Pheo
ID	°C	psu	<----ug/L---->	
6B	10/30/89	Time: 07:20	Lat:41o21.67'N	Long:65o01.80'W
2m	17.02	34.1108	0.479	0.179
10m	17.47	34.2680	0.465	0.169
25m	18.25	34.6401	0.443	0.207
75m	12.12	34.8989	0.147	0.129
100m	12.40	35.2003	0.057	0.067
125m	12.22	35.3447	0.013	0.025
150m	12.05	35.3408	0.017	0.037
200m	10.85	35.2823	0.027	0.029

Stn .	Temp.	Sal.	Chl. a	Pheo
ID	°C	psu	<----ug/L---->	
7B	Date: 10/31/89	Time: 01:28	Lat:42o12.97'N	Long:62o25.34'W
3m	14.70	33.2817	0.216	0.125
5m	14.66	33.3125	0.285	0.124
10m	14.65	33.3213	0.310	0.134
33m	15.46	34.2769	0.684	0.590
71m	13.78	35.3864	0.097	0.133
90m	13.63	35.5084	0.080	0.089
150m	12.65	35.5117	0.010	0.025
400m	7.08	35.0320		
8B	Date: 10/31/89	Time: 12:30	Lat:42o59.57'N	Long:59o59.94'W
3m	13.70	32.1313	0.446	0.216
5m	13.80	33.1952	0.558	0.227
10m	13.88	32.3867	0.431	0.228
25m	14.15	32.6251	0.445	0.223
50m	8.42	33.1978	0.242	0.205
75m	4.61	33.3933	0.067	0.023
101m	5.46	33.9169	0.017	0.040
150m	7.09	34.5957	0.008	0.028
12B	11/05/89	Time: 05:30	Lat:31o49.62'N	Long:64o10.07'W
2m	24.43	36.5565	0.072	0.027
5m	24.44	36.5559	0.078	0.023
10m	24.44	36.5538	0.075	0.029
25m	24.45	36.5571	0.067	0.023
50m	24.45	36.5661	0.083	0.030
75m	21.25	36.6834	0.462	0.450
100m	20.06	36.6485	0.197	0.439
12K	11/05/89	Time: 04:41	Lat:31o51.12'N	Long:64o11.35'W
150m	19.14		0.045	0.112
200m	18.85		0.015	0.028
13B	11/07/89	Time: 19:20	Lat:35o43.50'N	Long:72o10.65'W
3m	23.73	36.5857	0.179	0.060
6m	23.73	36.5568	0.191	0.062
10m	23.74	36.5720	0.176	0.082
25m	23.74	36.5917	0.208	0.079
50m	23.74	36.6307	0.223	0.083
75m	23.72	36.6181	0.238	0.100
100m	23.03	36.7146	0.256	0.365
150m	20.22	36.6392	0.052	0.124

Appendix C

Hydrolysis experiments: DDI results

Time (h)	OCS conc. nmol/L	Time (h)	OCS conc. nmol/L	Time (h)	OCS conc. nmol/L
	3°C		6°C		13°C
0.00	86.72	0.00	57.30	0.00	80.91
0.12	85.08	2.33	51.12	13.47	60.98
2.49	83.75	3.17	50.67	13.77	72.88
8.65	74.18	7.55	48.26	14.12	65.89
20.75	69.53	7.89	46.26	35.71	35.11
20.97	65.55	22.60	28.89	35.98	35.45
21.31	69.84	23.10	31.73	36.32	35.37
25.61	64.58	23.30	30.71	60.52	25.03
25.87	59.23	50.70	21.46	61.23	24.23
26.53	71.35	51.10	21.53	66.18	23.01
47.35	46.81	51.30	20.86	66.41	26.98
47.77	55.57	70.90	16.28	66.78	27.14
121.50	42.62	71.30	16.42	85.02	14.45
		71.80	14.07	85.42	13.11
		99.10	12.16		
		99.50	12.08		
		145.20	7.43		
		145.30	7.06		
		145.40	6.82		

Hydrolysis experiments: DDI results
(cont.)

Time (h)	OCS (nmol/L) 17.8°C
0.00	55.75
3.81	47.34
9.78	34.41
10.76	31.19
21.61	21.29
27.55	22.19
46.60	7.06
47.30	6.92
71.27	2.55

Time (h)	OCS (nmol/L) 24°C
0.00	16.36
18.86	6.90
19.19	6.34
19.29	6.56
19.41	6.68
19.53	6.87
19.61	5.94
22.38	6.12
22.46	5.62
22.71	5.58
37.03	3.23
37.11	2.89
37.21	3.22
37.32	2.94
37.39	3.47
37.81	3.27
69.83	2.61
70.26	1.69
85.93	1.23
86.11	1.31
86.27	1.22
91.94	1.15
92.15	1.21

Hydrolysis experiments: Sargasso Sea water results

Time (h)	OCS conc. (nmol/L) 3°C
0.65	88.78
1.35	86.11
2.33	83.93
3.51	73.12
3.72	65.03
5.18	60.35
5.71	62.01
9.41	58.71
10.41	52.47
21.87	49.02
22.19	45.03
22.43	46.32
26.82	46.69
27.13	47.17
27.43	48.33
30.19	45.96
46.78	31.85
48.55	29.22
49.05	30.45
100.4	12.27
100.7	11.86
102.2	9.12
126.6	9.45
127.1	8.65

Time (h)	OCS conc. (nmol/L) 6°C
0.65	68.74
1.38	64.61
1.53	59.16
2.73	61.57
7.97	65.30
20.41	55.71
20.68	46.77
22.21	47.29
22.42	51.19
22.74	48.09
26.21	48.37
26.78	45.88
47.09	35.44
47.49	35.12
74.76	20.48
75.14	18.65
75.44	20.38
95.08	14.45
96.04	14.16
122.72	9.08
123.48	9.13
124.16	8.72
169.32	4.18
170.52	4.26

Time (h)	OCS conc. (nmol/L) 13°C
0	76.2
0.03	70.20
0.53	65.60
4.57	62.10
4.85	54.30
10.12	46.50
10.45	42.30
24.72	18.36
25.05	19.20

Time (h)	OCS conc. (nmol/L) 17.8°C
0.13	76.0
0.433	79.02
4.23	58.33
4.63	51.36
9.97	26.43
10.3	31.58
24.59	6.71
24.87	5.89

Copper added

Time (h)	OCS conc. (nmol/L) 17.8°C
0.133	47.32
3.71	34.41
3.72	26.83
3.73	26.32
3.74	24.14
3.75	22.79
3.76	22.48
3.77	5.75
3.78	5.62
3.79	5.25
3.80	2.94

Mercury added

Time (h)	OCS conc. (nmol/L) 17.8°C
0.13	57.23
0.15	54.51
0.26	52.99
0.43	53.24
18.33	11.46
18.55	10.93
19.97	9.62
20.33	9.41
27.97	5.64
28.11	5.48
28.26	5.51

Zinc added

Time (h)	OCS conc. (nmol/L) 17.8°C
0.733	52.94
5.12	29.74
10.50	31.19
22.18	7.19
28.13	6.02
47.52	0.68
71.67	0.22

No metal addition

Time (h)	OCS conc. (nmol/L) 24°C
0	17.9
3.6	13.22
5.56	12.52
5.04	12.83
5.52	7.69
7.68	7.43
8.16	5.96
10.8	6.48
11.04	6.13
22.32	4.25
22.56	1.06

Appendix D

Equatorial Pacific Cruise Data Report: Ancillary Parameters and Dissolved Sulfide

Stn.: 1

Depth (m)	Salinity psu	NO3 uM	PO4 uM	SiO2 uM	Chl. a ug/L	Pheo. ug/L	pH (NIST)	oxygen uM
10					0.054	0.097		
15					0.081	0.097		
26	36.389	0.00	0.11	0.90			8.46	208.8
28					0.077	0.127		
44					0.063	0.085		
52	36.321	0.04	0.12	0.91			8.43	213.4
70					0.074	0.082		
76	36.302	0.02	0.26	0.88			8.42	216.67
100	36.282	0.00	0.12	0.85			8.43	223.03
107					0.124	0.109		
148	36.026	0.49	0.16	0.82			8.39	204.44
161					0.128	0.226		
199	35.953	1.16	0.23	0.78			8.40	196.67
259	35.538	2.78	0.19	1.10			8.31	177.35
303	35.227	4.79	0.22	1.73			8.28	177.33
410	34.536	15.60	0.98	5.73			8.14	175.31
517	34.245	25.20	1.58	12.50			8.03	178.79
620	34.187	27.10	1.49	14.30			8.01	194.42
1802	34.472	34.90	2.25	112.			7.91	158.18

Stn.: 2

Depth (m)	Salinity psu	NO3 uM	SiO2 uM	pH (NIST)	oxygen uM
26	36.405	0.11	0.90	8.45	196.7
52	36.402	0.04	0.86	8.45	201.8
200	35.984	3.93	0.96	8.28	178.4

Stn.: 3

Depth (m)	Salinity psu	NO3 uM	NH3 uM	SiO2 uM	pH (NIST)	oxygen uM
26	35.299	3.63	0.19	2.18	8.47	206.5
52	35.66	3.70	0.17	1.95	8.48	203.5
102	36.001	2.24	0.43	1.67	8.48	193.4
125			1.20			
151	36.114	4.10	0.00	1.40	8.38	175.7
202	35.546	8.18	0.11	2.80	8.26	175.4
1098	34.398	37.40		92.80	8.00	117.1

Stn.: 4

Depth (m)	Salinity psu	NO3 uM	NO2 uM	NH3 uM	SiO2 uM	pH (NIST)	oxygen uM
15	35.302	4.80	0.12	0.20	1.00	8.44	229.7
50	35.306	4.96	0.12	0.18	1.00	8.45	222.04
104	35.312	4.81	0.13	0.19	1.00	8.44	223.37
126	35.319	4.60	0.11	0.18	2.00	8.47	228.22
156	35.575	11.70	0.14	0.05	3.00	8.26	156.37
192	35.111	23.60	0.02	0.05	10	8.04	78.57
407	34.624	35.00	0.01		23	7.82	27.58
627	34.504	38.70	0.01		30	7.81	64.37
899	34.442	38.50	0.01		45	7.83	94.07
1188	34.489	38.00	0.01		66	7.85	117.9
1588	34.542	38.90	0.03		88	7.85	122.8
1990	34.566	37.10	0.04		85	7.9	138.36

Stn.: 5

Depth (m)	Salinity psu	NH3 uM	pH (NIST)	oxygen uM
27	35.382	0.53	8.23	217.89
51	35.396	0.52	8.25	212.52
114	35.679	2.29	8.21	198.88
152	35.23	0.18	7.87	74
200	34.934	0.60	7.71	32.15
252	34.909	0.23	7.72	53.41

Stn.: 6

Depth (m)	Salinity psu	NO3 uM	NO2 uM	NH3 uM	SiO2 uM	pH (NIST)	oxygen uM
23	35.381	6.00	0.52	0.28	2.42	8.24	211.62
77	35.503	7.92	0.62	0.39	2.89	8.25	193.49
102	35.623	11.90	0.05	0.24	3.82	8.18	147.39
124	35.317	12.60	0.02	0.30	6.34	8.14	143.09
148	35.181	15.50	0.01	0.56	9.11	8.09	149.96
249	34.904	25.20	0.01	0.41	18.9	7.92	117.9
303	34.894	29.50	0.02		21.6	7.82	73
403	34.745	38.10	0.02		33.1	7.63	28.75
500	34.684	38.80	0.02		38.6	7.62	47.48
751	34.6	40.80	0.01		54.6	7.64	74.54
1003	34.592	41.40	0.01		75.8	7.65	88.54
2094	34.678	39.90	0.02		126	7.73	117.02

Stn.: 8

Depth (m)	Salinity psu	NO3 uM	NH3 uM	SiO2 uM	pH (NIST)	oxygen uM
15	34.739	1.48	0.45	2.04	8.42	217.36
64	34.792	1.04	0.46	1.81	8.41	216.82
91	34.8	1.17	0.49	1.88	8.4	212.63
115	34.845	6.22	0.28	3.53	8.27	170.97
205	34.59	29.80	1.32	28.80	7.78	79.22
1098	34.522	42.60		96.90	7.66	73.9

Stn.: 9

Depth (m)	Salinity psu	NO3 uM	NO2 uM	SiO2 uM	pH (NIST)	oxygen uM
0						
25	33.966	0.01	0.00	1.01	8.27	201.03
48	34.509	0.05	0.01	1.85	8.14	206.71
65	34.518	6.07	0.49	5.84	7.98	174.98
90	34.55	25.50	0.09	23.00	7.64	29.86
108	34.608	24.80	0.09	25.30	7.55	15.95
144	34.636	30.90	0.05	27.60	7.61	34.04
502	34.528	37.20	0.01	100	7.54	66.25

Stn.: 10

Depth (m)	NO3 uM
20	0.13
30	1.09
50	0.27
75	0.21
100	0.18
150	5.43
200	20.20
300	31.50
500	37.40
750	41.20
1000	41.90

Dissolved sulfur species

Stn.: 1

Depth (m)	Sulfide* pmol/L	+/-	OCS pmol/L	+/-
5	37.4	1.3	157	11.3
15	87.4	1.7	503	42
26	42.6	6.1	79	3.7
52	44.6	12.6	57.3	21
76	27.8	4.3	46	23
100	29	2.8	43	4.9
148	0	0	100	9.3
200	15.9	1.9	335	22
259	25.2	4.2	128	36
303	22.2	1.8	70	21
410	0	0	11	7.2

Stn.: 2

Depth (m)	Sulfide pmol/L	+/-	OCS pmol/L	+/-
0	58.3	2.4	105	21
26	53.4	5.5	69	5.6
52	60.7	2.2	81	11.2
100	86.4	8.6		
125	59.2	0.85		
200	27.2	2.8		

Stn.: 3

Depth (m)	Sulfide pmol/L	+/-	OCS pmol/L	+/-
52	53.7	2	241	7.4

Stn.: 4

Depth (m)	Sulfide pmol/L	+/-	OCS pmol/L	+/-
0	26.4	4.9	418	2.9
25	20.9	6.3	117.3	1.8
50	33.7	0.7	129.6	27.9
75	37.1	3	0	0
104	76.2	4.3	93.2	5.9
126	0	0	56.8	20.7
200	19.58	6.7	17.7	1.9
225	12.7	2.7	104	45.7
250	10	4.1	15.6	2
328	5.46	3.3	0	
407	10.87	6	0	0
500	3.36	0.2	113	0.6
750	8.77	3.85	58.8	2
1000	0		0	

Stn.: 5

Depth (m)	Sulfide pmol/L	+/-	OCS pmol/L	+/-
0	10.68	1.53	130.4	12.5
27	27.8	0.48	40.33	6.12
51	38.88	0.38	48.62	11.96
114	0		85.3	9.23
152	0		21.58	5.59
200	16.51	0.47	16.32	11.4

Stn.: 6

Depth (m)	Sulfide pmol/L	+/-	OCS pmol/L	+/-
0	3.97	0	14.8	2.3
25	76.7	1.2	16.8	4
50	16	1.1	12.2	2.5
75	41	3.2	15.4	0.8
100	24.9	3	6	0.1
125	39.4	1.7	0	
150	10.5	0.5	29.1	5.5
175	12.1	1.7	8	0.7
200	27.2	1.1	17.9	0.6
250	43.52	2.9	12.5	6.7
500	11.3	0.1	8.5	0.7

Stn.: 8

Depth (m)	Sulfide pmol/L	+/-	OCS pmol/L	+/-
0	95.2	9.6	99.1	40
25	80.2	0.1	53.6	24
50	58.1	3	27	1
75	52.4	2.4	4.7	1
100	0	0	49.7	2.9
125	18.9	0.2	1.8	0.3
150	28.3	3	6.5	4.8
200	26.8	10.7	28.9	4.6
250	21.2	1	0.3	0.1

Stn.: 9

Depth (m)	Sulfide pmol/L	+/-	OCS pmol/L	+/-
0	46	2.72	10.04	0.38
25	90.45	1.76	9.7	0.21
50	78.64	0.89	5	0.14
75	11.7	1.59	21.44	0.2
100	20.1	0.32	13.03	3.31
125	24.91	0.2	15.05	1.28
150	39.08	1.45	22.28	1.12
200	25.24	0.8	13.75	0.45
250	18.82	0.63	12.46	0.67
300	10.03	0.91	12.89	2.19
400	10.36	0.86	7.06	1.42
502	9.33	2.8	8.52	0.76

Stn.: 10

Depth (m)	Sulfide pmol/L	+/-	OCS pmol/L	+/-
0	44.45	10.1	27.97	4
25	33.51	3.62	14.34	0.74
50	54.24	2.59	18.41	0.62
75	59.03	7.6	23.3	2
100	37.32	0.77	7.65	0.22
125	28.59	0.67	4.26	0.25
150	14.2	0.6	2.53	0.83
175	9.325	0.86	2.61	0.51
200	8.24	2.54	1.19	0.04

(*) Sulfide is total dissolved sulfide

Appendix E

Equilibrium studies of additions of copper and hydrogen sulfide to selected samples

Station 6, 200m pH=8.00

H2S added mol/L	Cu total mol/L	free sulfide* mol/L	S.D. mol/L	free bisulfide mol/L	log(K)
2.11E-09	1.96E-09	9.18E-10	3.90E-11	8.89E-10	9.27
2.11E-09	4.06E-09	3.03E-10	1.20E-11	2.93E-10	9.44
2.11E-09	7.21E-09	1.23E-10	6.00E-12	1.19E-10	9.51

Station 8, 25m pH=8.41

H2S added mol/L	Cu total mol/L	free sulfide mol/L	S.D. mol/L	free bisulfide mol/L	log(K)
1.06E-09	5.00E-10	8.49E-10	2.55E-10	8.38E-10	8.96
4.22E-09	3.65E-09	1.31E-09	2.10E-11	1.29E-09	9.5

Station 8, 500m pH=7.74

H2S added mol/L	Cu total mol/L	free sulfide mol/L	S.D. mol/L	free bisulfide mol/L	log(K)
1.41E-09	1.65E-09	1.10E-09	3.20E-11	1.03E-09	8.45
1.41E-09	2.70E-09	1.04E-09	2.80E-11	9.81E-10	8.28
1.41E-09	4.80E-09	3.64E-10	1.80E-11	3.44E-10	8.92
1.41E-09	7.95E-09	1.51E-10	0	1.43E-10	9.12
1.41E-09	1.22E-08	1.01E-10	0	9.54E-11	9.1

Station 9, 20m pH=8.27

H2S added mol/L	Cu total mol/L	free sulfide mol/L	S.D. mol/L	free bisulfide mol/L	log(K)
2.11E-09	1.00E-09	1.64E-09	1.41E-10	1.62E-09	8.77
2.11E-09	1.55E-09	1.14E-09	2.04E-10	1.12E-09	9.2
2.11E-09	2.05E-09	6.56E-10	5.40E-11	6.48E-10	9.58

Station 9, 1000m pH=7.55

H2S added mol/L	Cu total mol/L	free sulfide mol/L	S.D. mol/L	free bisulfide mol/L	log(K)
5.64E-09	2.05E-09	4.26E-09	2.03E-10	3.90E-09	9.16
1.41E-09	2.05E-09	4.74E-10	4.20E-11	4.34E-10	9.32
1.41E-09	3.10E-09	1.73E-10	6.00E-12	1.59E-10	9.63
1.41E-09	3.60E-09	3.97E-10	7.20E-11	3.64E-10	9.05

* free sulfide is the sum of free H2S, HS-, and S=.

Joël Radford-Knœry

Born in Strasbourg, France on March 21, 1963

Education

Bachelor of Science, Chemistry (*cum laude*), McPherson College (McPherson, KS), June 1986.

Diplôme d'Etudes Universitaires Générales, Physics/Chemistry, Université Louis-Pasteur (Strasbourg, France), June 1984.

Publications

- Hydrogen Sulfide and Radon in and over the western Atlantic Ocean, with T. Andreae, G. Cutter, N. Hussain and M. Andreae. **Journal of Geophysical Research** (96)18.753-18.760, 1991.
- Determination of Carbon, Nitrogen, Sulfur, and Inorganic Sulfur Species in Marine Particles, with G. Cutter. *In:* Marine Particles: Analysis and Characterization. Geophysical Monograph 63, D.C. Hurd and D.W. Spencer *Eds.*, American Geophysical Union, Washington, DC (U.S.A.), 57-63, 1992.
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- Determination of Carbonyl Sulfide and Hydrogen Sulfide Species in Natural Waters Using Specialized Collection Procedures and Gas Chromatography with Flame Photometric Detection, with G. Cutter. **Analytical Chemistry**, in press, 1993.

Honors and Professional Societies

- Special Doctoral Research Assistantship awarded by Old Dominion University, 1987.
- One-year full scholarship awarded by McPherson College, 1985.
- American Geophysical Union (Since 1986).
- Phi Kappa Phi Honor Society (ΦΚΦ, since 1989).