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SULFIDE IN SURFACE WATERS OF THE WESTERN ATLANTIC OCEAN

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Abstract. Using newly developed techniques, some preliminary data on hydrogen sulfide in surface waters of the western Atlantic have been obtained. Concentrations of total sulfide range from < 0.1 to 1.1 nmol/L, and vary on a diel basis. At these concentrations, sulfide may affect the cycling of several trace metals via the formation of stable complexes. Production of sulfide in oxygenated seawater may occur through the hydrolysis of carbonyl sulfide or by sulfate reduction within macroscopic particles in the water column. Removal mechanisms can include oxidation, complexation with particulate trace metals, and metal sulfide precipitation. However, the temporal and spatial distributions suggest a complex set of processes governing the behavior of sulfide in the surface ocean.

Introduction

The surface ocean is a natural source for several atmospheric sulfur gases, including dimethyl sulfide, carbonyl sulfide, and carbon disulfide (see Andreae, 1985 for a review). The most recent determinations of hydrogen sulfide in the marine atmosphere place its concentration in the low parts per trillion range [Cooper and Saltzman, 1987], and an oceanic source would seem unlikely since hydrogen sulfide is thought to be produced only in anoxic waters and sediments via microbial sulfate reduction. However, Elliott et al. [1987] postulate that hydrolysis of carbonyl sulfide (OCS) may produce hydrogen sulfide in oxygenated waters, and predict picomolar to nanomolar concentrations of sulfide in the surface ocean. Furthermore, at such concentrations sulfide could affect the activities of several trace metals. Until a single value in the western Atlantic (0.51 nmol/L) was reported recently [Cutter and Oatts, 1987], the prediction of Elliott et al. [1987] was only a testable hypothesis. In this paper we present some initial data on the temporal and spatial distributions of sulfide in surface waters of the western Atlantic Ocean, and examine potential production and removal processes.

Methods

The method used to determine sulfide for most of this work has been described previously [Cutter and Oatts, 1987]. Briefly, sulfide is preconcentrated via zinc sulfide precipitation and immediate filtration. Upon acidification, hydrogen sulfide is liberated from the filter and quantified using gas chromatography-photoionization detection. A direct determination of sulfide was also performed in which a 200 mL glass stripping vessel is filled with a water sample, followed by acidification to 0.5 M HC1. The evolved hydrogen sulfide

(from dissolved hydrogen sulfide and any metal sulfides) is cryogenically trapped, revolatilized, chromatographed on a 2 m Chromasil 310 column, and detected by photoionization. In order to intercalibrate the direct and precipitation methods, both were used on the same samples taken in July 1986. For the 4 samples analyzed in this fashion, the measured concentrations of total sulfide agreed within an average of 32% and show the same distribution with depth (actual data will be discussed below). The difference between the two methods may be due to the greater number of sample manipulations involved with the precipitation method (concentration of the direct method always higher). Precision for both methods is better than 8% (relative standard deviation).

The two analytical methods determine the total sulfide in a water sample (or total dissolved sulfide if the water is prefiltered), but cannot distinguish between free hydrogen sulfide ions (e.g., bisulfide) and sulfide complexed with metals. Two arguments suggest that the latter forms are the most likely sulfide species in oxygenated seawater. First, the thermodynamic calculations of Dyrssen [1988] and Elliott [1988] indicate that sulfide should be in complexes with metals such as copper, and to a lesser extent mercury. Secondly, the work of Zhang and Whitfield [1986] suggests that the oxidation of bisulfide by iodate is rapid enough to consume any free bisulfide (the surface water concentration of iodate in the North Atlantic is 330 ± 30 nmol/L [Jickells et al., 1988]). The formation of metal-sulfide complexes could stabilize sulfide against such oxidative removal [G. Luther, III, personal communication, 1988].

Study Sites

Samples were acquired in January 1986 during the GALE program (Generation of Atlantic Lows Experiment). Using the R.V. Endeavor, stations were occupied on a southeastern transect from Charleston, South Carolina to the western Gulf Stream (Figure 1). Water samples were collected with 5 L Niskin bottles on a CTD/rosette sampler, the water was not filtered, and total sulfide was determined using the zinc sulfide precipitation method. In July 1986, samples were taken at a station ca. 100 km off Virginia's coast (37° 35.8' N, 74° 31.8' W) using the R.V. Cape Henlopen. These samples were obtained with Go-Flo sampling bottles deployed on a CTD/rosette sampler. Both the direct and precipitation methods for determining sulfide were used on these samples. In addition, some of the July 1986 samples were filtered through 0.4 um Nuclepore polycarbonate membranes by pressurizing the Go-Flo bottles with nitrogen.

Results

During the January 1986 GALE cruise, a vertical profile of sulfide was obtained in the mid-morning at Station G21 (Fig-
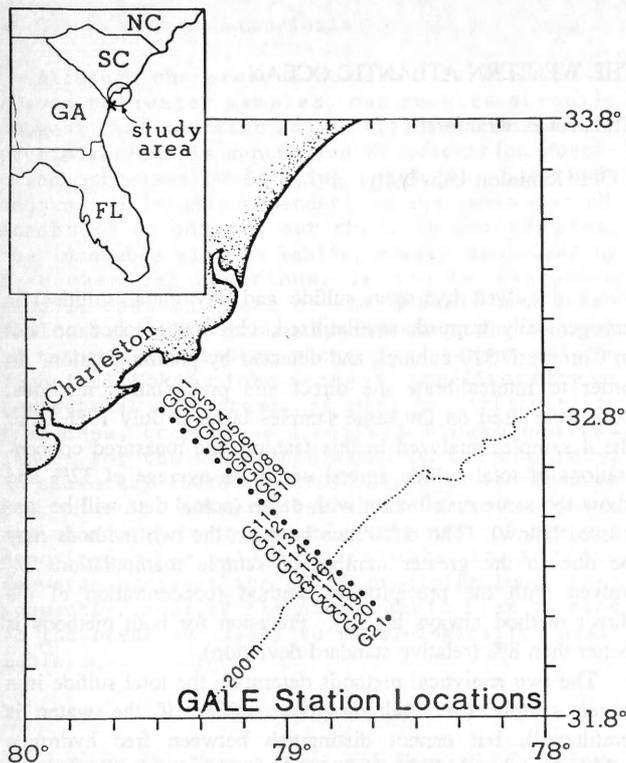
Fig. 1. Station locations for the January 1986 GALE cruise. The distance between Stations G1 and G21 is approximately 120 km.

ure 1). The data in Figure 2 show an increase in sulfide concentration from the surface to the top of the major thermocline (50 m), and a rapid decrease below this depth. At the depth of maximum sulfide, a maximum in chlorophyll a was also present. A diel study was performed at Station G21 by sampling at 4 m and 50 m every three hours. Large changes in concentration occur over a 24-hour period (Figure 3), with maxima at both depths just prior to sunrise (0715, local time). During this same period, temperature and salinity data indicate that potential artifacts from the mixing of other water masses were minimal. The temporal variability of sulfide suggests involvement in photochemical reactions (e.g., production of oxidants), although the time lag between changes at 4 m and 50 m seems to contradict such an interpretation.

Surface water samples were also obtained on the onshore/offshore transect (Figure 1). The data in Figure 4 show that nearshore sulfide concentrations are highest (0.21±0.11 nmol/L, Stns. G01-G03) and that concentrations farther offshore average 0.09±0.02 nmol/L (n=5, Stns. G11-21). Anoxic estuarine, marsh, and subtidal sediments could act as sources of sulfide in coastal waters. Assuming a 38-hour residence time for dissolved sulfide [Millero et al., 1987] and average surface current velocities of 10-30 cm/sec [Lee et al., 1985], sulfide could advect approximately 14-40 km from its source (e.g., from Stn. G01 to G09) before complete removal. This may be a conservative horizontal transport estimate since a residence time with respect to bisulfide oxidation was used, and metal sulfide complexes are likely more stable [G. Luther, III, personal communication, 1988].

Increased OCS concentrations nearshore (e.g., Ferek and Andreae, 1984) could also lead to elevated sulfide levels.

However, the transect data may actually be fortuitous since these samples were obtained at different times of day. The nearshore stations were sampled at night, when sulfide concentrations are highest according to the results in Figure 3. Therefore, the processes leading to elevated nearshore concentrations of sulfide cannot be uniquely resolved with the existing data.

In July 1986, unfiltered water samples from offshore Virginia were obtained at 5 depths, and were analyzed via the zinc sulfide and direct methods (intercalibration results discussed above). The data in Figure 5 show the surface water concentration of total sulfide to be over twice as high as those found during the winter GALE cruise. The higher sulfide concentrations may be due to increased summertime biological activity (e.g., anaerobic respiration, greater particulate material) or higher OCS concentrations (increased photo period leading to greater OCS production). In addition, the potential influence of outflows from the Chesapeake and Delaware Bays must be considered at this site.

Since all of the GALE samples were unfiltered, the reported sulfide concentrations include dissolved sulfide and metal-complexed sulfide, plus any suspended particulate sulfide (i.e., acid volatile sulfide). To evaluate the potential contribution of particulate sulfide to the total, three of the July samples (3, 24, and 32 m) were filtered before analysis. It was found that particulate sulfide averaged 30±14.5% of the total sulfide for these samples. While these data indicate that particulate sulfide is a potentially important fraction in coastal waters, future studies should make determinations of particulate sulfide directly on filtered material (i.e., analyze the filters) in order to minimize errors.

Potential Mechanisms for the Production and Removal of Sulfide

Overall, the results show that sulfide is found in the western Atlantic at roughly the concentrations predicted by Elliott et al. [1987] using a steady state model. Their calculation included OCS hydrolysis as a source of sulfide and oxidation as a removal mechanism. The western Atlantic data show that sulfide is not at steady state, and clearly additional production and removal reactions must also be involved. Indeed,
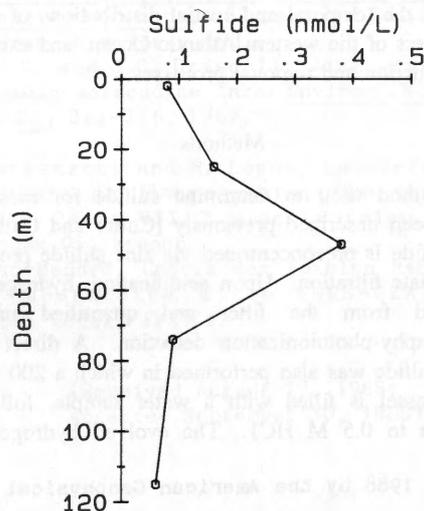

Fig. 2. Depth profile for total sulfide at GALE Station G21 at 0912 Hrs on January 29, 1986.

4 meters   50 meters
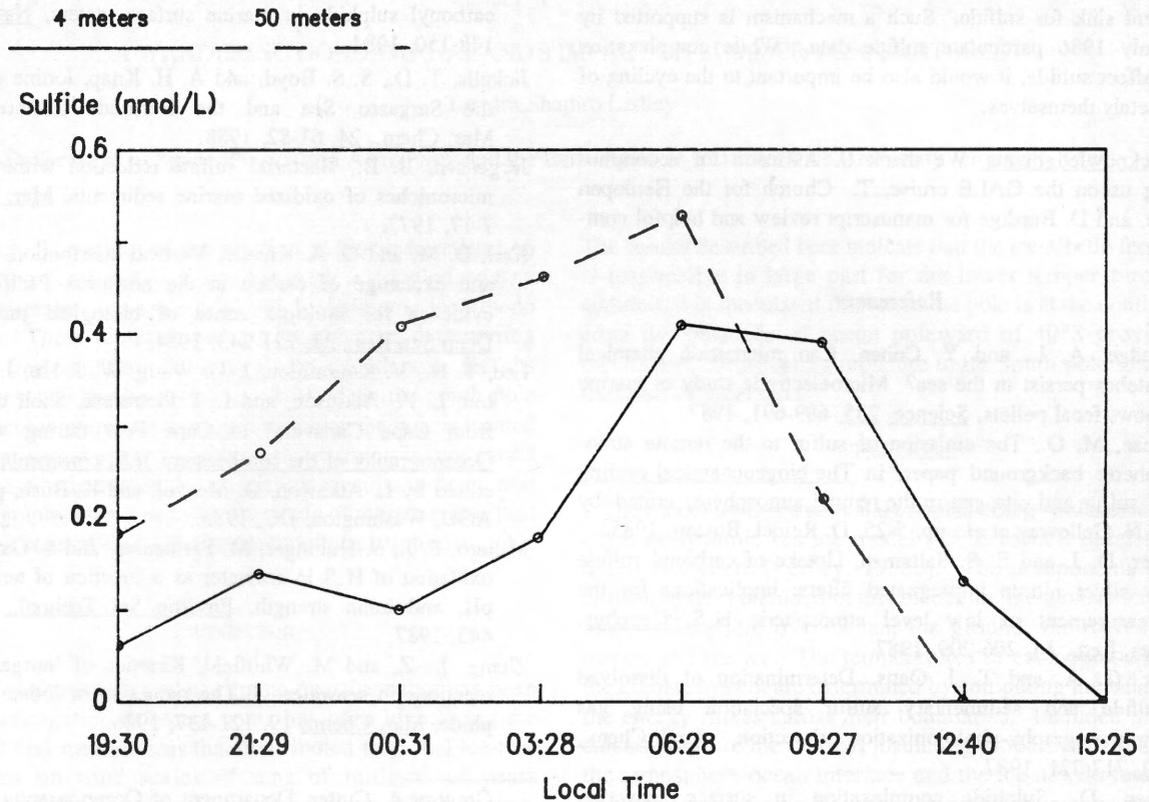
Sulfide (nmol/L)

Fig. 3. Diel variations of total sulfide at GALE Station G21 from January 25-26, 1986. Local sunrise occurred at 0715 Hrs.

Elliott and coworkers [1987] acknowledge that other production mechanisms for sulfide, such as biotic release, may exist. In light of the sulfide data presented here, some speculation on alternative sources and sinks for sulfide is justified.

Another source of sulfide in oxic waters may be anaerobic respiration (i.e., sulfate reduction) within micro-environments of organic detrital particles. Although no sulfide data are available, Karl and Knauer [1984] suggest that anaerobic decomposition occurs within particles collected by sediment traps. In the water column itself, large organic aggregates ("marine snow") are ubiquitous, and marked oxygen depletion within the interstitial waters of these particles is found [Alldredge and Cohen, 1987]. Sulfide production in such micro-environments is obviously speculative, but an analogous

scenario has been documented in oxic marine sediments [Jørgensen, 1977].

In addition to oxidation, other removal mechanisms for sulfide can be postulated. The formation of insoluble metal sulfides such as CuS [Elliott, 1988] can effectively remove dissolved sulfide. Similarly, the association of metal-sulfide complexes with sinking detritus (e.g., the reaction between sulfide and metals adsorbed to particles) could serve as an
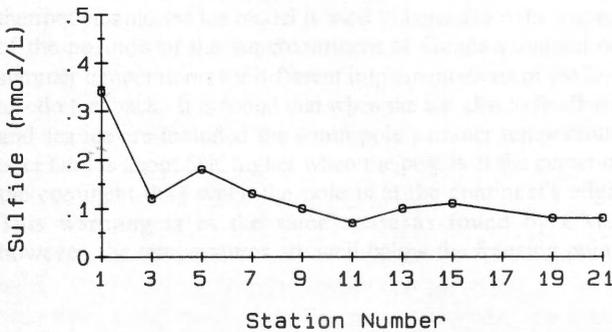

Fig. 4. Horizontal distribution of total sulfide at 2 m depth from GALE Stations G01 to G21. G01 was sampled at 1950 on January 28, 1986, and G21 was sampled at 0912 on January 29, 1986, with approximately 1-2 hours between stations.
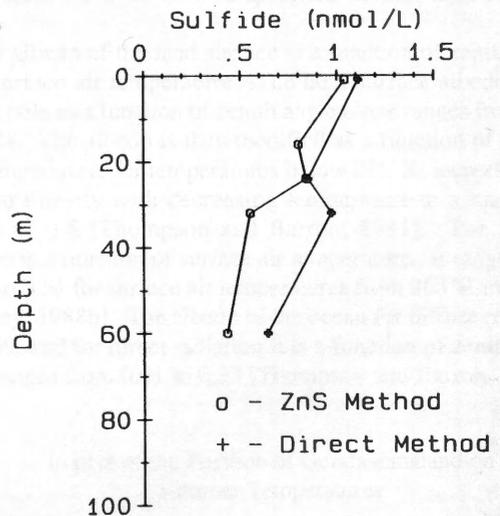

Fig. 5. Depth profile for total sulfide in the mid-Atlantic Bight at 0853 Hrs on July 13, 1986. All of the samples were determined in duplicate using the zinc sulfide precipitation method, while four of the five samples were also analyzed using the direct determination procedure.

efficient sink for sulfide. Such a mechanism is supported by the July 1986 particulate sulfide data. While complexation may affect sulfide, it would also be important to the cycling of the metals themselves.

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