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# Atmospheric Hydrogen Sulfide Over the Equatorial Pacific (SAGA 3)

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Atmospheric  $H_2S$  concentrations were measured over the equatorial Pacific on leg 1 of the third Soviet-American Gases and Aerosols (SAGA 3) cruise during February and March 1990. Five N-S transects were made across the equator between Hawaii and American Samoa. The concentrations ranged from below the detection limit of  $0.4 \pm 0.5$  (1 $\sigma$ ) to 14.4 ppt with an average value of  $3.6 \pm 2.3$  ppt (1 $\sigma$ , n=72). The highest concentrations were found on the easternmost two transects just south of the equator. The average concentration of 3.6 ppt observed on this cruise is the lowest reported value for background atmospheric  $H_2S$  over the tropical oceans. A lack of correlation between  $^{222}Rn$  and  $H_2S$  rules out a significant continental source. Model calculations indicate that the oceanic source of  $H_2S$  in this region is in the range of 9 to  $21 \times 10^{-8}$  mol m<sup>-2</sup> d<sup>-1</sup>. From this flux the concentration of free sulfide ( $H_2S + S^-$ ) in the surface mixed layer of the ocean is estimated to be in the range of 32 to 67 pmol L<sup>-1</sup>. In the atmosphere the oxidation of  $H_2S$  produces  $SO_2$  at a rate of 2.1 to  $4.4 \times 10^{-11}$  mol m<sup>-3</sup> d<sup>-1</sup> which is only a small fraction of that estimated from the oxidation of dimethyl sulfide (DMS) in this region. A diurnal cycle was not observed in the  $H_2S$  data recorded during this cruise.

### Introduction

'Hydrogen sulfide (H<sub>2</sub>S) is emitted into the atmosphere from a wide variety of marine and terrestrial environments, and its flux constitutes an important component of the atmospheric sulfur budget [Andreae, 1990]. Although the sea-to-air flux of hydrogen sulfide is thought to be a relatively minor source, current estimates are based upon an extremely limited data set [Slatt et al., 1978; Delmas and Servant, 1982; Herrmann and Jaeschke, 1984; Saltzman and Cooper, 1988; Andreae et al., 1991]. In fact, all previous studies of hydrogen sulfide in the marine boundary layer have been done in the Atlantic Ocean.

This work represents an extension of the data base to the equatorial Pacific Ocean, a region which should exhibit minimal atmospheric input from terrestrial and coastal sources. Measurements of atmospheric hydrogen sulfide were made on leg 1 of the third joint Soviet and American Gases and Aerosols (SAGA 3) cruise. The R/V Akademik Korolev made five transects across the equator between 10°N and 10°S on a cruise track from Hilo, Hawaii, to Pago-Pago, American Samoa, during February and March 1990 (Figure 1).

#### SAMPLING AND ANALYSIS

Atmospheric hydrogen sulfide was collected as Ag<sub>2</sub>S by drawing air through Whatman 41 filters impregnated with acidic silver nitrate and held in Teflon PFA filter holders [Saltzman and Cooper, 1988; Natusch et al., 1972]. The flow rate for collection was typically 9 L min<sup>-1</sup> with sampling times between 120 and 150 min. Filters were extracted using 20 ml of 0.1 M NaOH and 0.1 M NaCN. The sulfide was detected through the fluorescence quenching of a dilute solution of fluorescein mercuric acetate (20 nmol in 0.1 M NaOH added per sample). The fluorometer used was a Turner Designs model 10-853 with a blue lamp and 10-nm

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band-pass filters at excitation and emission wavelengths of 500 and 520 nm, respectively.

Calibration was done by standard addition of a freshly prepared sulfide standard to extracted blank filters. A 1 mmol  $L^{-1}$  stock solution of  $Na_2S$  was prepared in 0.1 M NaOH. The crystalline  $Na_2S$  was preweighed and stored under nitrogen in sealed glass ampules. The stock solution was diluted (1:50) to make a working standard. The standard solutions were prepared in glassware that had been conditioned and stored containing sulfide solutions. Aqueous sulfide standards prepared using this technique have been verified using thiosulfate titration during previous studies. The calibration has also been verified against a NIST gas standard during the recent NASA/GTE/CITE 3 experiment [Gregory et al., 1993]. The absolute accuracy of the calibration is estimated to be  $\pm 10\%$ .

The lower limit of detection for this method is determined from the variability of the blanks within each batch of filters. For this analysis, one batch of filters contained approximately 30 filters that were impregnated and dried at the same time. During this cruise the average variability within any given batch was  $13 \pm 15$  pmol  $(1\sigma, n = 40$  batches). This gives a detection limit of  $0.2 \pm 0.25$  ppt for each filter (150-min sampling time) or  $0.4 \pm 0.5$  ppt per sample as each sample involves measuring the sulfide found on two filters, a front filter and a backup filter.

Backup filters were used for each sample. Laboratory and field tests have shown that a single silver nitrate filter is >98% efficient for H<sub>2</sub>S removal [Cooper, 1986]. However, it has been shown that an artifact sulfide is formed on the filters during prolonged sampling periods. This artifact is thought to be caused from the hydrolysis of carbonyl sulfide on the filters and is assumed to generate equal sulfide concentrations on both the front and the back filters [Cooper and Saltzman, 1987]. Therefore the measured sulfide is corrected by subtracting from the front filter the amount of sulfide found on the backup filter. Cooper and Saltzman [1987] reported that a diurnal cycle was seen for the artifact sulfide due to a temperature effect with a maximum reported at noon when the filters became the warmest. During this cruise the filter holders were wrapped in a reflective white

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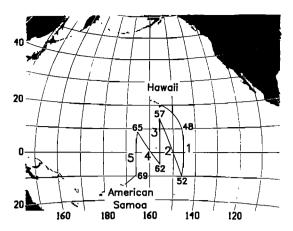


Fig. 1. Cruise track for R/V Akademik Korolev during the third Soviet-American Gases and Aerosols (SAGA 3) experiment, February 12 to March 12, 1990. Large numerals refer to transect numbers and small numerals refer to Julian dates for the beginning and end of each transect.

tape in an attempt to reduce the effect of the Sun on the temperature inside the holder.

In order to prevent contamination from the ship stack and ventilation ports, samples were collected on the bow of the ship. Sampling was done only while the ship was underway with the relative wind within 90° of the bow. The Teflon PFA filter holders were sealed with Teflon TFE plugs when not in use. The washing solution was stored in and delivered from a glass repipet and the extraction was done in sealed PFA vials in order to minimize contact of air with the reagents.

Each air sample was collected and analyzed in duplicate. Samples were presumed to be contaminated and were discarded if the front or back duplicate samples did not agree to within 25%. The results reported here are the averages of each set of uncontaminated duplicate samples. When only one of the samples in a set of duplicates exhibited signs of contamination, for example a high backup filter value, the remaining sample value is the one reported here. The average difference observed between duplicate samples was 0.40 ppt with a standard deviation of 0.28 ppt (n=39 sets of duplicates). We consider this a good measure of the precision of the method under field conditions.

The exposed filters were stored in the Teflon PFA filter holders (sealed with TFE end plugs) or in Teflon PFA vials until the analysis was performed. Storage time ranged from 10 min to 24 hours. Tests using duplicate samples showed that storage of the samples had no effect on the analysis.

### RESULTS

The atmospheric concentrations of  $H_2S$  measured during the SAGA 3 cruise are shown in Figure 2a. The concentrations ranged from below the detection limit (0.4 ppt) to 14.4 ppt with a mean of  $3.6 \pm 2.3$  ppt ( $1\sigma$ , n=72). Air mass trajectories for the cruise showed that the air masses encountered had been over the ocean for at least 7 days prior to sampling [Johnson et al., this issue]. The average concentration of  $H_2S$  found in this study is lower than those previously reported for North Atlantic marine air. Slatt et al. [1978] found concentrations ranging from 5 to 50 ppt over the North Atlantic. Delmas and Servant [1982] reported an average concentration of 14 ppt for the West African coastal

upwelling region. Herrmann and Jaeschke [1984] observed concentrations ranging from 11 to 118 ppt. Saltzman and Cooper [1988] reported an average concentration of  $8.5 \pm 5.3$  ppt  $(1\sigma)$  for the tropical Atlantic. A similar average concentration of  $7 \pm 4$  ppt  $(1\sigma)$  was reported for remote marine air masses over the temperate western North Atlantic Ocean by Andreae et al. [1991]. An average  $H_2S$  level (2.4 ppt) similar to that measured during this study has been reported for remote marine air masses over the South Atlantic Ocean [Cooper and Saltzman, 1993]. Of these previous measurements, those made before 1987 may be high due to the formation of artifact sulfide from the hydrolysis of OCS on the AgNO<sub>3</sub> filters [Cooper and Saltzman, 1987].

Atmospheric <sup>222</sup>Rn concentrations measured during this cruise are shown in Figure 2b. The time series data demonstrate a lack of correlation between 222Rn and hydrogen sulfide. There were two periods of elevated <sup>222</sup>Rn activity during the cruise, between days 45-49 and 62-67. These periods were not accompanied by increased H2S concentrations. High H<sub>2</sub>S concentrations encountered during days 50-53 were associated with a period of uniformly low <sup>222</sup>Rn activity (0.26–0.5 Bq m<sup>-3</sup>). This suggests that the higher  $H_2S$ concentrations reflect emissions from an oceanic source, rather than from the long-range transport of continentally produced  $H_2S$ . The lack of correlation between  $H_2S$  and  $^{222}Rn$  in this data set is markedly different from that found by Andreae et al. [1991] in the western North Atlantic. The region of elevated H<sub>2</sub>S levels was encountered just south of the equator during transects 1 and 2 (Figure 3). It can be seen from Figure 3 that this feature was absent from transects 3, 4, and 5. During transect 2 there appeared to be some correlation between the elevated H2S concentrations and the changes in ocean chemistry and biological activity (Figure 4). Atmospheric H<sub>2</sub>S and seawater dimethyl sulfide (DMS) [Johnson, this issue] both exhibit a general increase

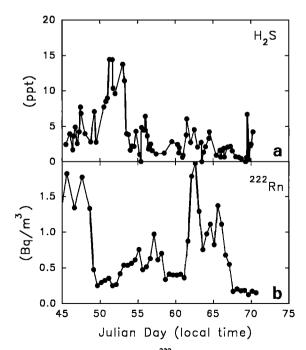


Fig. 2. Atmospheric H<sub>2</sub>S and <sup>222</sup>Rn concentrations measured during leg 1: (a) H<sub>2</sub>S and (b) <sup>222</sup>Rn.

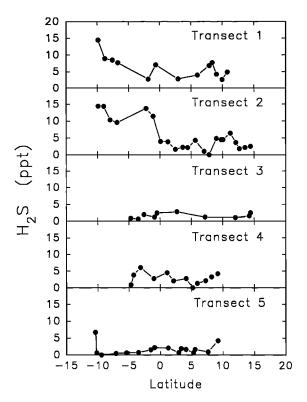


Fig. 3. Atmospheric  $H_2S$  concentrations shown by transect, from east (top) to west (bottom).

in concentration from north to south on this transect and both exhibit a sharp increase just south of the equator. This was apparently a region of active upwelling, as evidenced by the decrease in sea surface temperature and the increase in

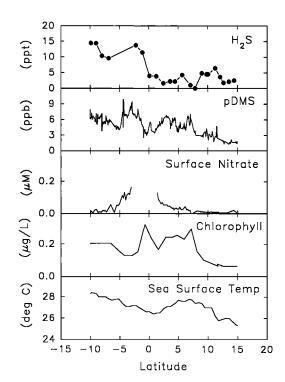


Fig. 4. A comparison of  $H_2S$ , partial pressure of dimethyl sulfide in air equilibrated with seawater (pDMS), surface nitrate, and chlorophyll on transect 2 (145°–155°W).

TABLE 1. Summary of the Parameters Used to Calculate OH Radical Concentrations

Concentration				
Species	Low O <sub>3</sub>	High O <sub>3</sub>	Reference	
03	9 ppb	20 ppb	Thompson et al.[this issue]	
Total O <sub>3</sub>	0.26 cm	0.26 cm	P. Newman (personal communication, 1990)	
NO	1.5 ppt	1.5 ppt	Torres and Thompson [this issue]	
CO	70 ppb	70 ppb	Bates et al. [this issue]	
CH <sub>4</sub>	1650 ppb	1650 ppb	Bates et al. [this issue]	

surface nitrate concentrations. Although indirect, these observations suggest that there may be a relationship between upwelling and  $H_2S$  emissions in this region. However,  $H_2S$  concentrations were generally lower and more constant at approximately 2.3 ppt for the remaining three crossings of the equator, although there was evidence for further upwelling on these transects as well. Therefore the dependence of  $H_2S$  emissions on upwelling may not be a simple one, and further work is needed to clarify this relationship.

### DISCUSSION

An estimate of the sea-to-air flux of hydrogen sulfide can be determined using a simple photochemical box model which balances the flux of H<sub>2</sub>S from the ocean with its destruction in the atmosphere due to reaction with the OH radical [Saltzman and Cooper, 1988]. The model does not include horizontal transport or downward mixing of H<sub>2</sub>S from the free troposphere. These processes should play a minor role in the H<sub>2</sub>S budget for this study, in view of the distance of the cruise track from terrestrial sources and the lack of correlation between  $H_2S$  and  $^{222}Rn$ . The  $H_2S$  lifetime in the boundary layer, as determined from the OH concentrations calculated for this study, is of the order of a day. We assume a constant mixing ratio in the marine boundary layer. A boundary layer height of 2 km was assumed, based on radiosonde profiles measured during this cruise. In this zero-dimensional kinetic model, a fixed time step (1 min) Runge-Kutta routine is used to solve the rate expressions for the reactions of H2S and DMS with OH radicals in the marine boundary layer. The simulation is carried out for several days, until consistent diurnal profiles of H<sub>2</sub>S and DMS are obtained.

OH radical concentrations are calculated using a steady state model where the photolysis rate of  $O_3$  is calculated using a radiative transfer scheme similar to that of *Isaksen et al.* [1977]. Two sets of conditions are used (Table 1). The low  $O_3$  case has an ozone concentration of 9 ppb to simulate the conditions observed at and south of the equator during SAGA 3. The high  $O_3$  case uses 20 ppb of ozone to simulate the conditions observed north of the equator [*Thompson et al.*, this issue].

The boundary layer model results are summarized in Table 2. The atmospheric oxidation of  $H_2S$  by OH ( $k=4.7 \times 10^{-12}$ ; *DeMore et al.* [1990]) results in an SO<sub>2</sub> production rate of  $2.1 \times 10^{-11}$  mol m<sup>-3</sup> d<sup>-1</sup> (0.53 ppt d<sup>-1</sup>) for the low ozone case and  $4.4 \times 10^{-11}$  mol m<sup>-3</sup> d<sup>-1</sup> (0.89 ppt d<sup>-1</sup>) for the high ozone case. This is only a small fraction of the 2.9 to  $6.2 \times 10^{-9}$  mol m<sup>-3</sup> d<sup>-1</sup> (72 to 153 ppt d<sup>-1</sup>) of SO<sub>2</sub> produced from local DMS emissions based on the observed

TABLE 2. Summary of the Model Results for H<sub>2</sub>S

	Oceanic Emission Flux, mol m <sup>-2</sup> d <sup>-1</sup>	Mean OH Concentration, molecules cm <sup>-3</sup>	SO <sub>2</sub> Production (From H <sub>2</sub> S), mol m <sup>-3</sup> d <sup>-1</sup>	Sulfide Concentration, pmol L <sup>-1</sup>
$O_3 = 9 \text{ ppb}$ $O_3 = 20 \text{ ppb}$	$9 \times 10^{-8}$ $21 \times 10^{-8}$	$3.5 \times 10^5$ $7.5 \times 10^5$	$2.1 \times 10^{-11}$ $4.4 \times 10^{-11}$	32 67

Twenty-four-hour averages.

atmospheric DMS concentration of 400 ppt [Huebert et al., this issue] and a 94% production of SO<sub>2</sub> from the oxidation of DMS ( $k = 6.3 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; Hynes et al. [1986]). This result indicates that the H<sub>2</sub>S oxidation contributes <1% of the SO<sub>2</sub> produced from the oxidation of reduced sulfur gases in remote marine air. This is lower than the proportion reported earlier by Saltzman and Cooper [1988] who found that the oxidation of DMS and H<sub>2</sub>S contribute 87 and 11%, respectively, of the non-sea-salt sulfate over the tropical Atlantic.

The model calculations indicate that a sea-to-air flux of 9 to  $21 \times 10^{-8}$  mol m<sup>-2</sup> d<sup>-1</sup> is needed to maintain a mean atmospheric concentration of 3.6 ppt. The concentration of aqueous hydrogen sulfide needed to support this flux is estimated using a simple model of air-sea exchange [Liss and Slater, 1974]. A piston velocity of 4 m d $^{-1}$  was obtained from the wind speed of 10 m s $^{-1}$  observed during the cruise and the wind speed versus piston velocity relationship determined by *Smethie et al.* [1985]. This value is corrected for the diffusivity of  $H_2S$  (2.14 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>; *Hayduk and* Laudie [1974]) assuming that gas exchange varies as  $D^{1/2}$ [Jahne et al., 1987]. The transfer velocity is controlled by the aqueous phase resistance. In seawater the aqueous free sulfide (H<sub>2</sub>S + HS<sup>-</sup>) is predominantly in the form of bisulfide (93%). Balls and Liss [1983] determined a chemical enhancement factor of 9.94 (pH = 8) for the sea-to-air exchange of H<sub>2</sub>S. The final value for the piston velocity used in this model is 3.86 m d<sup>-1</sup>. The resulting concentration of free sulfide (H<sub>2</sub>S + HS<sup>-</sup>) in the surface ocean is found to be in the range of 32 to 67 pmol L<sup>-1</sup>. At these concentrations the surface ocean is 6 to 12 times supersaturated in H<sub>2</sub>S with respect to the overlying atmosphere.

The calculated free sulfide concentration is lower than the <0.1-1.1 nmol L<sup>-1</sup> measured in the western Atlantic Ocean by Cutter and Oatts [1987] and Cutter and Krahforst [1988]. Their analytical method detects both free and complexed sulfide. Recently, Andreae et al. [1991] reported that free sulfide comprises only about 13% of the total sulfide and measured free sulfide concentrations ranging from 0 to 73 pmol L<sup>-1</sup>. This would indicate free sulfide levels in the western North Atlantic quite similar to those we calculate for the equatorial Pacific. However, in the Atlantic the ocean appears to act predominantly as a sink for atmospheric H<sub>2</sub>S. The average atmospheric H<sub>2</sub>S levels measured in that study were higher (7  $\pm$  4 ppt) than the SAGA 3 measurements (3.6 ± 2.3 ppt) and they observed a positive correlation between H<sub>2</sub>S and <sup>222</sup>Rn. This would indicate that the oceans can act as a sink for air masses strongly influenced by continental sources and a source in remote regions.

### SUMMARY AND CONCLUSIONS

Atmospheric H<sub>2</sub>S concentrations over the equatorial Pacific ranged from below the detection limit to 14.4 ppt with

an average value of  $3.6 \pm 2.3$  ppt ( $1\sigma$ , n = 72). The highest concentrations were found on the easternmost two transects just south of the equator. The average concentration of 3.6 ppt is the lowest reported value for background atmospheric  $H_2S$  over the tropical ocean.

Model calculations indicate that the atmospheric production of  $SO_2$  and sulfate from  $H_2S$  oxidation is minor (<1%) compared to that from DMS in this region. Diurnal variations are not observed in the data. They are probably obscured by spatial or temporal variability in the source.

The oceans appear to be a source of  $H_2S$  to the atmosphere over the equatorial Pacific. A sea-to-air flux of 9 to 21  $\times$  10<sup>-8</sup> mol m<sup>-3</sup> d<sup>-1</sup> is needed to balance the atmospheric oxidation. A surface ocean free sulfide concentration of 32 to 67 pmol L<sup>-1</sup> is required to support this flux.

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