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Ocean Color and Atmospheric Dimethyl Sulfide: On Their Mesoscale Variability

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The mesoscale variability of dimethyl sulfide (DMS) and ocean color is explored to determine the feasibility of a predictive relationship. During NASA's Global Tropospheric Experiment/Chemical Instrumentation Test and Evaluation (GTE/CITE 3), simultaneous shipboard and aircraft studies were carried out in the North Atlantic, followed by aircraft studies in the South Atlantic. Surface concentrations of chlorophyll *a* were measured with an airborne spectroradiometer, the Ocean Data Acquisition System (ODAS), with simultaneous determinations of tropospheric DMS. Shipboard measurements of DMS in air and water as well as in situ chlorophyll *a* were taken in the North Atlantic. No relation was observed between shipboard aquatic DMS and chlorophyll *a* or primary productivity. Higher levels of aqueous DMS were not always reflected by atmospheric DMS, although shipboard and aircraft measurements of atmospheric DMS agreed very well. A significant relationship between atmospheric DMS and ocean color was seen once at low altitudes in both the North and South Atlantic only under clean air conditions. Atmospheric DMS levels during the North Atlantic experiment were probably lowered by the presence of mostly polluted air masses in the study area and were, overall, probably not representative of the in situ sea-to-air flux of DMS. Changes in concentration of aircraft-sensed chlorophyllous pigments were not reflected by atmospheric DMS. If a predictive algorithm is to be found, phytoplankton blooms should probably be the first place to study an ocean color-DMS relationship.

1. INTRODUCTION

The first measurements of dimethyl sulfide (DMS) in the surface oceans and quantitative estimates of its sea to air flux were made more than a decade ago. Numerous subsequent shipboard measurements have confirmed the ubiquity of DMS in the surface oceans [Andreae, 1990 for review], and suggest that the flux of organosulfur into the troposphere provides a major source for sulfur aerosols in remote marine air masses [Nguyen *et al.*, 1983; Putaud *et al.*, 1992]. It has been proposed [Charlson *et al.*, 1987] that the distribution of sulfate aerosols in the marine atmosphere exerts significant control (either directly or indirectly) over the Earth's albedo. If true, then the response of the sulfur cycle to climate change could constitute an important feedback in the Earth climate system.

The major source of DMS in seawater is phytoplankton. The relationship between seawater DMS and chlorophyll

a (as an indicator of phytoplankton biomass), however, has been reported as highly variable both spatially and temporally. A lack of correlation between seawater DMS and chlorophyll *a* is most likely because only certain phytoplankton species are known to produce significant amounts of DMS. The biological production of DMS and its precursor dimethylsulfoniopropionate (DMSP) seems to be confined to dinoflagellates and prymnesiophytes (including coccolithophores) both in the field and in cultures [Ackman *et al.*, 1966; Barnard *et al.*, 1984; Turner *et al.*, 1988; Keller *et al.*, 1989]. There are numerous records of massive blooms of DMS-producing coccolithophores [Keller *et al.*, 1989; Matrai and Keller, 1993], other prymnesiophytes, and dinoflagellates [Holligan *et al.*, 1987; Turner *et al.*, 1988; Gibson *et al.*, 1990]. Based on the distribution of such bloom-forming species, it is evident that DMS and DMSP vary temporarily and spatially, dependent on the species composition of the flora and the environmental factors controlling their abundance.

Phytoplankton, by means of their pigment content, are easily visible from space. Remote sensing techniques might be used to perform a first-order estimate of DMS concentrations, given a good algorithm to convert water-leaving radiance to pigment concentration [Gordon *et al.*, 1993] or primary production [Balch *et al.*, 1992], and relations to predict DMS from these quantities. In general, the atmospheric concentrations of DMS appear to

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vary in concert with DMS in oceanic waters [Andreae *et al.*, 1985; Saltzman and Cooper, 1988; Matrai *et al.*, 1992]. To the extent that the DMS in air and water are covariant, one can relate either concentration to pigment concentration in sea surface. Nonetheless, because of the temporal and spatial scales involved in oceanic systems, the prediction of the global sea-to-air DMS flux will ultimately involve remote sensing techniques.

In this paper we investigate the feasibility of obtaining a predictive relationship between DMS emissions and ocean color as observed from an aircraft, on a regional basis. The Global Tropospheric Experiment (GTE) calibration comparison for airborne chemical sensors of sulfur gases (Chemical Instrumentation Test and Evaluation (CITE 3)) provided the opportunity to conduct coordinated shipboard and airborne measurements. Field seasons occurred over the polluted North Atlantic and the relatively unpolluted tropical South Atlantic, in an effort to contrast these two environments.

2. METHOD

The project was carried out in two phases, consisting of simultaneous shipboard (R/V *Atlantis II*) and aircraft studies in the North Atlantic ocean during July and August of 1989 followed by aircraft studies in the South Atlantic in September of 1989. The aircraft work was done in conjunction with the NASA CITE 3 program which involved airborne measurements of DMS and other sulfur gases [Cooper and Saltzman, this issue; Gregory *et al.*, this issue; Hoell *et al.*, this issue]. The Ocean Data Acquisition System (ODAS) [Campbell and Esaias, 1985] radiometer was mounted and operated aboard the NASA Electra aircraft to measure ocean color and sea surface temperature during a series of flights over the northern and southern Atlantic Ocean, including overflight of the ship's cruise track. Station location as well as flight paths are shown in Plate 1.

Every day at approximately local apparent noon we measured profiles of scalar irradiance using a PNF-300 optical profiling system (Biospherical Instruments) and collected samples for DMS, chlorophyll, primary productivity, nutrients, and cell counts with 10-L Niskin bottles attached to the wire. Pigment concentrations were determined in acetone extracts using a Turner-Designs fluorometer [Yentsch and Menzel, 1963]. ^{14}C -based productivity measurements were performed at each depth [Strickland and Parsons, 1972]. Spiked samples in 250-mL acid-cleaned polycarbonate bottles were incubated for 24 hours on deck under natural sunlight in seawater-cooled tubular incubators wrapped in blue acetate (Madico Film TS-51) to reduce the light intensity to the appropriate relative irradiance. Following the incubation, the samples were filtered onto Whatman GF/F filters, rinsed, and counted in Ecolume. Nutrient samples were filtered and frozen for analysis ashore of NO_3^- , NO_2^- , NH_4^+ , and PO_4^{3-} [Strickland and Parsons, 1972; Koroleff, 1983]. Water samples were preserved in lugols

iodine solution and settled once ashore for cell counts [Sournia, 1978], which were done with an Olympus BH2 microscope.

2.1. Ocean Color Measurements

Aircraft ocean color measurements were performed from the NASA Wallops Flight Facility Lockheed Electra leaving from Wallops Island, Virginia, for the North Atlantic Ocean flights and from Natal, Brazil, for the South Atlantic flights. In the North Atlantic missions, CITE 3 flight paths were planned to accommodate three sea-truth passes over the vessel. At those times, shipboard water and air samples were collected for DMS, and chlorophyll was measured in surface waters.

The ODAS measurements consisted of two primary instruments: an infrared radiometer (PRT-5) to measure sea surface temperature and a three-channel visible spectroradiometer for 460, 490, and 520 nm wavelengths. ODAS operates as a line-of-flight instrument. The instrument was calibrated before and after CITE 3 at the Goddard Space Flight Center in Greenbelt, Maryland, as well as after each flight. A compilation of calibrations run during 1988 and 1989 was finally used for each channel and at each gain setting (E. Itseweire, personal communication, 1992) [Harding *et al.*, 1992]. No atmospheric correction is necessary in the algorithm for aircraft altitudes of less than 150 m (500 ft) [Campbell and Esaias, 1983]. The upwelled radiances were simultaneously sampled every 0.1 s, then reduced to 2-s averages corrected for sunglint, reflection from other sources, and aircraft changes in elevation, pitch and yaw. Pigment concentrations were determined using a curvature algorithm [Harding *et al.*, 1992] that first calculates a ratio among the three radiances measured, then incorporates it into a linear regression with factors determined empirically from our data (in situ chlorophyll and ODAS measurements) collected during the ship overflights in the North Atlantic. Finally, the data for each flight were reduced to blocks of time matching those during which aircraft atmospheric samples of DMS were collected, usually 600 s long. Navigation data were obtained from ODAS or the aircraft system.

2.2. Dimethyl Sulfide Analysis

The shipboard determination of DMS in seawater and air is similar to that reported in Saltzman and Cooper [1988] and Cooper and Saltzman [1991], with a detection limit of 0.2 nM in a 5 mL sample. The precision of the method was better than 5% (plus or minus 1 standard deviation) for most of the working range and roughly 10% at the lowest concentrations. Standard additions were done routinely during the course of this study to confirm the accuracy of the measurements of atmospheric DMS.

Airborne analysis of DMS in the atmospheric boundary layer was done using an automated gas chromatography/flame photometric detection (GC/FPD) system with a

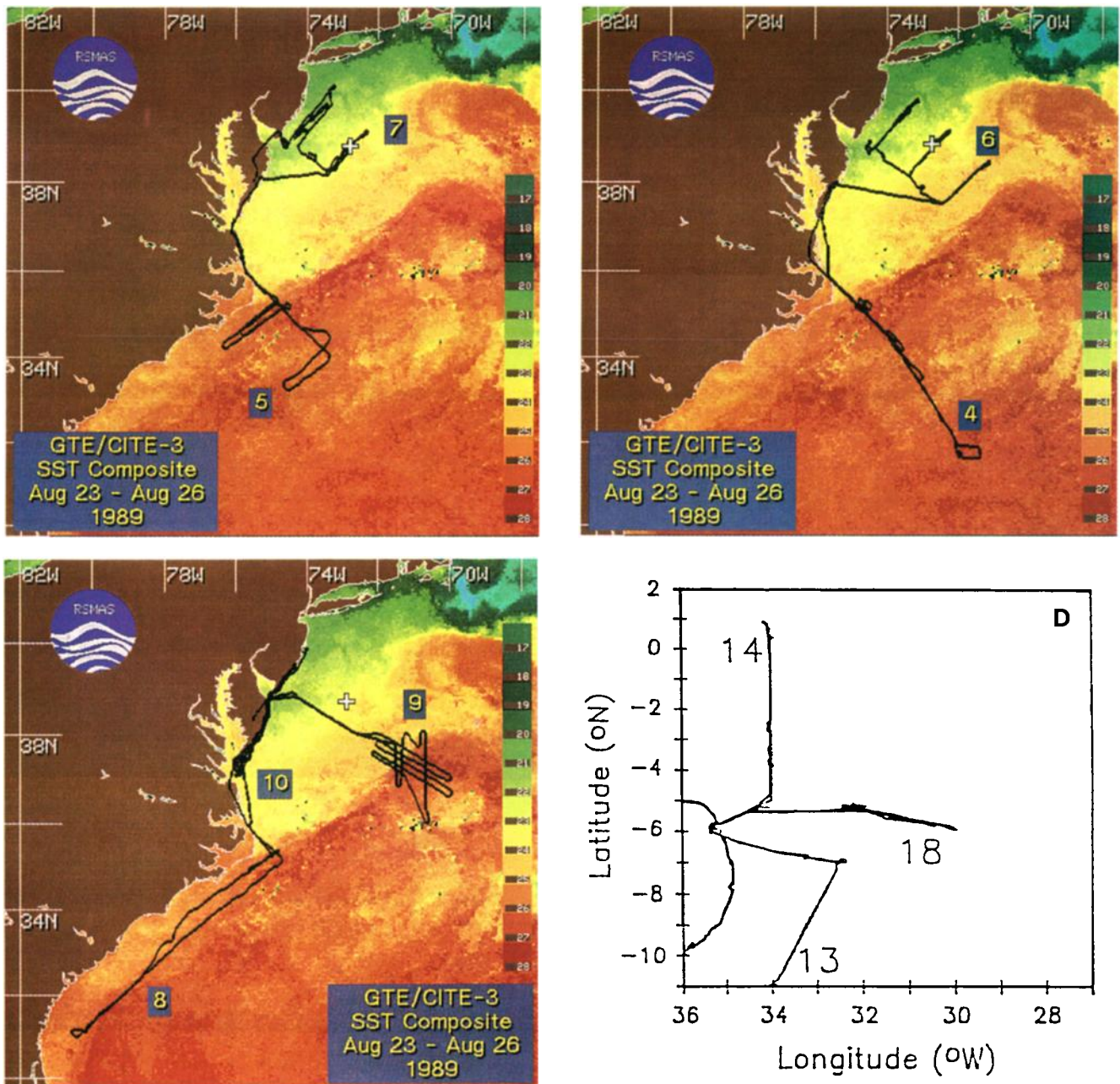


Plate 1 (a-c) Flight paths for NASA's aircraft and station position (crosses) for the R/V *Atlantis II* during the North Atlantic missions (flights 4-10) (August 22 to September 1, 1989) displayed on an AVHRR thermal composite for August 23-26, 1989 (courtesy of D. Olson, RSMAS, University of Miami) and (d) flight paths for the three ODAS sampling missions (flights 13-18) in the South Atlantic (September 1989).

sampling frequency of one sample every 600 s. The detection limit of this FPD was approximately 3 ppt of DMS in a 10-L air sample. Complete details are described in Cooper and Saltzman [this issue].

3. RESULTS

Depth distributions of DMS in the North Atlantic showed a subsurface maximum (except after one wind event, when uniform distributions reflected a well-mixed upper water column). This maximum, when present, was

generally shallower than the chlorophyll or the primary production maximum, with the latter usually located at the depth of the 1% light level. Surface chlorophyll was generally less than 1 $\mu\text{g/L}$ while the subsurface maxima reached concentrations as high as 4 $\mu\text{g/L}$. Except for an abundant but very patchy bloom of *Oscillatoria* sp. strictly in surface waters, diatoms were most abundant with dinoflagellates, small flagellates, and prymnesiophytes also present. Very low DMS concentrations were measured in surface waters dominated by *Oscillatoria* sp. Nutrient levels did not show any correlation with DMS

levels. Figure 1 presents the relationship between chlorophyll *a*, primary production and DMS. The North Atlantic scatter grams do not show any relation between these two measures of phytoplankton activity and DMS.

Shipboard DMS measurements in air were done throughout the North Atlantic cruise, both on a transect from St. George, Bermuda, to 38° 48'N 72° 47.2'W as well as while on station. These values are compared to DMS concentrations in surface seawater in Figure 2a. Higher levels of aqueous DMS were sometimes but not always reflected in the atmosphere. DMS in water and in air was, in general, lower in and over the oceanic areas than in the more coastal stations. The shipboard atmospheric DMS measurements corresponded well to the levels determined on board the aircraft during the ship overpasses at less than 150 m of altitude (Figure 2b), with the high-altitude (400 m) DMS levels being lower by a factor of 4.

Seven missions were flown over the temperate North Atlantic (Plates 1a-1c). The spatial coverage provided by ODAS indicated surface chlorophyll numbers ranging from 0.2 to 1.4 µg/L, while atmospheric DMS levels simultaneously measured aboard the aircraft averaged about 20 ppt, except during one mission (mission 4) in which values exceeding 80 ppt were observed along with

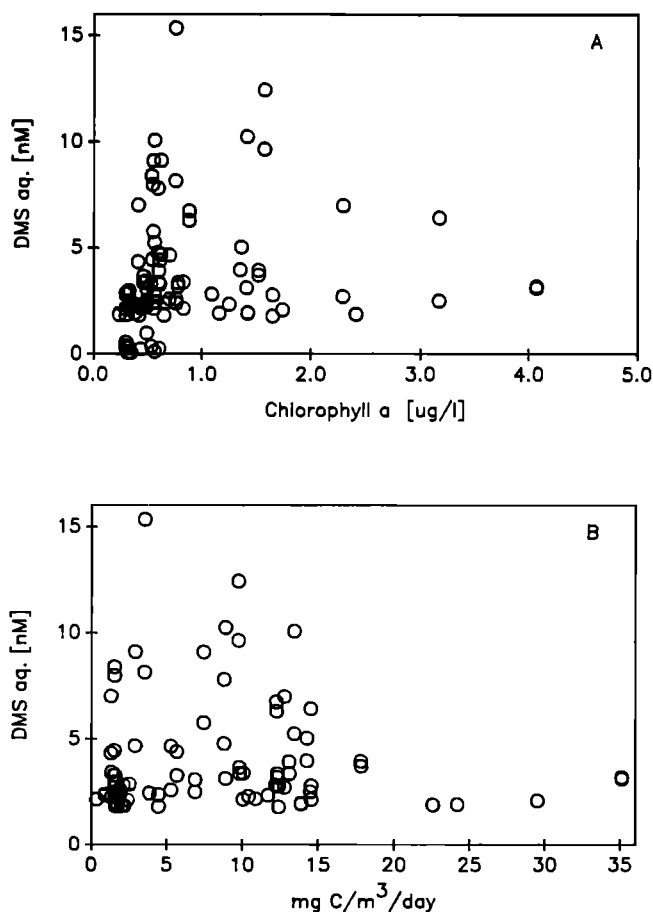


Fig. 1. (a) Seawater DMS versus extracted chlorophyll *a* and (b) primary productivity from on-deck incubations in the North Atlantic.

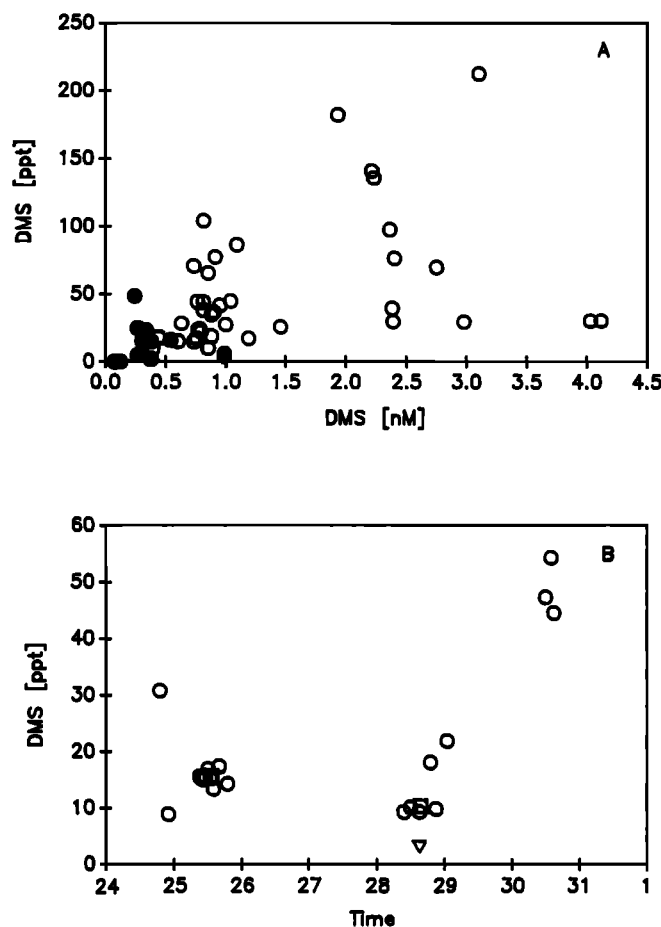


Fig. 2. (a) Shipboard atmospheric DMS concentrations in the North Atlantic during a transect from Bermuda to station (solid circle) and on station (open circle) versus surface seawater DMS concentration. (b) Comparison between atmospheric DMS concentrations on board ship (circles) and aircraft at 100-150 m (squares) and 1300 m (triangles) during three North Atlantic overflights.

the lowest ozone levels measured during the North Atlantic flights [Cooper and Saltzman, this issue]. Pigment values during this mission were in the range of 0.4-0.6 µg chl/L. This is the only North Atlantic mission when a significant relationship was observed between pigment levels and atmospheric DMS ($r=0.535$, $p<0.001$). Pigment concentrations observed only from altitudes of less than 150 m are plotted in Figure 3a. Overall, pigment observations from altitudes of 1300 and 5000 m were not significantly higher (range 0.4-1.4 µg chl/L) than those sensed from 150 m above sea surface (Figure 3b). Repeated ODAS sampling of one location from two altitudes (150 and 1300 m) with a delay of 1 hour resulted in a similar pigment concentration (within 3%).

A paucity of data for the South Atlantic flights is due mostly to the constant changes in altitude specifically programmed for those missions; ODAS provided usable data for only three of the seven missions flown. Hence, data from various altitudes are included in Figure 4. Atmospheric DMS concentrations were lower in the

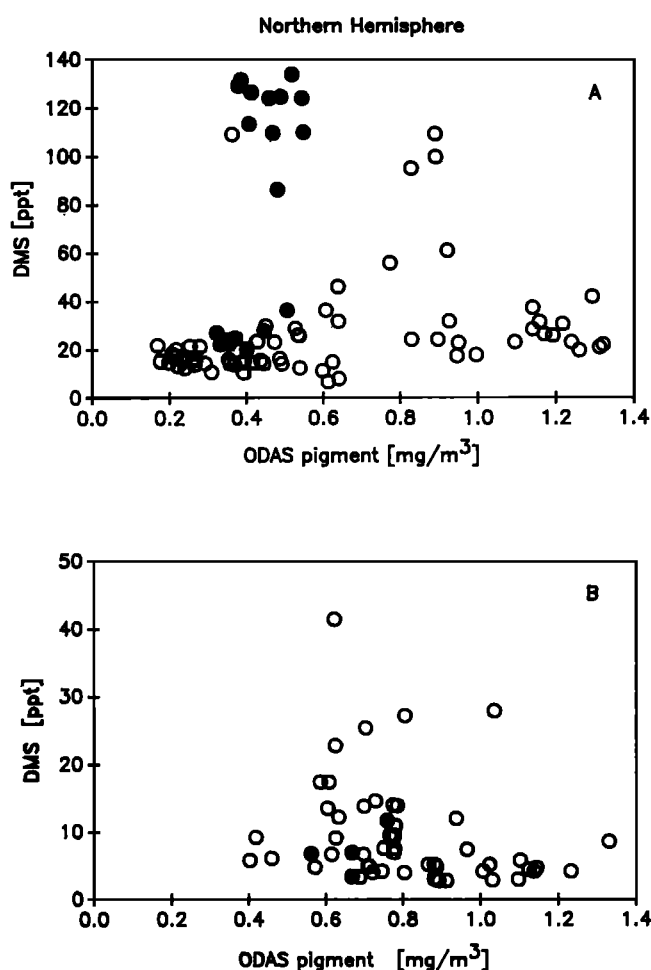


Fig. 3. Simultaneous atmospheric DMS versus ODAS chlorophyll *a* observations during all seven North Atlantic flights (*a*) in the boundary layer (150 m or less) (flight 4 observations represented by solid circles; see text for further explanations) and (*b*) at higher elevations of 1300 m (open circles) and 5000 m (solid circles)

Southern Atlantic, while pigment values ranged from 0.2 to 0.8 $\mu\text{g chl/L}$, overlapping well with those observed during the North Atlantic flights. Flight 13, southward along the Brazilian coast, observed the highest pigment concentrations, at about 0.7 $\mu\text{g chl/L}$ with little spatial variability. Field observations indicate the presence of haze and high sunglint during this mission, especially above 6000 ft. (approximately 2000 m). Atmospheric DMS during the same flight, on the other hand, showed an increase of about 25 ppt for several hours, most likely due to sampling of the lower boundary layer. Flight 14, northward along the Brazilian coast during a clear day, is the only South Atlantic mission when a significant relationship was observed between pigment levels and atmospheric DMS ($r=0.823$, $p<0.001$). It encountered little spatial variability for both atmospheric DMS and sea surface pigment, with values around 20–25 ppt and 0.2 $\mu\text{g chl/L}$, respectively. Flight 18, eastward, showed a distinct fourfold decrease in atmospheric DMS and threefold increase in chlorophyll *a*.

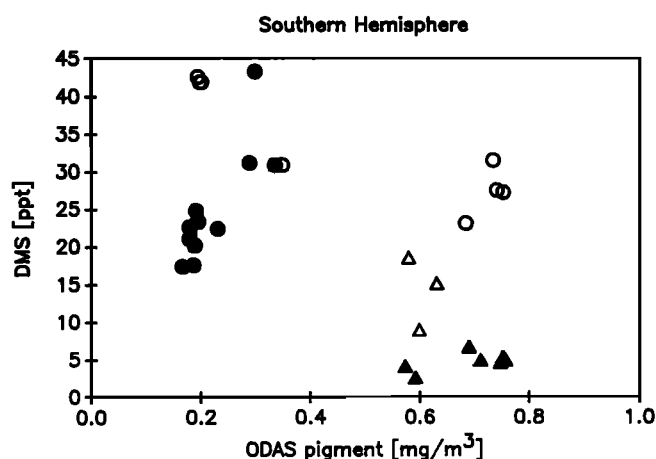


Fig. 4. Atmospheric DMS versus ODAS chlorophyll *a* observations during three South Atlantic flights at <150 m (open circles), 300 m (solid circles) (flight 14), 1300 m (open triangles), and >2000 m (solid triangles)

4. DISCUSSION

The rate of release of DMS from the sea surface is a complex function of the concentration of DMS at the sea surface, the physical state of the air/sea interface, and molecular properties of DMS which control its diffusivity in aqueous solution. In the atmosphere, DMS has a lifetime on the order of a day or less. To the extent that atmospheric DMS samples reflect emissions from the sea surface in the immediate vicinity, the signature of the sea-to-air DMS flux in polluted environments can be greatly disturbed by enhanced oxidant levels [Andreae *et al.*, 1985]. This means that changes in atmospheric DMS are unlikely to reflect any enhancement in the sea-to-air DMS flux due to a change in biological activity, assuming fairly constant winds.

Air mass trajectory analyses for CITE 3 confirm the presence of mostly polluted air in the North Atlantic [Shipham *et al.*, this issue]. Measurements of sulfur gases other than DMS and comprehensive support measurements collected during CITE 3 such as NO_x , CO, and ozone also indicate a substantial degree of pollution [Hoell *et al.*, this issue]. Continental air, either from the northeastern United States or of Canadian polar origin, was sampled during all the North Atlantic flights, except for flight 4 and the offshore leg of flight 5. These two flights sampled North Atlantic tropical maritime air masses, resulting in the highest atmospheric DMS values (Figure 3a) and the only instance when a significant relationship was observed between ocean color and atmospheric DMS. The mostly low and fairly uniform levels of DMS seen during the remaining North Atlantic flights probably resulted from such chemical interactions [Cooper and Saltzman, this issue].

During the South Atlantic flights, maritime air masses were transported westward across the equatorial Atlantic during all flights and at all flight altitudes, but the highest

ones [Shiphani *et al.*, this issue], implying that, unlike the North Atlantic, pollution would not be a good explanation for the apparent uniformity in DMS distribution. Cooper and Saltzman [this issue, and references therein] indicate that the DMS levels encountered during this period were considerably lower than those reported by previous studies over tropical waters, suggesting the low DMS may be due to a seasonal effect [Bates *et al.*, 1987; Nguyen *et al.*, 1992], as the sampling occurred at the end of the southern winter, perhaps prior to any spring phytoplankton bloom. It is also possible that although the air trajectories during the experiment did not indicate advection over land masses, the sources may have originated from different regions as evidenced by the presence of haze layers (ODAS operator field observations) and lack of homogeneity in the relative levels of various atmospheric gases [Cooper and Saltzman, this issue], encountered during some flights and at different altitudes during a single flight. If so, DMS levels would be lower and reflectances higher than expected.

Although logistics clearly restricted the number of overflights of the ship by the aircraft, pigment values calculated with the algorithm developed with our data (only case 1 waters, i.e., waters for which phytoplankton and their associated debris control the optical properties) were not significantly different from those calculated with an algorithm of mostly case 1 waters developed for the Multichannel Ocean Color Sensor, a 20-channel predecessor of ODAS [Campbell and Esaias, 1983; Campbell *et al.*, 1986]. ODAS has been extensively tested and used in one other study in the more turbid Chesapeake Bay [Harding *et al.*, 1992]; although a wide range of conditions and time scales were used in their study the accuracy of the ODAS chlorophyll *a* measurements was considered comparable to that of the coastal zone color scanner (CZCS). In the case of the South Atlantic, previous pigment measurements done in waters off Brazil indicate the ODAS-derived pigment concentrations were reasonable [e.g., Herbland *et al.*, 1985; DeMaster *et al.*, 1986]. However, the extent to which the extrapolation of our algorithm is possible for the South Atlantic waters, with no in situ data available, is unknown. Furthermore, our radiance-pigment conversion is valid for altitudes lower than 150 m; the apparent increase of chlorophyll levels as measured by ODAS when flown at higher altitudes suggests reflectance interference by other sources such as atmospheric aerosols, sunglint, and airborne pollen [Harding *et al.*, 1992].

The DMS data collected in and over the Mid-Atlantic Bight during the summer of 1989 were similar to previous shipboard [Andreae *et al.*, 1985; Cooper and Saltzman, 1991] and aircraft studies [Van Valin and Luria, 1988]. Phytoplankton biomass and productivity, as an indicator of the magnitude of the source of DMS, were fairly uniform in surface waters of the Mid-Atlantic Bight. The measurements taken by ODAS reflect best the in situ pigment measurements, not productivity. Other regional samplings have also failed to provide any simple

correlation of DMS in seawater and measured primary production [Barnard *et al.*, 1984; Bates *et al.*, 1987], even though large-scale, spatially averaged, aqueous DMS concentrations appear to be covariant with averaged productivity estimated from global maps [Andreae and Barnard, 1984]. Despite uncertainties such as winds and transfer rates and variations in regional DMS production and release, when we averaged all of our seawater DMS and productivity data, the mean would fit perfectly the spatially macroscale relationship between primary production and seawater DMS concentrations described by Andreae and Barnard [1984] for area-weighted biogeographical regions classified according to Koblenz-Mishke *et al.*'s [1970] productivity map. The error bars of our average, however, are large and tell us nothing about finer scale covariability in the entire range of values for DMS and primary production in the oceans. Given that airborne DMS samples were collected continuously with an integration time of 10 min per sample, this length of time represents an average distance of 60 km at the velocity of the aircraft. For phytoplankton spatial distribution, hence the ocean color signal sensed by ODAS, this is a large-scale average, not necessarily the most meaningful sampling distance [Haury *et al.*, 1978].

Two other large-scale estimates of the ocean-to-atmosphere flux of DMS have involved remote sensing. Thompson *et al.* [1990] used chlorophyll concentrations obtained from a CZCS monthly mean to derive a signal for the concentration of DMS in seawater for a specific region and time, assuming an empirical relationship between seawater chlorophyll and DMS [Andreae and Barnard, 1984]. This relationship was highly significant over a long transect across the Atlantic Ocean. Within the region of 0–35°N and 20–35°W, Thompson *et al.* [1990] calculate a regional mean DMS flux of similar magnitude or slightly higher than other published estimates [Barnard *et al.*, 1982; Erickson *et al.*, 1990]. Their large-scale averaging at 2.5° latitude probably smoothes over any mesoscale (~100 km) phytoplankton patchiness, similar to our averaging in the South Atlantic. Erickson *et al.* [1990] calculated DMS fluxes using an atmospheric general circulation model with DMS concentrations derived from incident solar radiation at the Earth's surface. No explicit calculation, simulation, or field data of global phytoplankton biomass or primary productivity were included in the model. The calculations were confined to oceanic regions only. The calculated DMS concentrations tend to underestimate the surface ocean DMS concentrations, especially in productive regions, while very high concentrations are calculated for polar regions, where DMS data are scarce. Determining the spatial and, most likely, temporal scale dependence of the relationship between biological activity and DMS concentrations is one of the major challenges in understanding the biogeochemical cycling of organic sulfur.

If our relationships between DMS in ocean waters and chlorophyll as well as between aqueous and atmospheric

DMS had been significant, as suggested in the literature, and given that ocean color is mostly a measure of chlorophyllous pigment concentration, a certain degree of covariability between atmospheric DMS and surface chlorophyll might have been expected. The presence of mostly polluted air masses during the North Atlantic section of the experiment as mentioned above may have masked the natural signal present. While up to 30% of the variability of DMS in seawater has been explained by its relationship to chlorophyll in different oceans [Cline and Bates, 1983; Andreae, 1990], the lack of relationship between DMS and chlorophyll as we saw has also been previously reported [Andreae and Barnard, 1984]. A correlation between pigment and DMS concentrations could also be dramatically affected by the physiological history of the cells: a healthy, blooming population of phytoplankton might produce much different quantities of DMS than a decaying bloom, yet the pigment values are the same [Matrai and Keller, 1993]. This is also a major factor preventing a good correlation between pigment and primary production [Balch et al., 1992]. In a similar manner, a "time-lag" approach might account for the effect of "stage of the bloom" in these relationships.

Spring phytoplankton blooms are occasionally, and often predictably, dominated by DMS-producing species for prolonged periods of time, covering mesoscale [Barnard et al., 1984; Holligan et al., 1987; Matrai and Keller, 1993] to megascale areas (500,000 km², south of Iceland) (P. Holligan and W. Balch, personal communication, 1992). During such cases, significant relationships have been observed between aqueous DMS, chlorophyll *a*, and/or cell numbers [Barnard et al., 1984; Turner et al., 1988; Matrai and Keller, 1993]. Whether such "hot-spots" of biological production of DMS, now known to be spatially significant, can still be considered to contribute the bulk of DMS to the atmosphere seems to be debatable [Andreae, 1990]. Nonetheless, these blooms are still the first place to study an ocean color-DMS relationship if a predictive algorithm is to be found.

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