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Frontal enhancement of dimethylsulfide concentrations across a Gulf Stream meander

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Abstract

Aqueous and atmospheric dimethyl sulfide (DMS) concentrations (0.4–4 nM, 5–350 ppt) were determined across a Gulf Stream meander in April 1989. Physical processes along and across the front were expected to result in biological changes also reflected in DMS levels. Highest concentrations of aqueous DMS (3–4 nM) were observed in surface waters coinciding with Slope waters at, or inshore of, the Gulf Stream north wall. This water also contained the highest chlorophyll levels (up to 2.6 μg chl/l) which co-varied with the sea surface DMS concentrations.

Concentrations of atmospheric DMS were lower and more constant (21 $\pm$ 9 ppt) outside the frontal area, either in Slope or Stream waters. At the northern wall of the Gulf Stream, a strikingly sharp increase in atmospheric DMS (up to 350 ppt) was observed.

1. Introduction

The sea-to-air flux of dimethylsulfide (DMS) is believed to be the single largest source of biogenic sulfur to the atmosphere on a global basis (Andreae, 1990, and refs. therein). The most recent estimates of the global flux range from 0.5 Tmol S(DMS)/yr (Bates et al., 1987) to 1.7 Tmol S(DMS)/yr (Andreae, 1990). Uncertainty in the global budget of DMS stems largely from (1) the parameterization of sea-to-air gas exchange rates, and (2) the geographic and temporal variability of sea surface DMS. Spatially, the greatest variability in DMS concentrations occurs in coastal waters in temperate and polar regions while oligotrophic waters tend to have lower concentrations and a more uniform distribution of DMS in surface waters (Bates et al., 1987; Cooper and Matrai, 1989; Andreae, 1990). Temporally, previous field and laboratory studies have shown that aqueous DMS can vary by several orders of magnitude as a result of phytoplankton speciation (Keller et al., 1989), seasonal blooms of phytoplankton (Barnard et al., 1984; Turner et al., 1988; Gibson et al., 1990; Matrai and Keller, 1993a), or physiological state of the phytoplankton (Dacey and Wakeham, 1986; Nguyen et al., 1988; Matrai and Keller, 1993b). These mechanisms may affect the production of DMS in surface waters while the lifetime of DMS may further be a function of exchange with the atmosphere (Kiene and Bates, 1990), bacterial con-

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sumption (Kiene and Service, 1991), photo-oxidation (Brimblecombe and Shooter, 1986), physical advection or diffusion, and perhaps particle adsorption.

In April 1989, as part of the BIOSYNOP Gulf Stream program, a cruise was dedicated to the study of frontal meandering in the open ocean. Numerous studies have coupled mesoscale features (e.g., rings, western edge) of the Gulf Stream circulation with phytoplankton biomass and primary production (Yentsch, 1974; The Ring Group, 1981; Hitchcock et al., 1987; Fryxell et al., 1985; Yoder et al., 1985). The meandering aspect of the Gulf Stream current along its northern wall results in physical and biological changes (Olson et al., 1994 and refs. therein) which are less well understood. Nonetheless, enhancement of phytoplankton biomass and macrozooplankton populations has been observed in the region between meander crest and through, associated with a combination of advection and mixing (Olson et al., 1994).

In this paper we present aqueous and atmospheric DMS data collected while sampling across a Gulf Stream meander, along the stream's northern wall. These areas were of particular interest because of the possibility of highly intensified biological activity resulting in elevated concentrations of DMS as observed across tidal and shelf fronts in the English Channel (Holligan et al., 1987). At times of low biological activity in surrounding waters, it is possible that the regional flux of biogenic gases could be dominated by these events.

2. Methods

The work presented here was conducted on board of the *R/V Columbus Iselin* on April 19–28, 1989 in the area between 65–70°W and 37–40°N. The sampling was constrained by several severe weather events. The cruise sampled the crest and trough of a Gulf Stream meander guided by real time advanced very high resolution radiometer (AVHRR) imagery. Seawater samples for DMS analysis were taken from either noon CTD casts while on station or from the ship's pumping system while underway. Samples were cryogenically preconcentrated by stripping the DMS from solution into a Teflon loop immersed in liquid oxygen. These samples were analyzed using a gas chromatograph with flame photometric detection (GC/FPD) system with a Chromosil 330 column (Saltzman and Cooper, 1988).

Atmospheric DMS samples were collected at the flying bridge level of the ship. Air was drawn through a 1/4″ OD Teflon tube with a Teflon filter into an automated sampling and analysis system located at the bridge level of the ship. This system was a prototype of the instrument described by Cooper and Saltzman (1993). Briefly, DMS was preconcentrated on Tenax GC (Alltech Assocs., Inc.) packed in a 1.5″ × 1/4′ ID Teflon tube. This sampling trap and an open tube, to remove moisture, passed through an aluminum block cooled to approximately −20°C by a thermoelectric module. The sample was thermally desorbed and the moisture trap dried by reversing the polarity of the module. The sample was loaded onto a smaller Tenax precolumn prior to injection onto the GC/FPD system with a Chromosil 330 column. Sulfur was added to the hydrogen flow from a DMS permeation tube immersed in an ice bath in order to optimize the sensitivity and linearity of the detector response.

Prior to DMS preconcentration, the air was drawn through neutral aqueous KI solution in order to remove oxidants from the gas stream. This step is essential for the prevention of sampling losses (Saltzman and Cooper, 1988; Cooper and Saltzman, 1991,1993). Both DMS systems were calibrated with liquid DMS standards. These standards were analyzed in an identical manner to the samples.

Chlorophyll was measured continuously and discretely following Yentsch and Menzel (1963). Cells were counted and sorted using a Becton–Dickinson FACS Analyser (Yentsch and Campbell, 1991). Particles were excited at 424 nm with a mercury lamp and chlorophyll fluorescence measured at > 650 nm. Cells were sized with the instrument's Coulter volume obtaining equivalent spherical diameters. Shipboard wind observations were averaged every 20 min.

3. Results and discussion

Despite severe weather during much of the cruise, a fairly comprehensive set of DMS measurements was obtained for the period of April 21–26, 1989 (JD 111–116). April 22 through 24 were spent crisscrossing the trough of the meander, after which the ship headed southwest. AVHRR imagery shows that by April 23, the curvature of the trough was maximum, with a narrow filament of cool Slope water entrained to the edge of the Gulf Stream near the shoreward apex of the trough (Fig. 1). At the seaward end of the trough, warm filaments of Gulf Stream water extended west. Two days later the cool filament had thinned and did not extend as far east as previously (Hitchcock et al., 1993). Cross sections of the Gulf Stream meander showed the highest levels of aqueous DMS (3–4 nM) in surface waters coinciding with Slope waters of lower salinity 35.53 ± 0.46‰, and temperature (16–19°C) at, or inshore of, the Gulf Stream north wall (Fig. 1). Consistent with this, strong subsurface DMS maxima (3–3.5 nM) at 5–10 m depth, were present on the Slope water side even if surface concentrations were relatively low (≤ 1 nM). This water also contained the highest chlorophyll levels, which were covariant with the sea surface DMS concentrations (Fig. 2). This increase in pigment concentrations on the northern edge of the meander's trough has been related to mixing of nutrients from nutrient-bearing waters near the Gulf Stream SST front (Hitchcock et al., 1993). Surface temperature and salinity at the core of the

Fig. 1. Sea surface DMS measurements in a Gulf Stream meander during April 21–26, 1989, plotted on a composite thermal image for the period.

stream were 23.06 ± 0.17°C and 36.43 ± 0.06‰, respectively. In the Stream as well as in Sargasso Sea waters, surface DMS concentrations were 0.93 ± 0.34 nM; vertical distributions of DMS concentrations were either uniform ranging 0.5–1.5 nM DMS down to a 100 m depth or decreased to less than 0.2 nM DMS below 50 m depth.

Since phytoplankton are the ultimate source of most DMS in ocean waters, an accumulation of aqueous DMS might be expected in areas where particle concentration (that is, DMS producers) exceeds loss by sinking, without forgetting the potential effects on net DMS concentrations of phytoplankton physiological state, microbial consumption, and zooplankton grazing. Cell numbers were highest in Slope waters (10^7 cells/1 vs. 2.4×10^6 cells/1 elsewhere, on average) at or north of the Gulf Stream front, although the particle size distribution did not significantly differ on either side of the front, with particles being 5–6 μ on average. Chlorophyll-containing particles were in a similar size range but represented 60% of all particles in colder waters while only 20–30% in warmer waters. Zooplankton biomass similarly showed a sharp (within 5 km) and striking increase at the north wall of the Gulf Stream by a factor of 100x (Ashjian et al., 1994). A study conducted in fall 1988 by Lohrenz et al. (1993) also found a large increase in pigment biomass and primary productivity across the Stream's northern wall on the Slope side (see also Yentsch, 1974) as well as variations in pigment distribution and primary production along the meander. During the spring of 1989, there was a clear difference in the surface distribution of aqueous DMS across the meander (Fig. 3). Holligan et al. (1987) report an increase in aqueous DMS in frontal areas and relate it to phytoplankton speciation. A survey of the mid-Atlantic Bight in April 1990 found low DMS concentrations in high-chlorophyll, shelf (1 nM DMS) and frontal (2 nM DMS) waters and higher levels in Sargasso Sea waters (~ 3 nM DMS) (Andreae, 1990); although this spatial variability was attributed to phytoplankton speciation, it was not tested. It is apparent that although enhanced nutrients can promote phytoplankton growth, it is most likely the interaction of all the above mentioned factors which resulted in the higher surface concentrations of surface DMS in the shoreward side of the Gulf Stream.

Concentrations of atmospheric DMS were lower and more constant (10–20 ppt) outside the frontal area, either in Slope or Stream waters

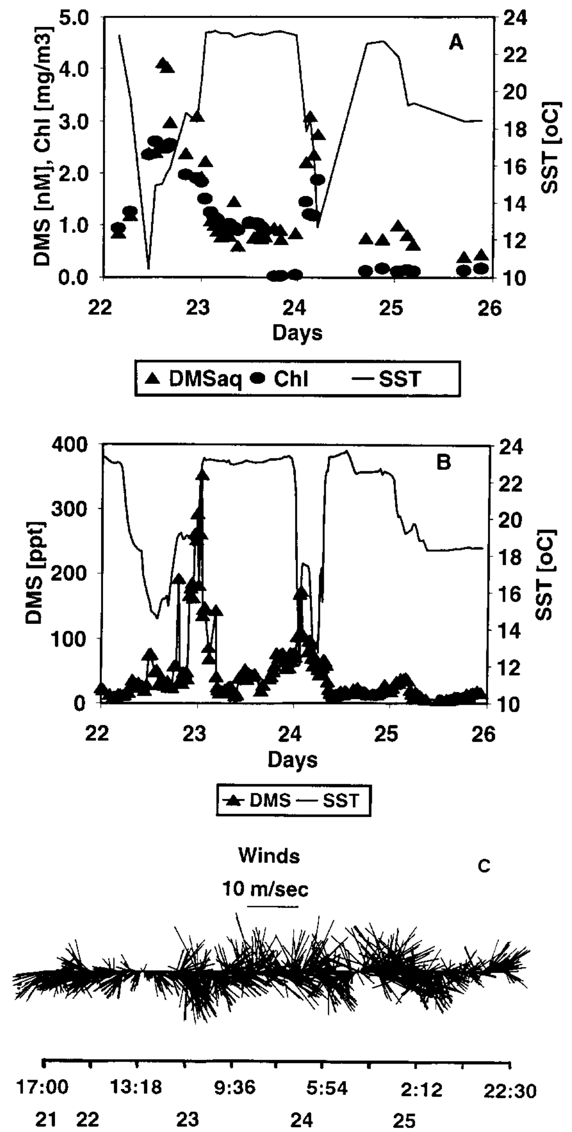

Fig. 2. (A) Sea surface DMS (▲), chlorophyll (•), SST (—), (B) atmospheric DMS (▲) and (C) wind direction and speed (m/s) measurements along the cruise track for the period of April 21–26, 1989.

(Fig. 2). At the northern wall of the Gulf Stream, a strikingly sharp increase in atmospheric DMS was observed (Fig. 4). Concentrations ranged from 11 to 354 ppt. Given average sustained winds of 10 ms^{-1} with gusts up to 25 ms^{-1} experienced in the sampling area (Fig. 2), it is remarkable that such strong and defined atmospheric DMS features were seen. The presence of an atmospheric DMS maximum at the western edge of the Stream must reflect a circulation pattern in the marine boundary layer of the area. Meteorological studies identify the north wall of the Gulf Stream as an extremely active site for cold-air outbreaks with formation of a strong marine atmospheric boundary layer front (Warner et al., 1990) and rapid development of cyclones (Sanders and Gyakum, 1980; Holt and Raman, 1990). The dynamic mechanisms responsible for this frontal circulation have not been conclusively identified although modeling studies suggest that this atmospheric frontal field can force local circulation in scales of half a day (Warner et al., 1990) to less than a week (Chao, 1992). Perhaps the sharp enhancement of atmospheric DMS at the Gulf Stream northern wall can be used as a tracer of atmospheric circulation patterns. Air spikes of DMS have been previously observed over Sargasso Sea waters (Andreae, 1985); it is suggested that such spikes result rather from the passage of fronts of continental air reducing atmospheric DMS concentrations through oxidation reactions.

In general, the atmospheric mixing ratio of DMS does not vary directly with the sea surface DMS concentrations. The aqueous and atmo-

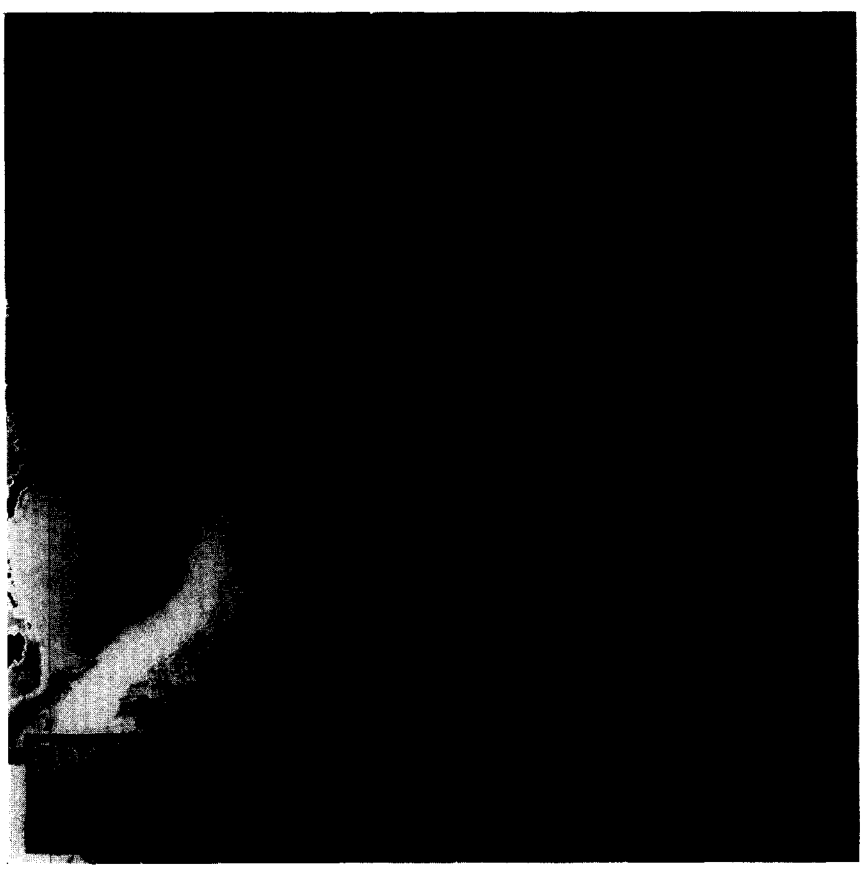

Fig. 3. Sea surface DMS measurements across a Gulf Stream meander during April 22–23, 1989, plotted on a composite thermal image for the period April 21–26, 1989.

spheric maxima of April 22 are clearly offset temporally even though the temporal resolution of the two data sets is different. The shipboard wind records indicate that this period of high atmospheric DMS corresponded to an area immediately downwind of an aqueous DMS maximum. These data indicate that the sea/air flux varied by a factor of > 30 across the frontal area. The winds during the second and third crossings of the Gulf Stream wall were variable enough (Fig. 2) to preclude any air trajectory analysis. On April 24th, it is likely that the atmospheric DMS was sampled upwind from its oceanic source region, as seen during the first crossing of the Gulf Stream (Fig. 1).

The DMS measurements made during the southwest transect away from the frontal area under steady meteorological conditions indicate correlation ($r = 0.54$) between atmospheric and aqueous DMS, indicating that continental effects were probably minimal in this study. This lends support to the argument that the lowest values of atmospheric DMS represent a change in the open ocean source rather than changes in atmospheric oxidant concentrations. It is hard to determine the relative importance of such a phenomenon to the regional atmospheric DMS budget for the mid-Atlantic Bight. However, assuming a constant increase along the meandering wall (since the spatial and temporal frequency of this phenomenon is unknown), a constant width of the Gulf Stream northern wall of 30 km (Von Arx, 1962) and a regional mean atmospheric DMS concentration of 15 ppt (mean of the range ob-

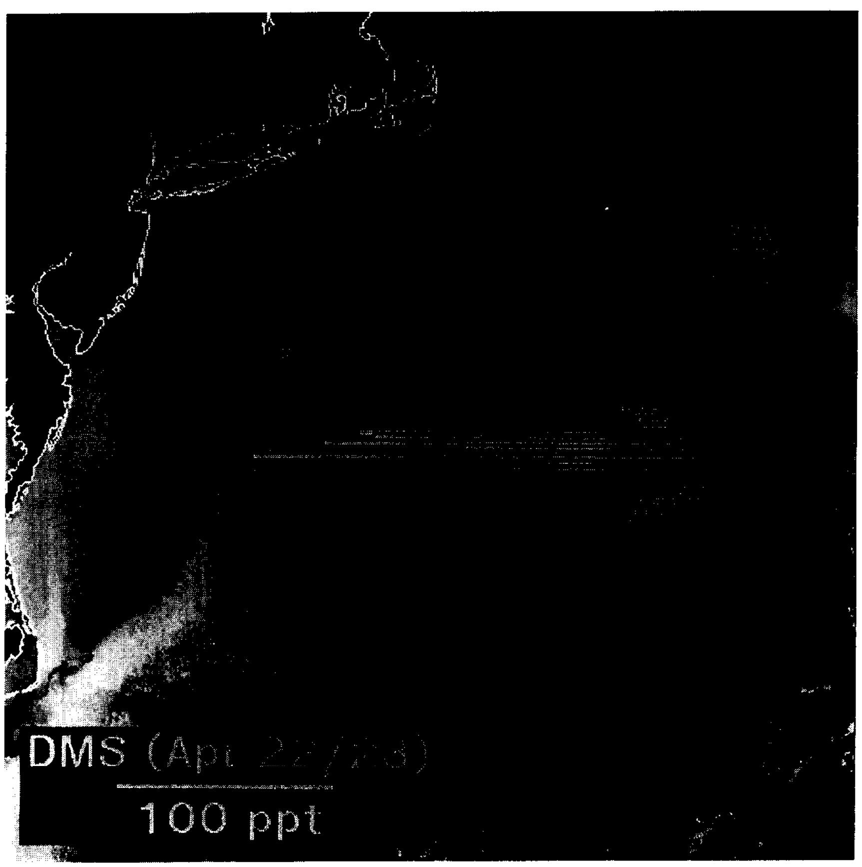

Fig. 4. Atmospheric DMS measurements across a Gulf Stream meander during April 22–23, 1989, plotted on a composite thermal image for the period April 21–26, 1989.

served away from the north wall of the time of sampling), these DMS spikes could represent as much as twice the background atmospheric DMS at that time. This calculation is based on the mid-Atlantic Bight extending as a triangle from Nova Scotia (46° N, 60° W) to Cape Hatteras, where the Gulf Stream turns east (35° N, 76° W) with the Gulf Stream forming the base.

The influence of meander circulation on aqueous DMS concentrations and its effect on atmospheric DMS concentrations has been explored. A sharp atmospheric signature was observed downwind from a sea-surface maximum, both located at the Gulf Stream front. The high winds present during this period might imply an enhanced DMS sea-to-air exchange while lowering the concentrations in surface waters.

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