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DMS air/sea flux and gas transfer coefficients from the North Atlantic summertime coccolithophore bloom

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[1] Dimethylsulfide (DMS) atmospheric and oceanic concentrations and eddy covariance air/sea fluxes were measured over the N. Atlantic Ocean during July 2007 from Iceland to Woods Hole, MA, USA. Seawater DMS levels north of 55°N ranged from 3 to 17 nM, with variability related to the satellite-derived distributions of coccoliths and to a lesser extent, chlorophyll. For the most intense bloom region southwest of Iceland, DMS air/sea fluxes were as high as 300 μmol m^{-2} d^{-1}, larger than current model estimates. The observations imply that gas exchange coefficients in this region are significantly greater than those estimated using most gas transfer parameterizations. South of 55°N, DMS levels were lower and the gas transfer coefficients were similar to those observed in other regions of the ocean. The data suggest that DMS emissions from the bloom region may be significantly larger than current estimates. The anomalous gas exchange coefficients likely reflect strong near-surface, water column DMS gradients influenced by physical and biological processes. **Citation:** Marandino, C. A., W. J. De Bruyn, S. D. Miller, and E. S. Saltzman (2008), DMS air/sea flux and gas transfer coefficients from the North Atlantic summertime coccolithophore bloom, *Geophys. Res. Lett.*, *35*, L23812, doi:10.1029/2008GL036370.

1. Introduction

[2] Oceanic emissions of DMS play a potentially important role in the earth's climate system, due to their role as a precursor for sulfate aerosol. For this reason, there has been considerable interest in understanding the biogeochemical controls on DMS (and its precursor, DMSP) in the surface ocean, on DMS air/sea exchange, and on DMS atmospheric chemistry. Because DMS levels in the surface ocean are biologically mediated, the potential exists for DMS involvement in feedback cycles involving climatic forcing and response of ocean ecosystems, aerosols, and clouds [*Charlson et al.*, 1987; *Shaw*, 1983].

[3] Estimates of the air/sea DMS flux are based on the expression: $F = k\Delta C$, where ΔC is derived from near surface (~1–5 m) seawater concentration measurements, and k is a gas transfer coefficient typically based on deliberate tracer and ^{14}C studies [*Nightingale et al.*, 2000a, 2000b; *Wanninkhof*, 1992]. These estimates assume that 1) subsurface DMS measurements are representative of "bulk" near surface DMS concentrations, and 2) the physics of transport of DMS across the air/sea interface is analogous to that of inert gases. The validity of these assumptions is supported by recent shipboard eddy covariance DMS flux measurements in tropical and subtropical Atlantic and Pacific open ocean waters [*Blomquist et al.*, 2006; *Huebert et al.*, 2004; *Marandino et al.*, 2007, 2008].

[4] In this study, shipboard measurements of atmospheric and oceanic DMS concentrations and eddy correlation air/sea fluxes were measured on a transect from Iceland to Woods Hole, MA, USA during July, 2007. The summertime high latitude North Atlantic Ocean is a region of extensive seasonal phytoplankton blooms, including some of the largest coccolithophore blooms in the world [*Balch et al.*, 1991; *Holligan et al.*, 1983]. Emiliania huxleyi, the main bloom-forming coccolithophore in this region, is a significant producer of DMSP, as demonstrated by both laboratory and field studies [*Archer et al.*, 2001; *Keller et al.*, 1989; *Malin et al.*, 1993].

2. Methods

[5] The Knorr_07 cruise left Reykjavík, Iceland on 17 July 2007, travelled SW, arriving at Woods Hole, MA, USA on 25 July 2007 (Figure 1). Environmental conditions changed from cloudy skies with positive (ocean to atmosphere) sensible and latent heat fluxes (SH and LE, respectively) from 55–63°N, to foggy with positive and negative SH and LE from 47–55°N, to sunny/partially cloudy skies with near zero/positive SH and LE fluxes from 43–47°N. DMS measurements in air and seawater were made using atmospheric pressure chemical ionization mass spectrometry (API-CIMS). Atmospheric DMS was sampled from the bow mast at 10 m height through a Teflon filter and 28 m of ½″ OD Teflon tubing at 30 L min^{-1} STP. DMS in air was detected using the instrument described by *Marandino et al.* [2007]. Three dimensional wind speed, direction, and virtual temperature were measured using a CSAT-3 sonic anemometer (Campbell Scientific) and ship motion was measured with a MotionPak II (Systron Donner). Seawater from the ship's scientific seawater system (intake 5 m depth, 1 L min^{-1}) was equilibrated with 60 cm^3 min^{-1} STP of purified air (Aadco Instruments) across a single-tube porous PTFE membrane equilibrator. The equilibrated gas stream was diluted with purified air, and analyzed for DMS using a second API-CIMS instrument. Seawater concentrations were computed using equilibrator temperature and the DMS solubility relationship of *Dacey et al.* [1984]. DMS mixing ratios in ambient and equilibrator air were quantified using an isotopically labeled internal standard (CD_3SCH_3). Data was acquired using single ion monitoring of $CH_3SCH_3^+$ and $CD_3SCH_3^+$ (m/z = 63 and 66) at 10 Hz for ambient air

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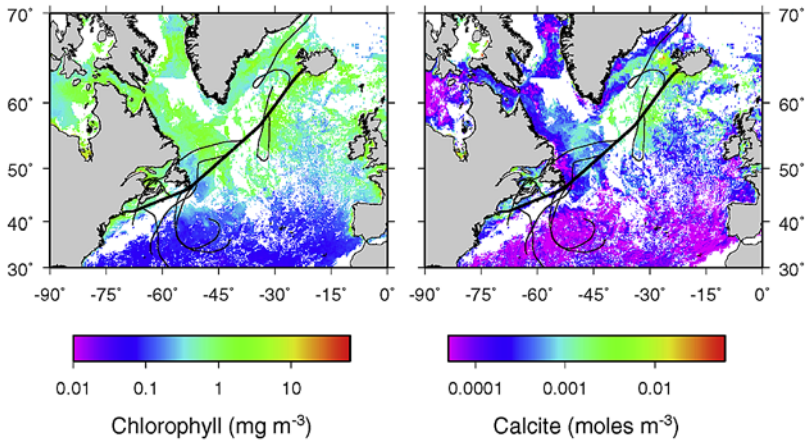

Figure 1. Knorr_07 cruise track (dark black line) with 5 day air mass back trajectories (light black lines) superimposed on MODIS 8 day (left) chlorophyll and (right) calcite images from July 12–19, 2007.

and 1 Hz for equilibrator air. DMS flux data processing was completed in 20 minute intervals. Details regarding the experimental setup, data processing, quality control, and ancillary data are given by *Marandino et al.* [2007].

3. Results and Discussion

3.1. Distribution of Seawater DMS

[6] The cruise track transited three oceanographic provinces as defined by *Longhurst* [1998]: the Atlantic Arctic (ARCT), the North Atlantic Drift (NADR), and the Northwest Atlantic Shelves (NWCS). The underway seawater DMS measurements are shown as a function of latitude in Figure 2, with shipboard flow-through chlorophyll fluorescence and satellite-based chlorophyll and calcite products from MODIS. The MODIS calcite product is derived from the reflectance of visible light from coccolithophore cells and detached coccoliths [*Balch et al.*, 1991; *Holligan et al.*, 1983].

[7] The highest DMS levels encountered on this cruise were observed in ARCT waters southwest of Iceland (55–62°N), in conjunction with the highest fluorescence, chlorophyll, and calcite signals. DMS levels in this region averaged 8.63 ± 2.77 nM (1σ), MODIS images show the appearance of coccoliths in these waters during July, a few weeks before this cruise and well after the onset of the spring chlorophyll bloom. Previous studies have reported comparable DMS levels of 2–25 nM in this region during June through July [*Jickells et al.*, 2008; *Simó et al.*, 2000; *Steinke et al.*, 2002].

[8] The NADR region, from 48–55°N, marked a transition to a region of lower DMS levels, 2.86 ± 1.12 nM. This region was characterized by slightly lower fluorescence and chlorophyll levels and significantly lower calcite levels than those to the northeast. There was no satellite evidence of coccolith blooms in these waters prior to July. There are few published DMS measurements from this region during summer. *Andreae et al.* [1985] reported 1–25 nM just south of this area in May and *Scarratt et al.* [2007] reported DMS levels around 1 nM from this region in September.

[9] Fluorescence, chlorophyll, calcite, and DMS levels dropped sharply (1 nM) as the cruise track crossed into the NWCS around 48°N. Through the Gulf of Maine towards Woods Hole, DMS levels became more variable, ranging from 2–5 nM. The average for this entire region was 2.00 ± 0.79 nM. At 44°N there is a region of elevated DMS that is coincident with a peak in fluorescence, chlorophyll, and calcite. *Matrai and Keller* [1993] reported July DMS values of 1–8 nM, similar to those found here.

3.2. Atmospheric DMS Levels and the Saturation State of the Sea Surface

[10] Atmospheric DMS levels followed a similar trend as the seawater DMS concentrations. The mean atmospheric mixing ratios in the three oceanographic regions were: 1459 ± 866, 371 ± 234, and 212 ± 124 ppt, respectively (Figure 3). Air mass back trajectories indicated that the air over the ARCT region came from higher latitudes, above waters that contained high levels of chlorophyll and calcite.

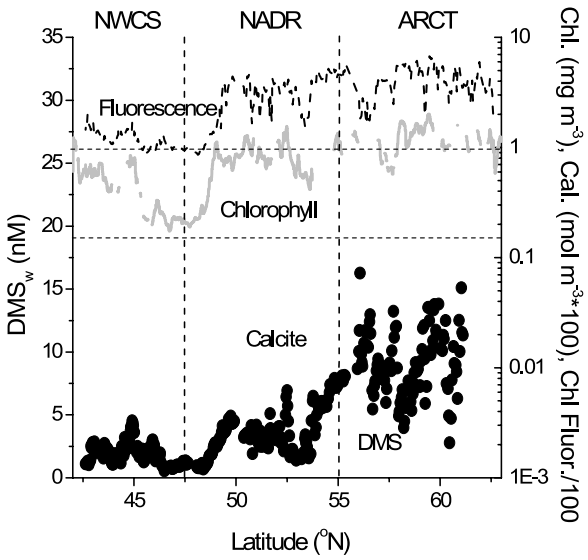

Figure 2. Latitudinal variations in seawater DMS (black circles), calcite (black line), chlorophyll (gray line), and shipboard fluorescence (unitless, dashed line). Vertical dashed lines indicate boundaries of oceanographic regions and the horizontal dashed lines indicate mean chlorophyll and calcite levels in the coccolith-rich bloom region.

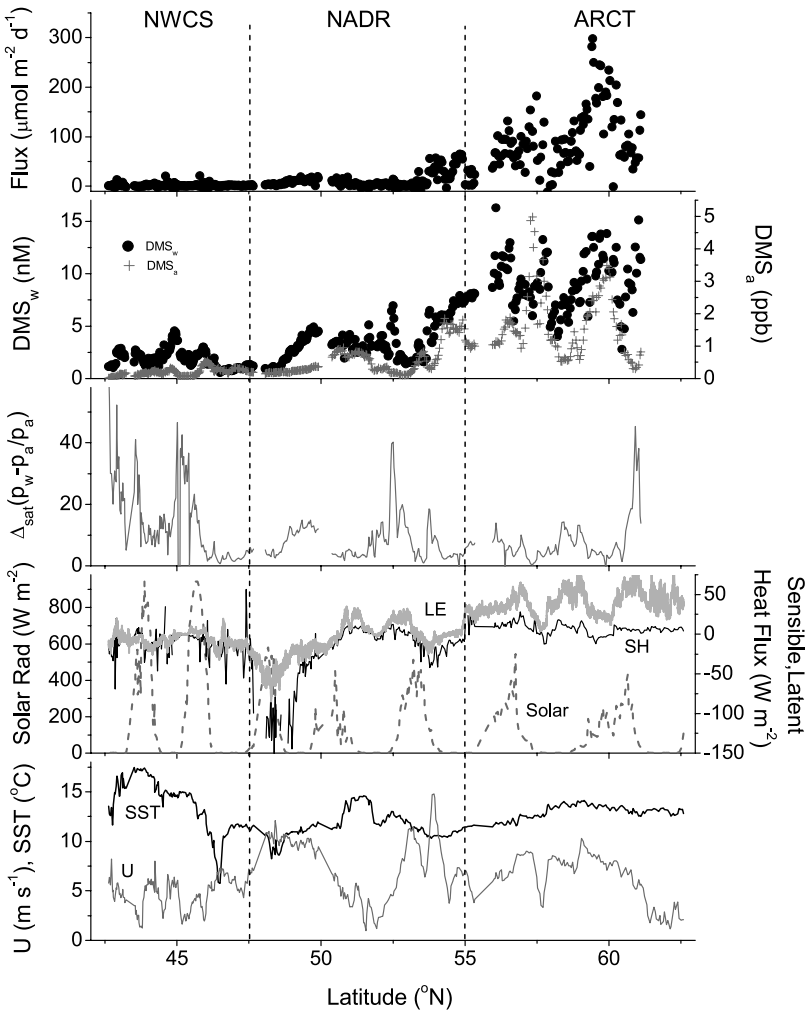

Figure 3. Shipboard DMS measurements from Knorr_07 cruise, eddy covariance air/sea flux, surface ocean (solid circles) and atmospheric DMS (plus signs), DMS saturation anomaly, downwelling short wave solar radiation (dashed gray line), calculated latent heat flux (gray line), and eddy covariance sensible heat flux (black line). Positive values indicate flux from ocean to atmosphere, sea surface temperature (black line) and horizontal wind speed (grey line).

The air sampled in the NADR region was largely from the North American coast, also above high chlorophyll and calcite waters. The NWCS air masses came mostly from the gyre region, over low chlorophyll and calcite waters.

[11] The sea surface DMS saturation anomaly was computed as $\Delta_{sat} = (p_w - p_a)/p_a$, where p_a and p_w are the DMS partial pressures in air and seawater (Figure 3). Δ_{sat} ranged from near equilibrium ($\Delta_{sat} = 0$) to 60-fold supersaturated. In general, the lower saturation states occurred in the ARCT and NADR regions, reflecting locally high DMS fluxes, air masses originating over high DMS waters, and cloudy conditions. The saturation anomaly exhibits an interesting apparent cyclicity, but did not maintain a systematic phase relationship to the diel cycle.

3.3. Air/Sea Fluxes and Gas Transfer Coefficients

[12] In general, the magnitude of the DMS air/sea fluxes varied with the levels of DMS in seawater. In the ARCT waters, DMS fluxes were extremely high, with an average of 96.7 ± 63.0 μmol m^{-2} d^{-1}. The fluxes were approximately an order of magnitude lower in the NADR region, with an average of 8.35 ± 5.19 μmol m^{-2} d^{-1}. In the NWCS waters, DMS fluxes were still lower, averaging 3.08 ± 2.64 μmol m^{-2} d^{-1}.

[13] Gas exchange coefficients were calculated from the measured fluxes and gradients between the bulk atmospheric and oceanic concentrations, as $k_{DMS} = F/\Delta C$ (Figure 3). For comparison with other datasets, the k values were normalized by $Sc^{-0.5}$, to $Sc = 720$, which is the value for DMS at 25°C [*Saltzman et al.*, 1993]. High and variable gas exchange coefficients were observed in the Arctic region from 55–62°N, which are markedly different from those observed for waters south of this region. This pattern is not simply a result of regional variations in wind speed, as illustrated in the plot of k vs. U (Figure 4). The data from southward of 55°N are similar to prior field measurements of oceanic DMS fluxes and are consistent with existing gas transfer parameterizations [*Marandino et al.*, 2008]. The elevated gas exchange coefficients from the more northerly coccolith-rich bloom region are anomalously high, and appear to exhibit a steeper wind speed relationship. The data from this region was carefully examined for analytical artifacts, but appeared normal in terms of the shape of the cospectra [*Kaimal et al.*, 1972], the influence of ship motion, the

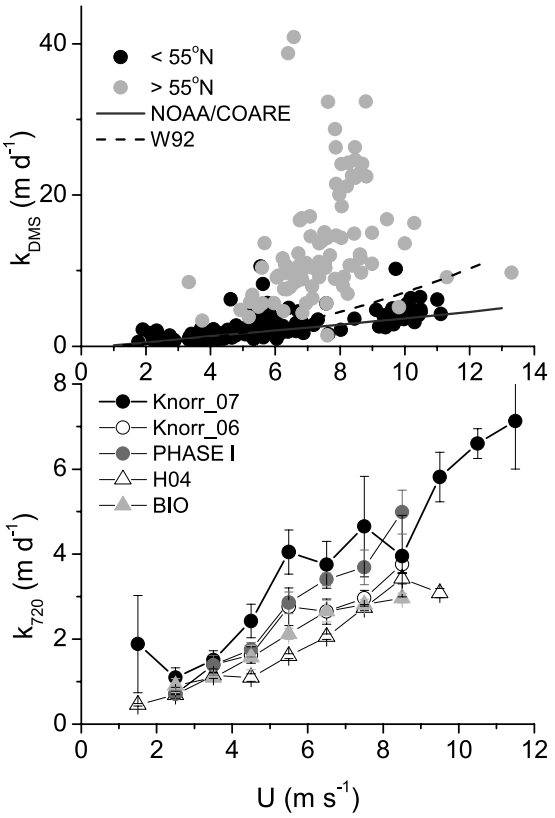

Figure 4. DMS gas exchange coefficients versus mean wind speed from this and previous DMS eddy covariance flux studies. (top) k_{DMS} from Knorr_07 segregated by latitude (●–>55°N, ●–<55°N), and parameterizations from *Wanninkhof* [1992] (W92) and the NOAA/COARE model for mean cruise conditions [*Fairall et al.*, 2000]. (bottom) Comparison of Knorr_07 data (<55°N subset only) to H04 [*Huebert et al.*, 2004], BIO [*Blomquist et al.*, 2006], PHASE I [*Marandino et al.*, 2007], and Knorr_06 [*Marandino et al.*, 2008]. The data are binned in 1 m s^{-1} intervals and normalized to *Sc* = 720.

response of the mass spectrometers to the internal standards, and the background spectra in the API-CIMS instruments. It is unlikely that the eddy covariance measurements were affected by non-neutral atmospheric stability caused by air and water temperature changes (e.g., during foggy/cloudy periods), because these conditions were present during and after the high flux measurements were made (Figure 3).

4. Implications

[14] The high concentrations of seawater DMS observed in the North Atlantic bloom region are not surprising and are similar in magnitude to those previously observed in biologically productive North Atlantic waters. What is surprising is the observation of DMS fluxes in the bloom region that are greater than expected, based on various gas transfer parameterizations [*Liss and Merlivat*, 1986; *Nightingale et al.*, 2000b; *Wanninkhof*, 1992]. A companion paper to this (S. D. Miller et al., submitted manuscript, 2008), shows that eddy covariance CO_2 fluxes measured in this region were not anomalous. Barring some major analytical error, the anomalous DMS fluxes observed in this field study suggest that there are unusual characteristics of the air/sea interface in the coccolith-rich North Atlantic bloom region.

[15] One possibility is that the air/sea gradient was underestimated due to strong near surface enrichment of DMS, relative to the level at the ship's 5m scientific seawater intake. Maintaining such strong enrichment at wind speeds of several m s^{-1} would require very active near surface biological cycling (perhaps at the interface itself), and near surface stratification. *Kettle and Turner* [2007] showed that under light-to moderate wind conditions, the ocean in this region tends to stratify to the surface. Stratification alone should lead to surface depletion of DMS due to photochemical destruction or air/sea gas exchange. The results here suggest enrichment, which requires that there be a near-surface source of DMS. Several previous studies have sought evidence of interfacial enrichment of DMS, with conflicting results [*Matrai et al.*, 2008; *Yang et al.*, 2008, 2005; *Yang and Tsunogai*, 2005; *Yang*, 1999; *Zemmelink et al.*, 2005a, 2005b]. This might be expected, given the difficulty of analyzing a dissolved gas in the thin film of a moving gas/liquid interface.

[16] This study is the first to indicate such a dramatic mismatch between DMS flux estimates from gas transfer parameterizations, and directly measured flux. One obvious implication of these observations is that models treating DMS as a passive tracer across the uppermost few meters of the ocean may not be accurate for extensive coccolithophore blooms. Another implication is that the DMS flux and the inferred DMS-derived sulfate aerosol production in the North Atlantic bloom region may be considerably underestimated by conventional parameterizations. Most models compute the biogenic contribution to sulfate aerosols from oceanic DMS using the *Kettle et al.* [1999] DMS climatology coupled with the *Liss and Merlivat* [1986] model for gas exchange [*Benkovitz et al.*, 1994; *Chin et al.*, 2000:, *Gondwe et al.*, 2003]. The directly measured fluxes in this study were more than 5-fold greater than those resulting from such calculations. This study suggests the need for more detailed physical, chemical, and biological studies of the near surface water column in this and other highly productive regions.

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