Field measurements of dimethyl sulphide and its oxidation products in the atmosphere

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SUMMARY

Dimethyl sulphide (DMS) is released into ocean waters by phytoplankton and may then cross the water–air interface into the atmosphere. Various models have been formulated to describe its behaviour in the atmosphere. Here, measurements of its concentrations and those of its major oxidation products, methane sulphonate, sulphur dioxide, non sea-salt sulphate and dimethyl sulfoxide, in both the gas and aerosol phases, in Atlantic air, are used to validate these qualitative descriptions of its oxidation. Behaviour consistent with day-time oxidation by the hydroxyl radical, with the yield of methane sulphonic acid being both temperature dependent and under the influence of the nitrogen dioxide mixing ratio, is seen. The rapid production of new particles also seems likely under certain conditions but it is not clear whether or not they enhance the concentrations of cloud condensation nuclei in the maritime troposphere. In maritime air a substantial fraction of the sulphate formed appears to be neutralized by reaction with ammonia to form ammonium aerosol.

1. INTRODUCTION

Dimethyl sulphide (DMS) is produced as a by-product of the metabolism of marine phytoplankton and is emitted into the atmosphere as a result of its very large concentration difference across the air–water interface. It is believed to be oxidized in the atmosphere to give a variety of gas and aerosol phase products (e.g. Hertel *et al.* 1994). It is possible that these products may influence cloud condensation nuclei (CCN) concentrations in the maritime atmosphere and hence may have direct and indirect effects on the planetary radiation balance and hence on global climate (Charlson *et al.* 1987; Schwartz 1988). In order therefore to be able to calculate the magnitude of such effects on climate it is necessary to have a detailed understanding of the rates of DMS emission from the oceans to the atmosphere and of the mechanisms that control DMS behaviour in the atmosphere. In particular it is necessary to understand what the yields of aerosol phase products are, and how these aerosol phase products themselves behave in the atmosphere.

Several attempts have been made to model the behaviour of DMS in the atmosphere and to construct chemical mechanistic schemes that describe DMS oxidation. These have largely been based on experimental data collected in controlled laboratory experiments. For example, Yin *et al.* (1986, 1990*a,b*) have proposed DMS oxidation mechanisms and validated them by smog chamber type experiments. Similarly, Barone *et al.* (1995) have used experimental and modelling studies to probe details of the DMS reaction scheme and have hypothesized that sulphur adducts play a crucial role in its oxidation in the atmosphere.

Much less emphasis has been placed on the use of field studies of biogenic sulphur in the atmosphere to elucidate details of the DMS reaction mechanism and its fate, and that of its products, in the atmosphere. Davison & Hewitt (1994) used information collected during a field campaign in NW Scotland to investigate the route of DMS oxidation and were able to show that the results obtained were consistent with the removal of DMS during the day-time by chemical reaction (presumably with the hydroxyl radical, OH) and that sulphur dioxide and sulphate aerosol are major oxidation products.

Here, we attempt to go further and to use field data collected at a number of sites bordering the eastern Atlantic and during a ship cruise from the United Kingdom to Halley Bay in the Weddell Sea area of Antarctica to test various hypotheses concerning DMS occurrence and behaviour in the atmosphere. The data used for this purpose are only a small selection of those published; we do not intend this paper to be a full review of DMS field studies. Neither is it possible to consider every possible hypothesis concerning DMS oxidation; we select for attention those hypotheses that are most pertinent to the possible DMS–climate link and for which we have relevant field data.

2. HYPOTHESES TESTED

Current understanding of the occurrence and behaviour of DMS in the atmosphere may be summarized as follows:

DMS is produced as a by-product of the metabolism of phytoplankton in ocean surface waters (Liss *et al.* 1994). Because of its high concentration in seawater

relative to that in air and its insolubility in water it is transferred across the water–air interface and enters the atmosphere (a process quantitatively described by Liss & Slater (1974)). There it is oxidized, in the day-time by the hydroxyl radical (OH) and at night-time by the nitrate radical (NO_3), to give a range of unstable, semi-stable and stable products (Yin *et al.* 1990a; Hertel *et al.* 1994). These products include dimethyl sulphoxide (DMSO), dimethyl sulphone (DMSO_2), sulphur dioxide (SO_2), sulphuric acid (H_2SO_4), non sea-salt sulphate (NSSS) in the aerosol phase and methane sulphonic acid (MSA), also largely present in the aerosol phase. The relative yields of each of these products may vary with differing environmental conditions. In particular, the yield of MSA relative to H_2SO_4 may increase with decreasing ambient temperature and with increasing ambient concentrations of nitrogen dioxide (Turnipseed & Ravishankara 1992). The formation of these aerosol phase products may lead to the production of new aerosol particles in the atmosphere (Ayers & Gras 1991). Charlson (1992) suggested that the concentrations of cloud condensation nuclei in the maritime atmosphere are controlled by gas-to-particle conversion processes (i.e. by the oxidation of gas phase precursors to aerosol phase products), but it is unclear at present whether or not the oxidation of DMS plays a major role in this (Hegg *et al.* 1991).

3. METHODS

(a) Sampling and chemical analyses

Various methods have been used for the determination of DMS in ambient air, but in the work described here air was pressurized into stainless steel cylinders using a Teflon headed pump. Air from the cylinders was then passed at a known rate via a mass flow meter through a 'Nafion' drier to remove water vapour and through a mixture of potassium iodide (KI) and magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$) to remove oxidants from the sampled air. DMS was preconcentrated from the air onto Tenax porous polymer held in a Teflon loop at -150°C . The sample was then thermally desorbed onto a Hewlett Packard gas chromatograph (GC) fitted with a Chromosil 330 column and a flame photometric detector (FPD), doped with COS to enhance sensitivity (Putaud *et al.* 1993; Davison & Hewitt 1992). The GC was calibrated daily using a DMS permeation tube. This method gives a detection limit for DMS in air of about 10 pptv with a precision and accuracy of better than $\pm 10\%$.

Sulphur dioxide was analysed using a pulsed fluorescence SO_2 analyser (Thermo Environmental Instruments) with a detection limit of about 0.1 ppbv. Data were logged every one minute. Calibration was performed using either an SO_2 permeation tube or a calibrated gas standard and a multipoint gas calibration system (Thermo Environmental Instruments).

In some cases sulphur dioxide was also determined using chemically impregnated (K_2CO_3 and glycerol) prewashed Whatman 54 filters. A 0.45 μm PTFE membrane was used as a front pre-filter to remove particulate sulphate already present in the atmosphere,

and the gaseous SO_2 was retained as sulphite (SO_3^{2-}) on the second filter. Filters were treated with H_2O_2 to ensure complete oxidation of the complexed SO_3^{2-} to SO_4^{2-} which was then analysed by ion chromatography (IC) (Davison & Hewitt 1992; Ferek *et al.* 1991).

Aerosol phase species were sampled using a high volume air sampler with Whatman QMA filters. Filters were extracted in 18 megaohm water and analysed for MSA, Cl^- , NO_3^- and SO_4^{2-} by IC using an AS4-A column on a Dionex 4000i instrument. Flame photometry was used for the analysis of Na^+ (Davison & Hewitt 1992). Detection limits of about 1 nmol m^{-3} for Cl^- and NO_3^- and 0.3 nmol m^{-3} for SO_4^{2-} were obtained.

A TSI 3025 ultrafine condensation particle counter (TSI, St Paul, MN) was used to measure the number concentration of the ambient aerosol in the size range 3 nm–5 μm diameter (the condensation nuclei).

Information on the chemical composition of the ambient aerosol was obtained with a thermal analytical or volatility technique. It consists of a heated quartz inlet tube in front of a PMS ASAP-X optical particle counter. The inflowing air is heated to 1050°C , causing fractions of the ambient aerosol to evaporate at specific, characteristic, temperatures and thus allowing the chemical composition of the aerosol to be inferred. With this method, sulphuric acid, ammonium sulphate/bisulphate, sea salt and soot carbon are some of the chemical species that can be identified (O'Dowd *et al.* 1992). The size range of the particles detected with this instrument is 0.1–3 μm diameter. The aerosol size characteristics determined by this method are independent of relative humidity (O'Dowd *et al.* 1993) since they are measured at about 30°C above ambient temperatures before being subjected to volatilization. They thus represent the size of the dry aerosol.

(b) Sampling locations

Sampling locations were generally chosen to allow the study of the biogenic sulphur system with minimum perturbation from possible anthropogenic inputs. To this end sites in remote locations on the west coast of Scotland (Isles of Lewis and South Uist) (Davison & Hewitt 1992), Mace Head on the west coast of Ireland and Pointe de Penmac'h in Brittany have been used on a number of occasions. All of these sites have a clean sector from north-west to south-west when relatively clean, unpolluted, Atlantic air can be sampled. In addition, Pointe de Penmac'h has extensive algal fields exposed at low tides, offering a significant local source of DMS, thus allowing the rapid atmospheric reactions of the gas to be investigated (Putaud *et al.* 1996). A site at Weybourne in Norfolk on the North Sea coast has also been used as this offers the possibility of sampling both relatively clean North Sea air in northerly air masses and recently polluted air in southerly air masses. The Antarctic offers the cleanest atmosphere available in which to study atmospheric processes, in particular new particle formation, and this has been utilized in an extensive series of measurements made aboard the RRS *Bransfield* on a cruise from the United Kingdom to Halley Bay (Davison *et al.* 1996).

4. RESULTS AND DISCUSSION

The first hypothesis concerning DMS testable with field data is whether or not DMS concentrations in air are related to phytoplankton productivity (Turner *et al.* 1988). If they are, then it would be expected that a strong seasonal variation in DMS concentrations would be observed, since it is clear that phytoplankton productivity is very strongly variable with season (phytoplankton blooms occurring in spring and summer). Figure 1 shows the concentrations of DMS in air measured at a coastal site at Lewis, in the Outer Hebrides, together with extrapolated values for periods when measurements were not available (Davison & Hewitt 1992). A clear seasonal signal is observed, with concentrations varying from < 1 to $885 \text{ ng (S) m}^{-3}$, with peak concentrations occurring in the late spring, coinciding with periods of phytoplankton bloom in the north Atlantic. Mean DMS concentrations at the site in 1989/90 were 58 ng (S) m^{-3} , and a simple steady-state model of the chemistry of DMS in the atmosphere was used to estimate that an ocean-to-atmosphere flux of $0.93 \mu\text{mole m}^{-3} \text{ day}^{-1}$ from the northern north Atlantic was necessary to sustain such atmospheric concentrations. If all the sulphur emitted by the north Atlantic contiguous with the United Kingdom is advected into the country, it is estimated this would equal about 10% of current (1996) SO_2 emissions in the U.K., on an annual basis.

Peak DMS concentrations have also been observed in the springtime in the Southern Hemisphere by Ayres *et al.* (1991). Although this is all only circumstantial evidence, it does suggest that oceanic phytoplankton are the major source of DMS in the atmosphere.

The second hypothesis concerning DMS is that it is

Figure 1. DMS concentrations in air, Outer Hebrides.

Figure 2. Diurnal cycle in DMS concentrations with estimated OH, NO_3 and DMS concentrations.

oxidized in the atmosphere by gas phase reactions initiated, in the day-time, by the hydroxyl radical, OH, and at night-time by the nitrate radical, NO_3 . The concentrations of OH in the troposphere are believed to vary with light intensity, the ultraviolet actinic flux, and the concentrations of water vapour, ozone, nitric oxide, methane and carbon monoxide (Hewitt & Harrison 1985). Although the concentrations of OH are too low to be routinely measured it is possible to estimate their magnitude by modelling calculations (Logan *et al.* 1981). They are believed to be essentially zero at night-time and to rise to a maximum of around 10^6 cm^{-3} at midday. In contrast, NO_3 concentrations are essentially zero during the day-time, because of its rapid photolysis by light of wavelength $< 670 \text{ nm}$, but may approach 0.5 pptv at night-time (Logan 1983).

Rate constants for the reactions of DMS with OH and NO_3 have been obtained from laboratory experiments (e.g. Tyndall & Ravishankara 1991) and it is believed that both reactions are important in the ambient atmosphere, in contrast to those of ozone and IO which are too slow to be appreciable sinks of DMS (Atkinson & Carter 1984; Daykin & Wine 1990; Maguin *et al.* 1990).

Figure 2 shows the diurnally varying concentrations of DMS measured at Lewis during April 1990 (mean of six days' data). Clear early morning maxima of 100 pptv and late afternoon minima of 45 pptv are apparent. In addition, the ambient concentrations of DMS, OH and NO_3 estimated from a simple model of the chemistry of the maritime troposphere (Andreae *et al.* 1985) are shown, with a day-time maxima for OH and a night-time maxima for NO_3 . The rates of change in DMS concentrations, assuming a constant flux from the ocean surface to the atmosphere, are broadly consistent with the rates of change and absolute magnitudes of the concentrations of the two oxidants, suggesting that current models of DMS oxidation by

Figure 3. Diurnal cycle in MSA concentrations at Weybourne.

OH, with oxidation by NO_3 being of secondary importance, are probably substantially correct.

The third hypothesis to be examined is that concerning the production of MSA from DMS. All current models predict that MSA is a stable product of DMS oxidation. If this is the case, given the relatively rapid rate of this reaction at ambient concentrations of OH, MSA concentrations would be expected to show a diurnal cycle with a day-time maxima (i.e. as DMS is removed during daylight hours, so MSA is produced). However, the yield of MSA is predicted to be rather low (< 10% of total oxidized DMS) in temperate latitudes.

Figure 3 shows aerosol-phase MSA concentrations obtained at the Weybourne sampling site during June 1995. MSA samples were obtained at 07.00, 13.00 and 18.00 GMT on each of 30 days. Mean concentrations of 140, 270 and 120 ng m^{-3} respectively were found, showing a statistically significant midday maximum, with lower early morning and evening concentrations, as predicted by current models of DMS oxidation. The amplitude in this signal of a factor or two is rather smaller than the amplitude in the DMS signal (factor of three) but it may be that the minimum concentrations of MSA were not observed, occurring later at night.

The fourth hypothesis to be tested is a detail of DMS oxidation that is predicted by several current reaction schemes (Yin *et al.* 1990a; Barone *et al.* 1995; Jenkin *et al.* 1996). It is that the yield of MSA relative to that of SO_4^{2-} increases as ambient temperature decreases. Earlier studies attributed this to changes in the branching ratio of the initial DMS–OH reaction, with the addition reaction being favoured at lower temperatures (Hynes *et al.* 1986). More recently, Barone *et al.* (1995) have suggested that the enhanced yield of MSA at lower temperatures is due to competition between the thermal decomposition of

Figure 4. MSA/NSSS ratio with temperature.

adducts such as CH_3SO_2 and their bimolecular reactions with other atmospheric species. Clearly, field studies are unlikely to be able to distinguish between these detailed chemical mechanisms. Nevertheless it does seem possible to test the general hypothesis that MSA production is enhanced at lower temperatures.

Figure 4 shows the ratio of MSA to non-sea salt sulphate (NSSS) concentrations obtained during the voyage of the RRS *Bransfield* from the United Kingdom to Halley Bay in the Weddell Sea area of Antarctica in 1992/93 plotted against ambient air temperature at the time of sampling. A very significant enhancement in this ratio is observed at temperatures below 280 K. Above this temperature, ratios of less than 0.05 were found, but below it ratios up to 0.6 (with one value in excess of 1.0) were observed. Jenkin *et al.* (1996) have used a simplified DMS reaction mechanism to predict the values of this ratio at varying temperatures, and the resultant curve is superimposed on the data in figure 4. It is apparent that the modelled values are substantially greater than the observed values at most temperatures, but nevertheless a curved relationship with temperature is both predicted and observed, suggesting that the current models of DMS oxidation are, at least qualitatively, correct in this detail.

A further detail of current models of DMS oxidation is that the ambient concentration of nitrogen dioxide, NO_2 , may affect the yield of MSA relative to NSSS, with increasing NO_2 concentrations leading to enhanced yields of MSA. Qualitative evidence for such an effect was observed in data collected in Lewis in 1988 to 1990 (Davison & Hewitt 1994). Unfortunately, ambient concentrations of NO_2 were not directly measured but backward air mass trajectories were used to distinguish between polluted and relatively unpolluted air masses, and the conclusion drawn that MSA concentrations, relative to those of NSSS, were enhanced in freshly polluted air which, it was assumed, contained higher concentrations of NO_2 .

One of the predicted intermediate, semi-stable, products of DMS oxidation is believed to be dimethyl sulphoxide (DMSO) (Yin *et al.* 1990*a*). There are rather few reliable measurements of this compound in ambient air (and none of its oxidation product, dimethyl sulphone). Berresheim *et al.* (1993) detected a diurnal cycle in DMSO concentrations, with a day-time maximum, in Pacific maritime air, consistent with its production from DMS oxidation. Recently, observations of its occurrence have been reported at a site in Brittany (Putaud *et al.* 1996) with concentrations in the range 0.25–65 pmol m⁻³, with a mean of 19 pmol m⁻³ ($n = 15$). A simple box model was used to estimate the yield of DMSO production from DMS oxidation necessary to sustain the observed ambient concentrations of the product. This was estimated to be about 1%.

The next hypothesis to be considered is that the aerosol phase acidic products of DMS oxidation may be neutralized by ammonia in the maritime atmosphere. O'Dowd *et al.* (1996) used a technique that investigates the volatility characteristics of the aerosol particles in sampled air to infer information about the chemical composition of the ambient aerosol. During the cruise of the RRS *Bransfield* in 1992/93 it was found that aerosol particles in polar air masses arriving from the Antarctic continent consisted mainly of H₂SO₄ in the accumulation mode size range, with inferred NH₄⁺ to SO₄²⁻ molar ratios close to zero. By comparison, air masses sampled in the northern Weddell Sea area but of temperate maritime origin were significantly neutralized, with molar ratios around unity. These results suggest a deficit of ammonia in polar air compared with that in maritime air.

The last hypothesis to be considered is that DMS emissions have an impact on the formation of new particles in the maritime atmosphere. O'Dowd *et al.* (1996) observed background condensation nuclei (CN) concentrations in the range 400–600 cm⁻³, with frequent bursts of high concentrations, with peaks up to 5000 cm⁻³. These periods generally coincided with periods of high DMS concentrations in areas of broken pack ice, and with a decrease in the surface area of the aerosol. Peak CCN concentrations of about 60 cm⁻³ were observed. Using a steady state approximation, background aerosol formation rates of around $(3-7) \times 10^{-4}$ cm⁻³ s⁻¹ were predicted, rising to about 3 cm⁻³ s⁻¹ during nucleation bursts. These 'new particles' rapidly coagulate, giving rise to a decay in the CN concentrations, returning concentrations to the background. In addition, the estimated rates of production seem to be too low to sustain the observed CCN concentrations, suggesting that other sources of these activated particles must be present in the boundary layer.

5. CONCLUSIONS

Many field studies of DMS and its oxidation products in the maritime atmosphere have been carried out. However, the data obtained have limitations which hinder their utility in the validation of models of

DMS oxidation. There are considerable logistical, practical and financial constraints on the number of field data obtained, on the locations of measurement sites, on the time resolution of samples and on the nature of the air masses sampled. The ambient atmosphere is an uncontrolled environment, in contrast to a chemical reactor in a laboratory or a computer simulation of the chemistry and physics of the oxidation of a gas. Hence it has to be recognized that the possibilities for the validation of detailed models of the behaviour of DMS and its products in the atmosphere are severely limited.

Despite these limitations, a qualitative agreement, at least, has been observed between current hypotheses concerning DMS oxidation and field measurements of DMS and its products. The seasonal and diurnal behaviour of DMS are consistent with its production as a result of biological activity in ocean surface waters and gas phase oxidation by the hydroxyl radical during the day-time and, at a slower rate, by the nitrate radical at night-time. Several predicted products of DMS oxidation are observed in the ambient atmosphere, including DMSO, MSA and H₂SO₄. The enhanced production of MSA, relative to N₂SSS, during periods of elevated NO₂ concentrations and at lower ambient temperatures are two features of current oxidation schemes that are supported by the field measurements presented here. In addition, the neutralization of acidic sulphur compounds by ammonia, probably itself of a biogenic maritime source, is also observable. The production of bursts of new particles resulting from gas-to-particle conversion processes is a clear feature of field studies of the ambient aerosol, but it is not possible at present to answer the question whether or not these particles contribute to the elevation of cloud condensation nuclei concentrations or whether they rapidly coagulate to give larger particles.

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Discussion

R. A. COX (*University of Cambridge, UK*). How do you reconcile the low yield of DMSO (1%) from DMS oxidation based on the observations in the atmosphere with the higher yield (up to 50%) implicit in the current picture given by Dr Ravishankara of the initial addition of OH to DMS?

N. HEWITT. At the Penmarch lighthouse site there is a very strong local source of DMS emissions. Given the very short travel times from the inter-tidal algal beds to the measurement point we do not expect DMS concentrations to be in equilibrium with those of its oxidation products. If we were able to measure DMSO further downwind we would expect to see a much higher yield as predicted by laboratory experiments.

R. TOUMI (*Imperial College, University of London, UK*). Given that most of the Northern Hemisphere sulphate is non-DMS derived, should you discard the MSA/NSSS ratio for the Northern Hemisphere? To look at the temperature dependence you would really only want a DMS-only influenced sulphur budget.

N. HEWITT. We agree that, ideally, the contaminated Northern Hemisphere should be excluded from the plot of MSA/NSSS against temperature. However, even when these data are excluded (10 out of 60 points) a strong temperature dependence is still evident.

G. P. AYRES (*Division of Atmospheric Research, CSIRO, Mordialloc, Australia*). The diurnal cycle in MSA at Weybourne seems different from what I would expect if it is photochemically driven. For example, a 50% loss of MSA from 1200 to 1800 implies a deposition velocity of 4 cm s^{-1} for a 1000 metre boundary layer. This seems too high for a sub-micron aerosol species. I would also expect no concentration change overnight. My guess is that local boundary layer meteorological processes dominate your data (unless you can use NO_3 oxidation to explain the night-time MSA).

N. HEWITT. MSA concentrations in air are controlled by the production rate (due to photochemistry), the removal rate (presumably due to wet and dry deposition) and dilution processes. At present we are not able to unequivocally distinguish between these, although further examination of these and other data may help in the future. In particular we wish to think about the effect that mist formation (which is common in the early evening at this site) has on the deposition rate of MSA.

A. R. RAVISHANKARA (*NOAA Aeronomy Laboratory, Boulder, CO, USA*). It is nice to see your measured variation of the MSA/NSSS ratio with temperature. There is a difference between your observations and calculation. The calculated ratio will better fit your data if you change the activation energy for some of the thermal decomposition reactions. Could you comment on this? Also a highly nonlinear dependence of the ratio on temperature could be due to heterogeneous processes. Such heterogeneous processes are likely to increase when temperature decreases. Further, their effect will be highly nonlinear.

N. HEWITT. Our field data for the temperature-dependent nature of the MSA/NSSS ratios seems to suggest that the activation energies currently used in model calculations may be incorrect and it would be helpful if these could be re-examined in the laboratory. We have not considered the role of heterogeneous processes but agree they might contribute to an increased ratio at lower ambient temperatures.