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Methanesulfonate in rainwater at Cape Grim, Tasmania

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ABSTRACT

Strong seasonal variation in rainwater methanesulfonate (MSA) concentration and wet deposition at Cape Grim is found to parallel the strong seasonal variation in aerosol MSA concentration previously reported for clean, maritime air at this site. The 4 years of rainwater MSA data available from mid-1983 to mid-1987 yield an estimated annual-average wet deposition rate to the ocean surface at 41°S of 0.096 ± 0.047 mmol m^{-2} yr^{-1}. This annual wet deposition of sulfur in the form of MSA represents only a small fraction (7%) of the 1.3 mmol m^{-2} yr^{-1} recently estimated for annual emissions of sulfur (in the form of dimethyl sulfide) from temperate oceans.

1. Introduction

The fate of dimethyl sulfide (DMS) in the marine atmosphere is of considerable contemporary interest, given the facts that DMS is apparently the major biogenic sulfur compound emitted from the ocean surface (Andreae and Raemdonck, 1983; Bates et al., 1987) and thus the major source of "sulfate" cloud condensation nuclei, which are hypothesized to act as mediators of global climate (Charlson et al., 1987).

DMS is oxidized in the atmosphere to sulfur dioxide, methanesulfonic acid (MSA) and excess (or non-sea-salt) sulfate (Grosjean, 1984; Atkinson et al., 1984; Hatakayama et al., 1985; Hynes et al., 1986). However, the relationship between these oxidation products under different oceanic and atmospheric conditions is yet to be fully clarified (Berresheim, 1987; Berresheim et al., 1988).

One of the areas still to be understood is the rôle played by MSA in the atmospheric part of the marine sulfur cycle, although it is thought that chemically the acid would act rather like sulfuric acid as a participant in homogeneous and heterogeneous nucleation processes (Kreidenweis and Seinfeld, 1988). Early measurements of aerosol MSA (Saltzman et al., 1983, 1986; Ayers et al., 1986) suggested that the MSA/excess sulfate ratio typically averaged about 0.07, which suggests a minor rôle for MSA in comparison with sulfate. However, more recent measurements at southern mid-to-high latitudes (Berresheim, 1987; Berresheim et al., 1988) and in Antarctic ice (Ivey et al., 1986) yielded ratios in the range 0.2 to 1, making the contribution of MSA to the sulfur budget considerably more important.

The purpose of this paper is to present data on MSA concentration in marine rainwater collected at Cape Grim (41°S). Unfortunately, high levels of sea-salt and contamination of rain by locally eroded dust renders accurate estimation of excess sulfate impossible (Ayers and Ivey, 1988), so the MSA/excess sulfate ratio in rain cannot be established. However, the data are still of interest on two counts: there is little other data on MSA in rain available, previously published studies on MSA having been confined mostly to the aerosol work cited above. Thus this work enables a first quantification of MSA wet deposition rate at southern mid-latitudes. In addition, the relationship of MSA in rain compared with aerosol MSA at the same site (Ayers et al., 1986) is of interest in view of the suggestion by Saltzman et al.

(1983) that in the atmosphere aqueous-phase MSA may be lost via conversion to excess sulfate.

2. Experimental

The Cape Grim site, collection method and analytical methods are fully described by Ayers et al. (1986) and Ayers and Ivey (1988). Briefly, the wet-only ERNI collector is situated approximately 100 m above the ocean surface at the seaward edge of the Cape, which juts out into the Southern Ocean directly into the prevailing southwesterly winds. Rainwater is only collected when prevailing winds are from the "baseline" sector, 190°–270°, while at the same time condensation nucleus concentration must be below 600 cm^{-3}. These criteria ensure as far as possible that atmospheric samples reflect clean, maritime conditions (Ayers and Gras, 1983). In practical terms this means that only about one third of all rain falling at Cape Grim is actually sampled.

Samples were analysed for sodium, sulfate and methanesulfonate: sodium by flame AA, sulfate and MSA by suppressed ion chromatography. All species were detectable well above the detection limits of the methods used, and are precise to better than 10% uncertainty for individual analyses (see Ayers and Ivey, 1988). The sampling interval was monthly from June 1983 to February 1985, and weekly from the beginning of March 1985 to the end of May 1987.

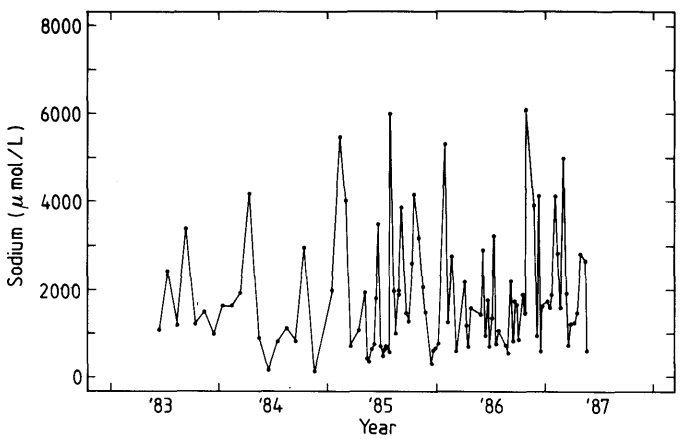

Fig. 1. Rainwater sodium concentrations at Cape Grim, Tasmania, from June 1983 to May 1987.

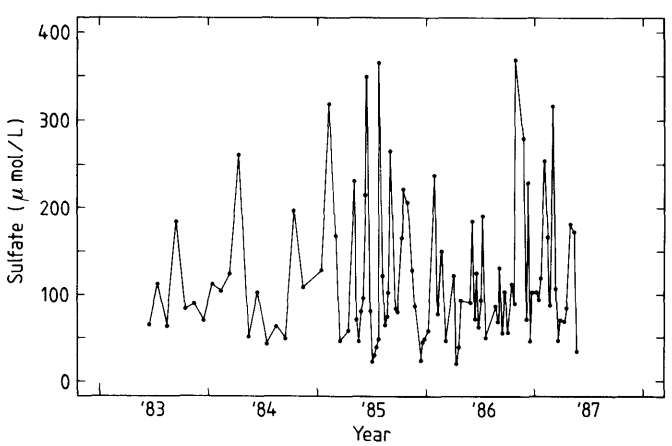

Fig. 2. Rainwater sulfate concentration at Cape Grim, Tasmania, from June 1983 to May 1987.

3. Results

Time series plots of concentrations of sodium, sulfate, and MSA are shown in Figs. 1–3. The points shown are plotted at the mid-point of each sample collection period. It should be mentioned that the weekly records necessarily contain some gaps when no sample was collected. Thus it is not clear what significance can be placed on the low MSA amplitude in Fig. 3 during the last summer sampled, since 2 weeks in late December and 1 week in January had no sample, and the summer maximum is sufficiently variable in time and short-lived perhaps for it to be associated with these "missing" sample periods. Finally, volume weighted mean concentrations covering all samples are given in Table 1.

Immediately evident from Figs. 1 and 2 is the very high sea-salt loading encountered in marine rainwater at this site, a consequence of the high wind speeds characteristic of the "roaring forties" (Ayers and Ivey, 1988). Excess sulfate is impossible to quantify against background sulfate concentrations from sea-salt averaging nearly 90 μmol L^{-1}, since excess sulfate is expected to be only about 2 μmol L^{-1}, based on results from Amsterdam Island at 39°S (Galloway and Gaudry, 1984) and Macquarie Island at 54°S (Ayers and Ramsdale, 1988). Analytical precision required to afford such estimation would need to be to better than 1% uncertainty for both sodium and sulfate, which is currently not possible. Even if such precision were available, estimation of excess sulfate would remain problematic, since erosion of soil dust from the Cape surface leads unavoidably to some local contamination of rainwater samples (Ayers and Ivey, 1988).

In contrast, the MSA record in Fig. 3 we consider to be free from obvious influence by local contamination, since MSA was not a significant constituent in the local soil samples analysed by Ayers and Ivey (1988).

Table 1. *Volume weighted mean concentrations, μmol L^{-1}, June 1983–May 1987*

Ion	Mean	Standard error	Number
sodium	1362	105	91
sulfate	87.6	6.4	91
MSA	0.12	0.03	91

4. Discussion

Given the impossibility of estimating excess sulfate concentrations, attention here is focussed on the MSA record, the most striking feature of which (Fig. 3) is the pronounced seasonal cycle in concentration, ranging from 0.02–0.05 μmol L^{-1} in mid-winter to as much as 1 μmol L^{-1} in mid-summer. This cycle is very similar in shape, relative amplitude and phase to that for aerosol MSA measured at Cape Grim in the interval 1976–1984, as published by Ayers et al. (1986).

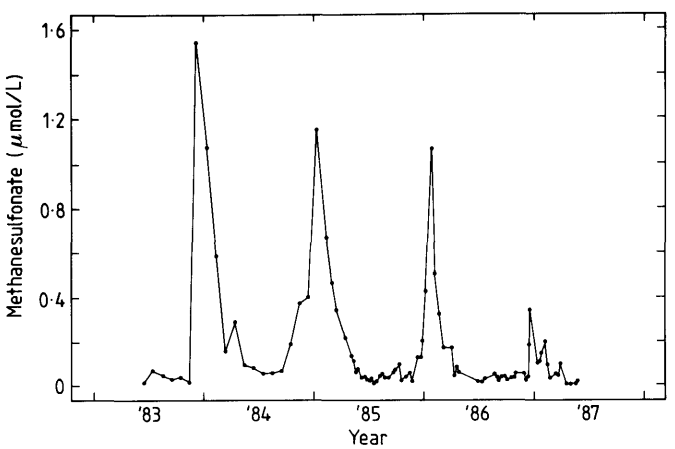

Fig. 3. Rainwater methanesulfonate concentration at Cape Grim, Tasmania, from June 1983 to May 1987.

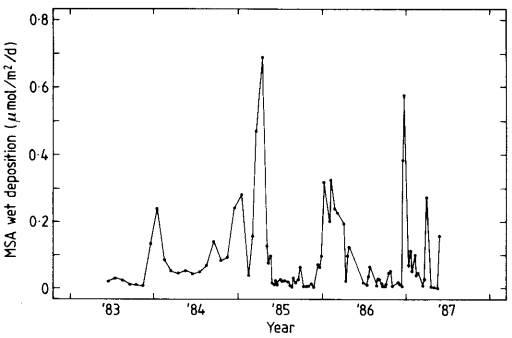

Fig. 4 Wet deposition of MSA calculated as an average daily rate for each sampling interval. Only rainfall collected in accordance with the "clean air" criteria (see text) contributes to this plot.

Indeed, the absolute concentrations for aerosol MSA in that work varied from about 0.02–0.05 μmol m^{-3} mid-winter to almost 1 μmol m^{-3} mid-summer, which would lead exactly to the rainwater MSA concentrations noted above if these average aerosol loadings for 1 m^3 were dissolved completely in 1 cm^3 of liquid water. Since 1 cm^3 liquid water per m^3 of air is a reasonable value (within a factor of 3 uncertainty) for actively raining clouds (Pruppacher and Klett, 1978), and in clean air nucleation scavenging is efficient (Jensen and Charlson, 1984; Vong et al., 1988), rainwater MSA concentrations at Cape Grim can readily be interpreted as arising from efficient nucleation scavenging of aerosol MSA. Thus, there is no obvious indication in the available data to suggest that aqueous-phase MSA in the atmosphere is rapidly lost via conversion to sulfate, as postulated by Saltzman et al. (1983).

Wet deposition of MSA calculated as an average value in μmol m^{-2} d^{-1} for each sampling interval, according to the rainfall amount actually sampled at the Cape, is displayed in Fig. 4. It must be kept in mind when viewing this plot that it is representative only of the 30% of total rainfall at the Cape which meets the sample collection criteria. However, it does reveal that the distinct annual cycle noted in concentration is again quite evident, though with some added variability since it is produced by convoluting the MSA concentration record with the rainfall record which is characteristically "noisy", partly as a result of our selective sampling criteria. At the same time, some attenuation of the very strong annual cycle in concentration must be expected in deposition, since the published rainfall data (BAPMoN, 1986) exhibit an out-of-phase annual cycle in rainwater deposition, as shown in Fig. 5.

Assuming that the volume weighted mean MSA concentration of 0.12 ± 0.06 μmol L^{-1} given in Table 1 and the total, long-term, annual mean rainfall of 80 cm at the Cape are represen-

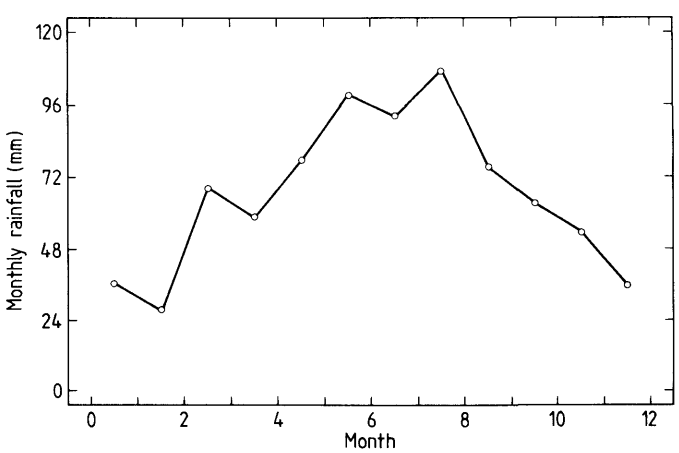

Fig. 5 Average distribution of total rainfall by month at Cape Grim, calculated from published records spanning the 8 years 1977–1984 (BAPMoN, 1986).

tative values for a completely marine site at this latitude, an estimate of mean annual MSA wet deposition to the ocean surface can be calculated. A figure of 0.095 ± 0.047 mmol m^{-2} yr^{-1} results. This may be compared with the annual mean figure of 0.040 mmol m^{-2} yr^{-1} at 66°S deduced by Ivey et al. (1986) from the Law Dome ice core results.

Bates et al. (1987) summarize all available DMS emission data for the global oceans. While this has been gathered almost completely over northern oceans, the few southern hemisphere data points available suggest that the resultant seasonal cycle in DMS emission rates as a function of latitude should not be greatly in error for the southern hemisphere. The seasonal cycle given by Bates et al. (1987) for the latitude band encompassing Cape Grim ("temperate oceans") is distinguished by about a factor of 7 or 8 amplitude for the winter to summer increase in DMS emission. Qualitatively, this seems very compatible with the seasonal variations in atmospheric MSA concentration and wet deposition under discussion here. Thus the MSA cycles may prove to be reasonable surrogates for the DMS emission cycle at Cape Grim.

On the other hand, an annual-average wet deposition rate of 0.096 mmol m^{-2} yr^{-1} for MSA is only 7% of the annual average DMS emission rate of 1.3 mmol m^{-2} yr^{-1} calculated by Bates et al. (1987) for "temperate oceans". In absolute terms then, if most of the sulfur emitted from the ocean surface as DMS is recycled within the marine boundary layer/cloud system, wet deposition of MSA appears to be a minor, rather than major pathway for return of sulfur to the ocean surface. However, an understanding of the complete sulfur budget at this site must await development of methods for accurate assessment of the annual cycle in rainwater excess sulfate and gas-phase sulfur dioxide.

5. Conclusions

A very pronounced annual cycle of summer maximum, winter minimum is found in rainwater MSA concentration and MSA wet deposition rate at Cape Grim, having close similarities in amplitude and phase to previously published seasonal cycles in aerosol MSA concentration at the same site. These cycles probably reflect similar seasonal variations in DMS emissions (although these are yet to be confirmed directly at Cape Grim). However, in absolute terms the annual wet deposition of MSA to the ocean surface at this latitude, 0.095 mmol m^{-2} yr^{-1}, represents only 7% of the 1.3 mmol m^{-2} yr^{-1} estimated by Bates et al. (1987) for the annual-averaged emission of DMS for the same latitude.

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