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# Sulfur dry deposition over the western North Atlantic: the role of coarse aerosol particles

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ABSTRACT

A number of investigators have observed substantial amounts of coarse fraction ($D > 1$ μm) non-sea-salt or excess sulfate ($XSO_4$) to prevail in marine boundary layer (MBL) aerosol. Its dry deposition velocity may be 1 cm $s^{-1}$ or more with low uncertainty relative to the dry deposition velocity of fine-fraction $XSO_4$. Estimates of total sulfur dry deposition using MBL ambient air data over the western North Atlantic Ocean are presented. It is shown, at distances of hundreds to 1000 km downwind from sulfur source regions, that sulfur dry removal from the western North Atlantic MBL is dominated by the dry deposition of $XSO_4$ rather than that of $SO_2$.

## 1. Introduction

Several studies of the sulfur budget in the marine boundary layer (MBL) have appeared in the literature (e.g., Kritz, 1982; Mészáros, 1982). In these studies, the removal of gaseous and particulate sulfur at the sea surface was accounted for by applying a dry deposition velocity $V_d$ to the mean concentration of sulfur species in the MBL. Kritz (1982) used a $V_d$ value for sulfur dioxide ($SO_2$) of 0.5 cm $s^{-1}$; a $V_d$ value for sulfate ($SO_4$) was not directly estimated, but his data implied a value of $<0.1$ cm $s^{-1}$. Mészáros (1982) used a $V_d$ value for $SO_2$ of 0.7 cm $s^{-1}$ and for $SO_4$ of 0.2 cm $s^{-1}$. The appropriateness of these values is discussed in Section 2. Uncertainty is not usually accounted for in sulfur budget calculations. It should be, however, since very large $V_d$ uncertainty exists, especially for $V_d$ of $SO_4$.

A major reason for the very large uncertainty in sulfur budget calculations is that dry deposition must be applied only to $XSO_4$ (the non-sea-salt-derived $SO_4$). This is because the total, wet plus dry deposition of sea salt $SO_4$ is balanced by the production of sea salt aerosol at the sea surface. The net mass exchange of $SO_4$ is due to $XSO_4$ deposition. MBL measurements (Andreae et al., [1986]; Gravenhorst, [1978]) of the mass size distribution of $XSO_4$ show that half or more of the $XSO_4$ mass may be found in coarse-fraction aerosol. Andreae et al. (1986) also observed that coarse-fraction $XSO_4$ about equals sea salt $SO_4$ in remote MBL areas over the Pacific Ocean. This remote-area coarse-fraction $XSO_4$ may result from sea-derived dimethyl sulfide (DMS). However, Luria et al. (1988), using a data base obtained over the western North Atlantic Ocean showed that less than half of the $XSO_4$ observed during WATOX-86 (Western Atlantic Ocean Experiment, 1986) was sea-derived DMS. Much of the sulfur dry deposition due to coarse $XSO_4$ may, therefore, not be balanced by DMS emissions from the sea's surface. Several investigators (e.g., Cahill, 1987; Okita et al., 1986; Whelpdale et al., 1987) observed a substantial portion of $XSO_4$ to be in coarse-fraction aerosol in coastal areas (50-500

km offshore) where the production of DMS was observed to be quite low.

A brief review of sulfur dry deposition measurements in Section 2 will establish that $<100\%$ uncertainty may be applied to the dry deposition of the coarse-fraction aerosol $XSO_4$; for fine-fraction sulfur (diameter, $D<1$ $\mu$m) an uncertainty of 500% (or more) may persist. Since $XSO_4$ is found to varying degrees in coarse-fraction aerosol, widely varying $V_d$ for $SO_4$ may be applied to the dry deposition of $SO_4$ at the air-sea interface. A major purpose of this paper is to identify (a) the magnitude of $XSO_4$ dry deposition over the Western North Atlantic, especially non-DMS-derived $XSO_4$, and (b) uncertainty in that magnitude.

## 2. Dry deposition of $SO_2$ and $XSO_4$: a brief review

Only a handful of observations of $V_d$ for $SO_2$, $V_d(SO_2)$, at air-water interfaces are available from the literature. No data exist on $V_d$ for $XSO_4$, $V_d(XSO_4)$, at the air-sea interface.

Four $V_d(SO_2)$ measurements at the air-water interface have been published: Shepherd (1974), Whelpdale and Shaw (1974), and Garland (1977) using the gradient technique; and Owers and Powell (1974), using a sulfur tracer technique. All three gradient measurements were over freshwater surfaces within the first few meters above the air-water interface. Shepherd found, at the 0.2-m mean height of measurement, $V_d(SO_2)$ was equal to $(0.024 \pm 0.004)$ $U_*$, where $U_*$ is the friction velocity. He made his observations during conditions of neutral thermal stability. Shepherd's results, at a $U_*$ of 16 cm s$^{-1}$, give $V_d(SO_2) = 0.38 \pm 0.06$ cm s$^{-1}$. Whelpdale and Shaw (1974) found, at a 4-m measurement height over Lake Ontario, a $V_d(SO_2)$ on the order of 1 cm s$^{-1}$. Wind speed data are not presented; however, a strong dependence on stability was noted. Therefore, the $V_d(SO_2)$ would range from 0.2 cm s$^{-1}$ during stable periods to 4 cm s$^{-1}$ during unstable periods. Garland's gradient data were obtained during relatively light wind speeds with an average $U_*$ of 16 cm s$^{-1}$. He found $V_d(SO_2) = 0.4 \pm 0.15$ cm s$^{-1}$. We see that the gradient measurements of Shepherd (1974) and Garland (1977) agree quite well. Owers and Powell (1974), using a radioactive tracer and a height above surface of 0.2 m (same as Shepherd), found $V_d(SO_2) = 0.5 \pm 0.2$ cm s$^{-1}$ during neutral stability, 80% RH, and 1.8 m s$^{-1}$ wind speed conditions. The friction velocity $U_*$ probably was in the range 5–15 cm s$^{-1}$. If Shepherd's formula is used, $V_d(SO_2)$ is 0.12-0.36 cm s$^{-1}$, which is somewhat lower than the $0.5 \pm 0.2$ cm s$^{-1}$ observed by Owers and Powell.

We conclude from these calculations that $V_d(SO_2)$ depends, perhaps linearly, on wind speed (or more accurately on $U_*$). Values $<0.25$ cm s$^{-1}$ are possible under light wind speed ($<3$ m s$^{-1}$) conditions and $>1$ cm s$^{-1}$ are possible under high wind speed ($>8$ m s$^{-1}$) conditions. Under moderate wind speed conditions, $V_d(SO_2)$ is 0.5–1.0 cm s$^{-1}$. We should note that (a) the authors themselves indicate that measurement uncertainties were $\pm 30$–40% and (b) the measurement height was less than one meter above the water's surface.

There are no definitive direct measurements of fine-fraction ($D<1$ $\mu$m) $SO_4$ deposition rates to water reported in the literature. Results from two attempts to measure it directly by the eddy flux technique, one over freshwater (Wesely and Williams, 1981) and one over seawater (Sievering et al., 1982), were inconclusive because of particle growth and decay mediated by the steep relative humidity gradients present over water. Given that essentially no data are available on $V_d(SO_4)$ at the air-water interface, we invoke theoretical modeling results. Slinn and Slinn (1980) presented the most often used model for particle dry deposition. A number of reflections upon this model (Williams, 1982; Slinn, 1983; Sievering, 1984) allow one to conclude that (a) $V_d$ for fine fraction $SO_4$ lies somewhere in the range 0.01–1 cm s$^{-1}$ and (b) $V_d$ for coarse-fraction $SO_4$ of mass median diameter $\geq 3$ $\mu$m is surely greater than 1 cm s$^{-1}$ during moderate and high wind speed conditions. We also conclude, with less confidence, that coarse-fraction $V_d(SO_4)$ is 10 times greater than fine-fraction $V_d(SO_4)$ during moderate and high wind speed conditions, remembering that $V_d$ is a strong function of the mass size distribution in the fine and coarse-fractions (see Section 3).

Globally averaged near-surface wind speeds usually fall in the moderate 3–8 m s$^{-1}$ range, although for some areas of the global oceans

average wind speeds may be greater than 8 m $s^{-1}$ (Erickson et al., 1986). For the western North Atlantic Ocean the average near-surface wind speed is 6–7 m $s^{-1}$. Thus, seasonally averaged $V_d(SO_2)$ are expected to be about 0.7 cm $s^{-1}$ with an uncertainty of $\pm 50\%$. Regarding $V_d(SO_4)$, we conclude that at least $\pm 500\%$ uncertainty must be applied to fine-fraction $V_d(SO_4)$; i.e., that this $V_d(SO_4)$ is in the range from 0.01 to 1 cm $s^{-1}$. This is in contrast to $V_d(SO_4)$ for coarse-fraction $SO_4$ for which $<100\%$ uncertainty may be applied.

## 3. Estimation of the dry removal of sulfur: western North Atlantic

It is clear from Section 2 that estimation of sulfur dry removal from the MBL demands that (a) the size distribution of $XSO_4$ be specified or (b) at least that the percentage of coarse- and fine-fraction $XSO_4$ be specified. The former is not available; however, the latter has been accomplished, using careful $Na^+$ and $SO_4^=$ ion chromatography analysis of fine- and coarse-fraction aerosols. One noteworthy study in this regard is the Western Atlantic Ocean Experiment (WATOX). During the 1986 WATOX field program (Galloway and Whelpdale, 1987), two aircraft with fine/coarse filter packs sampled 50-100 km off the northeastern US coast during January, 1986 and in the vicinity of Bermuda during February, 1986. Whelpdale et al. (1987) determined that about 20% of $XSO_4$ was present in coarse-fraction aerosol during the US coastal sampling. In the vicinity of Bermuda, Luria et al. (1988) found about half of $XSO_4$ in the coarse fraction. Gravenhorst (1978) also found half of $XSO_4$ in coarse-fraction aerosol over North Atlantic areas removed from the US coast.

DMS emitted from the sea converts to $XSO_4$. Luria et al. (1988) indicate that $\leq 0.3$ $\mu$g $SO_4$ $m^{-3}$ in the vicinity of Bermuda and $<0.05$ $\mu$g $SO_4$ $m^{-3}$ during US coastal sampling was derived from observed DMS concentrations. Thus, of the 1.9 $\mu$g $SO_4$ $m^{-3}$ observed in the vicinity of Bermuda, about 70% was non-DMS-derived $XSO_4$. One-third of that, 0.45 $\mu$g $SO_4$ $m^{-3}$, was found in the coarse fraction versus 0.9 $\mu$g $SO_4$ $m^{-3}$ in the fine fraction. Given that $V_d$ for the coarse-fraction $XSO_4$ may be 10 times $V_d$ for the fine fraction, the dry deposition of $SO_4$ in the vicinity of Bermuda is more than $\frac{3}{4}$ controlled by coarse-fraction $XSO_4$. Off the northeastern US coast Whelpdale et al. (1987) found about 0.4 $\mu$g $SO_4$ $m^{-3}$ in the coarse fraction versus 1.5 $\mu$g $SO_4$ $m^{-3}$ in the fine fraction. Cahill (1988) observed, 200 km downwind from the US coast, as much as half of $XSO_4$ to be in the coarse fraction. Thus, even in the US coastal area, where continentally-derived fine-fraction $SO_4$ contributes heavily, well over half of excess sulfate's dry deposition appears to be controlled by coarse-fraction $XSO_4$.

Given this dominance by coarse fraction over fine fraction in estimating $SO_4$ dry deposition, the estimation of total sulfur dry deposition to the western North Atlantic Ocean is worth pursuing since uncertainty in overall sulfur dry deposition may be reasonably low. Tables 1, 2 show the results of this calculation. Note that average concentration data are considered to have an uncertainty of $\pm 20\%$ or less (private communications: J. Boatman, Air Quality Group, GMCC, NOAA regarding $SO_2$ data; W. Keene, Department of Environmental Sciences, University of Virginia regarding $SO_4$ data). Note also that near-surface wind speeds were generally in the 4–8 m $s^{-1}$ range but nearly 20% of the sampling time had higher wind speeds prevailing. A somewhat larger $V_d$ was used with the US coastal coarse $XSO_4$ (not DMS derived) than with the Bermuda-area coarse $XSO_4$. Sievering et al. (1987) showed that the median diameter of coarse-fraction aerosol was 8.1 $\mu$m in the US coastal MBL versus only 5.5 $\mu$m in the Bermuda-area MBL. The entire coarse-mode aerosol size range of 1–47 $\mu$m diameter was very well fitted by a lognormal distribution. Thus, $V_d$ for the coarse-mode aerosol could then be specified with only 50–60% uncertainty because of the overwhelming contribution of very large aerosol (with relatively well specified $V_d$) to total coarse-mode dry deposition. It was assumed that coarse-fraction aerosol $XSO_4$ has the same size distribution as the coarse-fraction aerosol mass itself.

The values of $V_d$ shown in parentheses in the "dry deposition velocity" columns of Tables 1, 2 are the low and high confidence values used, along with the 20% uncertainty in the concentration data, to calculate the values found in the "uncertainty in dry flux" columns. The total

Table 1. *Western North Atlantic Ocean sulfur dry flux, US coast*

| | Concentration ($\mu g\ m^{-3}$) | Dry deposition velocity* ($cm\ s^{-1}$) | Median dry flux ($ng\ m^{-2}\ s^{-1}$) | Uncertainty in dry flux ($ng\ m^{-2}\ s^{-1}$) |
|---|---|---|---|---|
| S as $SO_2$ | $2.5 \pm 0.5$ | 0.7 (0.35,1.05) | 15 | 7–30 |
| S as fine $XSO_4$ | $0.5 \pm 0.1$ | 0.15 (0.03,0.75) | 0.75 | 0.1–4.5 |
| S as coarse $XSO_4$ (not DMS derived) | $0.15 \pm 0.03$ | 3 (2,4) | 4.5 | 2.5–7 |
| total dry flux | | | 20 | 10–42 |

* Values in parentheses are the low and high confidence values used, along with a 20% uncertainty in the concentration data, to calculate the "uncertainty in dry flux" values.

Table 2. *Western North Atlantic Ocean sulfur dry flux, Bermuda*

| | Concentration ($\mu g\ m^{-3}$) | Dry deposition velocity* ($cm\ s^{-1}$) | Median dry flux ($ng\ m^{-2}\ s^{-1}$) | Uncertainty in dry flux ($ng\ m^{-2}\ s^{-1}$) |
|---|---|---|---|---|
| S as $SO_2$ | $<0.15$ | 0.7 (0.35, 1.05) | $<1.5$ | – |
| S as fine $XSO_4$ | $0.30 \pm 0.06$ | 0.15 (0.03, 0.75) | 0.4 | $<0.1$–2 |
| S as coarse $XSO_4$ (not DMS derived) | $0.15 \pm 0.03$ | 2.5 (1, 4) | 4 | 1–7 |
| total dry flux | | | 5–6 | 2–10 |

* Values in parentheses are the low and high confidence values used, along with a 20% uncertainty in the concentration data, to calculate the "uncertainty in dry flux" values.

sulfur dry flux uncertainty is at the factor-of-2 level. This, despite the 2-order-of-magnitude uncertainty in the dry flux of fine $XSO_4$, since its contribution to the total flux is quite small. It is also very interesting to note the reversal in the sulfur dry flux due to $SO_2$ and coarse-fraction $XSO_4$ while progressing from the US coast to the Bermuda area. In the US coastal case (Table 1) the S as $SO_2$ dry flux is almost certainly greater than that for S as coarse-fraction $XSO_4$ and, probably, 2- to 4-times greater. In contrast to this, the Bermuda-area data (Table 2) show that dry flux S as coarse $XSO_4$ is greater than that for S as $SO_2$, and probably 3- to 5-times greater. Again it should be noted the latter result assumes that 0.1 $\mu g\ S\ m^{-3}$ as $XSO_4$ is DMS derived and further, that all of this 0.1 $\mu g\ S\ m^{-3}$ resides in the coarse fraction. Thus, the non-DMS-derived $0.15 \pm 0.03$ $\mu g\ S\ m^{-3}$ as coarse-fraction $XSO_4$ concentration could be still larger if a portion of the DMS-derived $XSO_4$ were to reside in the fine fraction. As a consequence, the median dry flux of S as coarse-fraction $XSO_4$, shown as 5 $ng\ m^{-2}\ s^{-1}$, could then be 6 $ng\ m^{-2}\ s^{-1}$ or more.

The importance of coarse-fraction aerosol $XSO_4$ dry flux to total sulfur deposition for the western North Atlantic Ocean is clear when we note that sulfur wet deposition to this area of the Atlantic Ocean is in the range of 10–16 $ng\ m^{-2}\ s^{-1}$ (Galloway and Whelpdale, 1987). The dry deposition of non-DMS-derived $XSO_4$ in the coarse-fraction aerosol probably causes total dry deposition of S from the MBL to surpass its wet deposition.

Okita et al. (1986) generated a sulfur data base for the western North Pacific Ocean. Using the same calculational procedure as above, the following results were obtained for the total MBL dry deposition of S. At 260 km from the Japanese coast and during offshore flow conditions, the median total sulfur dry flux is 10–30 $ng\ m^{-2}\ s^{-1}$. Of that total, about one-third appears to be due to

non-DMS derived, coarse-fraction aerosol $XSO_4$. At 800 km from shore, the median total sulfur dry flux is 5–15 ng $m^{-2}$ $s^{-1}$ with about two-thirds due to non-DMS-derived, coarse-fraction aerosol $XSO_4$. This $\frac{1}{3}$ to $\frac{2}{3}$ range in the 260–800 km downwind region off the Japanese coast is comparable to the $\frac{1}{4}$ to $\frac{3}{4}$ range in the 100-1000 km downwind region off the US East Coast.

## 4. Conclusions

We have shown that the role of coarse-fraction aerosol $XSO_4$ is critical to the estimation of sulfur dry deposition from the MBL. In the Bermuda area, over 1000 km removed from continental sulfur sources, about $\frac{3}{4}$ of sulfur's dry flux may result from the presence of non-DMS-derived coarse-fraction aerosol $XSO_4$. Nearer to shoreline areas with concentrated land-based sulfur sources, as little as $\frac{1}{4}$ of the sulfur dry deposition to the sea appears to result from coarse-fraction $XSO_4$ due to higher concentrations of $SO_2$ and fine-fraction $XSO_4$.

Given the distribution of $XSO_4$ in fine- and coarse-fraction aerosol, a weighted $V_d(XSO_4)$ of about 0.8 cm $s^{-1}$ may be expected in the first 1000 km downwind from continental sulfur source regions. A value of $V_d(XSO_4) < 0.5$ cm $s^{-1}$ is very unlikely. Previous sulfur global budget calculations (e.g., Kritz, 1982 or Mészáros, 1982) have significantly underestimated the dry deposition of $XSO_4$. It is possible that the dry deposition of $XSO_4$ equals that of sea-salt $SO_4$, 40-50 Tg $yr^{-1}$, as opposed to the 7 Tg $yr^{-1}$ suggested by Mészáros (1982).

It is possible that rapid $SO_2$ conversion in and on the surfaces of sea-derived aerosol may explain the observation that a majority of the $XSO_4$ is observed in coarse-fraction aerosol. Such a rapid conversion could be dependent upon the presence of the chloride ion and may also be a function of the water mass present in the MBL aerosol (Sievering et al. 1987). Large amounts of both the chloride ion and water mass are of course part of the sea-derived aerosol. It is, therefore, not surprising that relatively high concentrations of $XSO_4$ have been observed in coarse-fraction MBL aerosols.

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