Tellus (1982), *34*, 277–282

On the atmospheric input of sulfur into the ocean

By E. MÉSZÁROS, *Institute for Atmospheric Physics, P.O.B. 39, H-1675 Budapest, Hungary*

(Manuscript received June 1; in final form September 16, 1981)

ABSTRACT

The dry deposition of sulfur onto the ocean surface is calculated by using the results of trace gas observations and aerosol measurements carried out in the marine boundary layer as well as available information on the deposition velocity of different materials at the air–sea interface. The input by precipitation into the ocean is estimated on the basis of precipitation composition at three stations located in Hawaii, American Samoa and on the west coast of Ireland. It is found that the total air–sea transfer of sulfur is equal to 324 Tg yr^{-1}. The major part of this quantity (82%) is carried down by precipitation. 50% of the total input is due to the presence of excess sulfate in the marine atmosphere.

1. Introduction

The study of the pathway of trace substances in the atmosphere is one of the most important tasks of present meteorological research. This is explained by the fact that trace materials play an important part in the control of the climate. This field has become particularly important in recent decades since it has been demonstrated that human activity is able to modify the atmospheric budget of many trace species.

We have to emphasize that the investigation of the cycle of atmospheric trace substances (including pollutants) is also of interest for scientific fields other than meteorology, since the atmosphere is in a permanent material exchange with other parts of our environment. It follows from this fact that if we emit pollutants into the atmosphere, other media of the earth will also be polluted because of the deposition of the elements emitted on plants, soils and water surfaces.

Two types of atmospheric deposition can be defined: dry and wet deposition. Dry deposition denotes the vertical mass transfer of gases and aerosol particles due to diffusion and gravitational settling, while the removal of trace substances from the atmosphere by cloud and precipitation elements is termed wet deposition.

An important consequence of anthropogenic effects is the increase of acidity of atmospheric deposition owing to the increasing emission of substances like sulfur dioxide and nitrogen oxides. The aim of this paper is to determine the atmospheric input of sulfur into the ocean by calculating separately the wet and dry deposition rates as well as the sea-salt and excess sulfur fraction in the deposition. The results calculated are discussed from the point of view of the global atmospheric sulfur cycle. Whenever possible changes in the atmospheric deposition due to human activities will be identified.

2. Dry deposition of sulfur dioxide

Shipboard sulfur dioxide concentration measurements carried out in the air over the open ocean show (Mészáros, 1978) that, except over the North Atlantic, the SO_2 level is fairly constant, and is equal to about 0.1 $\mu g\ m^{-3}$ expressed as sulfur. Nguyen et al. (1978) speculate that this constant level reflects the effect of oceanic sources releasing a rather large quantity of dimethyl sulfide into the air. According to the results of more recent aircraft sampling (Maroulis et al., 1980) the average marine SO_2 concentration in the boundary layer is 0.16 $\mu g\ m^{-3}$. Maroulis and his co-workers found higher values in the free troposphere and they concluded that background SO_2 may originate from the oxidation of carbonyl sulfide emitted by

0040-2826/82/030277-06$02.50/0

biogenic and to a lesser extent by anthropogenic sources (Logan et al., 1979). It is felt that the higher SO_2 values over the North Atlantic are at least partly due to man-made sulfur dioxide emissions (Mészáros, 1978).

The deposition velocity of sulfur dioxide over water surfaces is estimated to be 0.7 cm s^{-1} on average (ISSA, 1978). By using this figure and a concentration of 0.1 μg m^{-3} for SO_2–S, a total deposition of 8 Tg yr^{-1} can be calculated for the world oceans (the deposition for unit area is given by the product of the concentration and deposition velocity).

It follows from the homogeneity of the results on SO_2 and excess sulfate concentration over the ocean, that average levels used in transfer calculations have a maximum error of about 50%. According to ISSA (1978) the deposition velocity of SO_2 over water ranges from 0.2 to 1.5 cm s^{-1}. The present author thinks that values above 0.5 cm s^{-1} are more probable considering the pH of the ocean water. Thus the accuracy of the value applied in this study (0.7 cm s^{-1}) can vary within a maximum factor of 2. This means that the total accuracy of SO_2 deposition calculated is about $\pm 100\%$ or a little bit more.

3. Dry deposition of aerosol particles

It is evident that in the atmospheric boundary layer over the oceans the major part of the aerosol loading is composed of sea-salt. However, on a number basis, the majority of the aerosol particles does not originate from marine-derived salts. This is due to the fact that many tiny particles are generated by gas-to-particle conversion. On the other hand even the composition of sea-salt particles can be modified owing to their interaction with smaller particles and trace gases. If we speak about the possible anthropogenic modification of the aerosol burden over oceanic areas, the study of this "excess' (not sea-salt) fraction of the particles is particularly interesting since aerosol forming trace gases (e.g. SO_2) can originate from global pollution.

Fig. 1 shows the average size distribution of the two main components of the marine aerosol on the basis of the data reported by Mészáros and Vissy (1974). These data were obtained by electron and optical microscopic evaluation of membrane filter samples taken on board the Soviet research ship *Prof. Vize*. Morphological studies demonstrated that smaller particles formed by gas-to-particle conversion are composed mostly of ammonium sulfate. The pointed distributions of sea-salt particles in Fig. 1 are calculated by correcting the original curves for isokinetic sampling conditions as proposed by Levin (1961).

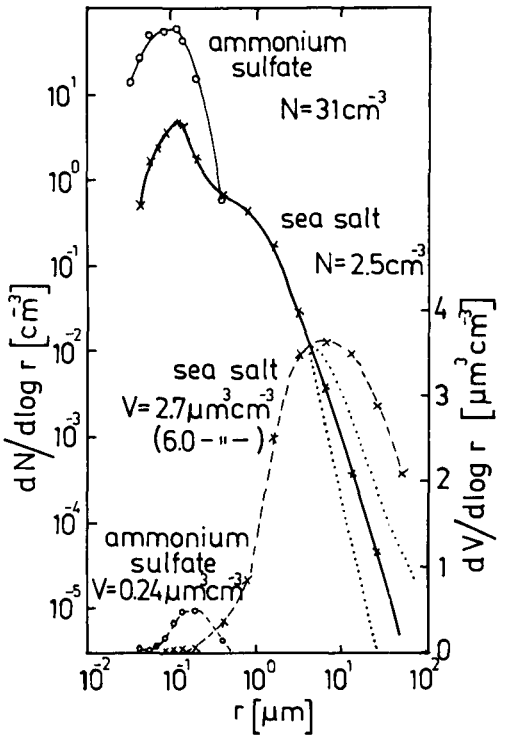

Fig. 1. Average size distribution of ammonium sulfate and sea-salt particles calculated from data in Mészáros and Vissy (1974). Pointed curves for sea-salt are corrected for isokinetic sampling conditions. The number in parenthesis at the value of the sea-salt volume gives the uncorrected volume concentration (the number concentration hardly changes because of the correction).

It follows from the volume of ammonium sulfate particles given in Fig. 1 that the sulfur quantity in this size range is equal to 0.11 μg m^{-3}. However, this value is substantially smaller than the excess sulfur mass concentrations measured by several workers by direct chemical analyses of shipboard filter samples. Thus, Gravenhorst (1978) reports for the North Atlantic an excess sulfur concentration of 0.3 μg m^{-3}, while according to the

publication of Bonsang et al. (1980) the mean SO_4–S excess concentration averaged for several sampling sites is 0.27 μg m^{-3}. Our own measuring program carried out over the Indian Ocean gives an average of 0.29 μg m^{-3} (Horváth et al., 1981). These results suggest a surprisingly constant excess sulfur concentration over the world oceans. By comparing the value of 0.3 μg m^{-3} for total concentration with the concentration of 0.11 μg m^{-3} resulting from Fig. 1, we can conclude that about 0.19 μg m^{-3} of excess sulfate can be found on larger sea-salt particles. This conclusion is supported by the finding of Gravenhorst (1978), demonstrating that about half of the excess sulfate belongs to particles larger than 0.45 μm. The excess sulfate in the range of larger particles can be formed by the interaction of sea-salt particles with SO_2 and sulfuric acid particulates (Hitchcock et al., 1980). For this reason, it is reasonable to believe that the excess sulfur on large particles (0.19 μg m^{-3}) is distributed according to the surface distribution of sea-salt particles (which can be calculated from the number distribution in Fig. 1).

According to the sea-salt volume given in Fig. 1, the aerosol particles over the ocean contain about 0.3 μg m^{-3} sea-salt sulfur. This means that in our oceanic model aerosol, the excess sulfur concentration is equal to that of sea-salt sulfur in agreement with the results of Bonsang et al. (1980).

Taking into account the deposition velocities of aerosol particles of different size over ocean water, as published by Sehmel and Sutter (1974) for a wind speed of 7.2 m s^{-1}, on the basis of Fig. 1, the following total dry depositions can be calculated. The sea-salt sulfur input of particles with radius smaller than 20 μm into the world oceans is equal to 42 Tg yr^{-1} while the corresponding value for excess sulfate-sulfur is 7 Tg yr^{-1}. A negligible part (0.13 Tg yr^{-1}) of this latter is due to particles smaller than about 0.5 μm referred to as ammonium sulfate in Fig. 1.

The variation of deposition velocities for a given particle size as measured by Sehmel and Sutter (1974) indicates that in the large size range, the accuracy of the excess sulfur deposition is not more than a factor of 2. However, the error may be higher in the case of small ammonium sulfate (or sulfuric acid) particles. A reasonable estimate from the dispersion of Sehmel and Sutter's data is a factor of 3 or 4. Fortunately enough, the deposition rate of these particles is very small. In this way the relatively low accuracy does not essentially influence the main points of this paper.

4. Wet deposition of sulfur

The composition of atmospheric precipitation over the world oceans is not well known. Precipitation samples taken on board ship over the Pacific Ocean were analysed by Selezneva (1974), while data on the composition of precipitation water collected on weather ships over the North Atlantic were reported by Nyberg (1977). According to Selezneva the median excess sulfur concentration calculated on the basis of sulfate and sodium levels is 0.64 mg l^{-1}. Nyberg gives average excess sulfur concentrations of 0.31 and 0.62 mg l^{-1} for a U.K. and a Dutch weather ship, respectively.

It is felt that precipitation chemistry data from stations operated regularly on islands are more reliable than episodic shipboard results. For this reason, the monthly precipitation chemistry data for three years (1975–1977) gained in the WMO Background Air Pollution Monitoring Network at two U.S. and one Irish stations are used (EDS, 1975; 1976; 1977) in this paper. The stations are Mauna Loa, Hawaii; Pago Pago (in 1977 Cape Matula), American Samoa and Valentia, Ireland. The geographical position of these stations as well as the monthly mean precipitation amounts for the years 1975–1977 are shown in Table 1. In this way we have three distinct types of station.[1]

[1] On the Faeroe islands there is also an oceanic BAPMON station. Unrealistically high concentrations were found, however, for this site in the EDS data reports.

Table 1. *Geographical position of the precipitation chemistry stations and the monthly mean precipitation amounts at the stations for the years 1975–1977*

Station	ϕ	λ	H (m)	P (mm/month)
Mauna Loa	19°32'N	155°35'W	3397	29
Pago Pago	14°20'S	170°43'W	3	107
Cape Matula	14°15'S	170°34'W	82	
Valentia	51°56'N	10°15'W	9	116

Firstly, Mauna Loa is a representative station for the marine free troposphere. It was found by Mendonca and Iwaoka (1969) that the properties of the trade wind inversion at the slope of Mauna Loa corresponded closely with that in free air. The only problem is the possible temporary modification of aerosol characteristics by local volcanic activity in the vicinity of the Mauna Loa Observatory (see e.g. Bodhaine, 1978). For the sake of simplicity, it is assumed in this paper that volcanic effects can be neglected for a longer time period. Secondly Pago Pago (Cape Matula) is a site situated in the marine boundary layer above the Pacific Ocean. Thirdly, the data obtained in Valentia give information on the chemical composition of precipitation formed mostly over the North Atlantic (Valentia is situated on the west coast of Ireland in the zone of the westerlies) the air of which is probably slightly polluted by human activities. This latter opinion is based on the spatial distribution pattern of the number concentration of aerosol particles (Podzimek, 1980) and sulfur dioxide (Mészáros, 1978).

In Table 2 the average concentration data, weighted according to the precipitation quantity, are tabulated. It is to be noted that the excess sulfur masses are calculated on the basis of sodium concentration and the mean composition of the ocan water ($SO_4/Na = 0.25$). The data tabulated show that the excess sulfur concentration for Valentia is in excellent agreement with the shipboard values of Nyberg (1977) reported for the open North Atlantic, while Selezneva (1974) measured higher excess sulfur levels over the Pacific Ocean than those measured at the Hawaii and Samoa stations.

Table 2. *Chemical composition of precipitation water under different oceanic conditions*

	Total S	Na	Excess S
Pacific Ocean M.F.T.	0.34	0.11	0.33
Pacific Ocean M.B.L.	0.58	3.1	0.32
Atlantic Ocean M.B.L.	1.2	8.9	0.48

The values are expressed in mg l^{-1}. M.F.T.: marine free troposphere; M.B.L.: marine boundary layer.

One can see from Table 2 that the concentration of excess sulfur in precipitation water collected in the marine boundary layer is practically the same as in the marine free troposphere. This finding suggests that the wash-out of smaller aerosol particles and trace gases by falling precipitation elements in the lower layers can be neglected. Thus the higher sulfur concentration near the ocean surface is due to the presence of large sea-salt particles in the air. As in the case of aerosols, the excess sulfur quantity in precipitation water is practically equal to the mass of sea-salt sulfur.

According to data gained at the Valentia station, the total sulfur, sodium and excess sulfur concentrations over the North Atlantic are higher than in precipitation collected near the surface of the Pacific Ocean. The higher sodium level at the Valentia station indicates higher sea-salt concentration *in precipitation* in this area in agreement with the spatial distribution of the concentration of giant sea-salt particles *in the air* (see Podzimek, 1980). On the other hand, the higher excess sulfur concentration in precipitation sampled at Valentia compared to the values for the Pacific Ocean probably suggests some anthropogenic effect. This effect increases the excess sulfur concentration by a factor of 1.5.

For calculating the wet deposition we assume that the precipitation chemistry data for Samoa represent the global undisturbed background. It is believed that the application of data from only one station is to a certain extent justified by the fact that SO_2 and particulate excess sulfur concentrations are practically constant in the air over the world oceans (see above). Taking a figure of $458 \cdot 10^3$ km^3 yr^{-1} for the precipitation amount over the oceans (see Petrenchuk, 1980) a total wet deposition value of 267 Tg S yr^{-1} can be obtained for the total area of the world oceans by multiplying the concentrations given in Table 2 with the above precipitation amount. The corresponding figure for excess sulfur is 147 Tg yr^{-1}. We should mention that the above total precipitation amount is equal to an average of 1267 mm yr^{-1} for the ocean. This figure is very close to that measured in Samoa (see Table 1). Among other things it follows from these data that the wet deposition of sulfur is much higher than the dry fluxes discussed above.

Finally we have to mention that the accuracy of

the chemical data reported in Table 2 is not better than about ±50% due to sampling and analytical errors. Considering the fact that the calculation was based on the data of one station and the possible error in the precipitation amount used, the accuracy of the total deposition values cannot be better than within a factor of 2. This clearly shows that more research and operational work are needed in this field.

Table 3. *Strength of the different components of the air–sea sulfur transfer*

	Total S	Excess S
Wet deposition	267	147
Dry deposition of aerosols	49	7
Dry deposition of SO_2	8	8
Σ	324	162

The values are expressed in Tg yr^{-1}.

5. Conclusion

The sulfur input into the ocean calculated in this paper is much higher than was previously proposed (e.g. Granat et al., 1976). This means that the atmospheric sulfur budget calculations have to be revised. This is particularly true concerning the strength of the sea-salt emission. According to our results summarized in Table 3 the wet and dry sea-salt sulfur deposition into the ocean surface is 162 Tg yr^{-1}. Considering that a certain part of sea-salt is removed from the air over the continents, this result means that the sea-salt sulfur emission is at least 4 times higher than the value of Eriksson (1960) accepted by several workers (e.g. Granat et al., 1976).

Further, the air–sea transfer of excess sulfur is very substantial. It is equal to the sea-salt sulfur input (see Table 3). This large amount of sulfur is removed from the atmosphere mostly by precipitation. It follows from the above discussion that the majority of the excess sulfur in precipitation is due to rain-out processes in the clouds (see Table 2). Much more research is needed to determine the anthropogenic fraction of the oceanic excess sulfur deposition.

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