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On the sulfate, chloride and sodium concentration in maritime air around the Asian continent

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ABSTRACT

On the basis of chemical analysis of aerosol samples collected over the seas around the Asian continent, the sulfate, chloride and sodium concentrations in maritime air are presented. By using the sodium content of the air and the average composition of the sea water, the magnitude of the chloride loss from sea-salt as well as the excess sulfate concentration are calculated. The results are discussed from the point of view of the HCl cycle and sulfate particle formation.

1. Introduction

In recent years it was demonstrated by morphological analysis of aerosol samples (Mészáros and Vissy, 1974; Butor, 1976) that the oceanic portion of the troposphere contains basically two kinds of aerosol particles. The particles with a radius larger than about 0.5 μm are composed of sea-salt, while the particles smaller than the above limit contain mostly sulfur species formed in the air by gas-to-particle conversion (excess sulfate). Results of measurements also show (Ketseridis et al. 1976) that these sulfur-containing particles are externally or internally mixed with some organics.

In spite of the importance of the maritime air (including aerosols) in many tropospheric phenomena, our knowledge of the characteristics of aerosol particles over the seas and oceans is rather limited.

The aim of this paper is to present the concentrations of the two main maritime aerosol components (sulfate and chloride) measured by direct bulk chemical analyses over such areas around the Asian continent where rather few measurements were carried out. In the program the sodium content of the air was determined in order to estimate the quantity of excess sulfate as well as the magnitude of the possible chlorine gas liberation from particulate sea-salt.

2. Sampling area and experimental procedures

The aerosol and gas samples were taken on board the Soviet RV *Okean* which participated in the second monsoon experiment ("Monsoon-77") organized in the GARP program to study different atmospheric and oceanic parameters. The trip was carried out between May 4 and September 15, 1977, from Vladivostok and back. However, all the sampling was done during the journey between Vladivostok and Calcutta before August 20 on the route represented in Fig. 1. Two of the authors of this paper (Antal, Simon) took part in the experiment as members of the international scientific staff.

The atmospheric particles were collected by membrane filters with nominal pore size of 0.3 μm (Synpore 6). The air was sucked through the filters by a small pump provided by the Millipore corporation. The flow rate, measured by a rotameter, was generally 0.8–0.9 $m^3\ hr^{-1}$, although it slightly varied as a function of sampling conditions. The sampling site on the upper board (14 m above the water level) depended upon the wind direction. It was chosen in such a way to avoid the contamination from the ship. Except some samplings, the air volume sampled was around 50 m^3

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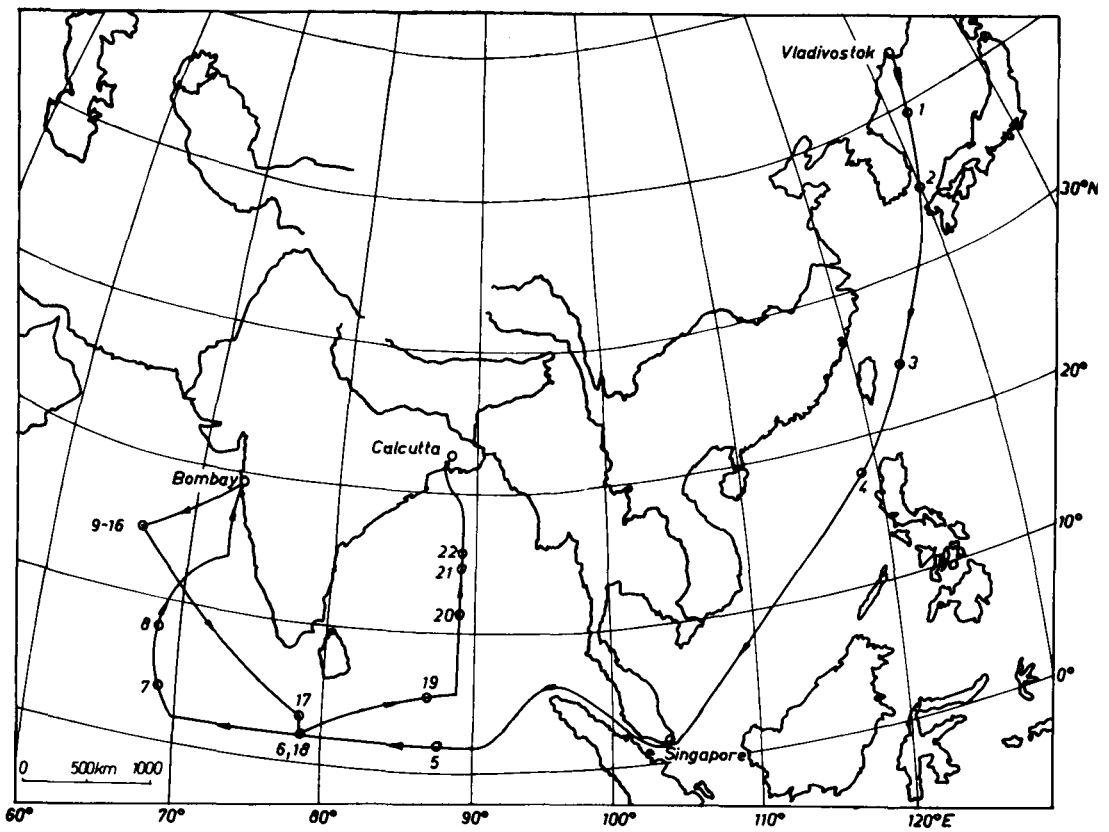

Fig. 1. Geographical representation of the sampling locations (the figures give the sample number).

(see Table 1). Fig. 1 gives the sampling positions of the ship. As the ship was moving, the point marked represents the position at the middle of the sampling time. After sampling, each filter was sealed in a small plastic box to be retained for analysis at the laboratory.

The samples were analysed in the chemical laboratory of the Institute for Atmospheric Physics of Budapest. The water soluble components were extracted from the filters by washing in 4 ml of 60 °C distilled water for 5 h. The sulfate content of the solution was determined by means of the isotope dilution analysis as described by Klockow et al. (1974). This analysis was repeated three times to gain more reliable results (0.5 ml of the solution was used for each analysis); 2 ml of the remaining part of the solution was diluted to 20 ml. Five ml of this latter solution was analysed for chloride with the spectrophotometric mercury thiocyanate-iron method (Zall et al., 1956), while 15 ml was used to determine the sodium concentration by means of a flame photometer in the usual way. The detection limit of the sulfate, chloride and sodium analysis in the solution is 0.1, 0.05 and 0.25 $\mu g\ ml^{-1}$, respectively.

It is to be noted here that each filter with a diameter of 3.5 cm, used for sampling, was cut from a larger one with a diameter of 5 cm. The filter pieces remaining were used to determine the sulfate, sodium and chloride blanks. By means of the procedure described above no sodium and chloride blanks were found. However, an average sulfate blank of 1.8 μg/filter was detected. In this way, using a 50 m^3 sample volume, the minimum detectable concentration of sulfate, sodium and chloride is 0.04 $\mu g\ m^{-3}$, 0.2 $\mu g\ m^{-3}$ and 0.04 $\mu g\ m^{-3}$, respectively (for sulfate we assumed that at least the same amount is necessary for an acceptable detection as the blank value).

3. Results and discussion

Table 1 shows the air volume sampled for aerosol analysis at different sampling locations as well as the chemical concentrations measured. The value of the wind speed averaged for the sampling periods and the wind directions (which were rather constant during one sampling) are also included. The concentration of excess sulfate in the table was calculated on the basis of the sodium content in the air and the average SO_4/Na ratio in the sea water (0.25) by assuming, which seems to be reasonable considering the wind directions, that the atmospheric sodium is entirely of maritime origin.

One can see from Table 1 that the chloride concentration varies between 0.73 and 9.4 $\mu g\ m^{-3}$ with an average value of 4.61 $\mu g\ m^{-3}$. The sodium concentrations are approximately in the same range. The average is 3.58 $\mu g\ m^{-3}$. The variation of the concentration of sea-salt components is mostly caused by the fluctuation of the wind speed (a correlation coefficient of about 0.6 is calculated between the concentrations and wind velocities, which gives a real relationship at a probability level of 0.01). The sodium and chloride concentrations obtained in this program are in a reasonable agreement with those published in the literature for other oceanic areas (e.g. Buat-Menard et al., 1974; Gravenhorst, 1978; Lodge et al., 1960) and with the figures measured over the Arabian Sea (Sadasivan, 1978). This means that in marine atmosphere the sea-salt concentration is rather uniformly distributed.

In agreement with the results of other workers (e.g. Buat-Menard et al., 1974; Martens et al., 1973, Sadasivan, 1978) an important chloride loss is detected in our aerosol samples as compared with the average Cl/Na ratio in sea water (1.80). This loss is equal to 26% on an average. Martens et al. (1973) believe that this loss is entirely due to the release of gaseous HCl owing to the interaction of HNO_3 vapor and sea-salt particles. However, recent measurements indicate that the concentration of NO_x (precursor of HNO_3) as well as the HNO_3 and nitrate levels (Huebert and Lazrus, 1978; Gravenhorst, 1978) are not sufficiently high

Table 1. *Main results of the sampling program (for sample number see Fig. 1), where V represents the air volume sampled for aerosol analyses, while NA means that no analysis was made*

Sample No.	V [m^3]	SO_4^{2-} [$\mu g\ m^{-3}$]	Na^+ [$\mu g\ m^{-3}$]	Cl^- [$\mu g\ m^{-3}$]	Cl^-/Na^+	Excess SO_4^{2-} [$\mu g\ m^{-3}$]	Wind direction and speed	[$m\ s^{-1}$]
1	9.05	NA	<1	0.73	—	NA	SE	11.7
2	8.65	NA	<1	1.01	—	NA	SSE	7.5
3	16.00	NA	<1	1.00	—	NA	SSE	7.7
4	4.80	NA	<2	2.03	—	NA	SE	4.5
5	52.50	0.61	1.65	2.08	1.26	0.20	WSW	6.8
6	24.20	0.20	0.79	1.26	1.59	0.00	WSW	5.4
7	57.90	0.61	1.02	1.37	1.34	0.35	WSW	6.7
8	55.70	2.23	3.59	4.74	1.32	1.33	WSW	12.2
9	55.60	1.02	3.09	4.58	1.48	0.24	WSW	14.7
10	53.40	2.72	8.46	9.53	1.13	0.60	WSW	10.8
11	52.40	2.36	2.82	2.37	0.84	1.65	SW	13.5
12	51.40	2.53	8.02	9.40	1.17	0.52	SW	12.3
13	54.70	2.48	6.58	9.18	1.40	0.83	SW	16.6
14	50.30	1.95	6.52	7.19	1.10	0.31	SW	12.6
15	55.00	2.36	5.09	6.95	1.37	1.08	SW	10.9
16	59.60	1.43	1.83	2.28	1.25	0.97	SW	12.2
17	58.10	1.55	2.69	4.93	1.83	0.88	SW	8.3
18	56.50	1.23	1.68	2.14	1.27	0.81	NW	5.5
19	45.30	2.03	3.13	3.82	1.22	1.24	SW	7.3
20	58.40	2.31	1.85	2.78	1.50	1.85	WSW	7.4
21	56.50	1.82	2.19	3.70	1.69	1.27	SW	11.8
22	59.30	2.43	3.51	4.68	1.33	1.55	SW	13.1
Average		1.77	3.58	4.61	1.34	0.87		10.0

to explain this phenomenon. Thus one expects that chloride loss may result from other processes, e.g. from the coagulation of H_2SO_4 particles and sea-salt droplets (Hitchcock et al., 1980) also liberating HCl vapor into the air. It is to be noted, however, that no correlation was found between the excess sulfate and chloride loss observed in this program. Thus, further studies are necessary to clarify this point.

We have to emphasize that the solution of this problem would be very important from the point of view of atmospheric chemistry since this process seems to be an important HCl source. The net production of chloride particles by the ocean is 10^2–10^3 Mt yr^{-1} (see Duce, 1969; SMIC, 1971) which gives on the basis of the loss measured in this program (26%) a global chlorine source strength between 26 and 260 Mt yr^{-1}. Further research is needed to determine the atmospheric cycle and importance of the chlorine released in this way.

The total maritime sulfate concentration range (0.22–2.72 $\mu g\ m^{-3}$) as well as the average value (1.77 $\mu g\ m^{-3}$) determined around Asia are in a good agreement with the results obtained over other parts of the world's oceans (Nguyen et al., 1974a and b). The level of excess sulfate (0.87 $\mu g\ m^{-3}$ on an average) is supported by the value of 0.9 $\mu g\ m^{-3}$ reported by Gravenhorst (1978) for the northern Atlantic. This agreement also points in the direction that the tropospheric background aerosol is fairly well mixed.

It is obvious that the excess sulfate is formed by gas-to-particle conversion. However, the origin and nature of precursor gases are not well understood. A possible candidate as precursor gas is the anthropogenic sulfur dioxide. However, taking into account the residence time of SO_2 (1–2 day) as well as the wind directions observed during the samplings this possibility can be probably ruled out. Nguyen et al. (1978) suppose that submicron sulfate particles form from a sulfur gas of natural origin, namely from dimethyl sulfide, the oceanic release of which is estimated to be 27 Mt yr^{-1}. On the basis of their laboratory work Cox and Sandalls (1974) reported that photochemically generated free radicals such as OH reacted rapidly with dimethyl sulfide to form aerosol particles. An important finding of these authors was the absence of SO_2 during the dimethyl sulfide oxidation.

Another reduced sulfur gas of natural origin is the hydrogen sulfide, having average background concentrations between 5–50 ppt (1 part in 10^{12} parts of the air) by volume as reported by Slatt et al. (1978). It was recently proposed that the reactions of carbonyl sulfide and carbon disulfide provide important sources for both H_2S (McElroy et al., 1980) and SO_2 (Logan et al., 1979). The latter authors postulated that the source of atmospheric SO_2 formed from CS_2 and COS can be as large as 12 Mt yr^{-1}, expressed in sulfur equivalents, and these compounds represent a very important SO_2 source in the marine troposphere. They also suggested that "the relative uniform distribution observed for COS suggests a globally distributed source". It is probable that this source is the ocean surface.

4. Conclusions

The comparison of our results with concentrations reported for other parts of the world's oceans clearly shows that sea-salt components (e.g. chloride and sodium) as well as excess sulfate particles are fairly uniformly distributed in remote oceanic atmosphere.

Much more research is needed in the future to determine the source strength and tropospheric cycle of HCl formed from particulate sea-salt. The need for further investigation of the formation mechanisms of excess sulfate particles and their gaseous precursors is also obvious.

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О КОНЦЕНТРАЦИЯХ СУЛЬФАТОВ, ХЛОРИДОВ И НАТРИЯ В ВОЗДУХЕ НАД МОРЕМ ВОКРУГ АЗИАТСКОГО КОНТИНЕНТА

На основе химического анализа проб аэрозоля, собранных над морями вокруг азиатского континента, представлены концентрации сульфатов, хлоридов и натрия в морском воздухе. С учетом содержания натрия в воздухе и среднего состава морской воды вычислены скорость потери хлоридов из морской соли, а также избыток концентрации сульфатов. Результаты обсуждаются с точки зрения цикла нсе и образования частиц сульфатов.