DISTRIBUTION OF ELEMENTAL AND ORGANIC CARBON AEROSOLS IN THE ATMOSPHERE BETWEEN JAPAN AND ANTARCTICA

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Abstract: During the period from November to December, 1988, aerosol samples were collected on board the research vessel "Shirase" between Japan and Antarctica. Carbon contents of the samples were determined using gas chromatography, after separating elemental and organic carbon by the conventional pyrolysis method. The concentration levels of elemental and organic carbon aerosols were found to be on the order of 100 ng/m³ over the Antarctic Ocean. These values were lower by two orders of magnitude than those in Tokyo Bay and higher by one order of magnitude than those at Syowa Station, Antarctica.

1. Introduction

Carbonaceous aerosols have been shown to account for 10–30% of the mass of ambient aerosols in Japanese rural areas (Nishikawa *et al.*, 1986), and consist of elemental carbon (mainly soot), carbonate (such as calcium carbonate) and organic carbon (Ohta and Okita, 1984). Elemental carbon aerosols reduce the atmospheric visibility and play an important role in the catalytic conversion of SO_2 to SO_4 on its surface (Novakov, 1984). Organic carbon aerosols are one of the important products in gas-to-particle transformation processes. Elemental and organic carbon aerosols are also dominant components of fine aerosols.

In spite of such importance, observations of carbonaceous marine aerosols are very sparse (Hoffman and Duce, 1977; Chesselet *et al.*, 1981; Ohta and Okita, 1984; Andreae *et al.*, 1984), especially over the Antarctic Ocean. We report here the concentration of carbonaceous aerosols measured on board the research vessel "Shirase" between Japan and Antarctica from November to December, 1988. The results are also compared with those from Syowa Station, Antarctica, 1988.

2. Experimental Procedures

2.1. Sampling

Aerosol sampling was done on the vessel using a β-ray-absorption-type-aerosol-monitoring system (DKK, MODEL DUB-32). Each sample was collected on a quartz-fiber-tape filter at the flow rate of 18 l/min. Thirty-two samples were taken by this procedure in areas of Tokyo Bay, the Pacific Ocean, the East Indian Ocean and the Antarctic Ocean. However, inspection of the record of the β-ray monitoring system showed that 20 samples were contaminated by exhaust dust from the vessel. The remaining 12 samples were analyzed for the concentration of elemental and organic carbon. The number of uncontaminated samples was 3, 5 and 4 for Tokyo Bay, the East Indian Ocean and the Antarctic Ocean, respectively. Aerosol samples were also collected by the same method at Syowa Station, Antarctica in December, 1988.

2.2. Analysis

A round filter sample 1 cm in diameter was punched from the filter tape which was kept rolling after sampling to avoid contamination during its storage. Organic and elemental carbons were separated by the pyrolysis method and their concentrations were determined using gas chromatography. The pyrolysis instrument used consists of a tunable furnace and a gas chromatograph with FID detector (Hitachi, 263 type), as shown in Fig. 1. Almost all natural organic aerosols can be vaporized anaerobically at below 600°C and elemental carbon burns to born CO_2 at 850°C in oxygen (HAYASHI et al., 1985; NISHIKAWA et al., 1986). Therefore, carbon found in helium carrier gas at 600°C was defined as organic carbon, and that in helium and oxygen-mixture carrier gas at 850°C was defined as elemental carbon. The CO_2 gas generated in the tunable furnace was led into the reduction furnace to remove interfering gases, and then into the methanizer through the separation column to change CO_2 into methane for detection by FID. Sulfanilamide was used for the standard material of organic and elemental carbon. For determinating the blank value of the filter tape, a round filter was also punched from the same filter tape, close to the position where each sample was taken. Both blank values of elemental and organic carbons thus obtained,
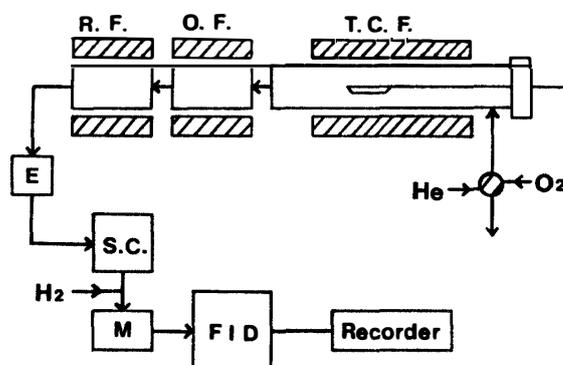

Fig. 1. Schematic diagram of the carbon analytical system. T.C.F.: tunable combustion furnace, O.F.: oxidation furnace, R.F.: reduction furnace, E: elimination trap for water vapor, S.C.: separation column, M: methanizer.

ranging between 10 and 50 ng/m³, were subtracted from each sample value.

3. Results and Discussion

3.1. Contamination by exhaust dust from the vessel

In the present study, the aerosol concentration was monitored by the β-ray absorption system to confirm contamination during aerosol sampling. In fact, contamination from the exhaust dust was apparently detected as occasionally abrupt increases in the response of the aerosol-monitor, as shown in Fig. 2. And the contaminated samples were discarded. To elucidate the effect of such contaminations, we collected the exhaust dust from the ship chimney and analyzed it. Table 1 shows the chemical composition of the sampled exhaust dust. High abundances of elemental carbon, organic carbon, NH_4^+, SO_4^{2-}, Ca, Fe and Zn are remarkable. In particular, elemental carbon and organic carbon account for 33 and 13% of the total weight, respectively. As shown in Fig. 3, almost all organic carbon extracted from the exhaust dust by n-hexane and benzene-methanol mixture were found in helium carrier gas at temperatures below
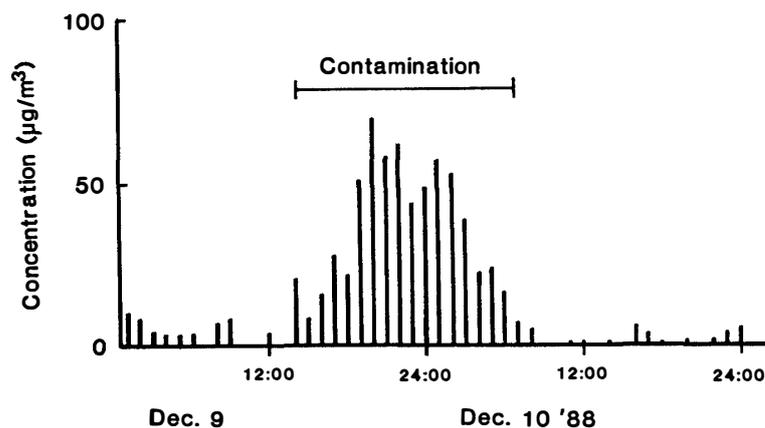

Fig. 2. Hourly mean concentrations of the atmospheric aerosols measured by the β-ray absorption system.

Table 1. Chemical composition of the exhaust dust from the ship-chimney of R. V. SHIRASE.

T-C	46.2%	K	150 (μg/g)
(Cae=33.3%)		Ca	19400
(Cao=12.9%)		Ti	37
SO_4^{2-}	95000 (μg/g)	V	68
Cl^-	<3	Mn	307
NO_3^-	30	Fe	42000
NH_4^+	5000	Cu	125
Na	305	Zn	1090
Mg	123	Sr	16
Al	100	Ba	16
P	1040	Pb	35

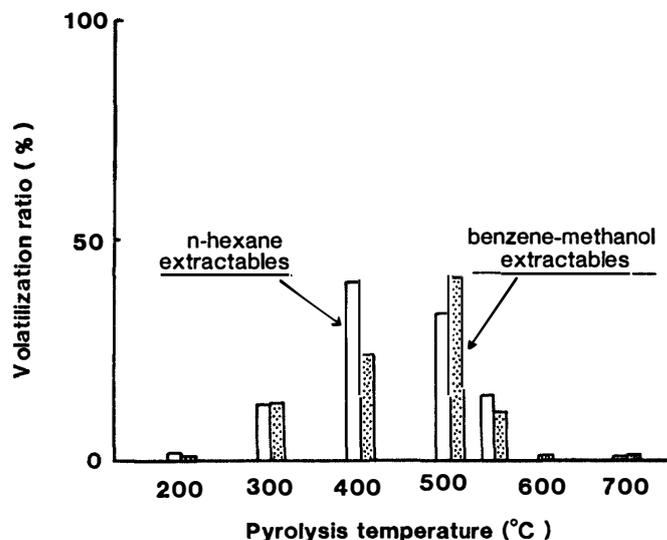T-C: total carbon
Cae: elemental carbon, Cao: organic carbon

Fig. 3. *Volatilization ratios of organic carbon extracted with two different solvents of n-hexane and benzene-methanol from the exhaust dust taken in the ship-chimney, as a function of pyrolysis temperature.*

600°C. This suggests its volatile nature, and hence, its possible highly dispersed state in the air. Therefore, contamination from the exhaust dust has high potentiality to affect the analytical results, and careful sampling is necessary for ship-board measurements of the aerosols.

It is also pointed out that high Zn content in the marine aerosols may be used as a measure of contamination by the exhaust dust.

3.2.   Distribution of the carbonaceous marine aerosols

Figure 4 shows average concentrations of elemental and organic carbon in aerosols in areas of Tokyo Bay, the East Indian Ocean, the Antarctic Ocean and Syowa Station. The concentrations found over the East Indian Ocean and the Antarctic Ocean were very close to each other at a level of $n \times 100$ ng/m^3, intermediate between those in Tokyo Bay and at Syowa Station. These organic carbon concentrations are in good agreement with 380–480 ng/m^3 in the Sargasso Sea area (CHESSELET et al., 1981) and 220–390 ng/m^3 at Bermuda, Hawaii and Samoa (HOFFMAN and DUCE, 1974, 1977). HOFFMAN and DUCE (1977) show that marine organic aerosols are produced by gas-to-particle conversion from gaseous organic substances, but it cannot be determined whether they are natural or artificial. CHESSELET et al. (1981) indicate by measurements of stable carbon isotopic composition that long-range transport of organic carbon of continental origin is the major source for the organic component of marine aerosols. If we accept their results, the organic aerosol concentration should be lower over the Antarctic Ocean than in other marine areas, because the Antarctic Ocean is sufficiently remote from land. Indeed, our results support this.

The concentrations of elemental carbon aerosols over the Antarctic Ocean are lower than 600–1400 ng/m^3 at Hachijo-jima and 400–1300 ng/m^3 at Chichi-jima in the Western Pacific Ocean (OHTA and OKITA, 1984). Because elemental carbon aerosols are produced by combustion of organic substances, its origin is also on land. Therefore, the marine organic and elemental aerosols show similar distributions, as observed in this
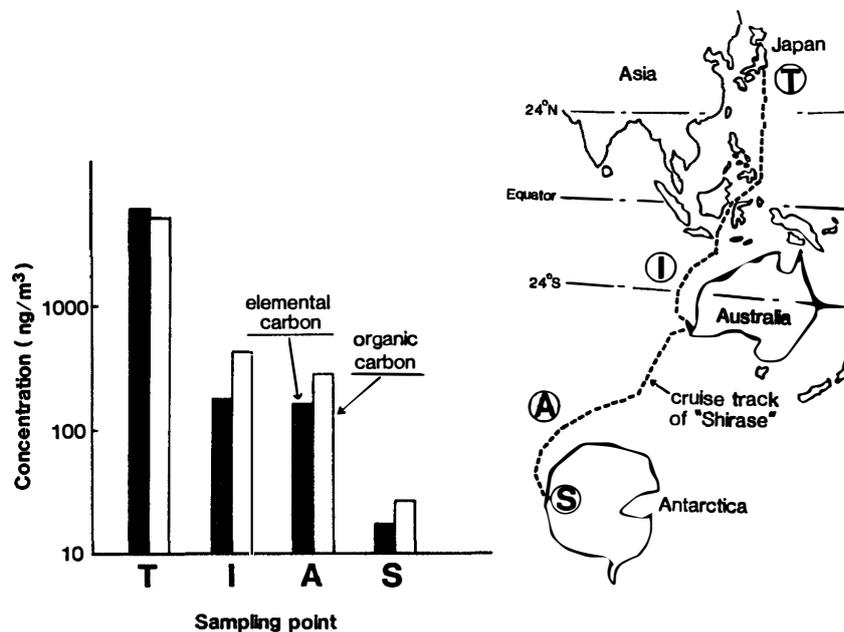
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Fig. 4. Average concentrations of elemental and organic carbon in the aerosol at each sampling point, and cruise track of R. V. SHIRASE from Japan (Nov. 15, 1988) to Antarctica (Dec. 18, 1988).

measurement. The levels of both carbon aerosols observed in the Antarctic Ocean indicate the global baseline concentrations of the marine carbon aerosols.

The difference in the organic and elemental carbon aerosol concentrations between the Antarctic Ocean and Syowa Station is quite marked. This big difference cannot be explained if we accept that the Antarctic Ocean and Syowa Station are covered with uniform air, because the distance separating both sampling sites is too short to result in a substantial decrease in the carbon aerosol concentrations by falling out. A different source of the airs over the Antarctic Ocean and Syowa Station is strongly suggested. This is also supported by the well accepted observation that fine sulfuric acid aerosol concentration greatly increases at Syowa Station in the austral summer season, which is not a common feature over the Antarctic Ocean. It is also consistent with the fact that the snow on Greenland, accompanying much aerosols from land, records the history of artificial air contamination, whereas that on Antarctica, which receives very low land aerosols, does not show such a trend due to the difficulty of aerosol transportation from the northern to southern hemisphere (MUROZUMI *et al.*, 1969). Though there is no direct evidence that the air over Syowa Station is highly affected by the Antarctic Ocean, the present observation of carbon aerosols suggests that the big gap between those over the Antarctic Ocean and Syowa Station is due to high contribution of Antarctic air with low carbon aerosol loading to the air over Syowa Station.

Acknowledgments

Appendix Data

We have already reported the concentration of chemical components, other than carbonaceous, of the marine aerosols over the Antarctic Ocean (NISHIKAWA et al., 1990). All chemical compositions of marine aerosols over the Antarctic Sea in the austral summer season of 1987 and 1988 are shown in the Appendix Table.

Appendix Table   Chemical composition of the marine
aerosol over the Antarctic Ocean.

T-C	460 (ng/m^3)	Na	100	(ng/m^3)
(Cae	170)	Mg	13	
(Cao	290)	Al	5.0	
		K	4.6	
NH$_4^+$	21	Ca	5.9	
Cl$^-$	172	Fe	4.7	
NO$_3^-$	17	Cu	(0.2)	
SO$_4^{2-}$	104	Zn	(0.4)	
CH$_3$SO$_3^-$	20	Sr	(0.04)	
		Pb	(0.07)	

soil aerosol: 60 (ng/m^3) was calculated assuming the
crustal average value of Al at 8%.

T-C: obtained in 1988, others: obtained in 1987

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