Modification of Sea-salt Aerosols over the Coastal Area in China

Li Fang (李 放), *Duan Minzheng* (段民征), *Lu Daren* (吕达仁)
LAGEO, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029
and *Kikuo Okada*
Meteorology Research Institute, Tsukuba, Ibaraki, Japan
Received September 8, 1997; revised March 24, 1998

ABSTRACT

Aerosol particles over the coastal area are subject to the modification of their chemical composition during their transport and diffusion. For examining the modification, the marine aerosol particles are collected at an island, East China Sea. Comparison of elemental composition of the marine aerosols with that of the samples collected at a coastal site, e.g. in Shanghai, was made. The results of chemical analysis show that the loss of chlorine component in aerosol particles is one of the main characteristics in the course of diffusion of marine aerosols into the coastal continent. Sulphur is a dominant component for fine particles in both marine and coastal aerosols. The relation of particle number concentration and particle size distribution to the meteorological conditions was discussed briefly. These results can be used as a reference in the estimation of equivalent refractive index of the aerosols for radiation transfer.

Key words: Marine aerosol, Modification, Elemental component, Coastal area

I. INTRODUCTION

Aerosol composition is a piece of important information for radiation transfer. Two parameters, namely, total loading and chemical composition, are of great significance (Li and Lu, 1995; and Li et al., 1995). Generally there are significant differences in physical and chemical properties between marine aerosols and continent aerosols (Ikegami et al., 1994; Mouri et al., 1995). For the physical-chemical modification of the dust-storm particles during their long-range transport from Asia inner continent to the western West Pacific many studies have been conducted (Okada et al., 1987; Okada et al., 1990; Mouri and Okada, 1993; Niimura et al., 1994; Fan et al., 1996; and Zhou et al., 1996). The re-crystallization and re-mixture are reported to be a basic process in the modification. About diffusion of the marine aerosol into the land or transform of sea particles affected by coastal area aerosols, however, there is little work up to the present. The fully understanding of the two-way modification makes it possible to characterize the coastal aerosols, which are a type of transition, between the continental and marine aerosols.

This paper aims at the investigation and analysis of the atmospheric aerosols over East China Sea and its near coastal city, Shanghai. The method of elemental analysis with EDX (energy diffusive X-ray) was adopted for the determination of the particle chemical composition. An Optical Dust Counter was used to measure the particle size distribution and concentration of the aerosols.

II. EXPERIMENTAL WORK

Aerosol particles were collected at two sites: one is located at Shengshan island, East China Sea, where there is an ocean observation station of National Oceanic Administration, and another is located at a coastal city, Shanghai (Fig. 1). The sampling date, time and meteorological conditions are shown in Table 1. The skies during the experiment appeared often in part cloud or overcast, fractional coverage of cloud being from 7/10~10/10. The prevailing wind was in the northeast direction, and wind speed was in the range of 2~6 m/s.

Table 1. Date, Time and Meteorological Conditions for the Field Sampling

Place	Date	Time	T(°C)	RH(%)	WS(m/s)	WD	FCA*	Vis. (km)
Island	17~22 Sept. 1995	12:10~12:15	24.3	62	5.0	NE	9/10	33
Shanghai	26 Sept. 1995	12:30~12:45	26.3	43	2.0	SE	8/10	15

* FCA—the fractional coverage of clouds.

1. *Measurement of Aerosol Size Distribution and Concentration*

The variation of aerosol content in the atmosphere with meteorological conditions is important for understanding the mechanism of particle product and growth. Optical Dust Counter of PM—730 type (made by Dan Industry Co., Ltd., Japan) was used in monitoring particle size distribution and concentration of atmospheric aerosols. With a flow rate of sampling air of 300 ml/min, the Counter gives a group of aerosol concentration and size distribution data every five minutes. The sampling entrance of the Counter is about 2.5 m above the ground so as to avoid the casual disturbance from the machine operating action.

2. *Collection of Aerosol Particles*

For examination of the modification from different size modes, the aerosol particles in

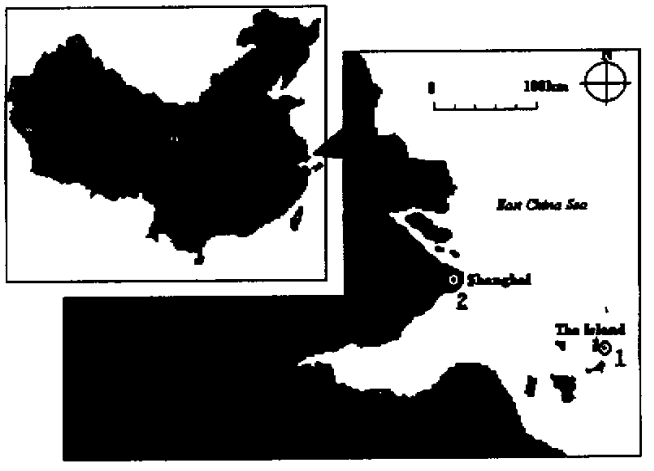

Fig. 1. Position scheme of observation stations. One is located at Shengshan island, (at 30°43′N, 122°48′E, 57 m (a.s.l.)) East China Sea, and another in Shanghai (at 31°10′N, 121°26′E, 2.8 m (a.s.l.)).

two size regions (fine and coarse) were collected on the matrix surface of carbon-coated nitrocellulose film supported on an electron microscope grid. Two different single stage impactors, one with a jet diameter of 0.5 mm and another of 1.0 mm were used for collection of aerosol particles. With the flow rates of 1.0 L / min and 1.3 L / min, the impactors collect aerosol particles efficiently down to 0.3 μ (fine particles) and 1 μ (coarse particles) respectively. The sample was examined with a transmission electron microscope (TEM) equipped with energy diffusion X-ray (EDX) for analysis of the elemental composition.

III. RESULTS

The meteorological parameters of the ground atmospheric layer during the observation on the six-day average basis are listed in the Table 1. There are about 96 sets of data in the style of total concentration and particle size distribution obtained with the Optical Dust Counter (ODC) at Shengshan island in East China Sea. Unfortunately the data measured by ODC at Shanghai site were missed due to the breakdown of the Counter in that time.

1. *Dependence of Aerosol Concentration on the Meteorological Condition*

Fig. 2 gives the hourly mean variations of atmospheric aerosol concentration with meteorological conditions on 20 September 1995 at Shengshan island, East China Sea from 0:04 ~23:00 LST. It can be seen from Fig. 2 that the number concentration of atmospheric aerosol particles is positive correlation with the ambient relative humidity by and large, which decreases slightly with the increase of the air temperature during the daytime. The wind speed in Fig. 2 shows inconsiderable effect on the aerosol concentration. This maybe because the magnitude of the wind speed is relatively constant, and is within the weak-influence range (Jaenicke, 1988).

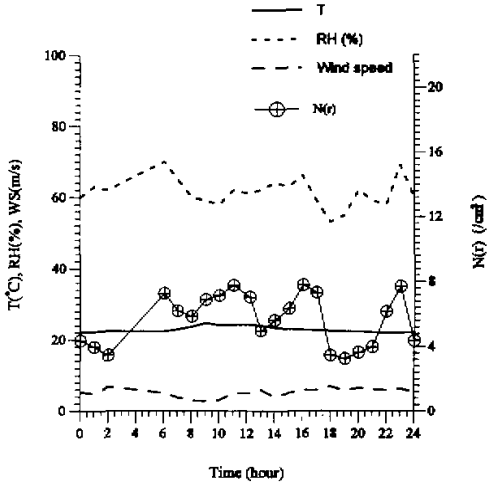

Fig. 2. Diurnal variation of the total concentration of atmospheric aerosols, the ambient temperature, relative humidity and wind speed for Shengshan island, East China Sea on 19 September 1995.

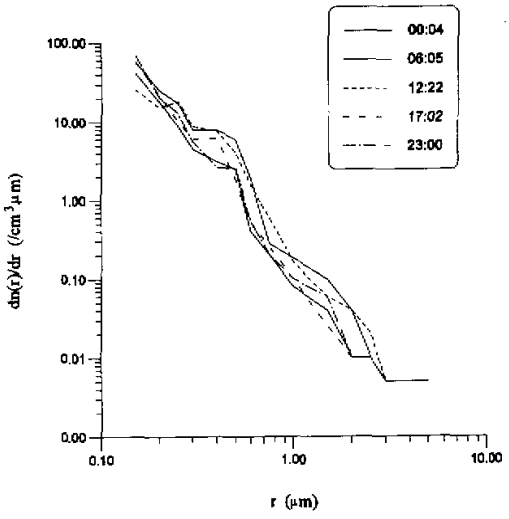

Fig. 3. Particle size distributions of atmospheric aerosols at Shengshan island at 0:04, 6:05, 12:22, 17:02 and 23:00 LST, on 20 September 1995.

Aerosol size distribution was measured in a duration including the time with the particle sampling. Fig. 3 gives the results observed at Shengshan island on 20 September 1995 at 0:04, 6:05, 12:20, 17:02 and 23:00 LST. It is seen from Fig. 3 that the common feature of size distributions is that there is a small hump located around 0.3 μm~ 0.6 μm size bins in the radius, which is a visible sensitive range. This implies that the formation of aerosol particles in this size range has probably a special mechanism with a high efficiency of the particle production as well as a low remove rate from the atmosphere (Twomey, 1977; Jaenicke, 1988). Only in the daytime the hump of the particle size distribution becomes considerable due to the involvement of photochemical reaction related to the gas–to–particle transformation (Graedel and Crutzen, 1993).

2. *Elemental Occurrence Frequency and Relative Concentration*

In order to investigate the mixed nature of an individual particle, elemental compositions contained in the particles were analyzed with an analytical electron microscope (Hitachi, H–600) fitted with the electron probe X–ray energy spectrometer. Fig. 4 gives EDX microanalytical results of fine particle collected in the island and in Shanghai respectively. For a sample of one hundred particles was randomly selected in the analysis. The occurrence frequency and relative concentration were measured for each element. The results are shown in Fig. 4(a) for fine particle samples, and for coarse particles seen in Fig. 4(b) respectively. The comparison between Fig. 4(a) and Fig. 4(b), shows that sulphur occurrence frequency is 100% for the sea fine aerosol particles, and 96% for coastal continent fine particles. From the histogram of the relative elemental concentration, sulphur is a dominant composition for the fine particles, regardless of sea aerosols or the coastal ones. Additionally sodium is a second main elemental component for the island particles, responding to the sea salt NaCl, but potassium is a second one for the coastal particles, suggesting a particle source related to

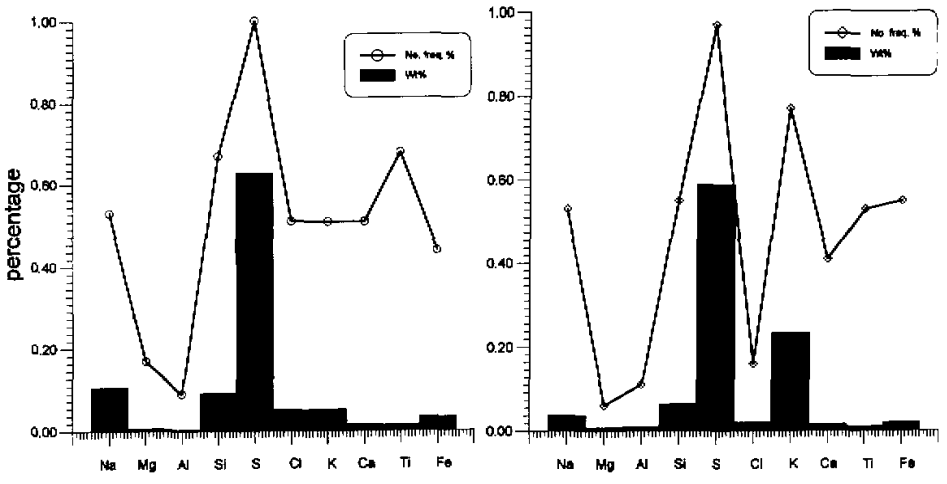

Fig. 4. Elemental compositions of atmospheric aerosols. Solid line denotes frequency of element occurrence and histogram is relative mass concentration in the particle collection. (a) at Shengshan island in East China Sea for 22 Sept. 1995, and (b) at a seaside city, Shanghai for 26 Sept. 1995, both sampling with an impactor of 0.5 mm jet in diameter for the fine particles.

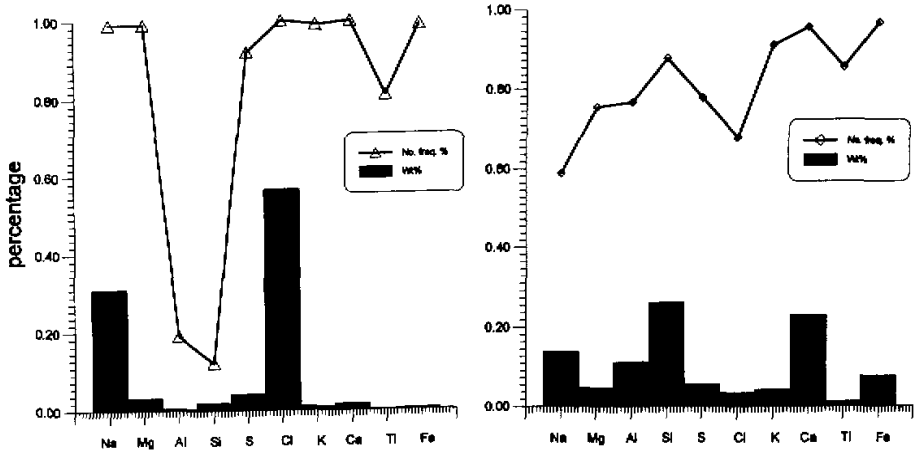

Fig. 5 (a) and (b). As in Fig. 4 but for 1.0 mm jet in diameter for the coarse particles.

biomass burning along the coastal area (Casareto et al., 1996).

In Fig. 5(a) and Fig. 5(b) for coarse particles, the relative contents of element Na and Cl are dominantly high for sea particles, compared to those for fine particles in Fig. 4. In the aerosol sample of coarse particles collected at the coastal area, silicium and calcium elements are main components according to the EDX analysis. This may be related with road dust and some airborne particles from building activities.

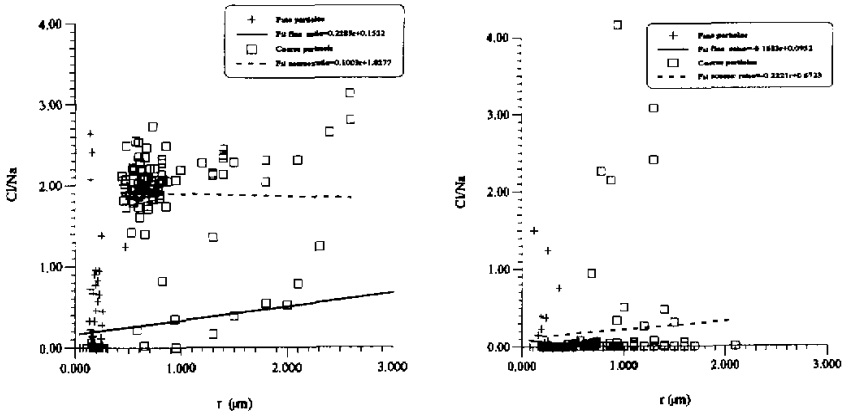

Fig. 6. Ratio of chemical element chlorine and sodium Cl/Na vs the particle radius. (a) at Shengshan island, East China Sea, and (b) in Shanghai.

3. *The Ratio of Chlorine/ Sodium*

In the sea water there is almost a fixed ratio of chlorine to sodium. To check the modification of aerosol particles transporting from marine to coastal area the ratio of Cl/Na against particle radius is examined. The results for the fine particles and for the coarse particles are illustrated in Fig. 6(a) and Fig. 6(b) respectively. For the particles collected at the island the Cl/Na ratio is fluctuated around the fitted line, of which the intercept is 1.8227, and very approximates the average value (1.8) of the sea water (Mouri and Okada, 1993). However the ratio in the fine particles is very low (0.1522), suggesting a low content of NaCl in fine particles. As for the coastal particles in Fig. 6(b), both the ratios for the coarse and fine particles are low. The modification of the aerosol particles must be included during their transport.

4. *Ternary Element Proportion*

In order to examine variation of the relative ratio between sodium, sulphur and chlorine in the particles, a ternary element graph is plotted in Fig. 7 for the island and the coastal aerosols. The values (x1,x2,x3) in the brackets of Fig. 7 are the percentages of the individual amount of Na, S, and Cl to the sum of the three components, respectively. Symbol I–C in Fig. 7 indicates the coarse particles of the island, I–F the fine particles of the island, S–C the coarse particles of the coastal area, and S–F the fine particles of the coastal area. Clearly the amount of sulphur element in the fine particles over the coastal area is high by an overwhelming majority, suggesting the dominant proportion of sulfate in this size range. Another important point needed to notice is that the ternary ratio of the coarse particles from the island is quite approximate to the ratio (35,3,62) (Ikegami, et al., 1993) of sea water, marked by a star symbol in Fig. 7. It seems that the ratio for the coarse particles tends to evolve as and approach to the ratio of Na_2SO_4 (marked by a triangle in Fig. 7) if one makes a line from the point I–C to the point S–C.

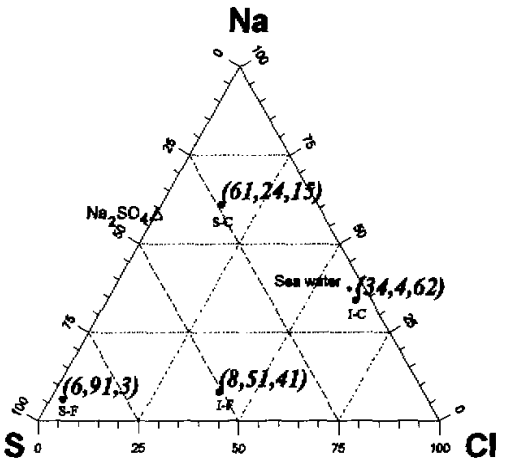

Fig. 7. Scheme of ternary elements for sodium, sulphur and chlorine of the aerosol samples, where I–F stands for the island fine particles; I–C for the island coarse particles; S–F for Shanghai fine particles; S–C for Shanghai coarse particles; " * " for the value of average sea water; and " Δ" for the value of Na_2SO_4.

IV. DISCUSSION

The variation of number concentration of aerosol particles behaves to a certain extent a positive correlation with the ambient relative humidity, although the time phase of both is not always consistent, as seen as in Fig. 2. This means that the moisture plays an important role in the microphysical process of particle formation and growth, and acts as an essential solvent for particle chemical transfer. In view of the complicated relation of aerosol concentration to the relative humidity, it is difficult to use a simple formula for description of the relation. Hanel (1976) had done some theoretical investigations on it, but his semi–empirical formula seems hard to be used into the other areas expect for his test cases (Li et al., 1995). Effect of the ambient temperature on the aerosol concentration is second important compared to the relative humidity, due to its implication to the particle chemical action rate as well as the particle collision remove from atmosphere. As to the wind speed, related with the sea surface spray and particles transport, the total effect of the wind can be referred to Fig. 2. In range of the wind speed in this experiment the wind transport seems to be a dominant process, for the particle concentration tends mostly to decrease as the wind speed increases.

In the daytime the formation of secondary particles in the atmospheric aerosols is more efficient due to the existence of sunshine that promotes the photochemical reaction of microparticle production. The aerosol size distributions in Fig. 3 shows the increase of the irradiance–related particles, focusing mainly on the radius range of 0.2～0.6 μm. It must be pointed out that aerosol concentration is usually controlled by multiple factors. For example, the aerosols in the size range of 0.15～0.3 μm at night at 23:00 LST (as seen in Fig. 3) show a little higher number concentration. This may be owing to the dominant effect of the heavy ambient moisture, the relative humidity reaching its top value at that time.

Sea salt component, NaCl is the essential ingredient of coarse particles collected at the island. Even for the case at the coastal city Shanghai, there is considerable NaCl composition in coarse particles. This suggests that one can use refractive index of NaCl to approach the equivalent refractive index of coarse sea salt particles when dealing with the climate effect of marine aerosols. For the fine particles, however, sulphur is always of overwhelming majority in the elemental weight percentage in both the cases at the island and at the coastal site, as seen in Fig. 4(a) and Fig. 4(b). It is shown that the gas–particle transformation from primary gaseous precursor, say, from dimethylsulfide (DMS) mainly over the sea area, from SO2 mainly over the coastal area, should proceed mostly in the fine bin range of the particle size distribution. These results deliver the messages of not only the ingredient proportion, but also the particle size range useful for estimating the refractive index of the aerosols (Stelson, 1990). They are important in atmospheric correction of the radiance transfer.

When marine aerosols diffuse over the continent, their composition is subject to the modification of the physical and chemical properties of the particles. The weight ratio of chlorine to sodium, Cl / Na, can indicate the change level of the sea salt composite. From Fig. 6, the ratio of Cl / Na for coarse particles has a dramatic decrease from 1.8227 near the value of sea water at the island, East China Sea, to 0.6723 in the coastal area, Shanghai. This point can be seen more obviously in Fig. 7, and Cl content in the particles for the coastal area has a significant loss compared with the one at the island. The loss process can be described mainly as following two reaction formulas,

$$2NaCl+H_2SO_4 \rightarrow Na_2SO_4+2HCl\uparrow,$$
$$NaCl+HNO_3 \rightarrow NaNO_3+HCl\uparrow,$$

and it has been reported that there are lots of chemical radicals, SO_4^- and NO_3^-, checked out in the coastal aerosol particles (Wu, et al., 1988), supporting the formulas of above modification mechanism. Additionally, content of potassium K in the fine particles in the coastal area has a considerable increase. This may be mainly a contribution of the burning of plant remains, because it is reported that plant cell well reserves a plenty of potassium (Casareto et al., 1996). That road dust (Si) and building material powder(Ca), as seen in Fig. 6(b), were found out in the coarse particles is not difficult to be understood in coastal area. This means that the modification of the aerosol composition also should include the influence from anthropogenic activities (Ji, et al., 1993). A long–term monitoring net of coastal area including the urban and rural is clearly necessary to make the more detail understanding for the modification from both ocean and continent.

A question that is often posed in discussion on representatives of analytical results is: "What is the proper number of sampling?" Obviously, there is no unique answer to that question, since many factors are involved, such as time scale in question and objectives. In the intensive campaign, the number of aerosol sampling is usually limited to a given time period. Aerosol concentration and size distributions at the Island were measured with an optical particle counter once an hour from day to night, and particle filter sampling was taken twice a day around noon. Relatively, as seen in Table 1, the number of the sampling over land appears poorer owing to the limitation of both requirements: the east prevailing wind (coming from the sea) and the sunshine midday for observation of aerosol optical properties in the campaign. The analysis of this paper is limited to aerosol measurements over the two places in the separate time, which is not sufficient for a detailed trajectory comparison of the two air

masses. The results in this work, however, show that modification of marine aerosol is in recognizable features, and deserves to be further explored.

V. CONCLUSIONS

Experiment for comparison of marine aerosols with coastal aerosols is carried out. The sampling stations are located at Shengshan island, East China Sea, and in a seaside city, Shanghai respectively. Variations of the particle number concentration and the size distributions with the meteorological conditions are briefly discussed for the marine aerosols. The EDX microscopy analyzer is used for determination of elemental relative proportion of the particles with two sampling systems, for fine and coarse particle collection in alternation. The following conclusions come to that

1). The total number concentration of marine aerosols is usually positive correlated with the ambient relative humidity. Temporal variation of the particle size distribution during the daytime is stronger than that during the nighttime, due to the photochemical reaction, which seems to have an explicit effect on the particles with the size 0.2—0.6 μ in radius;

2). For the marine aerosols, the coarse particles are rich in sea salt, NaCl, and fine particles consist of more than 60% sulphur element on a relative-mass percentage basis. This difference of the fine particles in the composition from the coarse particles is a piece of important information for modelling aerosol optical properties;

3). Chlorine loss of the coarse particles is one of the main features for the modification of the marine aerosols during diffusion in the continental atmosphere.

The authors wish to thank Mr. Yang Yulin, director of Shengshan Ocean Station, Chinese National Oceanic Administration for his facilities in sampling, and Dr. N. Niimura, University of Tsukuba, for her help for the test of artificial NaCl particles by the EDX. This work was in part supported by the National Natural Science Foundation of China. The first author gratefully acknowledges a fellowship awarded by the Science and Technology Agency of Japan.

REFERENCES

Casareto, B. E., Y. Suzuki, K. Okada and M. Morita (1996), Biological micro-particles in rain water, *Geophys. Res. Lett.*, **23**: 173–176.

Fan, X., K. Okada, N. Niimura, K. Kai, K. Arao, G. Shi, Y. Qin and Y. Mitsuta (1996), Mineral particles collected in China and Japan during the same Asian dust-storm event, *Atmos. Environ.* **30**: 347–351.

Graedel, T. E. and P. J. Crutzen (1993), *Atmospheric Change: A Earth System Perspective*, W. H. Freeman and Company, New York, 73–267.

Hanel, G (1976), The properties of atmospheric aerosol particles as functions of the relative humidity at thermodynamic equilibrium with the surrounding moist air, in *Advances in Geophysics*, **19**: 73–188, Academic Press, New York.

Ikegami, M., K. Okada, Y. Zaizen and Y. Makino (1994), Sea-salt particles in the upper tropical troposphere, *Tellus*, **46B**: 142–151.

Jaenicke, R. (1988), Aerosol physics and chemistry, *Landolt- B(nstein, Numerical Data and Functional Relationships in Science and Technology*, New Series, Group V: Geophysics and Space Research, Volume 4, Meteorology, Subvolume b, G. Fischer (editor), 391–457.

Ji, X., D. Jiang, S. Fei, H. Yuan, P. He, B. Ye, Z. Lei, and C. Feng (1993), Road dusts emission inventory for meteopolita area of Shanghai City, *Atmos. Environ*, **27A**: 1735–1741.

Li, F. and D. Lu (1995), Optical properties of atmospheric aerosols in the region of Mount Qomolangma in Tibet, *Chinese J. Atmos. Sci.*, **19**: 420–430.

Li, F., J. Liu and D. Lu (1995), Analyses of composite observations of optical properties of atmospheric aerosols in late summer over some areas of North China, *Scientia Atmospherica Sinica*, **19:** 235–242. (in Chinese)

Mouri, H., and K. Okada (1993), Shattering and modification of sea-salt particles in the marine atmosphere, *Geophys. Res. Lett.*, **20:** 49–52.

Mouri, H., K. Okada and S. Takahashi (1995), Giant sulfur-dominant particles in remote marine boundary layer, *Geophys. Res. Lett.*, **22:** 595–598.

Niimura, N., K. Okada, X. Fan, K. Kai, K. Arao and G. Shi (1994), A method for determining Asian dust-storm particles mixed internally with sea salt, *J. Meteor. Soc. Japan*, **72:** 777–784.

Okada, K., A. Kobayashi, Y. Iwasaka, H. Naruse, T. Tanaka and O. Nemoto (1987), Features of individual Asian dust-storm particles collected at Nagoya, Japan, *J. Meteor. Soc. Japan*, **65:** 515–521.

Okada, K., H. Naruse, T. TAnaka, O. Nemoto, Y. Iwasaka, P. Wu, A. Ono, R. A. Duce, M. Uematsu, J. T. Merrill and K. Arao (1990), X-ray spectrometry of individual Asian dust-storm particles over the Japanese island and the North Pacific Ocean, *Atmos. Environ.*, **24A:** 1369–1378.

Stelson, A. W. (1990), Urban aerosol refractive index prediction by partial molar refraction approach, Environ. *Sci. Technol.*, **24:** 1676–1679.

Twomey, S. (1977), Atmospheric Aerosols, Elservier North-Holland Inc., Amsterdam, 143–164.

Wu, P. M., and A. Ono (1988), X-ray spectrometry of individual nitrate-containing particles in the urban atmosphere, *J. Meteor. Soc. Japan*, **66:** 155–166.

Zhou, M., K. K. Okada, F. Qian, P. Wu, L. Su, B. E. Casareto, and T. Shimohara (1996), Characteristics of dust-storm particles and their long-rang from China to Japan- case studies in April 1993, *Atmospheric Research* **40:** 19–31.