Available online at www.sciencedirect.com
SCIENCE DIRECT®
Atmospheric Environment 40 (2006) 1205–1215
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

Coarse and accumulation mode particles associated with Asian dust in southwestern Japan

Daizhou Zhang[a,*], Yasunobu Iwasaka[b], Atsushi Matsuki[b], Kazunori Ueno[c], Tatsuya Matsuzaki[c]

[a]*Faculty of Environmental and Symbiotic Sciences, Prefectural University of Kumamoto, Kumamoto 862-8502, Japan*
[b]*Institute of Natural and Environmental Technology, Kanazawa University, Kanazawa 920-1192, Japan*
[c]*Kumamoto Prefectural Institute of Public Health and Environmental Science, Kumamoto 869-0425, Japan*

Received 19 May 2005; received in revised form 3 October 2005; accepted 14 October 2005

Abstract

Number and mass concentrations of atmospheric particles were measured at a surface site on the southwestern Japan coast from March to May 2002. Particles were collected when Asian dust appeared at the site in this period, and later characterized with their morphology and elemental composition from electron microscopic analysis. The mass concentration of suspended particulate matters with diameter smaller than 10 μm (SPM10) during dust episodes was predominated by particles larger than 1.0 μm (coarse particles), which were mainly mineral dust with a small fraction of sea salt. As dust-loading low-pressure systems were approaching, SPM10 and the number concentration of coarse particles decreased gradually until the arrival of cold fronts. After that, they increased due to dust arrival except during rainfall. Time series of the number concentration of coarse particles during dust plume passages was not in parallel with that of accumulation mode particles in the range of 0.1–0.3 μm and they were even inverse in some episodes, reflecting a horizontal structure with multiple intervals of dust and secondary particles. The electron microscopic analysis confirmed the frequent mixture of sea salt in dust particles and suggested that the probability for dust particles to become mixtures with sea salt was likely dependent on the vertical thermodynamic structure of the marine boundary layer, through which aloft dust particles descended to the ground. More mineral dust particles mixed with sea salt in cases with deep mixing layers than with shallow mixing layers. No correlation between the mixture degree and the transport time for dust particles to travel in the marine atmosphere from the Asian continent to southwestern Japan was found.

Keywords: Particle number concentration; Dust; Pollutant; Low-pressure passage

1. Introduction

Dust storms frequently break out in the arid and semiarid areas in the Asian continent, and aloft dust particles can, particularly in spring, spread in a wide range from East Asia to North America. The annual input of mineral dust into the North Pacific from the Asian continent is about 480 Tg, which is more than half of the global annual deposition of minerals into the ocean (Okada et al., 1990; Duce, 1995). Besides natural dust, the continent is recently characterized by rapid increase of industrial

*Corresponding author. Tel.: +81 96 383 2929x761; fax: +81 96 384 6765.
E-mail address: zdz@pu-kumamoto.ac.jp (D. Zhang).

1352-2310/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2005.10.037

pollution and biomass burning (Akimoto and Narita, 1994; Streets et al., 2001). The large and diverse aerosol emissions of these sources render the springtime outflow from the continent an extraordinarily complex synoptic-scale air parcel mixed with natural dust and anthropogenic pollutants. In the downstream areas, the air parcel encounters marine air masses abundant in water vapor and sea salt, which complicates the mixture further and stimulates chemical reactions sensitive to humidity. As a result, the composition and size of dust particles are severely changed during their long-range transport.

Dust particles, through surface uptake of gases such as SO_2 and NO_x, can enhance the production of particulate sulfate and nitrate in the downstream marine atmosphere over the Korean Peninsula and the Japanese archipelago (Kim et al., 1998; Kim and Park, 2001; Nishikawa et al., 1991; Ooki and Uematsu, 2005). Coagulations of dust and sea salt in the marine boundary layer can result in substantial growth in the size of dust particles (Andreae et al., 1986; Zhang and Iwasaka, 2004). These processes greatly change the hygroscopicity of dust particles and enforce their ability to act as nuclei for cloud droplet formation. At the same time, reactions on the surface of dust particles are expected to transfer part of the iron in the particles from non-bioavailable form into bioavailable form for phytoplankton growth, which subsequently enhances the primary bioproduction in surface sea water (Meskhidze et al., 2005). Since optical properties of dust particles depend on their size, shape and composition, the transformation will also affect their performance in the atmospheric radiation transfer.

The transformation occurs when dust plumes mix with other pollutants. It is naturally expected that mature intermingling of dust plumes and polluted airmasses will cause efficient dust transformation. Characterizing the mutual status of dust plumes and polluted airmasses during their dispersion is, therefore, essential for elucidating the transformation. Field measurements, postulated model simulations and the recently conducted ACE-Asia (Asian Pacific Regional Aerosol Characterization Experiment) have confirmed that the springtime outflow of Asian dust together with pollutant plumes has an extraordinary complicated structure in time and space. A detailed spatial structure of the atmosphere enclosing dust and anthropogenic pollutants was obtained by an airborne measurement of ACE-Asia (Seinfeld et al., 2004). Elevated layer structures of dust plumes were also identified in lidar network observations and model simulations (Sakai et al., 2002; Murayama et al., 2001; Uno et al., 2003). Since few long-term simultaneous observations on mineral dust, anthropogenic pollutant and sea salt are available to show their mutual status within low-pressure systems, the intermingling processes and weather conditions that induce dust particles to combine with sea salt and other pollutants as the systems move offshore from the Asian continent are poorly understood.

We conducted continuous measurements of aerosol particles in accumulation mode and larger size ranges when dust plumes passed southwestern Japan in spring 2002, and characterized individual dust particles which were collected during the dust passage. Here, we report the results and discuss dust properties in the context of meteorological conditions. In particular, we concentrate on the arrival time lags of accumulation mode particles and dust particles, and on the sea salt content in dust particles. The purposes are (1) to provide a more detailed insight into the distribution of dust plumes and polluted air masses within low-pressure systems at the downstream areas of the Asian continent and (2) to explore the processes responsible for the mixture state of dust particles with sea salt in the marine atmosphere.

2. Observation and analysis

Number concentrations of atmospheric particles with diameter larger than 0.1 μm and the mass concentrations of suspended particulate matters with diameter smaller than 10 μm were measured at the Takahama Environment Observatory, Kumamoto (32°23′N, 129°59′E), from February to May 2002. The observatory is located on the western coast of Amakusa island in southwestern Japan (Fig. 1); 160 m to the west is the East China Sea and to its east is the village of Takamama with a population of about 1700. Local inhabitants live on fisheries and agriculture. There is no industry or factory near the observatory. Anthropogenic influences on this site from local or regional surface emissions are supposed to be rare. Any non-pulse increases of air pollutants are attributable to long-range transport from upwind areas.

Two optical particle counters, Rion KC-01D and Rion KC-18 (Rion Corporation, Japan), were used to measure particle number concentrations. The

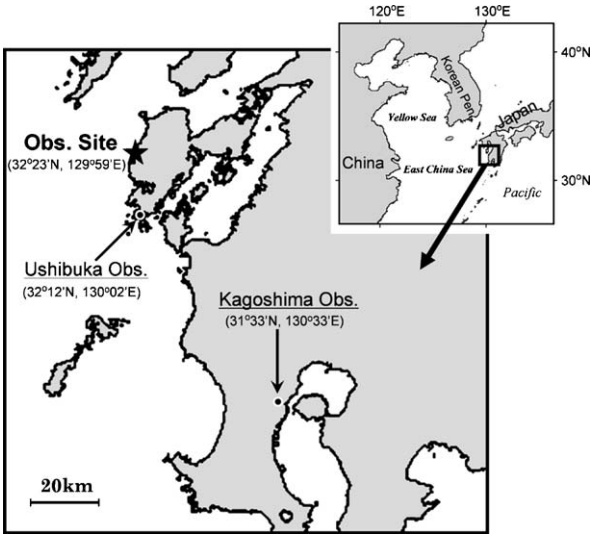

Fig. 1. Location of the observation site, Ushibuka Meteorological Observatory and Kagoshima Meteorological Observatory in southwestern Japan.

measurement ranges of Rion KC-01D are 0.3–0.5, 0.5–1.0, 1.0–3.0, 3.0–5.0 and $>5.0\,\mu m$, and the measurement ranges of Rion KC-18 are 0.1–0.15, 0.15–0.2, 0.2–0.3, 0.3–0.5 and $>0.5\,\mu m$. The Rion KC-18 was operated with an automatic dilution unit (Rion KD-06), which was set to dilute the particle concentration in inlet air to 1/100 before entering the Rion KC-18. Ambient air was introduced into these instruments from the outside of the observatory shed through two 2.8-m-long Teflon tubes, which have insulating surfaces. The flow rate of the Rion KC-01D was set at $0.5\,l\,min^{-1}$ and the flow rate of the Rion KC-18D was set at $0.3\,l\,min^{-1}$. Before starting the measurements, we investigated the particle loss due to the inlet tubes. We put the Rion KC-01D on the roof of the observatory shed where the inlet entrances were fixed and measured directly the concentration in the atmosphere for 15 min, at 1 min intervals. Then we moved the particle counter into the shed and measured the concentration through the inlet tube. The loss of particles in the range of 3.0–5.0 μm was about 5–10%. The loss of particles in smaller ranges was about 10–25%. These losses should be caused by the absorption of the inlet tubes. Our purpose is not to investigate the absolute particle concentration in a dust storm event, but to compare the concentrations of dust particles and their time series during different dust episodes. Systematic losses are not expected to degrade the discussions and conclusions in the following sections. The two particle counters measured number particle concentrations with 15-min intervals. To show time series of the concentrations, 1 h averages are applied in this study. Owing to technique problems, Rion KC-18 measurement was started from 22 March 2002.

Mass concentrations of suspended particulate matters (SPM) recorded by a DUB-12 SPM monitor (DKK-Toa Corporation, Japan) at the observatory during the observational period are used to show the scenarios of particulate matters in mass. The instrument was set up to monitor the air quality around the observatory. It measures the concentration with 1 h time resolution by quantifying β ray absorption of glass fiber filters (MILLIPORE, Filter Type: AP20) on which particulate matters are collected at a fixed flow rate ($18\,l\,min^{-1}$). Its detecting range is $0–5000\,\mu g\,m^{-3}$ with the sensitivity of $1\,\mu g\,m^{-3}$. A PM-10 cyclone inlet is set at the head of the air intake tube and, consequently, the measured concentration is for particles smaller than 10 μm. For convenience, the concentration measured by the monitor is described as SPM10 in the following sections.

When dust appeared in southwestern Japan, we collected particles on a cliff (32°23′N, 129°59′E) on the coast near the observatory (Fig. 1). The cliff faces the East China Sea to the west, and its altitude is about 34 m above the sea surface. We chose this position other than the observatory to collect particles, in order to avoid any possible local soil particles or road dust. The collection equipment was operated on a concrete stand which is 1.8 m high above the ground. It is unlikely that particle samples collected at this site contain mineral particles from local areas when wind is flowing from sea areas. Particles were collected onto electron microscope Ti grids (3 mm in diameter) using a single-stage cascade impactor. The jet diameter of the impactor is 1 mm. The volumetric flow rate of inlet air was kept at about $5.0\,l\,min^{-1}$. Under a given particle density of $2.3\,g\,cm^{-3}$, the 50% cut-off aerodynamic diameter of the impactor is about 0.25 μm, and the collection efficiency for particles larger than 0.6 μm is 1.0. The collection time for grids was from 30 s to 2 min depending on the visibility. Each grid after collection was preserved in a plastic capsule, and the capsules were sealed in plastic bags together with paper-packaged silica gel. Later, the bags were packaged into a box, and the box was preserved in a refrigerator in cooling until subsequent analysis. Table 1 lists the particle collection periods and

Table 1
Summary of dust collection time and surface weather conditions[a] at the particle collection site when dust particles were collected in 2002, together with the time (TIME) for the collected dust particles to travel from the Asian continent to southwestern Japan within the marine atmosphere

Sampling time (JST[b])		Temp.	RH	Visibility	Wind		TIME[c]
Date	Period	(°C)	(%)	(km)	Direction	Speed($m\,s^{-1}$)	(h)
9 March	1240–1330	15	36	~6	NWW	1	48
17 March	0850–0930	15	63	~8	NWW	2	50
21 March	1810–1900	12	70	~3	SW	4	21
2 April	1250–1410	24	48	~10	SSW	1	57
10 April	0840–0920	15	40	~5	W	5	24
14 April	0710–0800	18	72	~6	SSE	5	35

[a]Temperature, and relative humidity were recorded immediately after particle collection from monometers which we set up at the site before particle collection. Visibility was estimated by the naked eyes. Wind direction and speed were measured after the particle collection, with a delay of 1 min on average.
[b]JST—Japan Standard Time (UTC + 9 h).
[c]Time is estimated using the backward trajectories calculated from the online NOAA HYSPLIT model.

weather conditions when particles were collected. It is noted that all samples were collected under moderate weather. From surface weather charts and meteorological records published by the Japan Meteorological Agency, it is learnt that particle collections were carried out under approximately similar weather conditions, i.e., the local area was in the transition from low-pressure systems to high-pressure systems, the wind was weak and the weather was fine.

Morphologies and elemental compositions of collected particles were obtained by using the SEM-EDX system of the Solar Terrestrial Environment Laboratory of Nagoya University. The SEM-EDX analyses are the same as described in Zhang et al. (2003a). In terms of elemental composition, dust particles are defined as those containing silicon (Si) together with at least one of aluminum (Al), calcium (Ca) and/or iron (Fe). Sea salt particles are abundant in sodium (Na) and chlorine (Cl) and contain minor sulfur (S) and magnesium (Mg). If the content of Si was smaller than 2.0% and Al was not detected in a particle, it was not characterized as dust. We found that a few sea salt particles defined as above contained minor Si together with Ca and/or Fe, but they did not contain Al and their Si relative weight ratios were usually less than 2.0%. Mixture particles are dust particles which contain both Na and Cl besides mineral elements. Na-containing dust particles in which Cl was not detected were not identified as mixture particles. Na has a significant crustal origin, and surface uptake of acidic species such as sulfur dioxide and nitrogen oxides on mixture particles hardly result in a complete loss of chlorine in the sea salt parts in mixture particles (Zhang et al., 2003a, b; Zhang and Iwasaka, 2001). Fig. 2 shows examples of a SEM photograph and X-ray spectra of elemental composition of particles measured by the EDX.

Meteorological records of pressure, temperature, relative humidity and precipitation at the Ushibuka Regional Meteorological Observatory (32°12′N, 130°02′E, 3.0 m asl), which is located 19 km south of the Takahama Environment Observatory, are applied to show the weather during the observation period. Data from routine radiosondes launched at the Kagoshima Meteorological Observatory (31°33′N, 130°33′E, 4.0 m asl), which is located 69 km south of the Takahama Environment Observatory, are applied to show the vertical thermodynamic structure of the boundary layer.

3. Results and discussion

3.1. Dust dispersion associated with cold fronts

It is found that, during the whole observation period, particle concentrations in the ranges of 0.1–0.15, 0.15–0.2 and 0.2–0.3 μm showed the same trends, while particle concentrations in the ranges of 1.0–3.0, 3.0–5.0 and >5.0 μm showed the same trends. However, the scenarios of the two size groups were different in many episodes. Concentrations in the ranges of 0.3–0.5 and 0.5–1.0 μm were sometimes similar to particles in smaller ranges, and sometimes to particles in larger ranges. For this

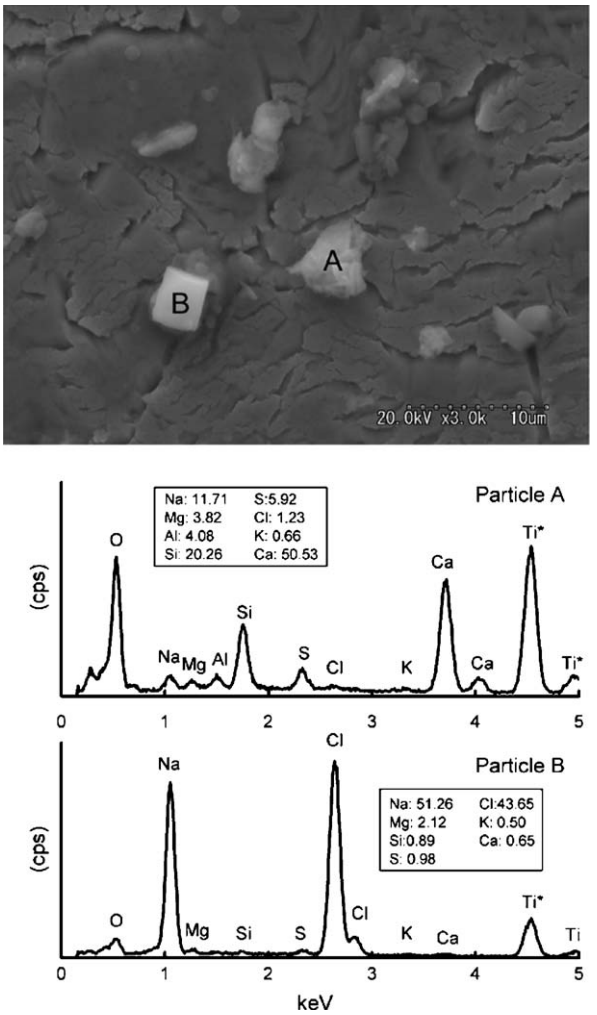

Fig. 2. SEM photograph of collected particles (the particles were collected on 9 March) and the X-ray spectra of a mixture particle of mineral dust and sea salt (particle A) and a sea salt particle (particle B). Data in the frames in each spectrum are the raw relative weight ratios of detected elements in the particles.

reason, here we will not discuss the particle concentrations in each available size range from the particle counters. Instead, we investigate the concentrations in two size ranges: 0.1–0.3 μm, which is the sum of particles in the ranges of 0.1–0.15, 0.15–0.2 and 0.2–0.3, and $>1.0\,\mu m$, which is the sum of particles in the ranges of 1.0–3.0, 3.0–5.0 and $>5.0\,\mu m$. Particles in the range of 0.1–0.3 μm are described as accumulation mode particles, and particles in the range of $>1.0\,\mu m$ are described as coarse particles, in the following description.

Fig. 3 shows the time series of SPM10 and the number concentration of particles at the Environment Observatory from 1 March to 20 April 2002, when Asian dust frequently appeared there. Surface weather records of pressure, precipitation, temperature and relative humidity are also shown in the figure. Cold front passages are marked by shaded bars in the panels and the particle collections are marked by arrows on the lower panel time axis in the figure. SPM10 variation is consistent with the concentration of coarse particles. Rapid increase/decrease of SPM10 always coincided with similar trends of coarse particles, suggesting SPM10 was dominated by particles larger than 1.0 μm. Single particle analysis showed that, in this size range, mineral dust particles including mixture and non-mixture ones, were always the majority, sea salt particles sometimes occupied a small fraction and other particles were rarely detected (Fig. 4), indicating that significant SPM10 at coastal areas in southwestern Japan is caused by Asian dust.

The time series of SPM10 and coarse particles around cold front passages show that, as dust-loading low-pressure systems were approaching, the coarse particle concentration and SPM10 usually decreased until the arrival of cold fronts. Then, both the concentration and SPM10 increased, sometimes gradually and sometimes rapidly, except in case of rainfall. For example, from 25 to 29 March, the number concentration of coarse particles decreased nearly by one order (the records show the concentration was about $2500\,l^{-1}$ in the morning on 25 March and about $450\,l^{-1}$ in the afternoon on 26 March) as a cold front was approaching. The cold front passed the site between 1900 and 2000 JST on 26 March. After that, the concentration and SPM10 showed a pulse reduction, which was caused by rainfall. Right after the rain, they were at far higher levels than usual, indicating dust's presence. Thus, Asian dust in a low-pressure system appears usually behind the cold front of the system in southwestern Japan. This is reasonable in view of the synoptic-scale structure of low-pressure systems. Asian dust plumes are initially stimulated by cold fronts of low-pressure systems (cyclone systems) in the arid and semiarid areas in the Asian continent, and move eastward in the cold and dry air following the fronts (Fang et al., 1997). Since dust particles are distributed within the atmosphere mainly by vertical convections, turbulence and horizontal advection, particles in the postfrontal air of a low-pressure system moving eastward in the northern hemisphere middle latitude (westerly region) are not expected to penetrate cold fronts to enter prefrontal air, i.e., the distinctive structure of low-pressure

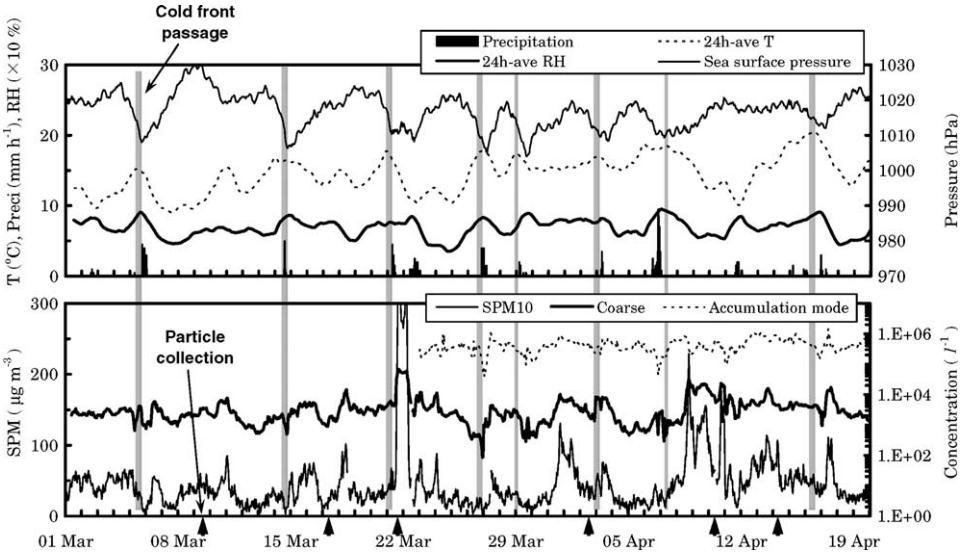

Fig. 3. Lower panel—time series of mass concentration of particles $<10\,\mu m$ (SPM10), coarse particle concentrations in the range of $>1.0\,\mu m$ and accumulation mode particle concentrations in the range of 0.1–0.3 μm at the Takahama observatory from the beginning of March to 20 April 2002. Upper panel—time series of precipitation per hour, 24-h average temperature (24h-ave *T*), 24-h average relative humidity (24h-ave RH) and sea surface pressure recorded at the Ushibuka Meteorological Observatory. Timings of cold front passages, which are identified from the variations of temperature, surface pressure and wind, and surface weather charts published by the Japan Meteorological Agency, are marked by shaded bars with their widths approximately proportional to the front strength. Timings of particle collections for single particle analysis are marked by arrows on the time axis in the low panel.

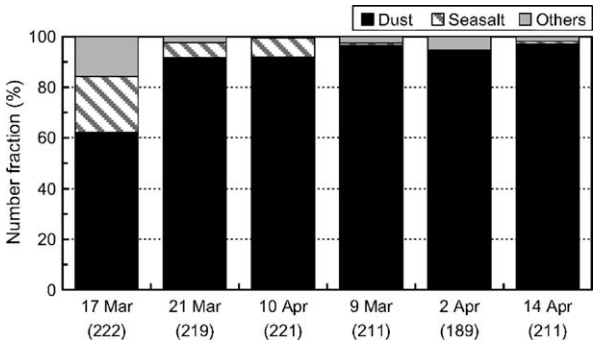

Fig. 4. Number fractions of mineral dust particles (including mixture and non-mixture ones), sea salt particles and others in particles detected by the SEM-EDX in each case. Total numbers of detected particles in each case are listed in parentheses. The fractions are not shown in the time order of dust events. For the convenience of discussions in the following sections, they are shown in two groups according to sea salt frequency detected in the particles.

systems make it impossible for postfrontal particles to easily enter the prefrontal regions. This was evidenced in a detailed case study of the spatial structure of a heavy dust-loading low-pressure system at a coastal site in China (Zhang et al., 2005) and a ship cruise in the marine areas around southern Japan when a dust-loading low-pressure system was encountered (Bates et al., 2004). From the above results, it can be confirmed that Asian dust plumes usually follow the cold fronts of low-pressure systems to arrive at southwestern Japan.

Fine natures of SPM10 and coarse particles after dust arrival in Fig. 3 further indicate that, within each dust event, the dust plume did not show a mono-peak spatial distribution across the plume. Dust plumes were usually composed of multiple intervals of high- and low-concentration dust. For example during 21–25 March, when a heavy dust plume passed, dust concentration peaked at least three times in different episodes. The eastward movement of Asian dust plumes is the result of synoptic scale advection by westerly flows in the middle latitude of the northern hemisphere. Dust particles observed are presumably those having experienced synoptic-scale movement and subsidence, simultaneously with gravitational settlement before arriving at the site. No sudden changes in the horizontal structures of dust plumes are expected except those caused by precipitation. Thus the up-and-down variations of SPM10 and the coarse particle number concentration across a dust plume indicate that the dust plume had sporadic horizontal distributions with multiple dense- and thin-dust intervals. This is consistent with previous results

from lidar measurements and model simulations at other sites around Japan (Murayama et al., 2001; Sakai et al., 2002; Uno et al., 2004). Therefore, dust plumes in the close downstream areas of the Asian continent are highly inhomogeneous even in the horizontal direction.

3.2. Passages of coarse particles and accumulation mode particles

The time series of concentration of accumulation mode particles from 23 March to 20 April are also shown in Fig. 3. They were not in parallel with the concentrations of coarse particles in a number of episodes. Before a front's arrival, the concentration of accumulation mode particles was frequently at high levels or even increasing with time, which is very different from the case with coarse particles. For example, as a cold front followed by dust was approaching during 25–26 March, the concentration of coarse particles decreased gradually, while the concentration of accumulation mode particles did not show systematic decrease or apparent changes compared to other periods. After a cold front's arrival with dust in postfrontal air, concentrations of coarse particles had remarkable increases, sometimes with the increase and sometimes with the decrease of accumulation mode particles. For example, concentrations of coarse and accumulation mode particles in cases of 27–29 March and 30 March–4 April were approximately synchronized, while in the case of 8–11 April they were approximately inversed.

As identified by single particle analysis, the majority of coarse particles are dust (mixed or non-mixed with sea salt) and sea salt particles. Such particles are typically primary particles emitted from arid and semiarid areas in the Asian continent and from the surface of the East China Sea, respectively. Many of them changed due to surface uptake of gaseous species and mutual interactions. In contrast, particles in accumulation mode are, in general, from the coagulation of nuclei mode particles and the condensation of vapors onto pre-existing particles (Seinfeld and Pandis, 1998). Such particles have the longest atmospheric life time, because particle removal mechanisms are least efficient in this regime. The high concentration of accumulation mode particles in an air parcel implies that the airmasses in the parcel are aged and contain, or have at one time contained, significant precursor gaseous pollutants favoring new particle formation. With a size-segregated Anderson sampler, we collected integrated aerosol samples at the Takahama Observatory during 19–22 March, and confirmed by later analysis that the major ion components in the particles smaller than 1.0 μm are sulfate and ammonium with a small fraction of nitrate. Therefore, the prior increase of accumulation mode particles as dust-followed cold fronts were approaching the observatory indicates that anthropogenic polluted air masses and dust plumes within the same low-pressure systems dispersed to Japan from the west with a time lag. Anthropogenic polluted air masses appeared ahead of dust plumes. Similar time lags were also reported from case data by Uematsu et al. (2002) and Matsumoto et al. (2003) around northern Japan. Aircraft observations also revealed that newly formed particles and dust were stratified in different layers in the marine areas between China and Japan (Hatakeyama et al., 2004; Fan et al., 1996; Buzorius et al., 2004).

The synchronizing increase of coarse particles and accumulation mode particles after dust arrival in some cases is very different from that found in the Asian continental atmosphere. Wehner et al. (2004) reported that dust arrival at Beijing was accompanied with rapid reduction of secondary particles, and they attributed this phenomenon to the replacement of local or regional anthropogenic air masses by the dust plume which contained less anthropogenic pollutants. In this regard, in southwestern Japan, dust plumes behind cold fronts of low-pressure systems intermingled, at least to some extent, with aged anthropogenic pollutants. The separated status of natural dust plumes and anthropogenic polluted air masses was confirmed at a coastal site in China (Zhang et al., 2005). Therefore, anthropogenic pollutants likely intermingled with dust plumes during the journey of the low-pressure systems from China to Japan. No observational data are yet available to interpret how they intermingle in the marine atmosphere. Low-pressure systems moving into the downwind marine areas from the Asian continent usually stimulate active cloud formation and enhance precipitation there because of the substantial supply of warm and humid air from sea areas. This will subsequently lead to a tendency for the boundary layers to be unstable and favorable for vertical exchanges of air masses at different levels. Other processes such as gravitational settlement of aloft dust particles can also lead to the mixing of different air masses. These hypotheses are very speculative. Observation data

and model simulations are essential to elucidate the intermingling processes. In addition, the consistencies and discrepancies of peak timings of coarse particles and accumulation mode particles indicate that the intermingling must be highly inhomogeneous.

3.3. Mixture of dust particles with sea salt

It is well known that dust particles appearing around Japan areas frequently mix with sea salt. This is also confirmed in this study. Here we compare the details of mixture situation in different dust events. Fig. 5 shows the number fractions of mixture and non-mixture dust particles to total detected dust particles in each event. Mixture particles are further segregated according to their mixture degrees of mineral and sea salt masses. Non-mixture particles are dust particles in which no sea salt was identified, mineral $\gg$ seasalt particles are those whose composition is dominated by mineral components, mineral$\sim$seasalt particles are those dominated by both mineral and sea salt, and mineral $\ll$ seasalt particles are those dominated by sea salt. According to the number fractions, the dust events can be separated into two groups as shown in Fig. 5. The first group includes dust events of 17 March, 21 March and 10 April. Mixture particles occupy about 90%, and only about one-tenth of dust particles do not contain sea salt in these events. The second group includes dust events of 9 March, 2 April and 14 April, in which mixture particles occupy around 70%, and about 30% dust particles do not contain sea salt. Compared to dust particles in the first group events, dust particles in the second group events are less mixed with sea salt. For convenience, we call the first group events well-mixed events and the second group events less-mixed events, in the following description.

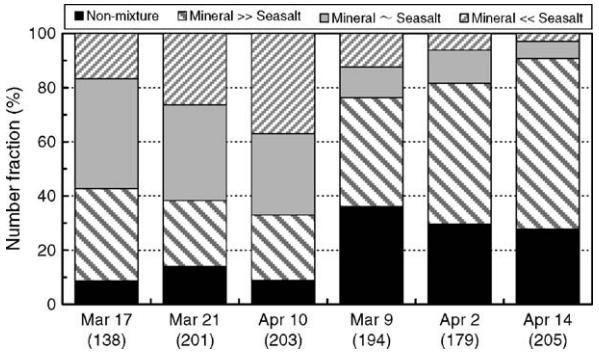

Fig. 5. Number fractions of non-mixture ($r = 0$), mineral $\gg$ seasalt ($0 < r < 0.35$), mineral$\sim$seasalt ($0.35 \leqslant r < 0.65$), and mineral $\ll$ seasalt ($0.65 \leqslant r < 1$) particles among the total detected mineral dust particles in each event. r refers to the mixture degree of sea salt to mineral components in dust particles and it is defined by $r =$ seasalt/(mineral + seasalt), where "mineral" is the sum of weight ratios of Al, Si and Fe, and "seasalt" is the sum of weight ratios of Na and Cl in individual mineral dust particles.

Number fractions in Fig. 5 further indicate that the composition of about 60% dust particles in the well-mixed dust events is dominated by sea salt or by both sea salt and minerals. In contrast, the relevant fractions in the less-mixed events are about 20% or less, and in most of the dust particles mineral components are dominant. This means that most of the dust particles in the well-mixed events have been largely modified by sea salt, but only a small fraction of dust particles in the less-mixed events have been so modified. Therefore, dust particles in the well-mixed dust events must have experienced an ambient environment which was more favorable for the mixing of dust and sea salt than the dust particles in the less-mixed events.

From backward trajectory analyses which were achieved by the NOAA online HYSPLIT model (http://www.arl.noaa.gov/ready/hysplit4), it is learnt that dust particles in some dust events penetrated the marine air between the Asian continent and southwestern Japan very fast, while in some other events the penetration was very slow. The approximate times taken by the collected dust particles to penetrate the marine areas are also listed in Table 1. It is from 21 to 50 h in cases of well-mixed events, and from 24 to 57 h in cases of less-mixed events. The mixture degrees are not proportional to the time that dust spent in the marine atmosphere. No correlation between the degree and time can be identified.

Number size distributions at the Takahama Observatory when particle collection was carried out are shown in Fig. 6. The distributions of less-mixed events are approximately consistent with each other. In contrast, distributions of coarse particles during the well-mixed events are largely sporadic, although dust particles in these events have a similar mixture state of mineral and sea salt. In the cases of the 21 March and 10 April events, particle concentrations of coarse particles were much higher than in other cases. So, the numbers of both dust particles and sea salt particles per unit volume of air in the two events were much larger than those in other events. However, the concentration of coarse particles on 17 March was apparently smaller than the concentrations of the less-mixed

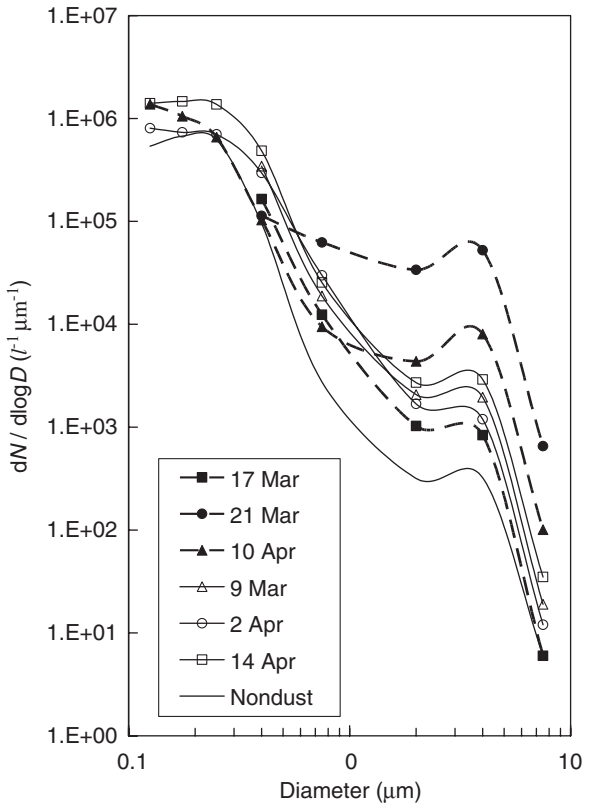

Fig. 6. 1-h average particle number–size distributions per liter airmasses measured by the particle counters when particle collection was carried out. A case of nondust period distribution, which was recorded around 0630 on 9 May, is added for comparison. The concentrations in the size range of 0.3–0.5 μm, which is overlapped by the two counters, are averages of data from the two counters.

events, in the same size ranges. From Fig. 5 it is learnt that there were a few sea salt particles in each well-mixed event, while sea salt particles were rarely detected in the samples of the less-mixed events. Since dust particles together with sea salt governed the coarse mode particles, among a fixed number of particles in an air parcel, there were more sea salt particles in the case of well-mixed events than in the case of less-mixed events. The absolute concentrations of coarse particles should not be important factors influencing the mixture state. Instead, the state should be closely relevant to the number ratios of dust particles to sea salt particles in the air.

From sea salt particle fractions in coarse particle mode (Fig. 4) and the number size distributions (Fig. 6), it can be confirmed that the number concentrations of sea salt particles in the air of well-mixed events were much larger than that in the air of less-mixed events. In other words, air parcels in the well-mixed events contained more sea salt particles than air parcels in the less-mixed events. Sea salt is originally emitted from the sea surface and then dissipates in the marine boundary layer with coagulation, dry and wet removal, and chemical transformation. The concentration of sea salt in the air depends on sea surface emission and atmospheric dissipation. Sea salt emission from sea surface to the atmosphere is governed by wind stress on the sea surface. The emission flux of sea salt particles at fixed size ranges is approximately proportional to powered wind speed at 10 m above the sea surface (Gong and Barrie, 1997). The dissipation is governed by air turbulent diffusion, advection and vertical convection. In particular, the vertical distribution of sea salt particles should be closely associated with gravitational deposition and vertical convection when there is no precipitation. There are no continuous records of wind speed at 10 m above the sea surface around the observation areas. Particles were collected under moderate weather, and wind was not strong when we collected the particles (Table 1). We checked the surface wind recorded at the Ushibuka observatory (3.0 m asl) in the last 6 h of each particle collection, and did not find obvious systematic discrepancies between the well-mixed event group and the less-mixed event group. The fluxes of sea salt to the atmosphere in these events were not anticipated to be so different as to result in systematic differences in sea salt content. Thus, the vertical distribution of sea salt might be the main reason accounting for the differences.

Fig. 7 shows the vertical thermodynamic structures from surface to 2000 m altitude at Kagoshima Meteorological Observatory around the timing of particle collection. The depths of mixing layers of well-mixed event group are obviously different from those of the less-mixed event group. In the cases of well-mixed events, the depths of mixing layers were about 450 m (21 March), 600 m (17 March) and 850 m (10 April), when the potential temperature was approximately constant, with similar water vapor content in the vertical direction. In contrast, in the cases of less-mixed events, the depths of mixing layers were always lower than 200 m, and above that were statically stable layers with pronounced decrease (9 March and 2 April) or increase (14 April) of water vapor content. Thus sea salt particles emitted from the sea surface in cases of the well-mixed events should have been vertically

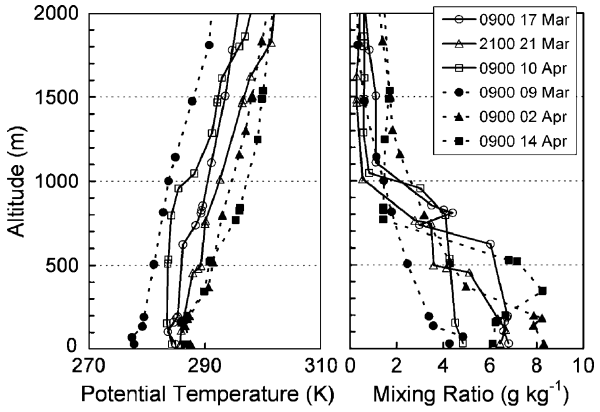

Fig. 7. Vertical profiles of potential temperature (left panel) and water vapor mixing ratio (right panel) from the radiosondings launched at the Kagoshima Meteorological Observatory around the timing of particle collection.

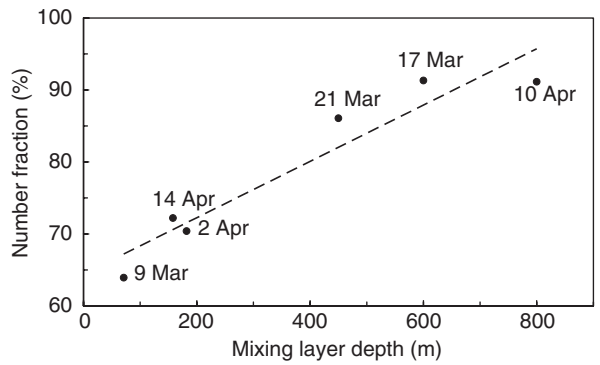

Fig. 8. Relationship between the number fractions of mixture particles among dust particles and the mixing layer depths in the six events. The depths were identified from the radiosonding data in Fig. 7. The dash line is the linear regression.

well-mixed up to about 450 m or higher, while sea salt particles in cases of the less-mixed events should have been mainly limited below 200 m. Consequently, dust particles that descended from elevated layers to the ground by gravitational settlement in the well-mixed events acquired more opportunities combining with sea salt particles than those in the less-mixed events. Although we cannot confirm direct links between the number fractions of mixture particles among dust particles and the mixing layer depths with the present data, we find that they are approximately proportional to each other (Fig. 8). Therefore, the vertical convection in the marine boundary layer is likely the key process influencing the sea salt–mineral mixture degrees in dust particles at the surface in marine areas.

4. Summary

From March to May 2002, a series of dust-loading low-pressure systems passed southwestern Japan. Accumulation mode particles in the range of 0.1–0.3 μm frequently showed different trends from particles >1.0 μm and SPM10 during dust plume passages, suggesting air parcels containing dust and anthropogenic pollutants had not, to a large extent, intermingled thoroughly with each other in these dust events. Anthropogenic pollutants arrived ahead of dust plumes, leading to an increase in the concentration of accumulation mode particles before the arrival of cold fronts in dust-loading low-pressure systems. Cold front arrival triggered rapid increases of SPM10 and the number concentrations of particles >1.0 μm with an exception of rainfall. Even within the same dust plumes, the horizontal distribution of anthropogenic pollutants in the plumes was highly non-homogeneous, and there were frequent intervals of accumulation mode particles with their concentrations opposed to particles >1.0 μm.

The mixture state of mineral and sea salt components in individual dust particles differed in different dust events. In some events, dust particles mixed well with sea salt while in other events they did not. Investigation of the mixing degree associated with weather conditions revealed that the degree seemed closely related to the vertical structure of the marine boundary layers. More dust particles were a mixture of mineral and sea salt in cases of deep mixing layers than in cases of shallow mixing layers. No correlations between the mixing degrees and lifetime of dust particles in the marine atmosphere have been identified.

Acknowledgments

This study was funded by the Japan Ministry of Education, Science and Technology under the Grant-in-Aid for Scientific Research on Priority Areas.

References

Akimoto, H., Narita, H., 1994. Distribution of SO_2, NO_x and CO_2 emissions from fuel combustion and industrial activities in Asia with $1^\circ \times 1^\circ$ resolution. Atmospheric Environment 28, 213–225.

Andreae, M.O., et al., 1986. Internal mixture of sea salt, silicates, and excess sulfate in marine aerosols. Science 232, 1620–1623.

Bates, T.S., et al., 2004. Marine boundary layer dust and pollutant transport associated with the passage of a frontal system over eastern Asia. Journal of Geophysical Research 109, D19S19.

Buzorius, G., et al., 2004. Secondary aerosol formation in continental outflow conditions during ACE-Asia. Journal of Geophysical Research 109, D24203.

Duce, R.A., 1995. Sources, distributions and fluxes of mineral aerosols and their relationship to climate. In: Charlson, R.J., Heintzenberg, J. (Eds.), Aerosol Forcing of Climate. Wiley, New York, pp. 43–72.

Fan, X., et al., 1996. Mineral particles collected in China and Japan during the same Asian dust-storm event. Atmospheric Environment 30, 347–351.

Fang, Z., et al., 1997. China Dust Storm Research (in Chinese). Meteorology Press, Beijing, pp. 158.

Gong, S.L., Barrie, L.B., 1997. Modeling sea-salt aerosols in the atmosphere 1. Model development. Journal of Geophysical Research 102, 3805–3818.

Hatakeyama, S., et al., 2004. Aerial measurement of air pollutants and aerosols during 20–22 March 2001 over the East China Sea. Journal of Geophysical Research 109, D13304.

Kim, B.-G., Park, S.-U., 2001. Transport and evolution of a winter-time yellow sand observed in Korea. Atmospheric Environment 35, 3191–3201.

Kim, Y.P., et al., 1998. Monitoring of air pollutants at Kosan, Ceju Island, Korea, during March–April 1994. Journal of Applied Meteorology 37, 1117–1126.

Matsumoto, K., et al., 2003. Chemical properties of outflow patterns of anthropogenic and dust particles on Rishiri Island during the Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia). Journal of Geophysical Research 108, 8666.

Meskhidze, N., Chameides, W.L., Nenes, N., 2005. Dust and pollution: a recipe for enhanced ocean fertilization? Journal of Geophysical Research 110, D03301.

Murayama, T., et al., 2001. Ground-based network observation of Asian dust events of April 1998 in East Asia. Journal of Geophysical Research 106, 18345–18359.

Nishikawa, M., Kanamori, S., Kanamori, N., Mizoguchi, T., 1991. Kosa aerosol as Eolian carrier of anthropogenic material. Science of Total Environment 107, 13–27.

Okada, K., et al., 1990. X-ray spectrometry of individual Asian dust-storm particles over the Japanese Islands and the North Pacific Ocean. Atmospheric Environment 24A, 1369–1378.

Ooki, A., Uematsu, M., 2005. Chemical interactions between mineral dust particles and acid gases during Asian dust events. Journal of Geophysical Research 110, D03201.

Sakai, T., et al., 2002. Free tropospheric aerosol backscatter, depolarization ratio, and relative humidity measured with the Raman lidar at Nagoya in 1994–1997: contributions of aerosols from the Asian continent and Pacific Ocean. Atmospheric Environment 34, 431–442.

Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. Wiley, Hoboken, N. J., p. 1326.

Seinfeld, J.H., et al., 2004. ACE-Asia: regional climatic and atmospheric chemical effects of Asian dust and pollution. Bulletin of American Meteorological Society 85, 367–380.

Streets, D.G., et al., 2001. Trends in emissions of acidifying species in Asia, 1985–1997. Water, Air and Soil Pollution 130, 187–192.

Uematsu, M., et al., 2002. Transport of mineral and anthropogenic aerosols during a Kosa event over East Asia. Journal of Geophysical Research 107, 4059.

Uno, I., et al., 2003. Regional chemical weather forecasting system CFORS: model descriptions and analysis of surface observations at Japanese island stations during the ACE-Asia experiment. Journal of Geophysical Research 108, 8668.

Uno, I., et al., 2004. Numerical study of Asian dust transport during the springtime of 2001 simulated with the chemical weather forecasting system (CFORS) model. Journal of Geophysical Research 109, D19S24.

Wehner, B., et al., 2004. Variability of the aerosol number size distribution in Beijing, China: new particle formation, dust storms, and high continental background. Geophysical Research Letters 31, L22108.

Zhang, D., Iwasaka, Y., 2001. Chlorine deposition on dust particles in marine atmosphere. Geophysical Research Letters 28, 3613–3616.

Zhang, D., Iwasaka, Y., 2004. Size change of Asian dust particles caused by sea salt interaction: measurements in southwestern Japan. Geophysical Research Letters 31, L15102.

Zhang, D., et al., 2003a. Mixture state and size of Asian dust particles collected at southwestern Japan in spring 2000. Journal of Geophysical Research 108, 4760.

Zhang, D., et al., 2003b. Mixture state of Asian dust particles at a coastal site of Qingdao, China. Atmospheric Environment 37, 3895–3901.

Zhang, D., et al., 2005. Separated status of the natural dust plume and polluted air masses in an Asian dust storm event at coastal areas of China. Journal of Geophysical Research 110, D06302.