Chemical composition of fine aerosol measured by AMS at Fukue Island, Japan during APEX period

Akinori Takami[a,*], Takao Miyoshi[a], Akio Shimono[b], Shiro Hatakeyama[a]

[a]*National Institute for Environmental Studies, Atmospheric Environment Division, Chemical Reaction Section, Onogawa 16-2, Tsukuba, Ibaraki 305-8506, Japan*
[b]*Sanyu Plant Service Co., Ltd., Hashimotodai 1-8-21, Sagamihara, Kanagawa 229-1132, Japan*

Abstract

The size distribution and chemical composition of ambient aerosols was analyzed using an Aerodyne aerosol mass spectrometer (AMS) at Fukue, Japan in the spring of 2003. The average concentration of ammonium, nitrate, sulfate, chloride and organics was 1.57, 0.56, 4.80, 0.07 and 5.03 $\mu g\,m^{-3}$, respectively. The size distribution showed that the modes of ammonium, sulfate and organics were all about 400–700 nm throughout the entire observation period with the exception of a few cases, indicating that these species were internally mixed. The average equivalent ratio of ammonium to sulfate was 0.88, which means that the aerosol was slightly acidic. When air masses came from China and Korea with high aerosol concentration (25–27 March and 6–7 April), nitrate was found in fine particles with ammonium and sulfate. The average ratio of organics to sulfate was 1.05, indicating that the contribution of organics is not negligible in this region. Mass spectra showed that the largest signal in organic fragments was $m/z = 44$, which shows that organic species are well-oxygenated.
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Keywords: Aerodyne aerosol mass spectrometer; Fukue; Chemical composition; Sulfate; Organics

1. Introduction

East Asia, one of the most rapidly developing regions in the world, shows continuously increasing energy consumption, which leads to considerable increase in anthropogenic emissions. According to a study by Streets et al. (2003), emissions of NO_x VOC and NH_3 have already increased significantly compared to the emission in 1994. Although the emission of SO_2 seems to decrease recently, the amount of emission is still large

(22.6 Tg). Aerosols are emitted from various sources such as car exhausts, factories, power plants and biomass burning. They are also produced from precursor gaseous species, such as SO_2, NO_x, and hydrocarbons, which are oxidized by oxidants and HO_x radicals and partly converted into aerosols.

Aerosols are considered to have a large impact on regional and global climate change. The direct effect of aerosols on the climate is the change in radiative forcing through their absorption and reflection of solar radiation. Aerosols also affect regional climate as cloud condensation nuclei (CCN), which changes the efficiency of cloud formation and rainfall. In both cases, chemical composition plays an important role as the determinant of aerosol optical properties and the efficiency of cloud

*Corresponding author. Tel.: +81 29 850 2509; fax: +81 29 850 2579.

E-mail address: takamia@nies.go.jp (A. Takami).

formation. Especially, organics are considered to act as an important CCN (Hori, 2003).

Japan is situated at the eastern end of East Asia, and a westerly wind prevails in the winter-spring period. Thus, aerosols are transported from the Asian continent to Japan. Several investigations have been carried out to measure the chemical composition of aerosols in Japan and its surroundings. For example, Mukai et al. (1990) measured the chemical composition of aerosols at Oki Island, Japan. Sulfate loading measured by filter sampling was about $3.59 \, \mu g \, m^{-3}$. Carmichael et al. (1996) measured aerosols using the filter sampling method at Cheju Island in Korea and found that sulfate loading was about $8.0 \, \mu g \, m^{-3}$. They also found that the equivalent ratio of nitrate to sulfate was as low as 0.13 for the long-range transport period. Their analyses are mainly focused on the inorganic species.

Recently, Aerodyne Research Inc. developed the Aerodyne aerosol mass spectrometer (AMS). The AMS is capable of delivering online quantitative data on mass concentrations and size distributions of fine particle components (Jayne et al., 2000). The usefulness of the AMS has already been shown during the ACE-Asia experiment (Bahreini et al., 2003; Topping et al., 2004). Especially, both organic and inorganic species were simultaneously measured with high time resolution. The AMS was deployed at Fukue Island during the APEX-E3 period (March–April 2003) in order to understand both the concentration level and chemical composition of aerosols in East Asia. Asian Atmospheric Particle Environment Change Studies (APEX) was a project to grasp future climate change in East Asia by investigating the direct and indirect effect of aerosols.

This paper presents the results obtained by the AMS. The characteristics of aerosol were analyzed using size distribution and chemical composition, including organics. The observation periods were classified using the characteristics of aerosol chemical composition, which is discussed with the air mass origin.

2. Experimental method

2.1. Site description

Fukue Island is situated at the western end of Japan, as shown in Fig. 1, and is close to northern East Asia including China and Korea. The sampling site was constructed at the northwest side of Fukue Island at $128.7°E$, $32.8°N$. There are no large industrial areas on the island. During the experimental period, weather and other meteorological data was recorded by local meteorological sites. The average temperature was about $13 °C$ and the humidity was about 70%. The wind blew mainly from the northwest and rainfall was recorded on
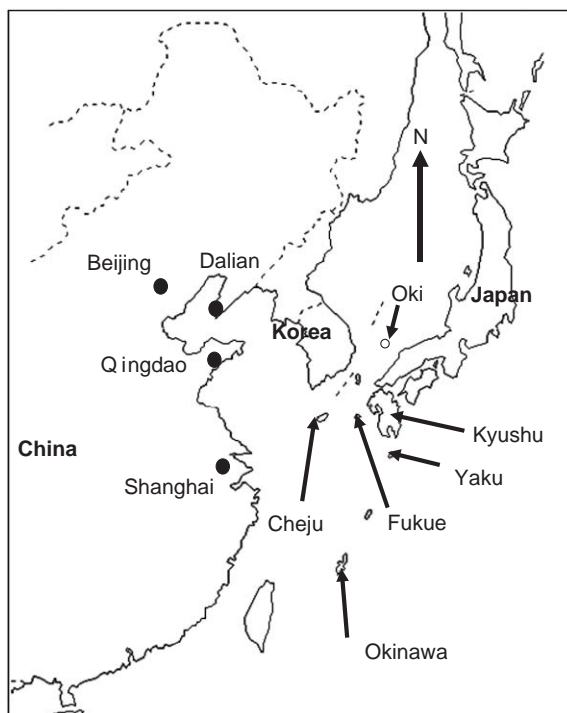

Fig. 1. Map of East Asia and the location of Fukue Island and surrounding islands.

16, 21–22, 27 and 31 March and on 1, 7 and 11 April (Hayasaka et al., 2005).

Aerosol sampling was carried out using a half-inch copper tube projecting from the top of the roof. The sampling height was about 4 m from the ground. A $PM_{2.5}$ cyclone was used to cut off large particles.

2.2. Instruments

Aerosol chemical composition was analyzed using an AMS produced by Aerodyne Research Inc. A detailed description can be found in other publications (Jayne et al., 2000; Allan et al., 2003a, b; Jimenez et al., 2003a). Briefly, aerosols are introduced through the AMS inlet orifice and are separated from gaseous species by aerodynamic lenses that focus an aerosol particle beam onto a vaporizer, as shown in Fig. 2. Particles of about $PM_{1.0}$, i.e., about 50% transmittance at $1 \, \mu m$ particle, pass through this aerodynamic lens. The vacuum aerodynamic diameter measured in the free molecule regime (Jimenez et al., 2003b; DeCarlo et al., 2004) is calculated from the time-of-flight (TOF) measurement. Aerosols are accelerated by supersonic expansion and the lighter aerosols obtain a faster velocity than the heavier ones. The traveling time from the chopper to the detector is the aerosol flight time. Chemical composition is analyzed by a quadrupole mass spectrometer after vaporization of aerosol at the vaporizer and ionization
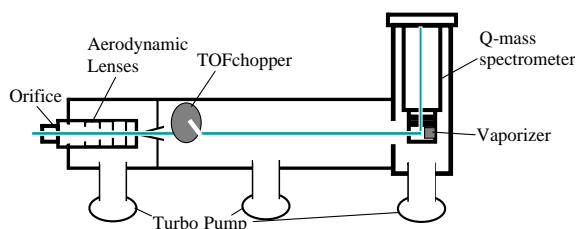
Fig. 2. Schematic diagram of the Aerodyne aerosol mass spectrometer.

by the standard 70 eV electron impact. Since the vaporizer is set to 600 °C, chemical composition vaporized at 600 °C can be analyzed by the quadrupole detector.

The AMS data were analyzed using the Igor-based software package described by Allan et al. (2003a, 2004b). The details of the analysis procedures are found in other publications (Allan et al., 2003a, b, 2004b; Jimenez et al., 2003a). Briefly, the ion current detected by the quadrupole mass spectrometer was converted into the mass concentration using the measured ionization efficiency (IE) of nitrate, which is calibrated by the ammonium nitrate aerosol (Jayne et al., 2000). As for other species, the relative ionization efficiency (RIE) is used, which was calibrated in laboratory studies, since each species has different ionization efficiency (Jimenez et al., 2003a; Allan et al., 2004b; Alfarra et al., 2004). The values of RIE for ammonium, nitrate, sulfate and organics used for this paper are 4.5, 1.1, 1.2 and 1.4, respectively. The particle collection efficiency (CE) in the AMS chamber is also taken into account to quantify the mass concentration. Previous studies have shown that the particle mass of sulfate dominated aerosol measured by the AMS is underestimated by a factor of 2, in comparing the AMS data to the data obtained by other instruments when the relative humidity is low (Drewnick et al., 2003, 2004; Hogrefe et al., 2003; Allan et al., 2004a; Zhang et al., 2005). For our observation, the accumulation mode of aerosol contained a significant amount of sulfate mass, the size distributions were similar for all species and the relative humidity in the inlet was low during the observation period. Therefore, a CE of 0.5 is used for all species. Organics defined here are the sum of signals that are not assigned to inorganic matter such as ammonium, sulfate, nitrate and chloride. Organic mass here includes the mass of organic fragments that contain C (carbon), O (oxygen), H (hydrogen) and N (nitrogen).

3. Results

3.1. Trend of aerosol mass concentration

The trend in mass concentration for major species is plotted in Fig. 3. The measurement period was from

3/19 to 4/16 (i.e. March 19 to April 16, and so on.) The mass concentration of sulfate was found to be high for 3/25–27, 4/7–10 and 4/12–14. It should be noted that no obvious diurnal variation was observed, as shown in Fig. 3. In most cases, the increase in concentration lasted several hours and high concentration continued for several days, indicating that our observation was not of local aerosol emitted from local vehicles and daily works but rather of regionally represented aerosol. Fig. 4 shows the results of back trajectory calculations (HYSPLIT4 Draxler and Rolph, 2003; Rolph, 2003). According to them, the observation of high sulfate loading indicates that the air mass came from the Chinese continent. A typical trajectory is shown in Fig. 4b for 3/26. Nitrate and ammonium showed similar trends in mass although the mass concentration was low compared to sulfate. Dust from China is often observed in the western Kyushu area during this period of the year (Murayama et al., 2001). However, a dust event was reported only on 4/13 according to the depolarization ratio obtained by the lidar measurements (http://www-lidar.nies.go.jp). The high sulfate events on
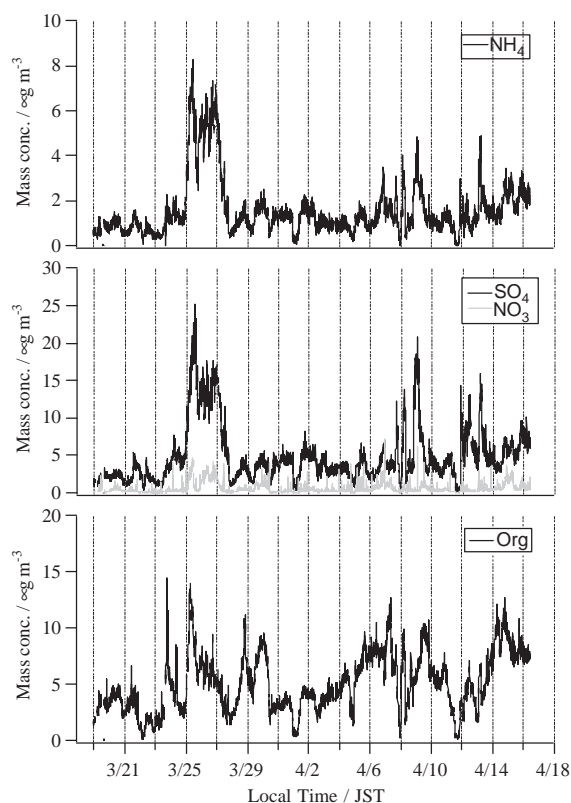

Fig. 3. Trend of mass concentrations of ammonium, sulfate, nitrate and organics measured at Fukue Island in spring 2003.
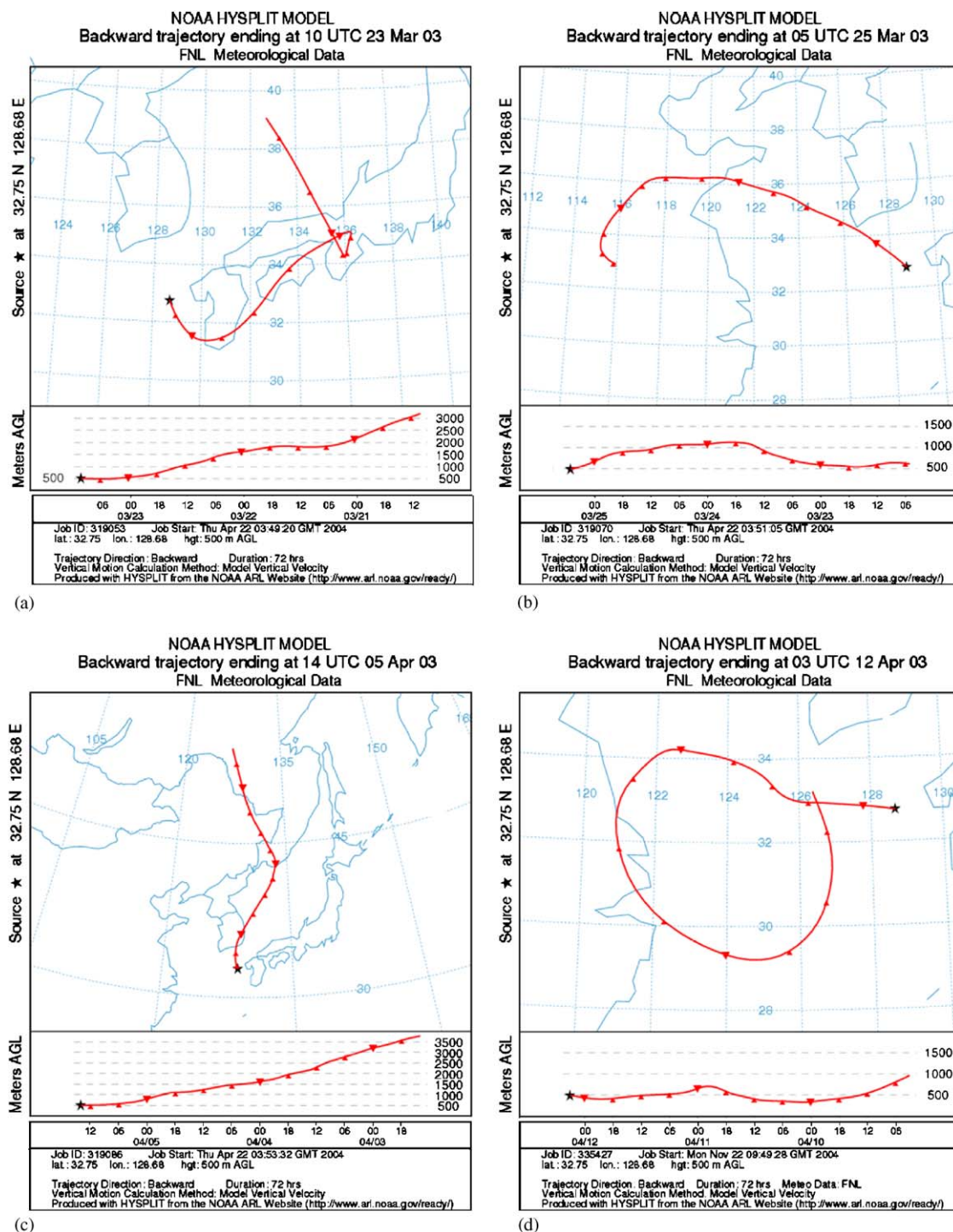
Fig. 4. Results of the back trajectory analysis using HYSPLIT4. The starting times are at (a) 10:00 23 March, (b) 5:00 25 March, (c) 14:00 5 April, (d) 3:00 12 April UTC. The time difference between UTC and the Japanese standard time is 9 h.

3/25–27 and 4/7–10 were not associated with a dust event. The average mass concentrations of sulfate on 3/25–27 and 4/12–14 were 12.8 and 6.15 μg m^{-3}, respec-

tively. It is interesting to note that sulfate loading is higher for non-dust periods. High mass loading of organics was observed for 3/23, 3/25, 3/28, 3/30, 4/5–7,

4/8 and 4/14. According to back trajectory calculations, the air masses passed over the Korean peninsula and Japanese islands. Typical trajectories are shown in Fig. 4a for 3/23, which shows a Japanese influence, and in Fig. 4c for 4/6, which shows a Korean influence. The trend in organic mass sometimes differed from that of ammonium, nitrate and sulfate. Especially, the change in organics on 3/23, 4/5–6 and 4/14 is very different from that in inorganic species, indicating that the chemical composition of aerosol varied during the different periods.

The average concentration of ammonium, nitrate, sulfate, chloride and organics during the observation period was 1.57, 0.56, 4.80, 0.07 and 5.03 $\mu g\,m^{-3}$, respectively. Sulfate and organics were more abundant relative to ammonium, nitrate and chloride. Although the maximum mass loading was higher for sulfate, the average mass concentration was slightly higher for organics. Nitrate was observed when both sulfate and ammonium were high. Peaks were observed for nitrate, which are considered to be associated with larger particles. This is because a large fraction of nitrate mass was observed at diameters larger than 1 μm when peaks appeared. It is possible that some of sea-salt and/or dust particles (1–2 μm) pass through the aerodynamic lenses and the nitrate adsorbed on the surface is evaporated and is detected as peaks. The mass concentration of chloride was very low throughout the observation period.

During the ACE-Asia experiments, two AMS measurements were carried out to investigate the aerosol composition in this area. Topping et al. (2004) reported the average mass concentration measured by AMS at Cheju, Korea from 4/13 to 4/29 in 2001. Cheju is about 200 km northwest of Fukue (see Fig. 1). The concentration of ammonium, nitrate, sulfate and organics was 1.48, 0.51, 3.09 and 3.49 $\mu g\,m^{-3}$, respectively, which is at the same level as our measurements at Fukue. Sulfate and organics were the dominant species and the nitrate mass was low and tended to be present in the larger size range. A higher organic mass loading relative to sulfate was also observed at Cheju. Their measurements are consistent with ours, which is reasonable since Fukue and Cheju are in the same area. During the ACE-Asia experiments, Bahreini et al. (2003) also measured aerosol chemical composition using AMS on a Twin Otter airplane, flying over the western area of Japan in which Fukue is included. Concentration levels similar to our measurements were observed at a flight altitude of 1000–3000 m, where the average concentration was 1.58, 0.55, 2.34 and 3.65 $\mu g\,m^{-3}$ for ammonium, nitrate, sulfate and organics, respectively. They observed a high nitrate mass concentration (2.31 $\mu g\,m^{-3}$) at ground-level observation. This may be due to local pollution at the Iwakuni Marine Corps Air Station where their airplane took off for the research flight.

3.2. Variation in chemical composition

The chemical composition of aerosol varies. For example, a high concentration of sulfate was observed several times, as shown in Fig. 3. During 3/25–27, the sulfate concentration increased to 25 $\mu g\,m^{-3}$, which was the maximum sulfate loading during the observation period. During this event, the mass concentration of ammonium and organics also increased to about 10 and 15 $\mu g\,m^{-3}$, respectively. The concentration of sulfate was much larger than that of organics. In contrast, a high concentration of organics was also observed several times. The concentration of organics increased to 10 $\mu g\,m^{-3}$ on 4/5–6 whereas ammonium and sulfate did not increase as much in comparison. Indeed, sulfate showed two small peaks during this period. The concentration of organics was much greater than that of sulfate. In order to examine the chemical variation, the mass fraction of each species was calculated. The mass fraction is the ratio of the mass of each species to the total mass concentration measured by AMS. The total mass here is defined as the sum of ammonium, nitrate, sulfate, chloride and organics. Total mass is normalized to 100%. For clarification, two major species (sulfate and organics) are shown in Fig. 5. The mass fraction of aerosol showed that nearly 80% of the mass in aerosol was composed of a sum of sulfate and organics. For the high sulfate periods (3/25–27, 4/7–10 and 4/12–14), the ratio of sulfate reached nearly 60% of the total mass. In contrast, the aerosol was composed of about 50% organics for the high organic loading period (4/5–6). It is important to recall that AMS measures only non-refractory $PM_{1.0}$ particles. Refractory and/or larger particles such as elemental carbon, dust and sea-salt aerosol were not measured. However, it is worth noting that there is a very high mass fraction of both sulfate and organics in fine aerosols in Eastern Asia. It is also important to note that the aerosol composition changed within several days. The mass fraction of sulfate and organics changed drastically between 3/25–27 and 3/28–29. As mentioned above, when the air
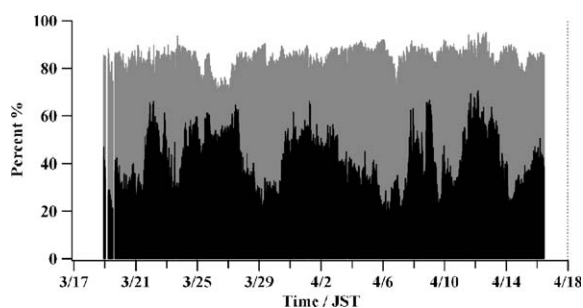

Fig. 5. Mass fraction of sulfate and organics to the total mass concentration measured by AMS at Fukue Island. Black: sulfate, gray: organics.

mass histories differed, the aerosol chemical composition varied, which is consistent with the previous results of ACE-Asia experiments (Topping et al., 2004).

3.3. Size distribution and mass spectra

Similarities and differences were observed for size distribution and mass spectra. Although the mass concentrations of sulfate and organics were very different on 3/25–27 and 4/5–6, size distribution and mass spectra of aerosol, as can be seen in Figs. 6 and 7, respectively, showed remarkable similarities. In Fig. 7, mass spectra of organic fragments are only drawn for the purpose of clarity.

The size distribution of sulfate in Figs. 6a (3/25–27) and b (4/5–6) is relatively similar in shape although the mass loading is different. Fig. 6c (4/12) is another example of similar size distribution of sulfate. For 4/12,
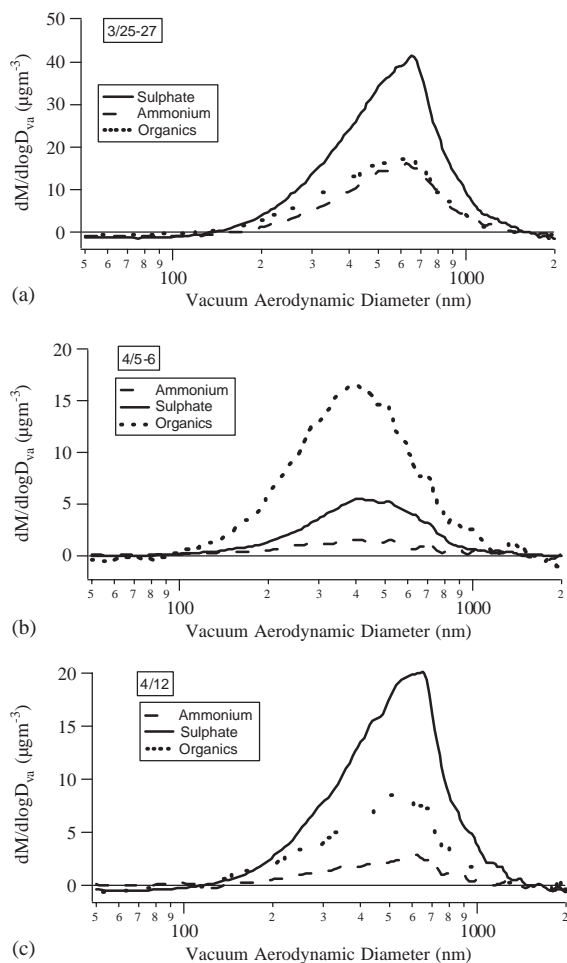

(a)

(b)

(c)

Fig. 6. Size distributions of ammonium, sulfate and organics measured by the AMS. Averaged over (a) 3/23 15:10—3/24 9:50, (b) 3/25 3:00—3/27 4:00, (c) 4/5 9:00—4/6 21:00.
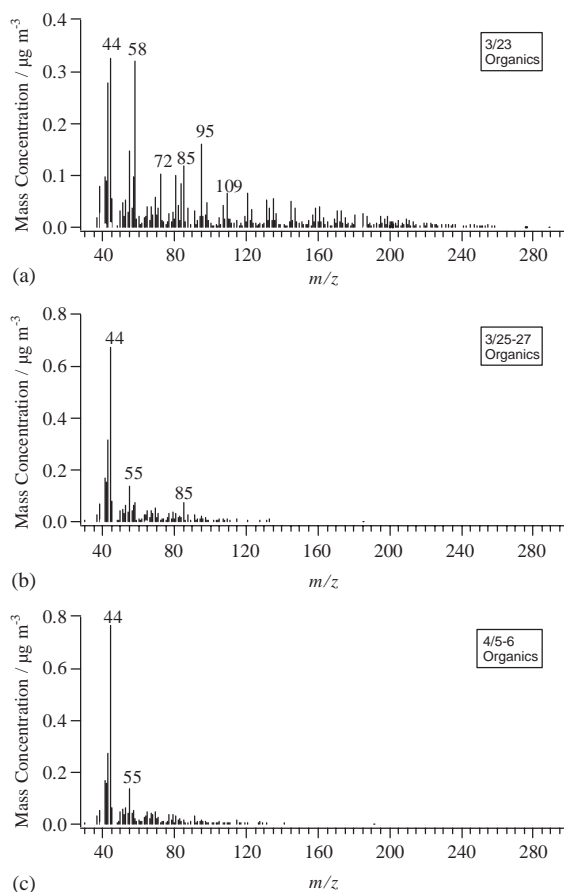

Fig. 7. Mass spectra of organics measured by the AMS. Averaged over (a) 3/23 15:10—3/24 9:50, (b) 3/25 3:00—3/27 4:00, (c) 4/5 9:00—4/6 21:00. The numbers in each panel are the selected m/z values.

it was a day of very low ammonium concentration, which means that sulfate in the aerosol was excessive relative to ammonium. According to the back trajectory calculation, the air mass stayed over the East China Sea. The typical trajectory is shown in Fig. 4d for 4/12, which shows marine influence. The mode of the vacuum aerodynamic diameter for sulfate was about 500–700 nm for these three examples, indicating that the sulfate size distribution belongs to the accumulation mode (not the nucleation mode ~0.01 μm). For these three cases, the size distribution of sulfate showed remarkable similarities although the air mass origin and the mass loading were very different. This is in good agreement with previous observations that the shape of the sulfate size distribution was relatively constant from day-to-day observation (Bahreini et al., 2003; Topping et al., 2004).

Fig. 6 also shows a similarity in size distribution of ammonium, sulfate and organics. In the urban area, the

size distribution shows bi-modal distribution, with modes of 100–200 nm and 400–500 nm, respectively. We observed bi-modal distribution at Tsukuba city where we carried out the initial conditioning of our AMS before going to Fukue. We took a sample from the air outside our institute in the evening. In this case, bi-modal size distribution was observed. Nitrate clearly showed bi-modal distribution, with modes of about 150 and 400 nm. The mode of the organic distribution was about 150 nm, while that of sulfate distribution was about 400 nm. These two modes are considered to correspond to "fresh" and "aged" aerosols, and species in different modes were not present on the same particles, i.e. the external mixtures. Compared to the observations from the urban area, the size distribution of ammonium, sulfate and organics in Figs. 6a–c shows remarkable similarity in shape. These facts suggest that the aerosols observed at Fukue were aged and that chemical species such as ammonium, sulfate and organics were on the same particles, that is, the internally mixed aerosol.

Mass spectra in Figs. 7b (3/25–27) and c (4/5–6) seem to show similar mass fragment patterns. Although the mass concentration of sulfate and organics was very different for these two periods, the mass spectra showed quite similar features, i.e., a mass of $m/z = 44$ is one of the largest peaks in the organics and a higher m/z signal ($m/z > 200$ amu) was not observed (m/z is mass to charge ratio). Figs. 7b and c are very different from Fig. 7a, which was obtained during another high organic loading period (3/23). According to the back trajectory calculation, the air mass passed over the Japanese islands as shown in Fig. 4a for 3/23. Signals of $m/z = 43$, 44 and 58 were high in the mass spectra in Fig. 7a. In a comparison with Fig. 7a, Figs. 7b and c show similar mass fragment patterns for organics. Since the $m/z = 44$ signal corresponds to COO fragments in the mass spectra, this indicates that oxidized organic species are one of the main components of the aerosol. It is considered that aerosol is aged (oxygenated) through the regional transport.

4. Discussion

4.1. Ion balances of inorganic species

As shown in Figs. 3 and 5, the aerosol chemical composition varies significantly during the sampling period. It is interesting to investigate how the ion balance is maintained in aerosols when the chemical composition changes. In order to see the ion balance between ammonium and sulfate, the equivalent ratio of these two species, which was calculated using neq m^{-3} units, are plotted in Fig. 8a. The dots show the ratio of each observation point, which shows a large variation,
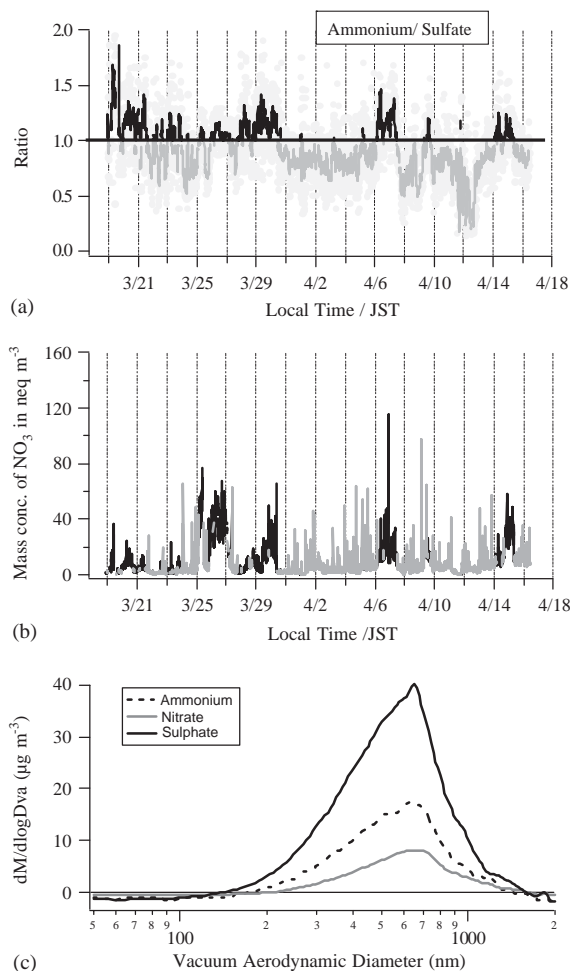

(a)

(b)

(c)

Fig. 8. (a) Equivalent ratio of ammonium to sulfate. Dots: ratio of each observation point. Solid line: nine average points. The black line corresponds to the period when the ratio is greater than unity, while the gray line corresponds to the period when the ratio is less than unity. (b) Concentration of nitrate in neq m^{-3} units. The black line corresponds to the period when the ratio of ammonium to sulfate in the panel (a) is greater than unity, while the gray line corresponds to the period when the ratio is less than unity. (c) Size distributions of sulfate, ammonium and nitrate averaged over 3/25 3:00—3/27 4:00.

indicating that the concentration of ammonium was seldom equivalent to the concentration of sulfate. In order to see the trend more clearly, nine average points were calculated, which are shown by the solid lines in Fig. 8a. The black line corresponds to the period when the ratio is greater than unity, while the gray line corresponds to the period when the ratio is less than unity. The ratio shows that it was often less than unity, especially for the low aerosol loading period. In addition, the average equivalent ratio of ammonium to sulfate for the entire observation period is 0.88. This means that sulfate was slightly excessive relative to

ammonium. It seems that aerosols measured at Fukue were slightly acidic if the ion balance of inorganic species is mostly determined by ammonium and sulfate in the fine particle mode.

As our AMS does not measure most of the dust and sea-salt particles using the current settings, it was necessary to examine the fraction of chemical species in the fine particle mode (0.1–1.0 μm) to the total suspended matter in order to assess the acidity. AMS mainly measures the fine particle mode ($PM_{1.0}$). The average concentration of ammonium, nitrate and sulfate was 89.6, 9.26 and 102 neq m^{-3}, respectively. Since the nitrate concentration is about 10% of the ammonium and sulfate, the contribution of nitrate to acidity is not large. This is supported by the fact that the ratio of ammonium to the sum of acidic species (nitrate, chloride and sulfate) in neq m^{-3} was 0.81, which is at the same level as the ratio of ammonium to sulfate.

Previous observations in this region support the findings that ammonium and sulfate are generally present in the fine particle mode. Shimohara et al. (2001) analyzed ions collected by Andersen samplers at Fukue and found that ammonium and sulfate were present in fine particles (~1.1 μm) and calcium and nitrate were present in coarse particles (>3.3 μm). Other ions such as calcium, magnesium, sodium and chloride were also present in coarse particles. They estimated that 85% of non-sea-salt sulfate was found in fine particles and 97% of nitrate was found in particles larger than 1.1 μm. Topping et al. (2004) reported a strong correlation between non-sea-salt sulfate and ammonium, particularly at the impactor stage 1 (0.2–0.5 μm). Hatakeyama et al. (2004) analyzed ionic species observed in total suspended matter, which they collected while flying over from Fukue to the south of Cheju at altitudes of about 3000 and 400 m in the spring of 2001. They found a good correlation between ammonium and sulfate with the ratio of ammonium to sulfate being 0.9, which is very close to our ratio measured at Fukue. On the other hand, no correlation was found between sulfate and calcium. This supports the findings that ammonium and sulfate are in the same particle mode and that nitrate and calcium are in a different particle mode. These facts indicate that ammonium and sulfate are the dominant inorganic species. Those of calcium, magnesium, sodium and chloride do not contribute to the ion balance in the fine particle mode. Thus, the aerosol measured at Fukue is considered to be slightly acidic since the ion balance of inorganic species is mostly determined by ammonium and sulfate in the fine particle mode.

One important aspect should be mentioned: the contribution of organics. As noted above, $m/z = 44$ is one of the largest signals in the organic fragments. This corresponds to the COO ion fragment, which is indicative of organic acids. Since the average equivalent ratio of ammonium to sulfate is 0.88 and the acidity is considered to be weak, organic acids may contribute to aerosol acidity.

Although nitrate was present mainly in coarse particles, our AMS sometimes detected nitrate. One of the reasons for this is that nitrate associated with relatively large particles (~2 μm) evaporated at the vaporizer, and produced some nitrate signals seen as peaks, since large particles give a relatively large signal even if the number is low. The other reason is that nitrate is actually present in the fine particles. For example, nitrate was continuously observed with a mass concentration of ~50 neq m^{-3} for 3/25–27, as shown in Fig. 8b. The size distribution of nitrate for 3/25–27 is similar to that of ammonium and sulfate, as shown in Fig. 8c, indicating that nitrate is present in the same particles that ammonium and sulfate are in. This means that nitrate is internally mixed with ammonium sulfate in the fine particles even after long-range transport from China. Hatakeyama et al. (2004) observed a weak correlation between ammonium and nitrate when they detected polluted air masses from the Chinese continent. This was observed when the polluted air mass was pushed down under a high-pressure system on 21 March 2001 and pollutions were present in front of the dust plume. In this case, the pollution and dust was not well mixed and nitrate was presumably held in the fine particles. In addition, the air mass traveled from the Chinese coastal region to the aircraft sampling point within two days. Before leaving the Chinese coast, the air mass stayed over central China where there are large cities and industrial areas near Shanghai. In our case, nitrate was continuously observed during 3/25–27, 3/28–30, 4/6–7 and 4/14–15 when the air masses came from both the Chinese and Korean regions. Since dust events occurred only on 4/13, there was little effect from dust. For these periods, aerosol mass loading was large, indicating that the polluted air masses reached Fukue. The typical time taken to reach Fukue from both regions was about two days or less as shown in Fig. 4b for 3/26 and in Fig. 4c for 4/6. It is known that nitrate is one of the dominant species in fine particles in the source region, i.e., in the city, urban and industrial regions. It seems that fine particles containing nitrate could reach Fukue directly from the urban and/or industrial regions. We consider that polluted air with a short transport time could hold nitrate in fine particles.

From the perspective of ion balance, the days of 4/11–12 are significant. The ratio of ammonium to sulfate was very low, with the minimum ratio reaching 0.2. However, the size distribution and mass spectra are not different. Fig. 6c shows that the size distribution of ammonium is similar to that of sulfate and organics. Mass spectra, which are not shown here, are also similar to Figs. 7b and c. These facts indicate that aerosol was apparently transported over a long-range distance with

oxygenation, and major chemical species were internally mixed. During this period, ammonium did not increase as sulfate and organics did. The back trajectory calculation in Fig. 4d shows that the air mass stayed over the East China Sea for about two days. We consider that this period was influenced by the marine air. In the marine boundary layers, it is probable that oxygenation occurs for sulfate precursors such as SO_2 and dimethyl sulfide (DMS) by ozone, which increases the sulfate level (Sievering et al., 1991; Arimoto et al., 1996; Topping et al., 2004). Organics are also expected
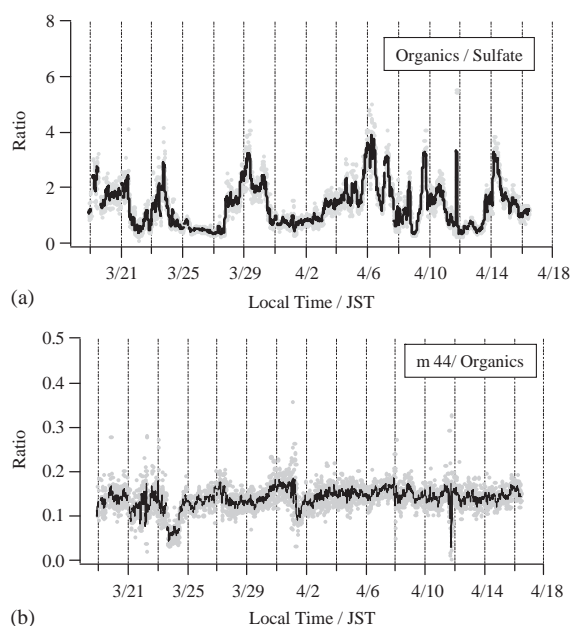

Fig. 9. (a) Ratio of organics to sulfate. Dots: ratio of each observation point. Solid line: nine average points. (b) Ratio of the $m/z = 44$ to the total organics. Dots: ratio of each observation point. Solid line: nine average points.

to be oxygenated during transport. However, there is less emission for ammonium over the sea. As a result, we see low loading of ammonium, while the concentration of sulfate and organics becomes high. Thus, the low ammonium to sulfate ratio was observed at Fukue with a long stay over the sea.

4.2. Organics in aerosols

Since organics and sulfate are the main chemical components of the measured aerosol, the ratio of these two species determines the chemical character of the aerosol. The ratio of organics to sulfate is shown in Fig. 9a. The ratios were often recorded to be more than 2. The average ratio of organics to sulfate is 1.05, indicating that organics is one of the main chemical components in the aerosol observed here. Using the back trajectory calculation, high organic periods relative to sulfate were the Korean- and Japan-influenced periods. Mass loadings of sulfate and organics for both Chinese and Korean periods are shown in Table 1. The organic loading is similar for both Chinese and Korean periods, while the sulfate loading is very different. Higher sulfate was observed in the Chinese-influenced period, indicating that the air mass from the Chinese continent contained more sulfate than that from Korea and Japan. Total mass loading for the Chinese-influenced period was also higher than that for the Korean and Japanese periods. Less sulfate was observed for the Korean and Japanese periods while organics for these periods were at the same level as for the Chinese-influenced period. This means that the emission patterns in Korea and Japan are very different from that in China. It is presumed that coal is still widely used as an energy source in China whereas oil is the main energy source in both Korea and Japan. This probably reflects the chemical composition of aerosols measured at Fukue. Although Korea and Japan emit less sulfate

Table 1
Four selected periods

Period	Sulfate in $\mu g\,m^{-3a}$	Ratio of org/SO_4[b]	Ratio of $m44$/org[c]	Ratio of NH_4/SO_4[d]	Origin of air masses[e]
A	14.6	0.49	0.13	0.98	China
B	3.46	2.21	0.15	1.00	Korea
C	4.37	1.33	0.06	0.83	Japan
D	6.41	0.52	0.14	0.41	Marine

Period A: 3/25 3:00—3/27 4:00, high sulfate.
Period B: 4/5 9:00—4/6 21:00, high organics.
Period C: 3/23 15:10—3/24 9:50, low ratio of $m/z = 44$ to organics.
Period D: 4/11 17:00—4/12 18:00, low ratio of ammonium to sulfate.
[a]Sulfate mass concentration in $\mu g\,m^{-3}$.
[b]Ratio of organics to sulfate.
[c]Ratio of the $m/z = 44$ to organics.
[d]Equivalent ratio of ammonium to sulfate.
[e]Back trajectories are calculated by NOAA HYSPLIT4 (Draxler and Rolph, 2003; Rolph, 2003).

than China does, organic emission is at the same level as China as far as we can determine from the aerosol composition. This means that the effect of organic emission in Korea and Japan is not negligible, but in fact will become more important for climate change in this region since organic materials serve as CCN (Matsumoto et al., 1998; Hori, 2003).

Although the ratio of organics to sulfate is very different, the size distribution of organics and sulfate is quite similar for both the Korean and Chinese periods as shown in Figs. 6b and c. This indicates that the sulfate and organics are in the same particles, i.e., sulfate and organics are internally mixed. Mass spectra in Figs. 7b and c also show the similarity for both periods. In both cases, $m/z = 44$ signals are one of the largest signals in organics, indicating high oxygenation. Oxygenated organics mixing with ammonium sulfate aerosol is reasonable since hydrocarbons consisting of only C (carbon atom) and H (hydrogen atom) are not water soluble and are not expected to produced an internal mixture with ammonium sulfate aerosol, which is water soluble. Oxygenated organics with a COO fragment are expected to be water soluble although it depends on the hydrocarbon chain lengths. Previous research reported that major species of oxygenated organics found in aerosols include oxo-, hydroxyl- and di-carboxylic acids and/or humic-like substances (Topping et al., 2004) that give $m/z = 44$ signals and are water soluble. The high fraction of oxygenated organics makes it possible to mix organic species with ammonium sulfate.

Fig. 9b shows the ratio of $m/z = 44$ signal to organics. Contrary to the significant variation in organics to sulfate ratio, $m/z = 44$ to organics ratio is fairly constant with the exception of 3/23. The average ratio is 0.14, and this value holds for both the high sulfate (3/25–27) and high organic (4/5–7) period. Even when the ratio of ammonium to sulfate changed drastically on 4/12, the ratio of $m/z = 44$ signal to organics is the same as in the other period with the ratio being 0.14. The ratio of $m/z = 44$ to organics is almost the same for all observation periods. During transport, oxygenation progresses in aerosol so slowly that the degree of oxygenation is determined by the long-range transport time, which results in the constant ratio of $m/z = 44$ to organics. Preliminary results of our measurements at Okinawa, which is about 700 km south of Fukue, show that the ratio is about 0.2, indicating that the longer transport distance provides enough time for slow oxygenation in the aerosol.

Decesari et al. (2005) analyzed the aerosol organic species sampled the ACE Asia experiment by liquid chromatography and the H-NMR method. They found the extensively oxidized species such as carbonyl and carboxyl groups, particularly in the accumulation mode size range. This is consistent with our findings, in which the $m/z = 44$ signals (carboxyl functional groups) are

one of the largest signals in the organics as shown in Fig. 7.

In addition, the H-NMR analysis was found to match up well with results from other polluted industrialized areas of East Asia and Europe. This suggests that aerosol emitted in the industrialized areas in China, Korea and Japan are the probable sources for the extensively oxidized organic species since the mass spectrum of the Chinese influenced period (Fig. 7b) is very similar to that of the Korean influenced period (Fig. 7c).

On 3/23, the ratio of the $m/z = 44$ signal to organics was very low, at about 0.08. The mass spectra are very different from that of other periods, as shown in Fig. 7a. A heavier mass signal was observed. The signals of $m/z = 43, 55, 57, 58, 67, 69, 72, 81, 84, 85, 95, 107, 109$ are prominent. For example, the signals of $m/z = 43$ and 55 are often seen in urban areas (Alfarra et al., 2004; Canagaratna et al., 2004). They are considered to be other oxidized species (aldehydes and ketones). The $m/z = 58$ is an amide functional group and the $m/z = 67$ is a typical mass of a cyclic compound. Some of them are typical signals for the organic functional groups. However, the signals of $m/z = 85$ and 95 are difficult to assign to the functional groups since there are several possibilities. The detailed analysis needs to understand the mass spectra shown in Fig. 7a, which is in progress. The back trajectory from 3/23 shows that the air masses came from the Japanese side. Local pollution is one possibility, but is unlikely since the low ratio started at 15:00 and continued throughout the night until the following morning (3/24 10:00). The local pollution does not last for such a long period since there are no large factories on the island. The effect of vehicle exhaust is typically observed during the morning period. We did not see this type of phenomenon for other periods and we do not know the exact reason for this event. The most probable reason is that "fresh" organics were injected into the industrial region in Japan when the air mass stayed over the western Japanese area. In addition, the air mass reached Fukue within a short period after leaving the Japanese coastal region.

5. Conclusions

Size distribution and chemical composition of aerosol was analyzed by an aerosol mass spectrometer (AMS) at Fukue in the spring of 2003. The average concentration of ammonium, nitrate, sulfate, chloride and organics was 1.57, 0.56, 4.80, 0.07 and 5.03 $\mu g\,m^{-3}$, respectively. Sulfate and organics were dominant species. Although the mass concentrations of sulfate and organics were very different for 3/25–27 and 4/5–6, size distribution and mass spectra of aerosols showed remarkable similarities. In most cases, chemical species in the fine

particles were oxygenated and ammonium, sulfate and organics were internally mixed. These results are consistent with previous measurements.

The average equivalent ratio of ammonium to sulfate was 0.88, indicating that the aerosol was slightly acidic. When the mass loading was large (3/25–27, 4/6–7), nitrate was also found in fine particles with ammonium and sulfate even after the long-range transport from China and Korea. The average ratio of organics to sulfate was 1.05, indicating that the contribution of organics is not negligible in this region. Mass spectra of organics show that the largest signal in most cases was $m/z = 44$, and the ratio of $m/z = 44$ to organics was almost constant throughout the observation period with the exception of 3/23. Organic species were well oxygenated and internally mixed with sulfate.

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