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Annual variability in chemical properties of particulate matter in Fukuoka based on measurements using an Aerosol Chemical Speciation Analyzer

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Abstract

Mass concentrations of chemical compounds in both fine (particle diameter, Dp < 2.5 μm) and coarse mode (2.5 < Dp < 10 μm) were measured in urban sites of the Fukuoka area using a continuous dichotomous Aerosol Chemical Speciation Analyzer (ACSA-12) at a time-resolution of 1 h throughout 2014. We found that mass concentrations of particulate matter (PM), sulfate, and water-soluble organic compounds in fine mode showed a predominant peak during the spring, indicative of long-range transport due to the prevailing westerly wind. Nitrate mass in fine mode showed an obvious warm-season-low and cold-season-high pattern; thus, it was difficult to accurately quantify the cross-boundary transport of nitrate because of the gas-aerosol phase equilibrium process, particularly under high temperature conditions. Mineral dust and sea salt were the two most important medians carrying coarse mode nitrates. This study found that the transported anthropogenic pollutants contributed to ambient PM mass in Fukuoka city, although urban emission was not negligible.

Keywords: *Anthropogenic pollutants, $PM_{2.5}$, sulfate, nitrate, East Asia*

1. Introduction

Substantial emissions of primary pollutants (NO_x, SO_2, CO, NMHCs, and soil dust) and secondary formation of anthropogenic aerosols (sulfate, nitrate, and organic aerosols) due to massive energy consumption in East Asia have recently resulted in consecutive severe haze pollution events [1]. Long-range transport (LRT) of anthropogenic pollutants in some episodic events also affected adherence to the National Ambient Air Quality Standard (NAAQS) in East Asian countries, and even in the west coast of North America [2]. In recent years, the issue of cross-boundary transport of particulate matter with an aerodynamic diameter of less than 2.5 μm ($PM_{2.5}$) has attracted great attention in both the scientific community and governments. The Kyushu area in Japan is frequently subject to the cross-boundary transport of pollutions, and is more affected by the $PM_{2.5}$ issue than other parts of Japan (such as the Kanto region), especially during the cold season when the westerly winds prevail. Recent studies on Fukue island (a remote marine site, 32.7N, 128.68E) demonstrated that the contribution from central north China (105°E–124°E, 34°N–42°N) could account for 50–60% of $PM_{2.5}$, except during the summer [3]. However, Kaneyasu et al. [4] performed observations at both remote and urban sites in the Kyushu area and found that the $PM_{2.5}$ concentration in the city area (Fukuoka) was primarily dominated by the inflow of LRT aerosols. It is believed that non-sea-salt sulfate concentration in Japan is mainly influenced by SO_2 emission in mainland China, and implementation of desulfurization activities in China during recent decades has decreased the tropospheric sulfate concentration in East Asia [5]. However, the contribution of nitrate from LRT remains unclear, especially in metropolis areas where nitrate formation from local NO_x emission was ubiquitously evident. Unfortunately, studies on the transport of nitrate in East Asia are not available, and comprehensive research in East Asia is important because of the increase in NO_x emission in China during recent decades [6]. Recent studies have shown that the co-existence of NO_x with SO_2, leading to the rapid conversion of SO_2 to sulfate, exaggerated the formation of Asian haze [7].

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Mineral dust aerosols are good carriers of anthropogenic pollutants (e.g., nitrate) in East Asia since the dust source regions (Taklimakan and Gobi desert) are close to populated/industrial areas in mainland China [8]. The formation of sulfate and nitrate on dust aerosols has been clearly observed using scanning electron microscopy (SEM) both in laboratory experiments and using field measurements [9]. In principle, nitrate in coarse mode presents in the form of calcium nitrate ($Ca(NO_3)_2$) and magnesium nitrate ($Mg(NO_3)_2$) since gaseous nitric acid (HNO_3) is a very sticky molecule in the troposphere. In the marine region, HNO_3 tends to react with sea salt (e.g., NaCl) to produce $NaNO_3$(aq) and gaseous HCl(g), resulting in the presence of NO_3^- in coarse mode. At this time, the environmental effect of fine mode nitrate has been well studied in East Asia; however, the ambient burden of coarse mode nitrate remains unclear, and the corresponding contribution of cross-boundary transport has not been discussed. In the present study, we report the annual/diurnal variation in anthropogenic pollutants in Fukuoka, and investigate the seasonal variability in fine/coarse mode nitrate, the contribution from outside of Japan, and the possible transport mechanism of nitrate in metropolitan areas.

2. Experimental

One-year observation of particulate matter (PM) and anthropogenic pollutant compounds (e.g., sulfate, nitrate, water-soluble organic compounds [fWSOC], black carbon) in both fine (particle diameter, Dp < 2.5 μm, marked as $PM_{2.5}$) and coarse mode (2.5 < Dp < 10 μm, mark as $PM_{2.5-10}$) were performed using a continuous dichotomous Aerosol Chemical Speciation Analyzer (ACSA-12, Kimoto electric co. Ltd) at a time-resolution of 1 h from October 2013 to December 2014. The instruments were installed at the roof of a three-floor building in the Fukuoka Institute of Health and Environmental Sciences (Lat: 33.51°N, Lon: 130.50°E) before September 2014, and were then moved to a six-floor building in the Chikushi campus of Kyushu University (Lat: 33.52°N, Lon: 130.47°E). The anthropogenic activity was very limited at both sites. ACSA-12 was designed to continuously measure mass concentrations of PM and water-soluble species at a specified time resolution and at a flow rate of 16.7L/min. The mass concentration of PM was determined using the beta-ray absorption method. The mass concentrations of nitrate ions and water-soluble organic compounds were determined using the ultra-violet absorption-photometric method. The mass concentration of sulfate ions was determined using the $BaSO_4$-based turbidimetric method after the addition of $BaCl_2$ dissolved in polyvinyl pyrrolidone solution. The acidity of particles (marked as $\Delta[H^+]$, representing the difference between measured and standard solution) was also determined based on an absorption spectrometric method after adding the pH indicator. The mass concentration of black carbon was determined optically using the near-infrared spectroscopy method; here, we defined it as OBC. Furthermore, light-polarization properties and size distribution of single particles at the observation site were measured using a Polarization Optical Particle Counter (POPC).

The depolarization ratio (DR), denoted as the ratio of the intensity of the *s*-polarized signal to the total intensity of the backward-scattering signal, was adopted to indicate the sphericity/non-sphericity of aerosol particles. A detailed description of POPC was reported previously [10]. In the present study, we adopted the filter-

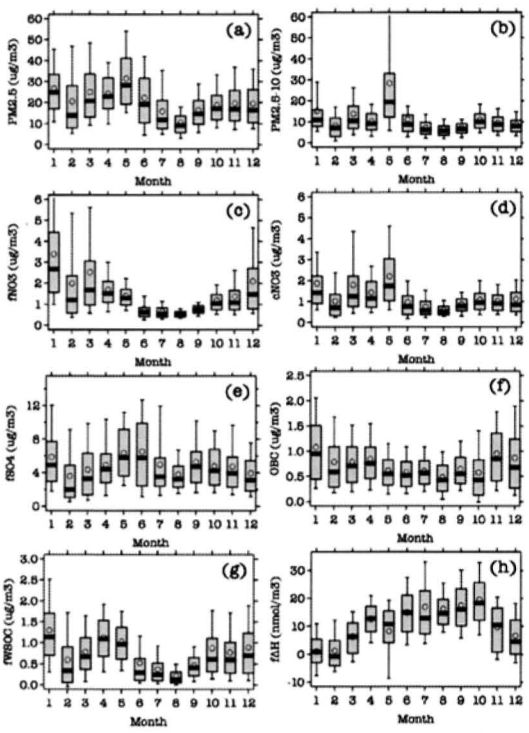

Figure 1. Monthly average concentrations of $PM_{2.5}$ (a), $PM_{2.5-10}$ (b), fNO_3 (c), cNO_3 (d), fSO_4 (e), OBC (f), fWSOC (g), and fΔH (h) in Fukuoka for 2014. The dark gray bar and black circle indicate the medium and mean values in each month, and the gray block and blue whisker indicate the 25th and 75th percentile and the 10th and 90th percentile values, respectively.

based off-line dataset provided by the Fukuoka Institute of Health and Environmental Sciences, and the mass concentrations of chemical species (e.g., sulfate, nitrate, ammonium, sodium) were analyzed based on ion chromatography (IC).

3. Results

3.1 Seasonal pattern

Concentrations of $PM_{2.5}$, $PM_{2.5-10}$, fine mode nitrate (fNO_3), coarse mode nitrate (cNO_3), fine mode sulfate (fSO_4), fWSOC, and $\Delta[H^+]$ ($f\Delta H$) showed clear seasonal variabilities, as shown in Figure 1. Monthly variation in mass concentrations of $PM_{2.5}$ showed a bimodal distribution with two peaks during the spring and winter, with minimum concentrations observed during the summer (Figure 1a). $PM_{2.5-10}$ concentration showed a pronounced peak in May due to the frequent impact by dust events in 2014 (Figure 1b). Mass concentrations fNO_3 during the cold season were much higher than during the warm season (Figure 1c) because of the frequent breakout of haze pollution in the mainland area of East Asia and transportation with prevailing westerly wind (as shown in the trajectory analysis in section 3.3). Second, the nitrate could be present in the gas phase (HNO_3) due to gas-aerosol equilibrium under high temperature conditions, resulting in an evident decrease in particulate nitrate mass. Lastly, the air masses in the summer typically originated from the west Pacific where anthropogenic pollutants were limited. The mass concentration of cNO_3 (Figure 1d) showed a similar pattern as $PM_{2.5-10}$, indicative of simultaneous transport with dust (discussed in section 3.4). The mass concentration of fSO_4 (Figure 1e) showed two peaks during January and June, respectively. The maximum concentration in June suggested that the conversion efficiency of SO_2 to sulfate played a vital role in tropospheric loading in East Asia. The mass concentration of OBC did not show clear seasonality, reflecting that local emission was a major contribution (Figure 1f). fWSOC mass showed a consistent variability with $PM_{2.5}$ (Figure 1g), although the photochemical activity of organic aerosol was high during the summer [11]. Thus, the transport contribution on the ambient fWSOC exceeded local formation in Fukuoka city; however, more detailed model simulations are required to confirm this observation. $f\Delta H$ showed a moderate peak during the warm season, and was close to zero in winter, suggesting that the acidic species in $PM_{2.5}$ were mostly neutralized; however the acidic species was obviously superfluous, especially during the summer.

3.2 Diurnal variation

Diurnal variation in $PM_{2.5}$, fSO_4, $PM_{2.5-10}$, fNO_3, NO_3, fWSOC, OBC, and $f\Delta H$ for different seasons during the observation period are illustrated in Figure 2. As expected, the mass concentrations of $PM_{2.5}$ and fSO_4 did not show evident diurnal variability (Figure 2. a1-a4 and b1-b4), which suggested that the local formation had a minor contribution to ambient mass in the Fukuoka area. The median values of $PM_{2.5}$ were 28 $\mu g/m^3$, 12 $\mu g/m^3$, 18 $\mu g/m^3$ and 20 $\mu g/m^3$ for spring, summer, autumn, and winter, respectively. The median value of fSO_4 concentration was 3.5–4.5 $\mu g/m^3$. The mass concentration of $PM_{2.5-10}$ showed a daytime-high and nighttime-low pattern (Figure 2c1–c4), which could be partially attributed to anthropogenic activities. In addition, the observation site was located near a coastal area of the Fukuoka prefecture, and the wind speed normally reached its peak at noon due to both topographic effects and land-sea breeze circulation. Therefore, the corresponding transport of sea salt contributed to the mass in coarse mode. No increase in coarse mode particles was observed during the summertime (Figure 2c2) because of frequent precipitation and high dry deposition velocity of large particles under high humidity conditions. The mass concentration of fNO_3 showed diurnal variability to some extent during the spring and winter (Figure 2d1 and d4). The peak appeared at 1000 JST near rush hour and reflected the preferential formation of nitrate due to the emission of NO_x. Mass concentration of fNO_3 during the summer was generally less than 1.0 $\mu g/m^3$ throughout the day, mostly as a result of the gas-aerosol equilibrium of particulate nitrate mass under high temperature conditions. cNO_3 mass showed an entirely different diurnal variation than fNO_3 (Figure 2e1–e4), suggesting that cNO_3 had more complicated origins (e.g., transport with dust plume). fWSOC mass, particularly during the summer (Figure 2f2), showed a moderate peak at noon. This was consistent with observations in Tokyo, which showed that oxygenated organic aerosols (chemical WSOC) were substantially formed due to high photochemical activity. The increase in fWSOC during the daytime in autumn and winter was not evident. OBC mass showed a pronounced peak during rush hour in the morning due to vehicle emission, and gradually decreased to the minimum at 1500 JST in the afternoon due to full development of the planet boundary layer (PBL). The weak peak at night was mainly due to depressed PBL after sunset. Figure 2h1–h4 shows the diurnal variation in $f\Delta H$ for all seasons, and the acidity of $PM_{2.5}$ was not significantly influenced by the local emission.

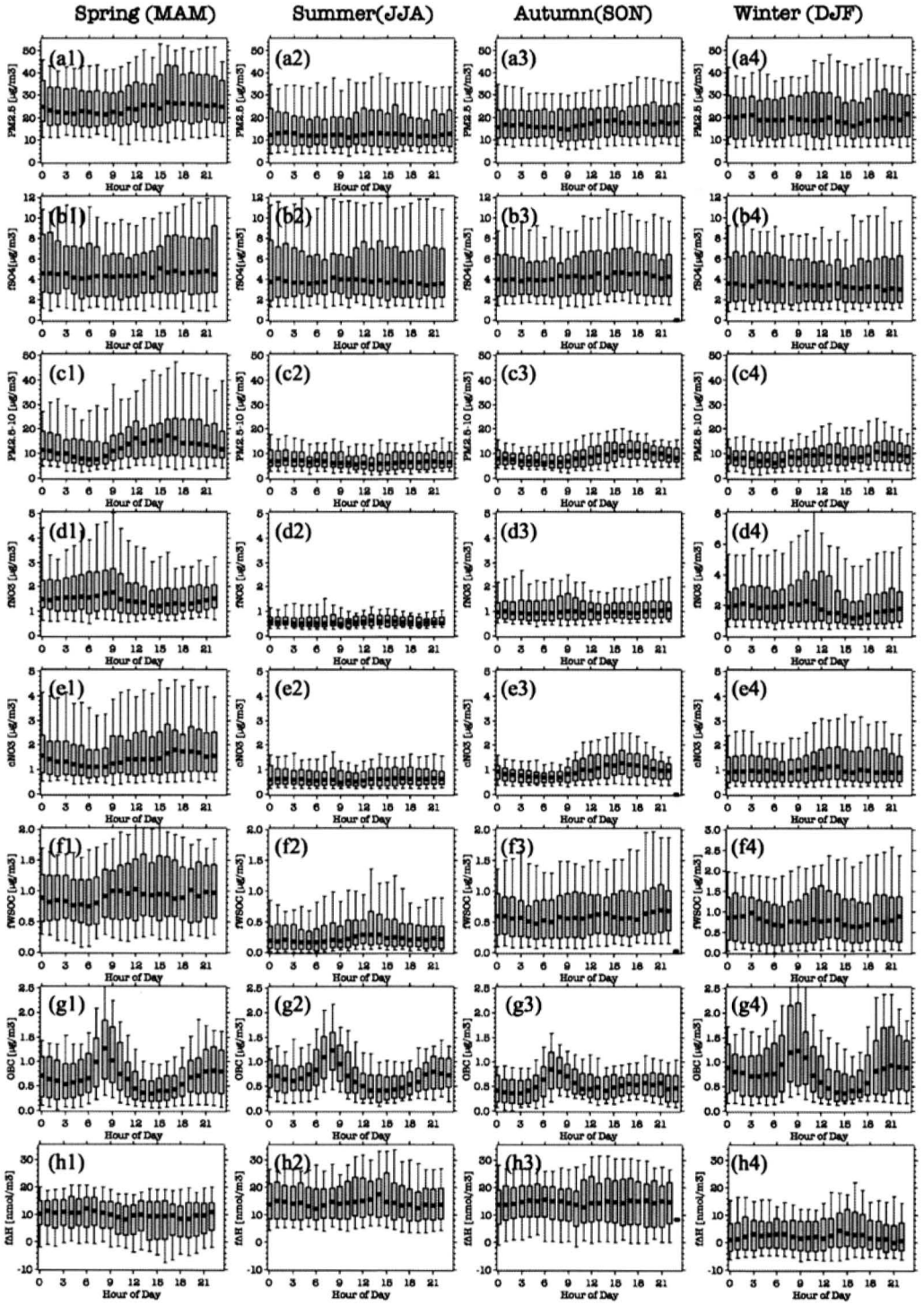

Figure 2 Diurnal variations in $PM_{2.5}$, fSO_4, $PM_{2.5\text{-}10}$, fNO_3, cNO_3, fWSOC, OBC, and fΔH for different seasons in 2014. The black bar indicates the medium value in each hour and the gray block and whisker indicate the 25th and 75th percentile and the 10th and 90th percentile values, respectively.

4. Discussion

4.1 Potential source regions of pollutants in Fukuoka

Variation in average concentrations of $PM_{2.5}$, $PM_{2.5-10}$, fSO_4, fNO_3, cNO_3, and OBC as a function of wind speed and wind direction during the observation period are shown in Figure 3. To avoid local geographic impacts on the wind field, the meteorological sounding data (twice a day at Fukuoka, JMA, Latitude: 33.58N, Longitude: 130.38E at 0900 JST and 2100 JST, http://weather.uwyo.edu/upperair/sounding.html) at a height of 1000-hPa was used in the plot. Based on Figure 3a, the mass concentration of $PM_{2.5}$ was significantly enhanced when the observation site was exposed to a prevailing westerly wind, and it almost exceeded the daily Ambient Air Quality Standard (35 μg/m^3) in Japan when the air masses originated from the northwest at high wind speeds (> 6 m/s). Averaged $PM_{2.5}$ mass from southwest was also found to be higher than that from the east. This suggested that the contribution of LRT was important for adherence to the National Ambient Air Quality Standard (NAAQS) in Fukuoka. The mass concentration of $PM_{2.5-10}$ as a function of wind direction generally showed a similar pattern as $PM_{2.5}$ (Figure 3b). The high $PM_{2.5-10}$ mass (larger than 40 μg/m^3) from the west was due to the impact of a long-lasting dust event

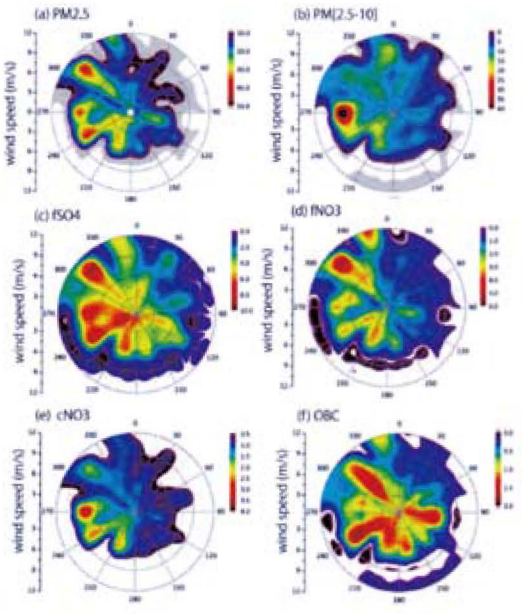

Figure 3 Dependence on the average concentration of $PM_{2.5}$ (a), $PM_{2.5-10}$ (b), fSO_4 (c), fNO_3 (d), cNO_3 (e), and OBC (f) on the wind speed and direction during the observation period.

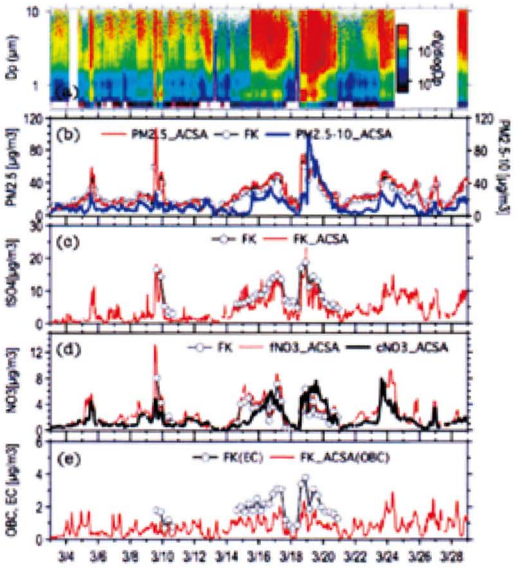

Figure 4 Time series of volume size distribution of particles and mass concentrations of $PM_{2.5}$, fSO_4, fNO_3, cNO_3, OBC, and sodium ion in March in Fukuoka.

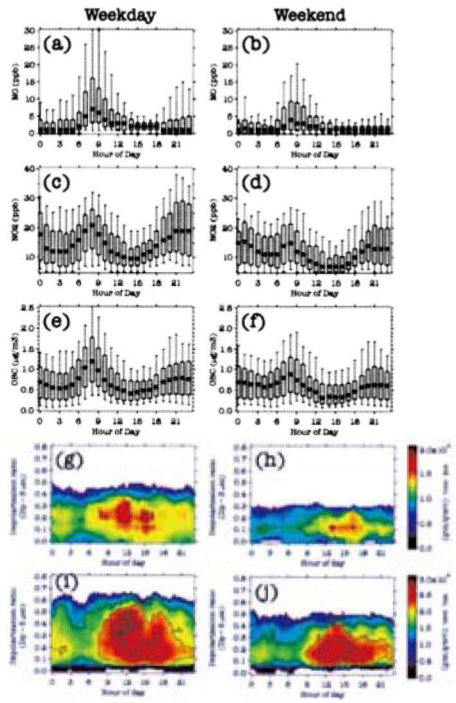

Figure 5 Weekday effect of local anthropogenic emission on NO, NO_2, OBC, and depolarization ratio for coarse mode particles at Dp = 3 μm and at Dp = 5 μm. The left and right panels represent the diurnal variations at the weekday and weekend, respectively.

from May 26th–June 2nd, 2014 [12]. The sea salt aerosols due to sea-land breeze from northwest in Fukuoka city also contributed some fraction of coarse mode particles. fSO_4 is the key component of $PM_{2.5}$, and it showed a similar spatial distribution with $PM_{2.5}$ (Figure 3c). For fNO_3 (Figure 3d), the concentration of fNO_3 increased when the northeast wind was prevailing. We noted that a high nitrate concentration under strong northerly wind conditions (wind speed higher than 10 m/s) was observed, suggesting that LRT contributed to fine mode nitrate in the urban area, excluding local formation. Mass concentration of cNO_3 as a function of wind direction (Figure 3e) was similar with that of $PM_{2.5-10}$, because cNO_3 could simultaneously transport with dust and sea salt aerosols. These observations were confirmed by several previous reports [9]. Figure 3f demonstrated the spatial variability in OBC at urban sites of Fukuoka; the mass concentration of OBC increased under three distinct wind directions (northwest, southwest, and east), irrespective of the wind speed. This reflected that the contribution from local emissions (as demonstrated in Figure 2g1–g4) in Fukuoka city is a key factor.

4.2 Transport of anthropogenic pollutants with dust in March 2014

Figure 4 shows temporal variation in mass concentrations of chemical species during several different anthropogenic pollution events in March 2014. To examine the reliability of ACSA observations, the filter-base analysis results at Fukuoka were included in the plot (indicated by "FK" in the legend). The on-line measurements of $PM_{2.5}$, fSO_4, fNO_3, and cNO_3 showed good agreement with off-line analysis using ion-chromatography techniques. The volume size distribution of particles as a function of time (Figure 4 a) was used to indicate the variability of aerosol types in Fukuoka. We can see that the observation site was influenced by a typical anthropogenic pollution event on March 9th 2014 and a polluted dust event on March 19th 2014 because the volume concentration of coarse mode particles was distinctly different, although mass concentrations of pollutant species were similar. On March 9th 2010 JST, the mass concentrations of $PM_{2.5-10}$ and cNO_3 were 29 $\mu g/m^3$ and 5 $\mu g/m^3$, respectively; however, they increased to 101 $\mu g/m^3$ and 8 $\mu g/m^3$, respectively, on March 19. Temporal variability in cNO_3 was generally consistent with that of $PM_{2.5-10}$. However, temporal variation in mass concentration of fNO_3 correlated well with that of fSO_4, indicating that fNO_3 was simultaneously transported with sulfate species from outside of Japan. Regarding OBC, ACSA measurement was generally lower than the filter-based analysis during dust events. The two possible explanations for this observations were: i) coverage of dust layer on the PTFE filter in ACSA could evidently increase scattering capacity of the sampled aerosol layer, resulting in an underestimation of black carbon loadings by ACSA; or ii) for the filter-based analysis, BC concentration (elemental carbon by strict definition) was determined based on thermo-optical-transmission methods, which could classify some fraction of pyrolyzed organic carbon as elemental carbon, leading to an overestimation. A detailed comparison of BC between ACSA and other instruments (e.g., multi-angle absorption photometer, single particle soot photometer) is required. In this sense, the transport of BC from outside of Fukuoka city was not well supported by field observations.

4.3 Local contribution

Figure 5 depicts the diurnal variation in NO, NO_2, OBC, and depolarization ratios of coarse mode particles during weekday and weekend periods in 2014. We can see that the mixing ratio of NO, NO_2, and OBC in Fukuoka city peaked when the anthropogenic activities were intensive, in particular during rush hour (0600-0900 JST). The mixing ratio of NO during rush hour on weekdays showed a medium value of 7 ppb (sometimes exceeding 20 ppb), higher than that (3 ppb) on the weekend (Figure 5a, 5b). Mixing ratios of NO_2 during rush hour were 22 ppb and 15 ppbv for the weekday and weekend, respectively (Figure 5c, 5d). Similar diurnal variability was observed for OBC with a medium peak of 1.4 $\mu g/m^3$ on weekdays and 0.8 $\mu g/m^3$ on weekends, respectively (Figure 5e, 5f). The moderate increase in NO_2 and OBC during the night was due to depression of the urban boundary layer. The diurnal variation in volume concentration of coarse mode particles (e.g., Dp = 3 μm and Dp = 5 μm) provided interesting results, which reflected the impact of anthropogenic activities and land-sea circulation, the latter of which could introduce considerable amounts of sea salt particles into the inner part of Fukuoka city. As shown in Figure 5g, the average volume concentration of coarse mode particles at both Dp = 3 μm and Dp = 5 μm in the daytime of weekdays were considerably higher than that on the weekend due to the impact from anthropogenic activities. It was also noticeable that the depolarization ratio of the coarse particles during the week were larger than those on the weekend, suggesting that human activities in the urban area could produce substantial amounts of non-

spherical particles (e.g., local fugitive dust). For particles with Dp = 5 um, both the volume concentration and depolarization ratio start to increase from 0800 JST, earlier than that on the weekend. The peaks at noon indicated that local vehicle activities may play a key role in enhancement of ambient loading of coarse mode particles in Fukuoka. Another interesting feature was that, even on the weekend, an obvious diurnal variation in volume concentration of coarse mode particles were observed. Such variability could be mostly attributed to the effect of land-sea circulation that periodically introduced sea salt aerosols into the inner land area.

5. Summary

We investigated the mass concentrations of anthropogenic pollutants based on high-temporal-resolution measurements of ACSA in Fukuoka. Their seasonal and diurnal variation, as well as possible origins, were discussed. We found the following: (1) the $PM_{2.5}$ in Fukuoka city was influenced by long-range transport from outside of Japan, but local sources were partially responsible for ambient loading of $PM_{2.5-10}$ during the non-dust period; (2) nitrate mass in coarse mode in Fukuoka was comparable to that in fine mode, and both showed a minimum during the hot season due to gas-aerosol equilibrium of nitric acid under high temperatures; the occurrence of dust events in spring resulted in the transport of substantial amounts of cNO_3; and (3) anthropogenic activities in Fukuoka were mostly responsible for variability in black carbon.

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