Analysis of Organic Aerosol in Fukuoka, Japan Using a PMF Method

Akinori Takami1*, Takao Miyoshi1, Satoshi Irei1, Ayako Yoshino1, Kei Sato1, Atsushi Shimizu1, Masahiko Hayashi2, Keiichiro Hara2, Naoki Kaneyasu3, Shiro Hatakeyama4

1 National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan
2 Faculty of Science, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka, Fukuoka 814-0180, Japan
3 National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan
4 Graduate School of Agriculture, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan

ABSTRACT

Aerosol chemical species were measured using an Aerodyne quadrupole aerosol mass spectrometer (Q-AMS) in spring 2010, in Fukuoka. The main species were sulfate and organics. Organic data were analyzed using the Positive Matrix Factorization (PMF) method. Two distinct periods (Period 1 and 2) were selected. Period 1 (from March 19 at 19:50 to March 20 at 10:00) was influenced by trans-boundary air pollution. Low-volatile, oxygenated organic aerosols (LV-OOA) were dominant and the hydrocarbon-like organic aerosols (HOA) fraction was as low as 15%. About one-fourth (26%) of the observation period in Fukuoka was influenced by trans-boundary air pollution. In Period 2 (from March 22 at 00:00 to March 22 at 23:50), both local emissions and trans-boundary air pollutants influenced Fukuoka air quality. The HOA fraction was relatively high, although the LV-OOA fraction was about one-third of OA. The trans-boundary air pollution was analyzed using the oxidation state of organic aerosols (OA), obtained by the PMF method.

Keywords: AMS; Organic; Sulfate; PMF; LV-OOA.

INTRODUCTION

Emissions in East Asia have increased because of the rapid economic development in this region (Ohara et al., 2007; Lu et al., 2010; Kurokawa et al., 2013). The emission in 2008 and the growth rate between 2000 and 2008 of nitrogen oxides (NOx) for China are 27.0 Tg and +89%, respectively. Those of non-methane volatile organic compounds (NMVOCs) for China are 27.1 Tg and +71% (Kurokawa et al., 2013). Since primary and secondary products of gas and aerosol emitted in China are transported to Japan by the winds of the seasonal monsoon, the air quality is influenced by trans-boundary air pollution in the western and southwestern areas of Japan, namely Kyushu and Okinawa (see Fig. 1) (Takami et al., 2005, 2007; Ohara et al., 2008; Kanaya et al., 2010; Hatakeyama et al., 2011; Kaneyasu et al., 2011; Hatakeyama et al., 2014).

Fukuoka is one of the largest cities of Kyushu, Japan, and its local emissions are expected to be large. In addition, Fukuoka is also influenced by trans-boundary air pollution since Fukuoka is located in northern Kyushu (Takami et al., 2005; Ohara et al., 2008; Kaneyasu et al., 2011). The air quality in Fukuoka is therefore, influenced by both local emission and trans-boundary air pollution. In order to improve the air quality in Fukuoka, it is necessary to assess both contributions.

The Aerodyne aerosol mass spectrometer (AMS) is well recognized as a useful instrument to measure the chemical composition of aerosols (Jayne et al., 2000; Jimenez et al., 2003; Takami et al., 2005; Canagaratna et al., 2007; Takami et al., 2007). Factor analysis methods have been developed to interpret AMS organic data (Lanz et al., 2007; Zhang et al., 2007; Lanz et al., 2008; Ulbrich et al., 2009). Organic aerosol (OA) is typically classified into hydrocarbon-like organic aerosols (HOA) and oxygenated organic aerosols (OOA) (Zhang et al., 2007). It was found that more than 90% of the OA occurred as OOA, and less than 10% was HOA, on remote islands (e.g., Fukue and Okinawa) in the East China Sea region in spring; while about 60% of OA was OOA, and nearly 40% was HOA in Tokyo in summer and winter. This indicated that OA transported long distances contained higher fractions of OOA, and that OA from local emissions contained higher fractions of HOA.

We have applied a factor analysis method to assess the influences of both local and trans-boundary air pollution in Fukuoka. Aerosol chemical composition was measured in...
Fukuoka City in spring, using an AMS. The East Asian monsoon prevails in winter-spring season, and it is expected that the trans-boundary air pollution occurs frequently. Period for the local air pollution or the trans-boundary air pollution in Fukuoka was determined using the AMS data (inorganic chemical composition and size distribution), numerical simulation and air-mass backward trajectory. Then, we elucidate the variation of concentration and fraction of the OOA and HOA components for the two study periods, of both local and trans-boundary air pollution in Fukuoka City.

**MATERIALS AND METHODS**

**Sampling Location, Instruments and Sampling Method**

Aerosols were sampled at Fukuoka University in Fukuoka City (Fig. 1). Fukuoka is one of the largest cities in northern Kyushu, Japan, which faces the Korean peninsula and the Chinese continent. The seasonal monsoon winds in the winter and spring seasons, transport air pollutants to the study area (Kaneyasu et al., 2011). The population of Fukuoka is about 1.5 million, and there is substantial
infrastructure within the metropolitan area (shipyard, airport, railway stations, and city highways). There are also large industrial and commercial areas in the city (See Fig. 1). Fukuoka University is located 5 km from the downtown area, and within the residential area. There is a subway station at the edge of the campus and the city highway runs several hundred meters south of the university. Sampling was performed on the 4th floor of the Science Building of Fukuoka University (130.3°E, 33.5°N).

The chemical composition of the aerosols (PM$_1$) was measured and analyzed using a quadrupole type aerosol mass spectrometer (Q-AMS, Aerodyne Research, Inc.). A detailed description of the Q-AMS can be found elsewhere (Jayne et al., 2000; Allan et al., 2003a, b; Jimenez et al., 2003; Takami et al., 2005; Canagaratna et al., 2007; Takami et al., 2007). A brief introduction follows here. Ambient air is introduced through an aerodynamic lens. The particles form a particle beam and hit the vaporizer, within which the temperature is set to 873 K (600°C), and where non-refractory species are vaporized. The vaporized molecules are ionized by electron impact ionization at 70 eV. The ions are then analyzed by the quadrupole mass spectrometer.

The sulfate, nitrate, ammonium, and chloride content are calculated from the fragment signals of the mass spectra. Organics are calculated by subtracting the known inorganic and gaseous species (e.g., sulfate, nitrate, nitrogen, oxygen, and argon) from the total mass. The particle mass was calibrated using ammonium nitrate (NH$_4$NO$_3$) particles (Jayne et al., 2000). The ionization efficiency (IE), and the relative ionization efficiency (RIE), were determined for NH$_4$NO$_3$ particles with a diameter of 350 nm using standard procedures (Jayne et al., 2000; Allan et al., 2003a, b; Jimenez et al., 2003; Takami et al., 2005; Canagaratna et al., 2007; Takami et al., 2007). The IE used here was $3.21 \times 10^{-6}$, and the RIE for NH$_4^+$ was 3.2. The collection efficiency (CE) for all the measured species was 0.5, which is a standard value for the AMS (Canagaratna et al., 2007). Q-AMS can measure the size distribution by measuring the flight time of the particle. The flight time is converted to the vacuum aerodynamic diameter. The flight time is calibrated to the size-distribution using the known size of poly-styrene latex and NH$_4$NO$_3$ particles (Jayne et al., 2000; Allan et al., 2003a, b; Jimenez et al., 2003; Canagaratna et al., 2007).

The size-distribution for each chemical component is called “Chemically resolved size-distribution (CRSD)”. The AMS data were analyzed using the standard AMS analysis software (Allan et al., 2004; Canagaratna et al., 2007).

The sampling inlet was set up about 20 m above the ground. A PM$_{2.5}$ cut cyclone (URG-2000-30ED) was attached at the inlet to remove coarse particles. The flow rate of sampling line was 3 L min$^{-1}$. A stainless steel tube with an outer diameter of half an inch was used as the main sampling line. Taking into account isokinetic sampling, the main sampling line was connected to the Q-AMS inlet tube (outer diameter, 1/8 inch).

**PMF Analysis**

Positive Matrix Factorization (PMF) was originally invented by Paatero (Paatero and Tapper, 1994; Paatero, 1997), and is a receptor-only factorization method. Since we measured the aerosol chemical composition only in the receptor area (Fukuoka City) of the trans-boundary air pollution, we adopted the PMF method to analyze our AMS organic data. We used the PMF analysis software version 2.04 developed by Ulbrich et al. (2009). Details of the analysis method can be found in their publication (Ulbrich et al., 2009) and on their web page (http://cires.colorado.edu/jimenez-group/wiki/index.php/PMF-AMS_Analysis_Guide).

**RESULTS**

**Chemical Composition Measured by AMS**

Aerosol was measured from the beginning of March until the end of May in 2010. In this paper, a period between March 18 and March 24, 2010 was selected for intensive analysis. These two period are the test cases to see the variation of concentration and fraction of the OOA and HOA components for local and trans-boundary air pollution in Fukuoka City. The time series of the chemical composition measured using Q-AMS is shown in Fig. 2. The average mass concentrations and standard deviations (expressed in $\pm 1\sigma$) of ammonium, nitrate, sulfate, chloride, and organics were $3.4 \pm 1.8$, $2.0 \pm 2.3$, $5.9 \pm 4.0$, $0.1 \pm 0.2$, and $5.7 \pm 2.4$ µg m$^{-3}$, respectively. No precipitation was observed during this period.

**Fig. 2.** Variation of mass concentrations (sulfate, nitrate and organics) measured using Q-AMS at Fukuoka city.
The average CRSD of the organics are shown in Fig. 3. The peak mode of the vacuum aerodynamic diameter ($D_{va}$) was 600 nm (single peak), when high concentrations of sulfate were observed from March 19 at 19:50 PM to March 20 at 10:00 AM (hereafter, Period 1). Double peaks were observed at the peak modes of $D_{va} = 200$ and 600 nm, when higher concentrations of organics (compared to sulfate) were observed from March 22 at 00:00 AM to March 22 at 23:50 PM (hereafter, Period 2). In previous studies, a single peak with the peak mode $D_{va} = 600–800$ nm was observed on remote islands in the East China Sea (Fukue and Okinawa), when the aerosol was transported a long distance (Takami et al., 2005, 2007). Double peaks were observed in the suburbs, when the aerosol was a mixture of local emissions and transported pollutants (Alfarra et al., 2004).

**Backward Trajectory Analysis and Numerical Simulation for Sulfate in Aerosol**

Backward trajectories (BT) were calculated using the NOAA Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) (Draxler and Rolph, 2012; Rolph, 2012). In addition, the results of the Chemical Weather Forecasting System (CFORS) numerical simulations were also used to investigate the spatial distribution of sulfate (Uno et al., 2003, CFORS WEB page: http://www-cfors.nies.go.jp/~cfors/). The BT and CFORS results are shown in Fig. 4. In Period 1, when the sulfate concentration was high, the air mass was transported from the Chinese continent. The CFORS simulation also shows that the main stream of the wind vector (arrows in the figure) was from the Chinese continent to Japan. The high concentration of sulfate was spread from the coastal region of China to Japan during that time. In Period 2, the air mass was transported from northern China via the Korean peninsula. The air mass had traveled over the Kyushu region for 18 hours before it reached Fukuoka. The CFORS simulation shows that the main wind stream in the East China Sea was southerly, and sulfate concentrations were low in Fukuoka.

**Organic Aerosol Speciation by PMF Analysis**

The organic spectra were analyzed using the PMF method (Ulbrich et al., 2009). Results of the mass spectra and time series are shown in Fig. 5. Fig. 5(a) shows the two-factor case, and Fig. 5(b) shows the three-factor case. The purpose of this paper is to see variation of concentration and fraction of the OOA and HOA components for the two study periods as written in the Introduction section. Therefore, we chose the two and three factor cases. For the two-factor case, the mass spectra of Factor 1 show the distinctive signal of $m/z = 44$, which is typical of OOA. The spectra of Factor 2 show the distinctive signal of $m/z = 41, 43, \text{and } 55$, which is typical of HOA (Jimenez et al., 2009; Ulbrich et al., 2009). For the three-factor case, the mass spectra of Factor 1 show the distinctive signal of $m/z = 44$, which is typical of LV-OOA. The spectra of Factor 2 show the distinctive signal of $m/z = 43$, which is typical of SV-OOA. Those of Factor 3 show distinctive signals of $m/z = 41, 43, 55 \text{ and } 57$, which are typical of HOA (Jimenez et al., 2009; Ulbrich et al., 2009). The variation of each fraction against time is shown in Fig. 6.

**DISCUSSION**

Two periods were selected for the intensive data analysis. Period 1 was from March 19 at 19:50 PM to March 20 at 10:00 AM, and Period 2 was from March 22 at 00:00 AM to March 22 at 23:50 PM.

In Period 1, high concentrations of sulfate were observed, and the CRSD shows a single peak with $D_{va} = 600$ nm. BT and CFORS show that the air mass was transported from the Chinese continent. These results indicate that this period was typically influenced by trans-boundary air pollution (Takami et al., 2005). In this period, the PMF analysis for the two-factor case shows that mass concentrations of OOA, and HOA were 4.4 and 2.6 $\mu g \text{ m}^{-3}$, respectively. The calculated fractions of OOA and HOA were 62.8% and 37.2%, respectively. The PMF analysis for the three-factor case shows that mass concentrations of LV-OOA, SV-OOA, and HOA were 3.9, 2.0, and 1.1 $\mu g \text{ m}^{-3}$, respectively. The fractions of LV-OOA, SV-OOA, and HOA were 55.4%, 29.2%, and 15.3%, respectively. The fractions of both OOA and LV-OOA are dominant components in the two-factor and three-factor cases, respectively. The results of the two-factor case are similar to those from the previous analysis of HOA and OOA by Zhang et al. (2007), in which the average HOA and OOA fractions in urban areas in the
northern hemisphere were 37% and 67%, respectively. However, the HOA fraction of the three-factor case was much lower than the fraction in urban areas calculated by Zhang et al. (2007). The reason is that the SV-OOA component for the three-factor case was included in both OOA and HOA components for the two-factor case because the signal of $m/z = 43$ in the SV-OOA mass spectra, consists of aldehyde (CH$_2$CHO) and hydrocarbon (C$_3$H$_7$) in Q-AMS. Therefore, the results of the three-factor case should be used to analyze the influence of trans-boundary air pollution. OOA and sulfate are produced by oxidation of VOCs and sulfur dioxides, respectively, during long-range transport. Therefore, they are expected to be highly correlated to each other. In Fig. 7, LV-OOA shows a positive correlation with sulfate. This supports the idea that LV-OOA is transported long distances, and probably from the Chinese continent, since sulfate mainly originates in China (Takami et al., 2005, 2007).
In Period 2, we observed relatively high concentrations of organics compared to sulfate. BT shows that the air mass was transported from northern China via the Korean peninsula. The height of the trajectory of 500 m at the starting point (i.e., Fukuoka) was kept very low, which is considered to be influenced by the Fukuoka local emissions. Although the BT from 1000 m and 1500 m shows that the air mass was transported from the Chinese continent and the Korean peninsula, the CFORS shows that sulfate concentrations in the Fukuoka area were relatively low, which agrees with the AMS results. The CRSD shows double peaks with $D_a = 200 \text{ nm}$ and 600 nm, which is typical of a mixture of both local emission and long-range-transported air masses (Alfarra et al., 2004). These results indicate that Period 2 was influenced by local air pollution. In this period, the PMF analysis for the two-factor case shows that the mass concentrations of OOA, and HOA were 2.3 and 3.2 µg m$^{-3}$, respectively. The calculate fractions of OOA and HOA were 42.2% and 57.6%, respectively. The PMF analysis for the three-factor case shows that the mass concentrations of LV-OOA, SV-OOA, and HOA were 2.0, 2.0, and 1.5 µg m$^{-3}$, respectively, and that the fractions of LV-OOA, SV-OOA, and HOA were 36.4%, 36.3%, and 27.4%, respectively. For the two-factor case, the HOA fraction was much higher than that found in urban areas by Zhang et al. (2007). For the three-factor case, the fraction of SV-OOA consists of one-third OA component. As mentioned above, the mass spectra of SV-OOA consists of signals for aldehyde (CH$_2$CHO) and hydrocarbon (C$_3$H$_7$) in Q-AMS. Therefore, it is suggested that the fraction of hydrocarbon that is not oxygenated, is large in the SV-OOA component. Period 2 is considered to be influenced largely by local emissions. In Period 2, LV-OOA still consists of one-third OA. BT shows that the air mass came from the Korean peninsula, and stayed around the Kyushu region for 18 hours. The CRSD shows the double peak for OA. OOA was produced during the transport from Korea or originated in the Kyushu region. The fraction of OOA is 42.2% for the two factor case and those of LV-OOA and SV-OOA are 36.4% and 36.3%, respectively, for three factor case. In SV-OOA, both aldehyde (CH$_2$CHO) and hydrocarbon (C$_3$H$_7$) are included, for example, at $m/z = 43$. However, the Q-AMS cannot separate them since Q-AMS measures the unit mass. Therefore, we infer that the OOA fraction of 42.2% for two factor case is at least oxygenated organic aerosol. Since OOA is considered to consist mainly of secondarily produced, organic aerosol (SOA), about 40% of OA is considered to be SOA in Fukuoka in spring, even though the influence of local emissions is large. As shown above, the HOA fraction was 15.3% in Period 1, and was largely influenced by trans-boundary air pollutants. Therefore, the fraction of HOA is used to judge the period when the trans-boundary air pollution is predominant. Here, 15% is considered a threshold indicating a trans-boundary-
Takami et al., Aerosol and Air Quality Research, 16: 314–322, 2016

Fig. 6. The time series of the fraction of each component. Upper panel: two-factor case, Factor 1: OOA, Factor 2: HOA, Lower panel: three-factor case, Factor 1: LV-OOA, Factor 2: SV-OOA and Factor 3: HOA.

Fig. 7. Plots of LV-OOA against sulfate.

air-pollution dominated period. During the observation period March 18–March 24, 2010, the length of time when the HOA fraction was below 15% was 36.3 hours, which was 26.2% of the total observation period. One-third of this observation period may be largely influenced by trans-boundary air pollution. One of the features of the period with low HOA fractions is that the wind speed was high.

In half of these periods, the wind speed was more than 5 ms\(^{-1}\). The strong wind, due to the seasonal monsoon, blows away locally produced particles and brings in long-range transported particles.

CONCLUSIONS

Aerosol chemical species were measured using Q-AMS in spring 2010 in Fukuoka. The main species were sulfate and organics. Organic data obtained from Q-AMS were analyzed by the PMF analysis.

Two distinct periods (Period 1 and 2) were selected and were analyzed using chemical composition, CRSD, BT, CFORS, and PMF results. In Period 1, high concentrations of sulfate were observed with a single peak of CRSD, and the air mass came from the Chinese continent. This period is considered to be influenced by trans-boundary air pollution. The fractions of OOA and HOA in the two-factor case were 62.8% and 37.2%, respectively. Those of LV-OOA, SV-OOA, and HOA in the three-factor case were 55.4%, 29.2%, and 15.3%, respectively. When the trans-boundary air pollution was dominant, both OOA and LV-OOA were dominant, and the HOA fraction was as low as 15%. Using the HOA fraction, we estimate that for about one-fourth (26%) of the observation period, Fukuoka air quality was...
influenced predominantly by trans-boundary air pollution. In Period 2, high concentrations of organics were observed with double peaks of CRSD, and the air mass came from the Korean peninsula and from the Kyushu/Fukuoka area. At this time, both local emissions and trans-boundary air pollutants influenced the air quality in Fukuoka. The fractions of OOA and HOA in the two-factor case were 42.2% and 57.6%, respectively. Those of LV-OOA, SV-OOA, and HOA were 36.4%, 36.3%, and 27.4%, respectively. The HOA fraction is relatively higher, although the OOA and LV-OOA fractions were not small.

The oxidation state of OA (i.e., the PMF analysis results) is very different in Fukuoka when the air quality is influenced by trans-boundary air pollution, compared to periods when it is influenced by local emissions. This indicates that the oxidation state of OA is usable to classify the trans-boundary air pollution in the same way as chemical composition (sulfate and nitrate), CRSD and BT are.

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