Transboundary Secondary Organic Aerosol in the Urban Air of Fukuoka, Japan

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Abstract: Studies providing quantitative information regarding secondary organic aerosol (SOA), the least understood subject in atmospheric chemistry, are important to evaluating secondary transboundary pollution. To obtain quantitative information of long-range transported SOA in the air of Fukuoka, we conducted simultaneous field studies during December 2010 and March 2012 at a rural site in northern Kyushu and at an urban site in Fukuoka City. During the studies, we collected airborne particulate matter (PM) on filters and extracted the low-volatile water soluble organic carbon (LV-WSOC) component, which is possibly dominated by SOA, from the filter samples and analyzed it to determine the carbon concentration and stable carbon isotope ratio. Under the assumption that the LV-WSOC at Fukuoka had both transboundary and local origins, we then applied end-member mixing analysis (EMMA) to the stable carbon isotope ratio data from both sites to estimate the fraction of LV-WSOCs from these origins in the Fukuoka air. Independently, we also analyzed the organic component of fine PM (OA) using an aerosol mass spectrometer (AMS) at both sites during the study periods, and further analyzed the OA mass spectra using positive matrix factorization (PMF) analysis. We then compared results from the EMMA and the PMF. Results from the PMF analysis showed that the OA at Fukuoka was deconvoluted into two loadings: low-volatility oxygenated organic aerosol (LV-OOA), possibly the long-range transport origin, and hydrocarbon-like organic aerosol. The comparison of LV-OOA and LV-WSOC estimated by PMF and EMMFA, respectively, showed disagreement. Since the m/z 44 signals produced by the AMS measurements and the LV-WSOC concentrations from the filter analysis were found be correlated strongly, the inconsistency suggests that the LV-WSOC observed at Fukuoka during the study periods predominantly consisted of SOA.

Introduction

The recent severe air pollution in China has led to high levels of public concern in neighboring countries in north-east Asia, because the prevailing wind during the fall, winter, and spring seasons often carries pollution across international boundaries. Air quality in Japan can be strongly influenced by this pollution. Fukuoka is the largest city in the Kyushu region of Japan, which is the westernmost region closest to the Chinese continent. Approximately 1.5 million people reside in the city, and thus with respect to public health, it is important to quantitatively understand the influence of transboundary pollution on local air quality. When evaluating air pollution, assessments should not only consider the primary pollutants, which are emitted directly from emission sources, but also secondary pollutants, such as ozone, peroxyacetyl nitrate, and secondary organic aerosol (SOA) that are formed during transport. The estimation of SOA is important due to the potential association with its impact on climate and its adverse health effects (Anderson et al., 2003; Dockery et al., 1993), but this is difficult because no unique molecular marker has been identified. To the best of our knowledge, positive matrix factorization (PMF) analysis of organic aerosol mass spectra obtained by aerosol mass spectrometry (AMS) measurements is the only method currently used for assessing atmospheric SOA (Zhang et al., 2005 : Ng et al., 2010). However, a recent report demonstrated that stable carbon isotope ratio ($\delta^{13}C$) measurements of particulate low-volatile water soluble organic carbon (LV-WSOC) at rural sites in the Kyushu and Okinawa regions captured evidence of SOA (Irei et al., 2014). Due to the lack of a large emission source of anthropogenic SOA precursors near the sites and the transport of air masses from the Chinese continent during the study period, the SOA was concluded to be transboundary air pollution, with a secondary origin. It would be no surprise to discover that significant amounts of SOA exist in the urban air of Fukuoka, but the LV-WSOC may also contain primary particulate LV-WSOC from local emissions. This is important to evaluate for the management of air quality.

Our objective in this study was to quantitatively determine transboundary SOA in the urban air of Fukuoka. We analyzed LV-WSOC possibly containing primary LV-WSOC and SOA formed during long-, middle-, and/or short-range transport to determine the carbon concentration and $\delta^{13}C$. We then compared the results with those previously published for a rural site in the northern Kyushu region to apportion the transboundary SOA and the primary LV-WSOC using End Member Mixing Analysis (EMMA).

Theory: EMMA

EMMA is a mass balance approach that is often used in isotope chemistry (*e.g.*, Phillips et al., 2005; Yevenes and Mannaerts, 2012). Given that the stable carbon isotope ratio of the LV-WSOC mixture sampled in urban air ($\delta^{13}C_{Mix}$) consists of i types of LV-WSOCs, which have distinct $\delta^{13}C$ values, the $\delta^{13}C_{Mix}$ can be expressed as follows:

$$\delta^{13}C_{Mix} = \sum w_i \cdot \delta^{13}C_i$$

where w_i and $\delta^{13}C_i$ are the fraction and stable carbon isotope ratio of the type i LV-WSOC, respectively. For a binary mixture, the equation above can be written as:

$$\delta^{13}C_{Mix} = w_{Local} \cdot \delta^{13}C_{Local} + (1 - w_{Local}) \cdot \delta^{13}C_{Trans} \qquad (1)$$

where $\delta^{13}C_{Local}$, $\delta^{13}C_{Trans}$, and w_{Local} are the stable carbon isotope ratios of LV-WSOCs from local emissions and transboundary origins, and the fraction of LV-WSOC from local emissions in the LV-WSOC mixture, respectively. To solve for w_{Local}, the known values of $\delta^{13}C_{Local}$ and $\delta^{13}C_{Trans}$ need to be introduced. Note that the $\delta^{13}C$ values of the source organic carbon would reflect the $\delta^{13}C_{Local}$ because particulate primary LV-WSOC originates from anthropogenic emissions (i.e., the emissions from high temperature combustion processes), while the $\delta^{13}C_{Trans}$ varies depending on the extent of the production reaction(s). By applying a variety of possible $\delta^{13}C_{Local}$ values from the literature and the $\delta^{13}C_{Trans}$ of the particulate LV-WSOC observed at a background site in northern Kyushu, equation (1) is solved for w_{Local}.

Experiment

We conducted simultaneous field studies at the Fukue atmospheric monitoring station (32.8°N, 128.7°E) and at Fukuoka University (33.6°N, 130.4°E) (Figure 1) during two periods: from 6 to 16 December, 2010 and from 8 to 17 March, 2012. The measurements and results of the field studies in 2010 at both sites and those in 2012 at Fukue have been presented and discussed previously (Irei et al., 2014; Irei et al. 2015).

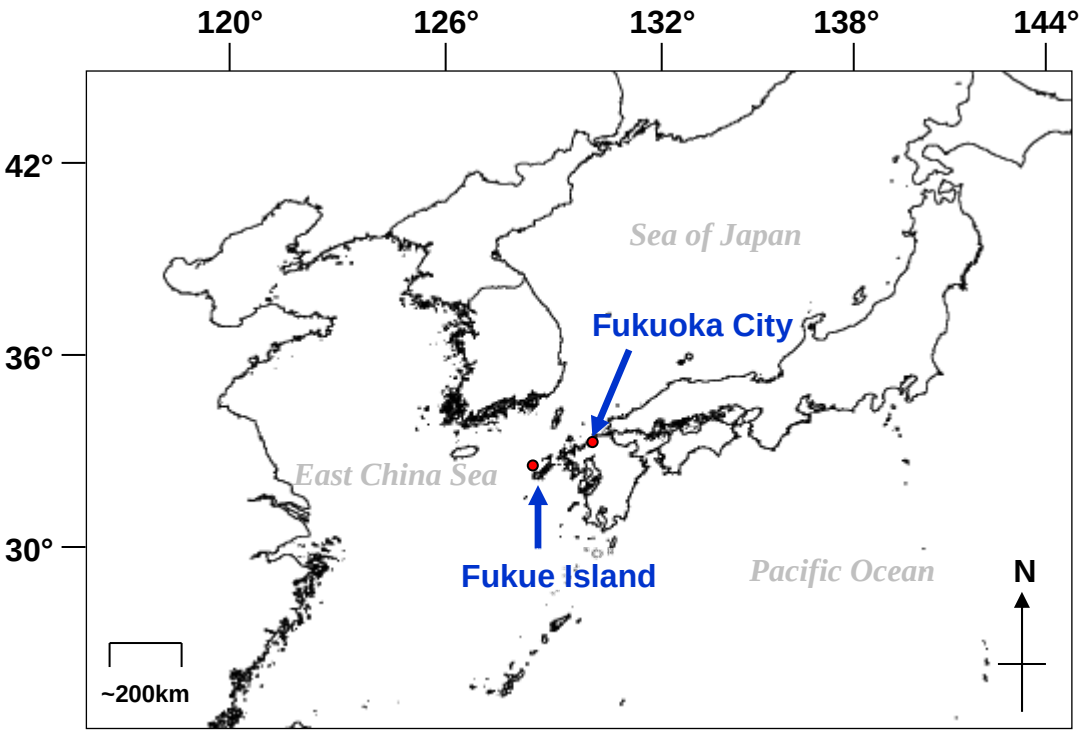

Figure 1. Map showing the locations of measurement sites.

Therefore, only the experiments conducted during the study at Fukuoka 2012 are described here. Total suspended particulate (TSP) was collected every 24 h on pre-baked (773 K for 12 h) quartz fiber filters (8 × 10 inch Tissuquartz, Pall Corp., New York City, NY, USA) using a high-volume air sampler (HV-1000: Sibata Corp., Saitama, Japan). We used a quarter of each filter sample for the LV-WSOC analysis. The details of the preparation procedure for LV-WSOC extracts has been described previously (Irei et al., 2014). Briefly, LV-WSOC was extracted with ultra-pure water (Wako Pure Chemical Industries, Ltd., Osaka, Japan) via sonication. The extract was filtered (PURADISC 25 TF, Whatman Japan K.K., Tokyo, Japan) and then concentrated to ~0.1 mL using a rotary evaporator (R-205 and B-490: Nihon Büchi K.K., Tokyo, Japan) and a gentle flow of 99.99995% pure nitrogen (Tomoe Shokai, Tokyo, Japan). The final volume of the concentrated extract was determined by weighing the extract, assuming unit density. An aliquot of the concentrated extract was pipetted into a 0.15-mL tin cup for elemental analysis (Ludi Swiss AG, Flawil, Switzerland) and then completely dried under a gentle flow of pure nitrogen. Finally, a drop of 0.01 M hydrochloric acid (Wako Pure Chemical Industries, Japan) was spiked into the dried sample for the removal of carbonate, and the sample was re-dried. Extracted samples prepared in this manner were analyzed by an elemental analyzer (Flash 2000: Thermo Scientific, Waltham, MA, USA) coupled with an open-split interface (Conflo IV: Thermo Scientific), followed by

an isotope ratio mass spectrometer (Delta V Advantage: Thermo Scientific) to determine the carbon mass and δ^{13}C value. Here, δ^{13}C is defined as follows:

$$\delta^{13}\mathrm{C} = \left[\frac{(\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}})_{\mathrm{sample}}}{(\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}})_{\mathrm{reference}}} - 1 \right],$$

where $(^{13}C/^{12}C)_{sample}$ and $(^{13}C/^{12}C)_{reference}$ are the $^{13}C/^{12}C$ atomic ratios for the sample and the reference (Vienna Pee Dee Belemnite), respectively.

During the study period, we also used a quadrupole aerosol mass spectrometer (AMS, Aerodyne Research Inc., Billerica, MA, USA) to measure the chemical composition of fine aerosol (~$PM_{1.0}$) during the study at Fukuoka in 2012. The details of these instruments and the theory for determining the concentration of chemical species have been described previously (Jayne et al., 2000; Allan et al., 2004). The details of our AMS measurements are described elsewhere (Irei et al., submitted). Briefly, the AMS was set to output mean concentrations of chemical species every 10 minutes. The scanning range of *m*/*z* was from 1 to 300, and the AMS flash vaporizer was set to 873 K. The AMS was calibrated with 300–350-nm dried ammonium nitrate particles at the beginning of the study period for quantitative analysis. The ionization efficiency was 6.2×10^{-7} counts molecule^{-1}. The collection efficiency used for the calculation of the concentrations was one.

Results and discussion

Concentration and δ^{13}C

In this paper, our fundamental data analysis focuses on the data acquired during the study in March 2012 since such analysis for the study in December 2010 has been published already (Irei et al., 2014). A time series of the carbon concentration and δ^{13}C of LV-WSOC during the field study in March 2012 showed that the concentrations at Fukue were typically higher than those at Fukuoka (Figure 2). The carbon concentration of the sample collected on March 13th was not available due to a failure in the weighing procedure of the final extract that should have determined the extract volume. The higher concentrations at Fukue could be due to its proximity to the source(s) of precursor(s) of LV-WSOC: the closer to the sources, the less dilution of airborne substances. The δ^{13}C values of LV-WSOC at Fukue were consistently higher than those at Fukuoka (except for March 9). This can be explained by the additional LV-WSOC from the local source(s) having lower δ^{13}C values than the transboundary LV-WSOC. We found the same overall trend in the LV-WSOC concentrations during the study in

December 2010. The $\delta^{13}C$ trend was similar, but there were some exceptions; e.g., the

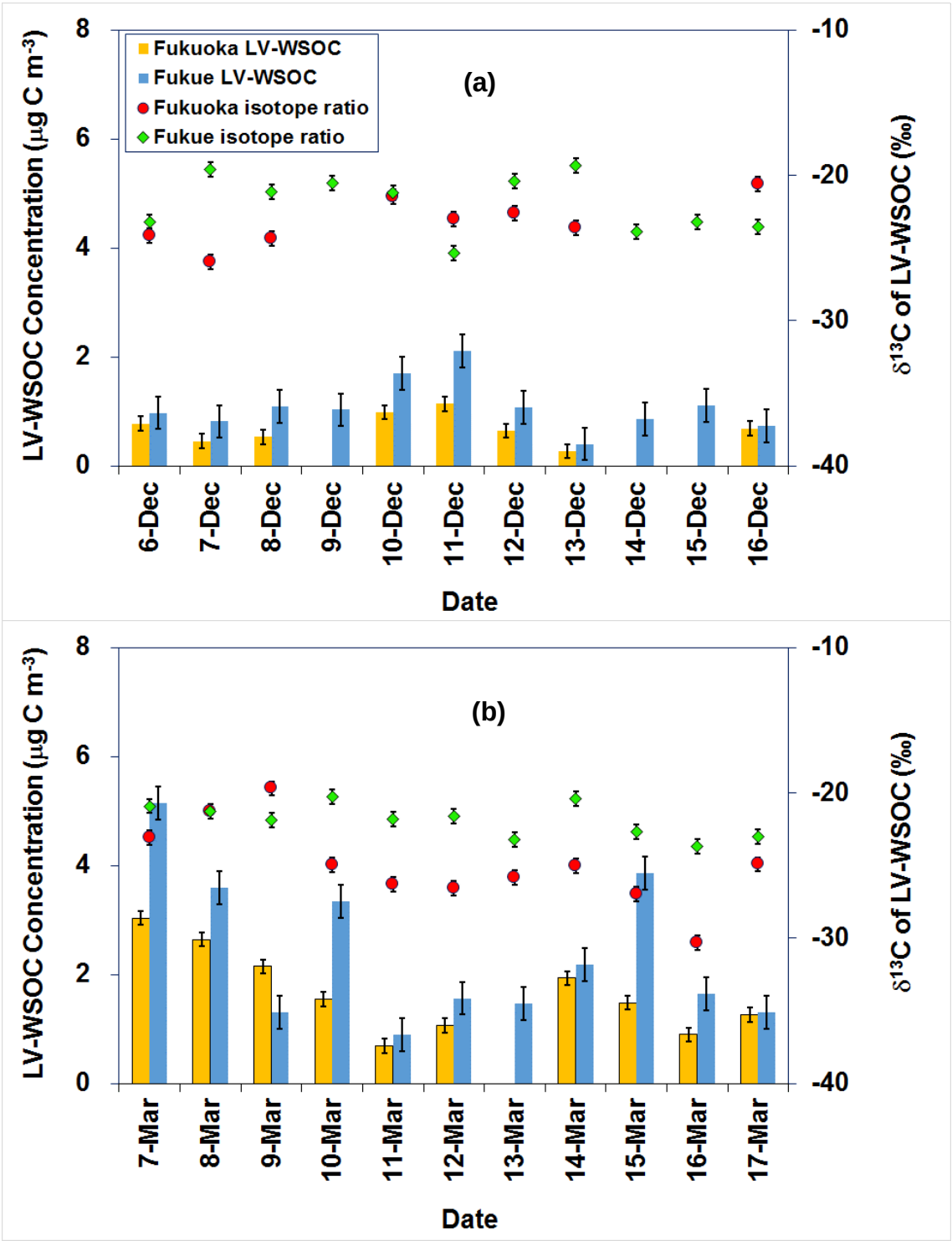

Figure 2. Time series plot of the concentration and $\delta^{13}C$ of LV-WSOC observed at Fukuoka and Fukue during the field studies in (a) December 2010 and (b) March 2012. The data points of December 9, 14, and 15 and March 13 at Fukue and of March are not available at Fukuoka.

samples collected on December 11 and 16 had higher $\delta^{13}C$ values at Fukuoka than at Fukue. These inverted $\delta^{13}C$ values likely indicated a contribution of LV-WSOC from a different source at Fukuoka.

A time series of OA and *m/z* 44 during the two study periods at Fukue showed that their variations coincided and that the variation of f_{44} (*m/z* 44 divided by the organics) was small (Figures 3a and 3c). This implies that the composition of OA at Fukue was simple and made of carboxylate-related substance(s), an indication of aged organics. The plots at Fukuoka also showed coinciding variations, but there was a larger variation in f_{44}. This can be explained by both the carboxylic acid(s) contribution to the OA concentrations at Fukuoka, and the contribution from primary emissions of OA, with a local origin. Sharp rises and falls in the observed OA concentrations indicate a contribution from local sources. This explanation becomes more convincing as the data obtained from the two sites were analyzed more in detail: two-hour averaged concentrations of *m/z* 44 at Fukue (*x*-axis) were correlated with those at Fukuoka (*y*-axis) (Figure 4a). The linear regression obtained was $y = 0.375 \pm 0.032x + 0.224 \pm 0.031$ ($r^2 = 0.507$). Such plots of OA also showed a proportional increase, but more scattered and a larger slope (Figure 4b). The linear regression obtained was $y = 0.456 \pm 0.048x + 2.61 \pm 0.27$ ($r^2 = 0.395$). The larger slope with lower correlation for the OA is

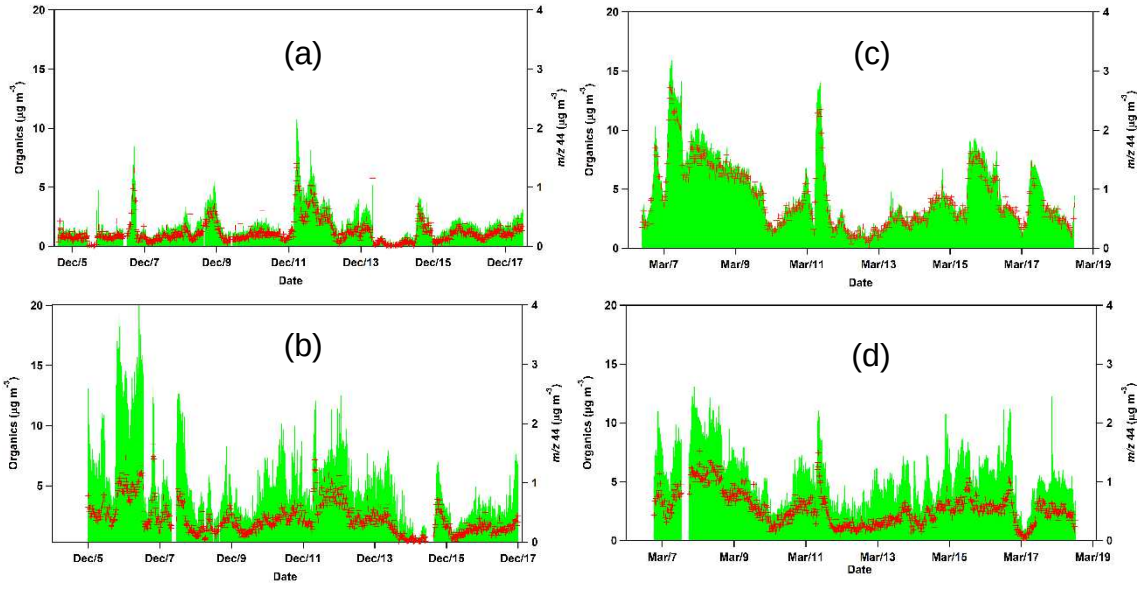

Figure 3. Time series plot of OA (green filled) and m/z 44 (red cross) concentration observed during the field studies in 2012 by AMS measurements at (a) Fukue in December 2010, (b) Fukuoka in December 2010, (c) Fukue in March 2012, and (d) Fukuoka in March 2012.

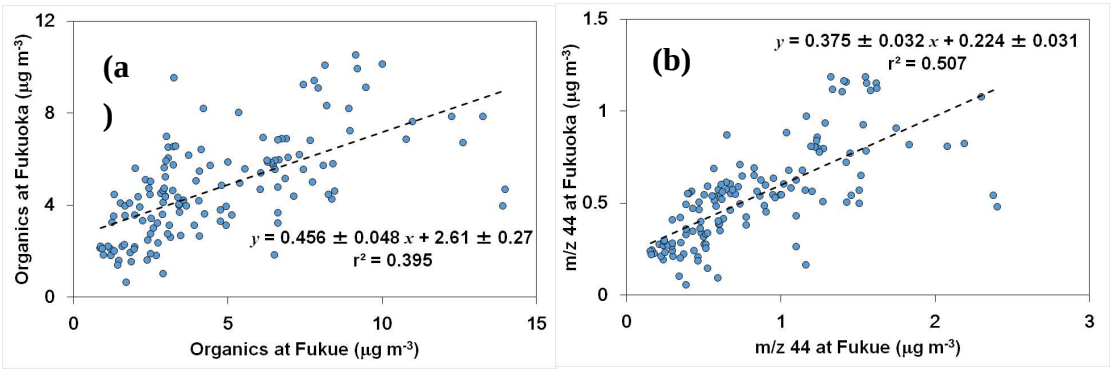

Figure 4. Scatter plot of two-hour averaged concentration of OA (a) and m/z 44 (b) at Fukuoka as function of Fukue.

probably due to the irregular contribution of OA from the local sources in Fukuoka. It should be noted different degree of the atmospheric dilution between the two sites also causes lower correlation. Nevertheless of such irregular sources, the overall trends (*i.e.*, the slopes of the linear regressions) at Fukue and Fukuoka were similar and significant, implying that transboundary OA is predominant even in Fukuoka City. Modeled back trajectories of air masses arriving at Fukue and Fukuoka during the study period of March 2012 by HYSPLIT (Draxler et al., 2013) were similar (Figure 5), suggesting the same air masses in macro scale and possibility of influence of transboundary air to the local air quality at Fukuoka. The similar pattern has been observed in the previous study in December 2010.

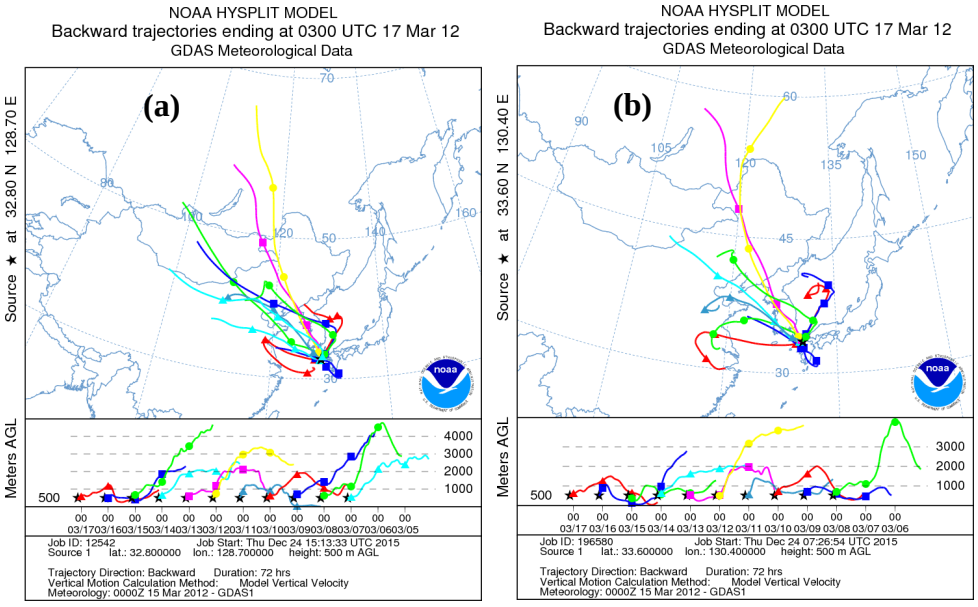

Figure 5. Three-day back trajectories of air masses arriving at Fukue (a) and Fukuoka City (b) during the study period in March 2012.

Comparison of LV-WSOC with OA

If LV-WSOC predominantly consisted of SOA, a high correlation between the LV-WSOC concentrations and the *m/z* 44 concentrations would be observed. As with the results reported for December, 2010 (Irei et al., 2014), the LV-WSOC concentrations determined by the filter sample analysis and the *m/z* 44 or OA concentrations determined by the AMS measurements were strongly correlated at both Fukue (r^2 = 0.91 and 0.94, respectively) and Fukuoka (0.75 and 0.60, respectively) (Figures 6a and 6b). The m/z 44/LV-WSOC and OA/LV-WSOC ratios were 0.28 and 1.7 μg μgC^{-1} at Fukue, respectively, and 0.30 and 2.0 μg μgC^{-1} at Fukuoka, respectively. We compared the OA/LV-WSOC ratios with the organic mass (OM) to organic carbon (OC) ratios of OA in (see the following sub-section) to evaluate the differences in LV-WSOC between TSP and $PM_{1.0}$.

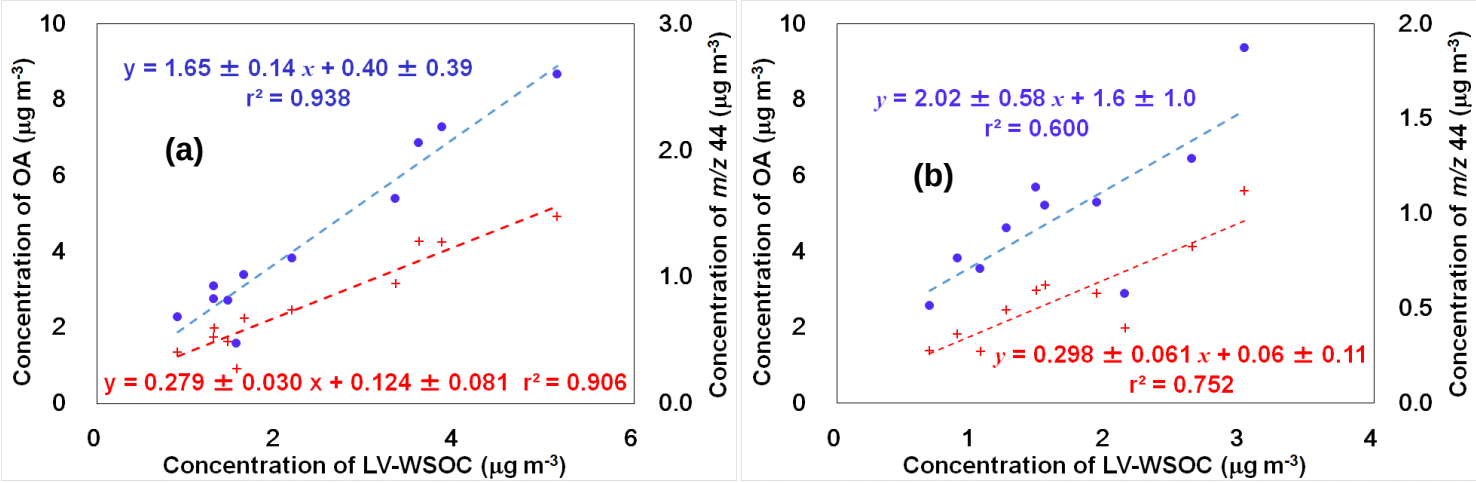

Figure 6. Plot of LV-WSOC concentration from the filter sample analysis versus the OA concentration (blue) and m/z 44 concentration (red) measured by AMS at (a) Fukue and (b) Fukuoka, March 2012.

We observed previously that the $\delta^{13}C$ values of LV-WSOC had a proportional relationship with the photochemical age of NO_x, but that a similar relationship with the f_{44} of OA was case-dependent (Irei et al., 2014; Irei et al., 2015). We hypothesized that f_{44} could be an oxidation indicator if LV-OOA with a high f_{44} (*i.e.*, an SOA origin) is mixed with a constant amount of hydrocarbon-like organic aerosol (HOA) with a low f_{44}. If this hypothesis were correct, the f_{44} values of OA during the field study at Fukuoka in March 2012 could be used as an oxidation indicator because, as discussed in the next section about the PMF analysis, the OA during this study was a mixture of low-volatility oxygenated organic aerosol (LV-OOA) and HOA. Indeed, plots of the

$\delta^{13}C$ values of LV-WSOC versus the f_{44} of OA (Figure 7) indicated a positive correlation (r^2 = 0.646). The linear regression obtained was $\delta^{13}C$ = (138 ± 34)‰ × f_{44} – (40.1 ± 3.8)‰. Compared to the linear regression observed during an earlier field study at Cape Hedo, Okinawa (Irei et al., 2014), the slope was more than five times steeper. The slope depends on kinetic isotope effects (KIEs) during the loss and production of particulate carboxylic acids. The steeper slope may imply the production of SOA via different processes. Given that the f_{44} of OA is ~0.08 or lower at emission, the $\delta^{13}C$ derived from the linear regression at the f_{44} of 0.08 (-29.0‰), is expected to represent the upper limit of the $\delta^{13}C$ for the background LV-WSOC or for the SOA at a very early stage of oxidation processing.

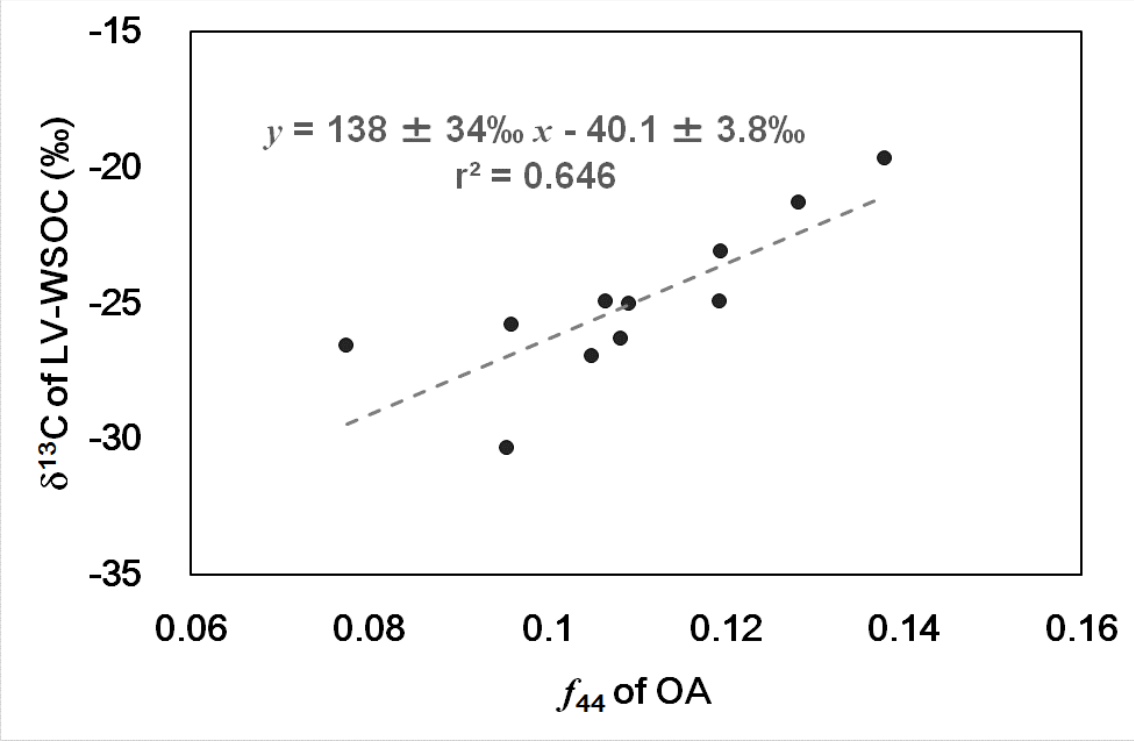

Figure 7. Plot of $\delta^{13}C$ of LV-WSOC from the filter sample analysis versus f_{44} of organic aerosol measured by AMS at Fukuoka, March 2012.

PMF analysis of OA mass spectra

We performed PMF analysis on the organic aerosol mass spectra using a PMF evaluation tool (Ulbrich et al., 2009). The results of the PMF analysis during the field studies in December 2010 at Fukue and Fukuoka, in March 2012 at Fukue, and in December 2010 to May 2011 at Fukue are discussed in detail elsewhere (Irei et al., 2014; Irei et al., 2015; Irei et al., submitted). Briefly, with respect to spectral patterns, a two-factorial analysis gave the most feasible results for the dataset of December 2014 at

Fukue and Fukuoka, and these loadings were often identified as LV-OOA and HOA (Figures 8a and 8b). For a longer time period of study in this season (from December 2010 to May 2011), the PMF analysis resulted in a feasible solution with the two-factorial analysis, comprising HOA and LV-OOA loadings. For the study in March 2012 at Fukue, one-factorial analysis resulted in the most reasonable solution, with the extracted loading identified as LV-OOA (Figure 8c).

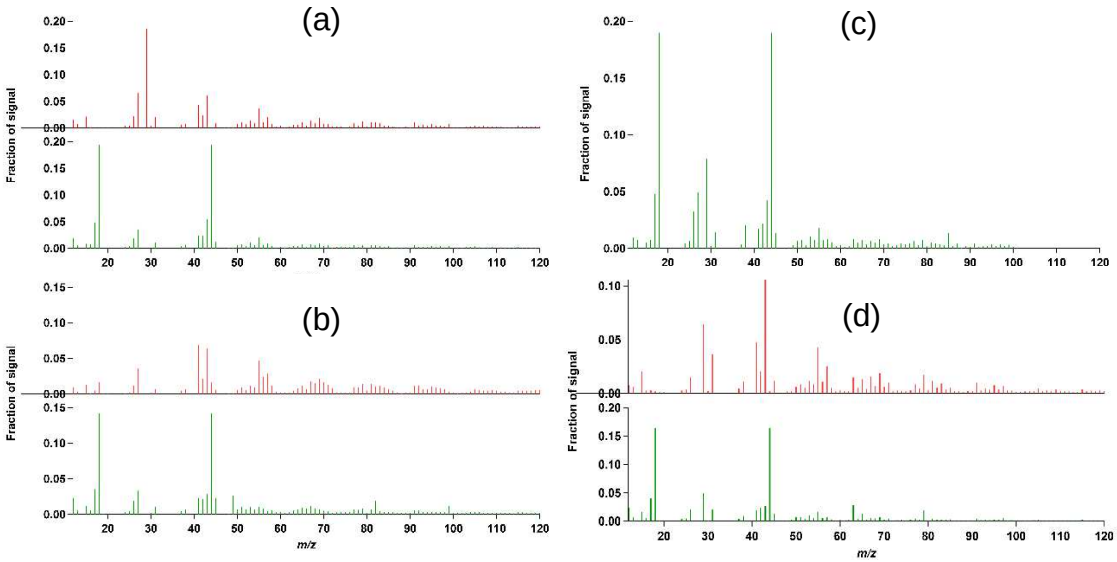

Figure 8. Loading (m/z 12 to m/z 120) yielded from PMF analysis on organic mass spectra for (a) the two factorial solution of Fukue December 2010, (b) two factorial solution of Fukuoka December 2010, (c) one factorial solution of Fukue March 2012, and (d) two factorial solution of Fukuoka March 2012. The extracted loadings shown are LV-OOA (green) and HOA (red).

PMF analysis of the organic mass spectra observed during the field study in March 2012 at Fukuoka showed that a two-factorial analysis gave the most reasonable results: loadings corresponding to LV-OOA and HOA (Figure 8d), with average fractions of 72% and 28%, respectively. In this PMF analysis, the signal at *m/z* 27 was excluded due to the large amount of noise caused by N_2 at the edge of the slightly wider peak width at *m/z* 28. A comparison of the extracted loadings at Fukuoka with the loading at Fukue referred to in the earlier March 2012 studies revealed that the LV-OOA at Fukuoka coincided with the LV-OOA at Fukue. The HOA at Fukuoka was then explained by OA of local origin.

According to the method used by Zhang et al. (2005), we calculated the

OM/OC ratios for the deconvoluted loadings produced by the PMF. The OM/OC ratios for LV-OOA and HOA during the study in March 2012 at Fukuoka were 4.7 and 2.9 μg μgC^{-1}, respectively. According to these OM/OC ratios and the previously determined fractions of LV-OOA and HOA, we calculated the overall OM/OC ratio for the OA (i.e., the mixture of LV-OOA and HOA) to be 4.2 μg μgC^{-1}. The OM/OC ratios for LV-OOA and HOA observed at Fukue and Fukuoka during the different field studies are listed in Table 1.

We compared the overall OM/OC ratio at Fukuoka with the linear regression slope for the plots in Figure 6 and the OA/LV-WSOC ratio of 2.0 μg μgC^{-1}. The comparison provides information regarding the difference between the LV-WSOC in TSP filter samples and the OA in $PM_{1.0}$ measured by the AMS. The OA/LV-WSOC ratio was half of the OM/OC ratio, indicating that for particle sizes larger than $PM_{1.0}$ there was more than twice as much OC as was measured by the AMS.

Table 1. OM/OC ratio calculated for PMF loadings

Field studies	LV-OOA	HOA
December 2010, Fukue[b]	3.6	1.2
December 2010, Fukuoka[b]	3.5	1.2
December 2010, Hedo[b]	3.8	n.a.[a]
March 2012, Fukue[c]	4.3	n.a.[a]
March 2012, Fukuoka	4.7	2.9
December 2010 through May 2011, Fukue[d]	5.0	2.8

[a] Not available because the PMF analysis ended with only the LV-OOA loading.
[b]Adopted from Irei et al. (2014). [c]Adopted from Irei et al. (2015). [d]Adopted from Irei et al. (submitted).

EMMA for the evaluation of the mixing state of LV-WSOC

We applied the EMMA presented in the theory section to the $\delta^{13}C$ values observed at Fukue and Fukuoka to evaluate the w_{Local} in the LV-WSOC mixture collected from Fukuoka. In this calculation, the parameter $\delta^{13}C_{Local}$ had to be derived first; therefore, we tested a $\delta^{13}C_{Local}$ value between -34‰ and -27‰ to determine if the calculation gave a reasonable w_{Local}, i.e., between 0 and 1. The results showed that, except for December 11 and 16 in 2010 and March 9 and 16 in 2012, the w_{Local} values varied in a feasible range when the $\delta^{13}C_{Local}$ vale was lower than -28‰ (Figure 9). This

range was consistent with the $\delta^{13}C_{Local}$ of -29‰ indicated by the intercept of the linear regression of the plot of $\delta^{13}C$ against f_{44} shown in Figure 7. It is likely that the $\delta^{13}C$ of organic carbon from the vehicular emissions is between -27‰ and -26‰ (Kawashima and Haneishi, 2012), and therefore this does not indicate a possible local source of LV-WSOC. Compared to the literature $\delta^{13}C$ values, the possible source may be biomass

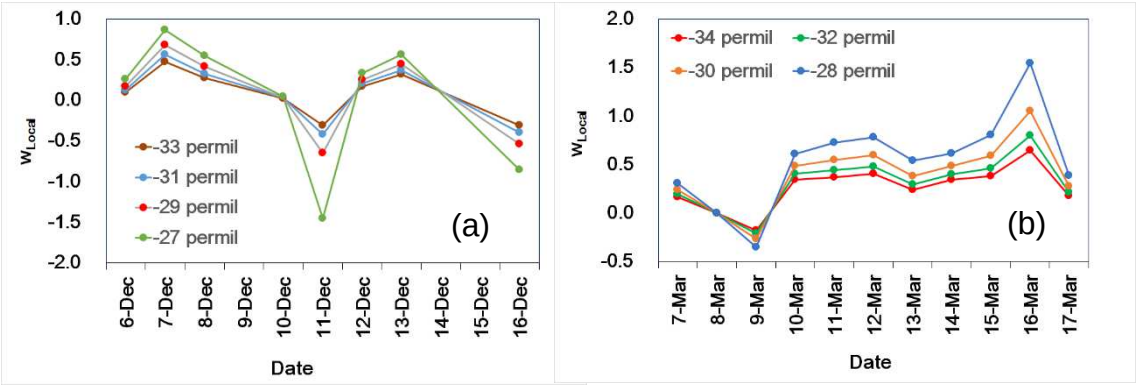

Figure 9. Calculated fraction of LV-WSOC from the local origin (w_{Local}) using different $\delta^{13}C_{Local}$ values during the field study in (a) December 2010 and (b) March 2012. The $\delta^{13}C_{Local}$ values used are shown in the legend.

burning, but this is highly speculative. Under the assumption that the observed LV-WSOC concentrations are a binary mixture of LV-WSOC, with transboundary and local source origins, and the $\delta^{13}C_{Local}$ of LV-WSOC is -29‰ (using the previously determined $\delta^{13}C$ as f_{44} = 0.08 in Figure 7), we estimated the fractions of the transboundary and local source origins using EMMA (Figure 10). Except for the four data points referred to previously, the calculation indicated that a transboundary origin was slightly more predominant than the local origin during the study in December 2010, with almost the same magnitude for both origins during the study in March 2012. To determine if the results of the EMMA were feasible, we compared the fractions determined with the results of the PMF analysis that were discussed previously.

We used the w_{Local} values to estimate the concentrations of LV-WSOC with a transboundary origin ($LV\text{-}WSOC_{Trans}$), and the $LV\text{-}WSOC_{Trans}$ values were then compared to the LV-OOA concentrations extracted by the PMF analysis. For March 2012, the correlation between the LV-OOA determined by the PMF and the $LV\text{-}WSOC_{Trans}$ determined by the EMMA (r^2 = 0.330) was significantly lower than that between the LV-OOA and the LV-WSOC (r^2 = 0.753), indicating that the EMMA produced less consistent results. For the study in December 2010, both correlations were weak (Figure 11). Overall, the fractions determined by the EMMA were inconsistent with the results for fine OA produced by the PMF analysis. This

inconsistency likely indicates that in Fukuoka most of the LV-WSOC observed was comprised of a single component, which had a transboundary origin.

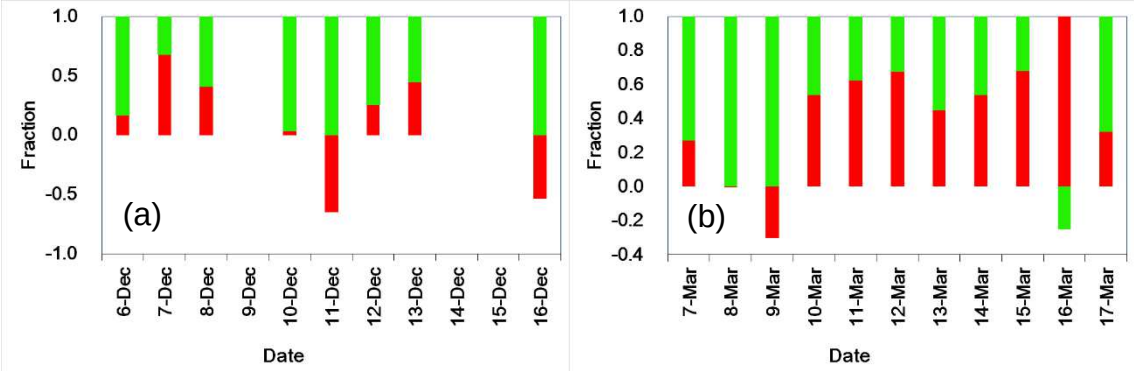

Figure 10. Calculated fractions of LV-WSOC from the transboundary (green) and the local origin (red) using two EMMA with the $\delta^{13}C_{Local}$ of -29‰during the field study in (a) December 2010 and (b) March 2012.

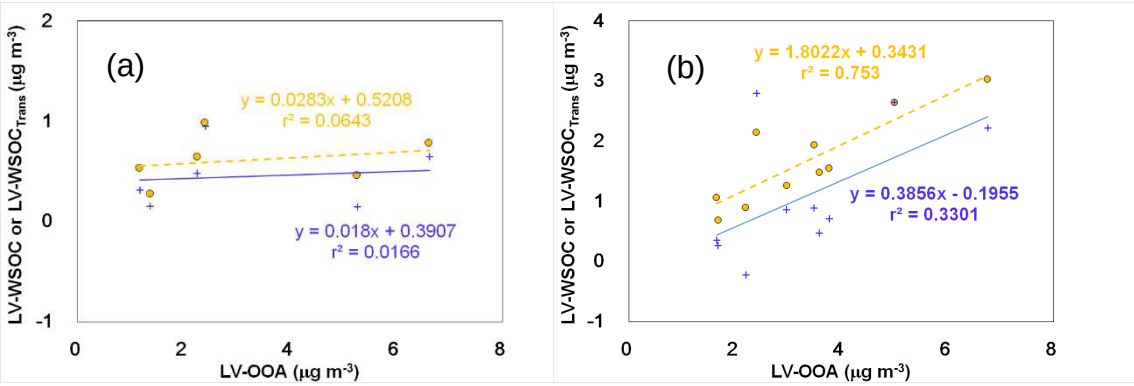

Figure 11. Plot of LV-WSOC (yellow) or LV-WSOC$_{Trans}$ (blue) concentration as function of LV-OOA concentration extracted by PMF analysis (24-average) during the field study in (a) December 2010 and (b) March 2012.

Summary

We conducted simultaneous field studies at the Fukue monitoring station and Fukuoka University during December 2010 and March 2012. During the studies, LV-WSOC from the TSP filter samples were analyzed by an off-line method and OA in fine PM was analyzed by AMS. The measurements showed that LV-WSOC concentrations at Fukuoka were lower than those at Fukue, indicating the proximity of an emission source of precursor organics in the gas-phase and/or condensed phase at Fukue. The f_{44} values of OA at Fukuoka were significantly lower than at Fukue, indicating a contribution of OA from local primary emissions at Fukuoka. The PMF

analysis of OA mass spectra revealed that the OA at Fukuoka consisted of HOA and LV-OOA. As with the plots previously observed at Cape Hedo, Okinawa, the $\delta^{13}C$ values of LV-WSOC were proportional to the f_{44}, indicating a strong association of LV-WSOC with SOA.

We estimated the daily fractions of LV-WSOC with a transboundary origin, $LV\text{-}WSOC_{Trans}$, using EMMA, and compared the quantitative results with the magnitudes of LV-OOA extracted from the PMF analysis. The $LV\text{-}WSOC_{Trans}$ values estimated by the EMMA were more inconsistent than were the LV-OOA concentrations. Because the total LV-WSOC concentrations were more strongly correlated with the LV-OOA concentrations, the results of our analysis imply that the LV-WSOC observed at Fukuoka predominantly consisted of material with a transboundary origin.

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References

Allan, J.D., Delia, A.E., Coe, H., Bower, K.N., Alfarra, M.R., Jimenez, J.L., Middlebrook, A.M., Drewnick, F., Onasch, T.B., Canagaratna, M.R., Jayne, J.T., Worsnop, D.R., 2004. A generalized method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data. *Journal of Aerosol Science*, 35, 909-922.

Anderson, T. L., Charlson, R. J., Schwartz, S. E., Knutti, R., Boucher, O., Rodhe, H., Heintzenberg, 2003. J. Atmospheric Science: Climate Forcing by Aerosols—A Hazy Picture. *Science*, *300*, 1103–1104.

Dockery, D. W., Pope, C. A., 3rd, Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris,

B. G., Jr., Speizer, F. E., 1993. An Association between Air Pollution and Mortality in Six U.S. Cities. *New England Journal of Medicine, 329,* 1753–1759.

Draxler, R.R.; Rolph, G.D., 2013. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/HYSPLIT.php), NOAA Air Resources Laboratory, College Park, MD.

Finlayson-Pitts, B.J.; Pitts, Jr., J.N. Chemistry of the upper and lower atmosphere. Academic Press, San Diego, U.S.A., **2000**.

Irei, S.; Takami, A.; Hayashi, M.; Sadanaga, Y.; Hara, K.; Kaneyasu, N.; Sato, K.; Arakaki, T.; Hatakeyama, S.; Bandow, H.; Hikida, T.; Shimono, A., 2014. Transboundary secondary organic aerosol in western Japan indicated by the $\delta^{13}C$ of water-soluble organic carbon and the *m/z* 44 signal in organic aerosol mass spectra. *Environmental Science and Technology*, 48 (11), pp 6273-6281.

Irei, S.; Takami, A.; Sadanaga, Y.; Miyoshi, T.; Arakaki, T.;, Sato, K.; Kaneyasu, H.; Bandow, H.; Hatakeyama, S., 2015. Transboundary secondary organic aerosol in western Japan: An observed limitation of the f_{44} oxidation indicator. *Atmospheric Environment*, 120, pp 71-75.

Irei, S.; Takami, A., Sadanaga, Y.; Nozoe, S.; Yonemura, S.; Bandow, H.; Yokouchi, Y., 2015. Photochemical age of air pollutants and oxidation products in transboundary air observed on Fukue Island, Nagasaki, Japan. Atmospheric Chemistry and Physics Discussion (submitted).

Jayne, J.T., Leard, D.C., Zhang, X., Davidovits, P., Smith, K.A., Kolb, C.E., Worsnop, D.R., 2000. Development of an aerosol mass spectrometer for size and composition analysis of submicron particles. *Aerosol Science and Technology*, 33, 49-70.

Kawashima, H. and Haneishi, Y., 2012. Effects of combustion emissions from the Eurasian continent in winter on seasonal d13C of elemental carbon in aerosols in Japan. *Atmospheric Environment*, 46, 568-579.

Kleinman, L.I.; Daum, P.H.; Lee, Y.-N.; Senum, G.I.; Springston, S.R.; Wnang, J.; Berkowitz, C.; Hubbe, J.; Zaveri, R.A.; Brechtel, F.J.; Jayne, J.; Onasch, T.B.; Worsnop, D., 2007. Aircraft observations of aerosol composition and ageing in New England and Mid-Atlantic States during the summer 2002 New England Air Quality Study field campaign. *Journal of Geophysical Research [Atmosphere]*, 112, D09310, doi: 10.1029/2006JD007786.

Ng, N.L.; Canagaratna, M.R.; Zhang, Q.; Jimenez, J.L.; Tian, J.; Ulbrich, I.M.; Kroll, J.H.; Docherty, K.S.; Chhabra, P.S.; Bahreini, R.; Murphy, S.M.; Seinfeld, J.H.; Hildebrandt, L.; Donahue, N.M.; DeCarlo, P.F.; Lanz, V.A.; Prevot, A.S.H.; Dinar, E.; Rudich, Y.; Worsnop, D.R., 2010. Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry. *Atmospheric Chemistry and Phys*ics, 10, 4625-4641.

Phillips, D.L.; Newsome, S.D.; Gregg. J.W., 2005. Combining sources in stable isotope mixing models: alternative method. *Oecologia*, 144, 520-527.

Takami, A.; Miyoshi, T.; Shimono, A.; Hatakeyama, S., 2005. Chemical composition of fine aerosol measured by AMS at Fukue Island, Japan during APEX period. *Atmospheric Environment*, 39, 4913-4924.

Takami, A.; Miyoshi, T.; Shimono, A.; Kaneyasu, N.; Kato, S.; Kajii, Y.; Hatakeyama, S., 2007. Transport of anthropogenic aerosols from Asia and subsequent chemical transformation. *Journal of Geophysical Research [Atmosphere]*, 112, doi 10.1029/2006JD0081

Takami, A.; Miyoshi, T.; Irei, S.; Yoshino, A.; Sato, K.; Shimizu, A.; Hayashi, M.; Hara, K.; Kaneyasu, N.; Hatakeyama, S. 2016. Analysis of organic aerosol in Fukuoka, Japan using a PMF method. Aerosol and Air Quality Research (in press).

Takegawa, N.; Kondo, Y.; Koike, M.; Chen, G.; Machida, T.; Watai, T.; Blake, D.R.; Streets, D.G.; Woo, J.-H.; Carmichael, G.R.; Kita, K.; Miyazaki, Y.; Shirai, T.; Liley, J.B.; Ogawa, T., 2004. Removal of NOx and NOy in Asian outflow plumes: Aircraft measurements over the western Pacific in January 2002. *Journal of Geophysical Research [Atmosphere]*, 109, D23S04, doi: 10.1029/2004JD004866.

Ulbrich, I.M.; Canagaratna, M.R.; Zhang, Q.; Worsnop, D.R.; Jimenez, J.L., 2009. Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, *Atmospheric Chemistry and Physics*, 9, 2891-2918.

Yevenes, M.A.; Mannaerts, C.M., 2012. Untangling hydrological pathways and nitrate sources by chemical appraisal in a stream network of a reservoir catchment. *Hydrology and Earth System Sciences*, 16, 787-799.

Zhang, Q.; Worsnop, D.R.; Canagaratna, M.R.; Jimenez, J.L., 2005. Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: insights into sources and processes of organic aerosols. *Atmospheric Chemistry and Physics*, 5, 3289-3311.