Characterization and Source Apportionment Studies of PM$_{2.5}$ Using Organic Marker -based Positive Matrix Factorization

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Abstract

In this study, organic marker compounds in fine particulate matter （PM$_{2.5}$） were observed during four seasons at forested （Akagi）, suburban （Maebashi） and urban （Saitama） sites in the Kanto region of Japan, and the source contributions of PM$_{2.5}$ were evaluated. Organic compounds were analyzed using an extraction-derivatization GC/MS method. PM$_{2.5}$ samples were also analyzed for ion components, organic carbon, elemental carbon and metallic elements. At both urban and suburban sites, the concentrations of levoglucosan （a biomass burning marker） increased in winter and fall, whereas dicarboxylic acids （photo-oxidation products） increased during warm seasons. At the forested site, the concentration of 2-methyltetrols （a biogenic secondary organic aerosol （BSOA） marker from isoprene） tended to increase during warm seasons, especially in summer. The levels of organic markers for cooking and vehicle emissions were higher at the urban site than the other sites. As a result of positive matrix factorization analysis using a PM$_{2.5}$ component data set, it was possible to apportion 80-90％ of PM$_{2.5}$ mass concentration to 12 sources, including sources of organic particles such as biogenic primary/secondary origin, biomass burning and cooking. The contribution ratios of these sources involved in organic aerosols in PM$_{2.5}$ were estimated to be 41％ at the urban, 39％ at the suburban, and 46％ at the forested site. These results will provide basic data for planning of future PM$_{2.5}$ reduction measures in Japan.

Key words: biogenic source, biomass burning, levoglucosan, organic carbon, secondary organic aerosol, source contribution

1. Introduction

In Japan, air quality standards for fine particulate matter （PM$_{2.5}$） （35 μg/m^3 for 24-hour mean and 15 μg/m^3 for annual mean） were introduced in 2009 to reduce the adverse effects on human health. Following that, monitoring of PM$_{2.5}$ concentrations has been conducted by local governments. The results of nationwide PM$_{2.5}$ monitoring show the air quality standard achievement ratio to be not so high. Therefore, measures to reduce PM$_{2.5}$ concentration are required. There is also concern about transboundary PM$_{2.5}$ air pollution from East Asia to Japan. To create policies to achieve air quality standards, it is necessary to know the major sources and formation mechanisms of PM$_{2.5}$.

PM$_{2.5}$ can be classified into primary particles directly emitted from the sources as particulate matter and secondary particles which are formed from gaseous substances by photochemical reactions. In Japan, regulations on vehicle exhaust emissions have been gradually tightened, whereby PM concentration has declined moderately over the last two decades （Iijima & Kumagai, 2012）. On the other hand, the proportion of secondary particles has become relatively large. To ameliorate PM$_{2.5}$ pollution, deepening our understanding of the dynamics of the secondary particles and source contributions will be indispensable.

Although organic aerosols （OA） are the most important constituents of PM$_{2.5}$ in Japan, the chemical properties, environmental behavior and the contribution of potential sources have not been sufficiently elucidated due to chemical complexity. OA is not only directly emitted from potential sources but also formed by photochemical reactions of volatile organic compounds in the atmosphere （Turpin *et al*., 2000）. OA is classified into primary organic aerosols （POA） and secondary organic aerosols （SOA）, and further classified into anthropogenic OA （APOA, ASOA） and biogenic OA

（BPOA, BSOA） from the viewpoint of its origin. It is important to clarify the source contributions of organic particles in PM$_{2.5}$. Recently, organic tracer-based source apportionment methods have been employed to determine the contributions of specific primary organic sources to ambient OA concentrations （Schauer *et al*., 1996; Kleindienst *et al*., 2007; Fabbri *et al*., 2009）. For example, levoglucosan, which is formed by combustion of cellulose （Simoneit, 2002）, is well known as a biomass burning tracer （Simoneit, *et al*., 1999; Kleeman *et al*., 2008; Fabbri *et al*., 2009）. Dicarboxylic acids are related to photo-oxidation products of organic precursors of both anthropogenic and biogenic origin （Kawamura *et al*., 1996; Kerminen *et al*., 2000）. Sugars, such as glucose and arabitol, are derived from pollen and fungal spores, so they are treated as biogenic primary compounds （Schauer *et al*., 2002; Graham *et al*., 2003; Medeiros *et al*., 2006; Bauer *et al*., 2008）. 2-methytetols are formed from the oxidation of isoprene （Claeys, 2004）, and pinonic acid is formed from the oxidation of α-pinene （Kleindienst *et al*., 2007; Fu *et al*., 2010）. The ambient behavior of organic marker compounds will help elucidate the sources and formation of OA. In Japan, many studies and monitoring surveys on PM$_{2.5}$ components have been done, but knowledge about organic compounds in PM$_{2.5}$ remains deficient.

In this study, we focused on the characteristics of source-specific molecular markers of organic aerosols with other components in PM$_{2.5}$. Multicomponent analysis of each organic marker of various sources, such as biomass burning, photo-oxidation products, BSOA, BPOA, cooking and vehicles, was developed using an extraction-derivatization GC/MS （gas chromatography– mass spectrometry） method. Then PM$_{2.5}$ source apportionment was carried out using positive matrix factorization. One more purpose of this study was to provide an organic marker measurement method and source apportionment method for policy making in Japan that can be applied to monitoring methods in Japan.

2. Methods

2.1 Observation Sites

We conducted PM$_{2.5}$ observations at the three different locations, forested, suburban and urban, in the Kanto region of Japan （Fig. 1）. The suburban site, Maebashi （36.4054° N, 139.0945° E）, was selected in a suburban city situated inland on the Kanto Plain, about 100 km northwest of central Tokyo. The sampling site was surrounded by residential areas and agricultural fields. The forested site, Akagi （36.5380° N, 139.1818° E） was selected in a mountainous area north of the Kanto Plain. The sampling site was surrounded by deciduous trees and had snow cover in winter. There were no anthropogenic sources around the Akagi sampling site. The straight-line distance between Akagi and Maebashi was approximately 16 km. The urban site, Saitama （35.8642° N, 139.6079° E）, was selected in the Tokyo metropolitan area on the Kanto Plain, characterized by a
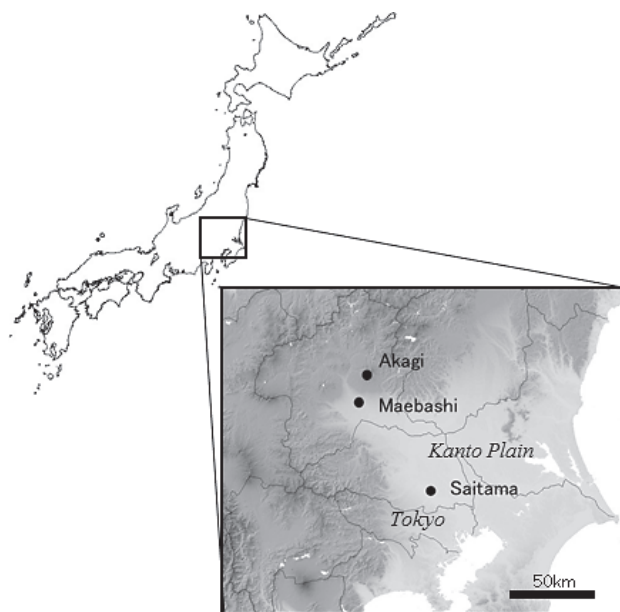

Fig. 1 Locations of the observation sites: Akagi （forested site）, Maebashi （suburban site）, and Saitama （urban site）. The shading of the enlarged map represents the topographic image.

large population and heavy traffic. Its location was about 30 km northwest of central Tokyo.

Regarding the atmospheric environment, the Kanto Plain, where these sampling sites were located, has characteristic meteorological conditions. On this plain, a sea breeze produces a southerly wind during the daytime during the warm seasons. This wind can bring polluted air from the Tokyo metropolitan area. Contrastively, a strong, dry northwest wind frequently blows down from the mountainous area during the cold seasons.

2.2 Sampling and Analytical Methods

PM$_{2.5}$ sampling was conducted during four seasons; winter （from December 3 to 18, 2014）, spring （from May 26 to June 8, 2015）, summer （from August 7 to 21, 2015）, and fall （from October 5 to 19, 2015）. Samples were collected on quartz fiber filters （ϕ 47 mm, 2500 QAT-UP, Pallflex, USA） and PTFE （Polytetrafluoroethylene） membrane filters （ϕ 47 mm, R2-PJ047, Pallflex, USA） with low-volume air samplers （FRM2025, Thermo Fisher Scientific Inc., USA, 16.7 L/min, or MCAS-SJ, Murata Keisokuki Service Co., Ltd., Japan, 30.0 L/min）, respectively. Although high-volume air samplers are often used in field studies targeting organic particulate matter （Alves *et al*., 2010; Offenberg *et al*., 2011; Wang *et al*., 2011）, we used low-volume samplers because they are commonly used in PM$_{2.5}$ monitoring surveys in Japan. The sampling period was 24 hours, starting at 10 a.m. Japan Standard Time （JST）. The quartz filters were pre-cleaned to remove carbonaceous components present originally in the filters by baking for one hour at 350℃. We obtained particulate mass with the PTFE filters by the gravity method under conditions of constant temperature and humidity （21 ± 1.5℃ and 35 ± 5% RH）.

The PM$_{2.5}$ filter samples collected at the three sites were analyzed for organic marker compounds, ion components, carbonaceous components, and metallic elements. The detailed components are summarized in Table 1. Ion components, oxalic acid (C$_2$) and water soluble organic carbon (WSOC) on the PTFE filters were ultrasonically extracted with ultrapure water, and subsequently their solutions were filtered through hydrophilic syringe filters. The ion components and WSOC were measured with an ion chromatograph (Dionex ICS1100, Thermo Fisher Scientific Inc., USA) and a total carbon analyzer (TOC-V, Shimadzu, Japan), respectively. Organic carbon (OC) and elemental carbon (EC) on the quartz filters were determined using a thermal/optical carbon analyzer (DRI Model 2001, Atmoslytic Inc., USA) by following the IMPROVE protocol (Chow $et~al.$, 2001). Metallic elements on the PTFE filters were determined by acid digestion ICP-MS. The sample preparation procedure is described in detail elsewhere (Iijima $et~al.$, 2009). Metallic elements (e.g., Al, V, Zn, Fe, Cu) were determined by ICP-MS (7500cx, Agilent Technologies Inc., Japan). Blank filters were analyzed for all components, and blank values were subtracted for some detected components.

Organic marker compounds were determined by a derivatization GC/MS method (Kumagai $et~al.$, 2010). This method is widely used for measurement of levoglucosan, and can also be used for measuring other polar organic compounds (e. g., Fabbri $et~al.$, 2009, Fu & Kawamura, 2011). We carried out preliminary observations of PM$_{2.5}$ at Maebashi and Akagi by using high-volume air samplers and determined the operational conditions for multicomponent analysis. The organic compounds we targeted were as follows: levoglucosan, mannosan and β-sitosterol as biomass burning tracers; dicarboxylic acids (e. g., malonic acid, C$_3$; succinic, C$_4$; malic, hC$_4$, azelaic, C$_9$) as photo-oxidation products; pinonic acid as a BSOA marker of α-pinene; 2-methyltetrols (2-methylthreitol and 2-methylerythritol) as BSOA markers of isoprene; arabitol and glucose as BPOA markers; oleic acid, linoleic acid and cholesterol as cooking markers; and hopanes (17α(H)21β(H)-30-norhopane, HP29, and 17α(H)21β(H)-hopane, HP30) as vehicle markers. One half of each quartz filter was extracted with a dichloromethane and methanol mixture (2:1, v/v) by ultrasonic agitation for 15 minutes. Each sample was spiked with internal standards (d_7-levoglucosan and cis-ketopinic acid). The extracts were filtered and dried in a nitrogen stream and then derivatized with 50 μL of N, O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) containing 10% trimethylchlorosilane. The samples were heated to 70°C for two hours for the derivatization reaction. Organic compounds were analyzed using a GC/MS instrument (7890GC/5975MSD, Agilent Technologies, USA). The instrument was equipped with a fused silica capillary column (DB5MS, 60 m × 0.25 mm-i.d. × 0.25 μm film thickness, Agilent Technologies, USA). For further details on the GC/MS analysis conditions, see Kumagai $et~al.$ (2017).

2.3 PMF Modeling

Source apportionment was conducted using a positive matrix factorization (PMF) model (EPA PMF 5.0). In this model, a speciated data set can be viewed as a data matrix X of i by j dimensions, in which i number of samples ($i = 1, \cdots, m$) and j chemical species ($j = 1, \cdots, n$) have been measured, with uncertainty u (US EPA, 2014). The goal of PMF is to solve the mass balance between measured species concentrations and source profiles, as shown in Equation (1), with number of factors p ($1, \cdots, k$), the species profile f of each source, and the amount of mass g contributed by each factor to each individual sample:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad \cdots (1)$$

where x_{ij} is the concentration of species j in sample i and e_{ij} is the residual of each sample/species. Factor contributions and profiles are derived by the PMF model minimizing the objective function Q as defined in Equation (2):

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{e_{ij}}{u_{ij}} \right)^2 \qquad \cdots (2)$$

where u_{ij} is the uncertainty of each sample/species. If the model is appropriate, then $(e_{ij}/u_{ij})^2$ approximates 1 and the expected Q (Q$_{exp}$) will correspond to the degree of freedom ($mn - p(m + n)$) of the fitted dataset.

Our dataset for PMF modeling consisted of 167 samples with 38 selected species: PM$_{2.5}$ mass concentration, seven ions, OC, EC, 10 elements, and 18 organic markers, as shown Table 1. Uncertainties of the

Table 1 Summary of measured components in PM$_{2.5}$ and species selected for the PMF (positive matrix factorization) model.

Compounds	
Mass*	
Ions	Cl$^-$*, NO$_3^-$*, SO$_4^{2-}$*, Na$^+$*, NH$_4^+$*, K$^+$*, Mg^{2+}, Ca^{2+}*
Carbonaceous components	OC*, EC*, WSOC
Metallic Elements	Li, Be, B, Na, Mg, Al*, K, Ca, Sc, Ti, V*, Cr, Mn*, Fe*, Co, Ni, Cu*, Zn*, Ga, Ge, As*, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd*, Sn, Sb, Te, Cs, Ba*, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Ir, Pt, Au, Pb*, Tl, Bi, Th, U
Organic markers	Levoglucosan*, Mannosan, β-Sitosterol*, Dicarboxylic acids (oxalic acid, C$_2$*; malonic, C$_3$*; succinic, C$_4$*; malic, hC$_4$*; glutaric, C$_5$*; adipic, C$_6$*; pimelic, C$_7$; suberic, C$_8$; azelaic, C$_9$*; maleic acid, phthalic acid*), Pinonic acid*, 2-Methyltetrols* (2-methylthreitol and 2-methylerythritol), Arabitol*, Glucose*, Oleic acid*, Linoleic acid, Cholesterol*, Hexadecanoic acid*, 17α(H)21β(H)-30-norhopane* (HP29), 17α(H)21β(H)-hopane (HP30)

*Species selected for the PMF model.

respective data were calculated using the error estimation function (Polissar *et al.*, 1998) with obtained method detection limits and error fraction of 10%. The extra modeling uncertainty was set at 5%. The uncertainties of duplicated variables (PM$_{2.5}$ mass and OC) and HP29 with low S/N ratios were down-weighted by setting them as "weak" in the modeling. By considering the Q/Q$_{exp}$ ratio, correlation coefficient between obtained and modeled data, distribution of residuals and bootstrap error estimation, we could resolve a twelve-factor solution using PMF.

3. Results and Discussion

3.1 Chemical Characterization of PM$_{2.5}$ at the Three Sites

3.1.1 PM Mass Concentration and Major Components

The average concentrations of PM$_{2.5}$ mass obtained in the four seasons from December 2014 to October 2015 were 7.2 (minimum 0.5–maximum 21.9), 12.3 (1.9–31.9), and 12.7 (3.5–36.0) μg/m^3 at Akagi, Maebashi and Saitama, respectively. The relatively most abundant component in PM$_{2.5}$ was OC, with average concentrations of 1.3, 2.8, and 3.9 μg/m^3; then SO$_4^{2-}$, with average concentrations of 1.8, 2.1, and 2.4 μg/m^3 at Akagi, Maebashi, and Saitama, respectively. Overall, the concentrations of PM$_{2.5}$ mass and its chemical components were higher at the urban and suburban sites than at the forested site.

Figure 2 shows the temporal variations in concentrations of PM$_{2.5}$ mass and major chemical components during the observation period. In winter, at Maebashi and Saitama, the range of PM$_{2.5}$ concentrations was larger than during other seasons. High concentrations of PM$_{2.5}$ observed in winter were caused by increasing OC and NO$_3^-$ concentrations at Maebashi and Saitama, as shown in Fig. 2. EC and Cl$^-$ also tended to increase at Saitama in winter. This was considered to result from a strong influence by anthropogenic emissions. On the other hand, the PM$_{2.5}$ concentration remained low in winter at Akagi, attributed to a relatively low influence of air pollution from human activities in the area due to the prevailing north wind. In spring, mass concentrations of PM$_{2.5}$ were observed to be relatively high at all the sites, the major components being OC and SO$_4^{2-}$. High concentrations (approximately 100 ppb) of photochemical oxidants (Ox) were observed several times during our sampling period. The increase in OC and SO$_4^{2-}$ could be attributed to secondary formation through photochemical activity. In summer, photochemical activity is generally high, but the mass concentrations of PM$_{2.5}$ were relatively low during the sampling period, except for August 7, on which day high Ox concentrations were observed. The PM$_{2.5}$ concentrations may have remained low due to rain from typhoons. OC and SO$_4^{2-}$ were predominant components in PM$_{2.5}$ in summer. In fall, relatively high concentrations of PM$_{2.5}$ were observed at Maebashi, when OC was the dominant component. The proportions of SO$_4^{2-}$ and NO$_3^-$ were high, second to OC. OC was commonly
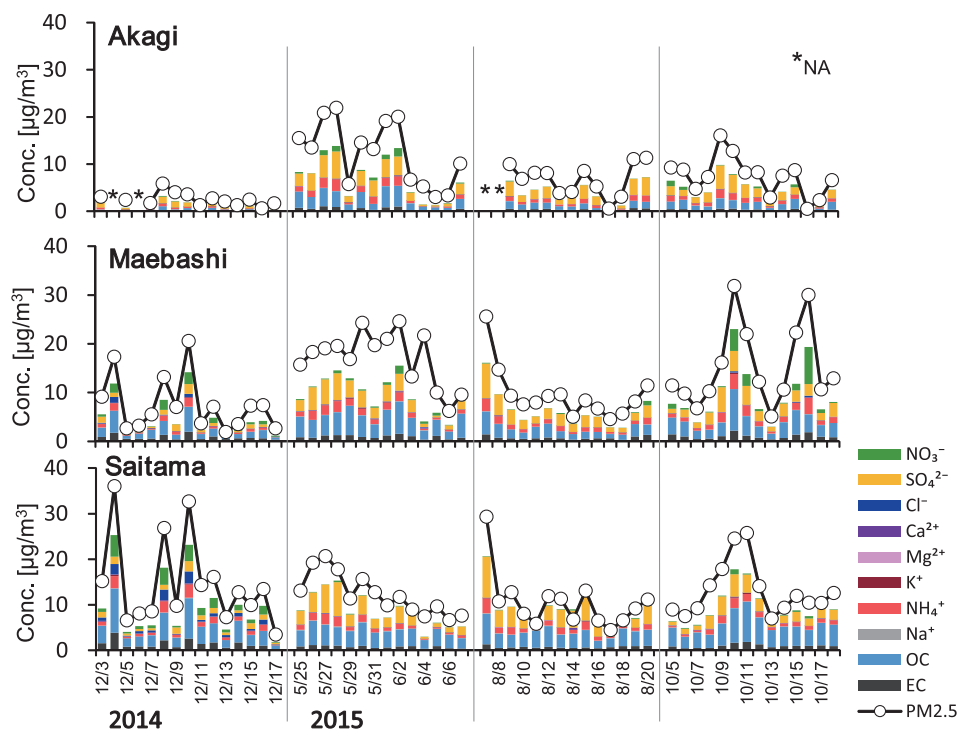

Fig. 2 Temporal variations in PM$_{2.5}$ mass, ion components, OC (organic carbon) and EC (elemental carbon) during the sampling period (winter: December 2014, spring: May–June 2015, summer: August 2015, fall: October 2015) at the three sites specified in Fig. 1.

dominant, but there was no increase in NO$_3^-$ at Saitama or Akagi. OC was the dominant component of PM$_{2.5}$ throughout the four seasons.

3.1.2 Seasonal Variation of Organic Markers in PM$_{2.5}$

Figure 3 shows seasonal average concentrations of organic marker compounds in PM$_{2.5}$ collected at the three sites. Biomass burning markers, levoglucosan and mannosan increased in concentration during the cold seasons (winter and fall) in urban and suburban areas. The average concentrations of levoglucosan were found to be 175 ng/m^3 in winter and 96 ng/m^3 in fall at Saitama, and 93 ng/m^3 in winter and 94 ng/m^3 in fall at Maebashi, respectively. The levoglucosan concentrations obtained were strongly correlated with OC concentrations at Maebashi and Saitama during these seasons ($r = 0.92$-0.99). A similar relationship between OC and levoglucosan at Maebashi also was observed in our previous study (Kumagai et al., 2010). The concentration of levoglucosan at Akagi increased slightly when the main wind direction was southerly on the Kanto Plain, but overall the concentration was lower than at the other sites. From these results, biomass combustion should be noted as an important regional source of organic particles during the cold seasons.

The most abundant dicarboxylic acid in PM$_{2.5}$ was oxalic acid, which was common at all the sites and its average concentrations in spring were the highest among all seasons: 111 ng/m^3 at Maebashi, 108 ng/m^3 at Akagi, and 82 ng/m^3 at Saitama, respectively. The highest concentrations of the other dicarboxylic acids were also observed in spring, as shown in Fig. 3. The Ox concentration level during the sampling period was higher in spring than in summer, indicating photo-oxidation activity was higher during the spring period. Concentrations of low-molecular diacids such as C$_3$-, C$_4$-, and hC$_4$- diacid were found to be significantly high at Akagi, followed by Maebashi. Low-molecular-weight diacids are most likely to be generated by photochemical reactions (Kawamura & Ikushima, 1993). These results show that SOA formation increases during the warm seasons (spring and summer). At Saitama, C$_9$ diacid was found at a relatively higher abundance than the other diacids. C$_9$ diacid is an oxidation product of unsaturated fatty acids (Kawamura & Ikushima, 1993). Long-chain diacids can be oxidized to short-chain diacids by photochemical reactions (Kawamura & Yasui, 2005). Therefore the differences in compositions of dicarboxylic acids observed at each site were thought to indicate differences in aging of organic aerosols. In the Kanto area, as the southerly wind blew dominantly in the daytime during the warm seasons, as previously mentioned, the air mass was transported from the metropolitan area as photochemical reactions occurred. The organic aerosols inland in the Kanto region (the suburban and forested sites in this study) are considered to have undergone advanced aging compared to those within the metropolitan area.

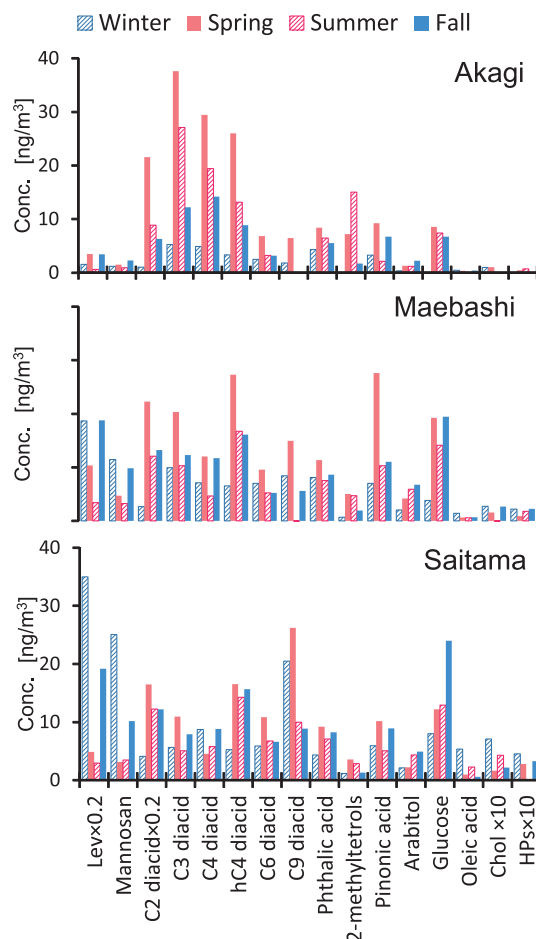2-methyltetrols, which are oxidation products of

Fig. 3 Seasonal average concentrations of organic marker compounds in PM$_{2.5}$ at the three sites specified in Fig. 1. Lev: levoglucosan, Chol: cholesterol, HPs: hopanes

isoprene, increased notably during the warm season. The average concentration of 2-methyltetrols was 15.1 ng/m^3 in summer at the forested Akagi site, which was 3–5 times higher than at Maebashi and Saitama. In this study, we conducted simultaneous measurement of VOC when the isoprene concentration level increased significantly in summer at Akagi. Our observation results suggested that the high concentration of 2-methyltetrols was related to isoprene emissions and photochemical activity. Similar seasonal trends in isoprene oxidation products were reported by Kleindienst et al. (2007). The concentration of pinonic acid, which is an oxidation product of α-pinene, was high in spring at Maebashi but was detected throughout all seasons. In contrast with isoprene, α-pinene existed at the same order of concentration during all seasons. These results suggest that isoprene BSOA increases during the warm seasons and α-pinene BSOA is present during all seasons.

Oleic acid and cholesterol, as organic markers for cooking (Schauer et al., 1999), and hopans, as specific markers for vehicular emissions (Schauer et al., 2002), were detected at relatively higher concentrations at Saitama than at Maebashi, and increased in winter. The influence of anthropogenic emissions is thought to have arisen strongly under the stable meteorological

Table 2   Assignment of decomposed factors by the PMF model to their respective sources.

Factor	Source	Indicated components	Comparison between sites[1]	Seasonal characteristics[2]
F1	BPOA	Arabitol, Glucose	MA＞＞ST＞AK	Sp, Sm, Fl
F2	BSOA from monoterpene	Pinonic acid, C_5-C_6 diacids	MA＞AK≒ST	Wn, Sp
F3	BSOA from isoprene	2-methyltetrols, C_3-C_4 diacids	AK＞＞MA＞ST	Sp, Sm
F4	Cooking	Cl^-, Linoleic acid, Oleic acid, β-sitosterol	ST＞＞MA≒AK	Wn
F5	Urban site organic aerosol	C_{16} acid, C_9 diacid, Na^+	ST＞＞MA≒AK	Sp, Sm
F6	Biomass burning	K^+, Levoglucosan	MA＞ST＞＞AK	Fl, Wn
F7	Vehicular and road dust	Ca^{2+}, EC, Mn, Cu, Zn, Ba, Hopane	ST＞MA＞AK	All seasons
F8	Nitrate	NO_3^-, NH_4^+	MA＞ST＞AK	Wn, Fl
F9	Sulfate from fuel combustion	V, C_2 diacid, SO_4^{2-}	ST≒MA＞AK	Sp, Sm
F10	Sulfate from coal combustion	NH_4^+, SO_4^{2-}, As	MA≒ST＞AK	Sm, Fl
F11	Transboundary pollution	As, Cd, Pb	MA≒AK≒ST	Sp, Fl
F12	Soil	Ca^{2+}, Al, Fe	MA＞＞AK≒ST	Sp

1） Predominant sites in order of contribution. MA: Maebashi, AK: Akagi, ST: Saitama.
2） Predominant seasons with higher contributions. Wn: winter, Sp: spring, Sm: summer, Fl: fall

conditions of winter. In many samples collected at Akagi, these compounds were below the detection limit.

As described above, the concentration levels of various organic markers had different characteristics according to the season and surrounding environment at each site.

3.2 Source Apportionment by PMF

Each of the 12 factors has a distinctive grouping of species that can be associated with a specific source sector（F1: BPOA, F2: BSOA from monoterpene, F3: BSOA from isoprene, F4: cooking, F5: urban site organic aerosol, F6: biomass burning, F7: vehicular and road dust, F8: nitrate, F9: sulfate from fuel combustion, F10: sulfate from coal combustion, F11: transboundary pollution, and F12: soil）. These are summarized in Table 2. Conventional studies on $PM_{2.5}$ source contribution by PMF analysis based on datasets with ion components, carbon components and metallic elements showed six to seven factors, typically including nitrate, sulfate, transboundary pollution, vehicle exhaust, oil burning, soil, road dust, etc.（Iijima & Kumagai, 2012; Belis *et al*., 2013; Toyonaga *et al*., 2017）. In many cases, it was difficult to identify certain sources that were supposed to be present as origins of organic particles. By using organic markers for receptor modeling, six factors; F1-F6 related to OA could be determined in this study.

Source contributions of $PM_{2.5}$ at Akagi, Maebashi and Saitama are shown in Fig. 4. OC concentrations were converted to organic matter concentrations by multiplying them with a coefficient of 2.1 at Akagi and Maebashi, and 1.6 at Saitama（Turpin & Lim, 2001）.

Although the $PM_{2.5}$ mass concentrations were approximately comparable at Maebashi and Saitama, the source contributions were found to be significantly different for each site, as shown in Fig. 4. At Akagi, at the forested site, the most abundant factor was F3（BSOA from isoprene, 27%）, followed by F10（15%）. At Maebashi, the suburban site, the most abundant factor
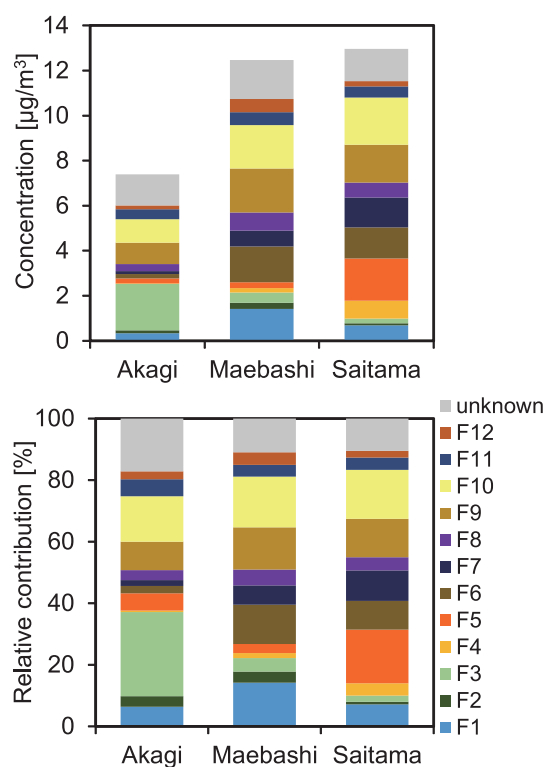

Fig. 4   Average factor contributions to $PM_{2.5}$ concentrations（upper）and percentages（bottom）at Akagi, Maebashi, and Saitama. F1: BPOA, F2: BSOA from monoterpene, F3: BSOA from isoprene, F4: cooking, F5: urban site organic aerosol, F6: biomass burning, F7: vehicular and road dust, F8: nitrate, F9: sulfate from fuel combustion, F10: sulfate from coal combustion, F11: transboundary pollution, F12: soil.

was F10（sulfate from coal combustion, 17%）, followed by of F1（BPOA, 14%）, F9（sulfate from fuel combustion, 14%）, and F6（biomass burning, 13%）. At Saitama, the contribution of F5（urban site organic aerosol, 17%）was dominant, followed by F10（16%）and F9（13%）.

Regarding the source contribution of OA, the following characteristics were observed when focusing on seasonal trends. Biomass burning was presumed to be the most influential source during the cold seasons at Maebashi and Saitama. The contribution of BSOA derived from isoprene was remarkably high at Akagi in spring and summer, and it was characteristic at the forested site. The contributions of urban site organic aerosols were the predominant source during the warm season at Saitama, but the specific source was unclear. More detailed seasonal characteristics of source contributions are now under consideration. Source contribution ratios of organic aerosols, which are associated with the total of F1 to F6, could be estimated to 39％ at Maebashi, 46％ at Akagi, and 41％ at Saitama. Thus, organic markers were shown to be useful for source apportionment of PM$_{2.5}$. It was concluded that countermeasures against sources of organic aerosols would be effective for reducing PM$_{2.5}$ mass concentration.

4. Conclusions

In this study, we observed organic marker compounds and other chemical components in PM$_{2.5}$ at forested（Akagi）, suburban（Maebashi）and urban（Saitama）sites in the Kanto region of Japan, and evaluated the source contribution of PM$_{2.5}$. As a result of our observation, we could clarify the seasonal and regional characteristics of various organic marker compounds at these sites. The concentration of levoglucosan significantly increased during the cold seasons（winter and fall）at Saitama and Maebashi. Organic markers of cooking and vehicles had relatively higher concentrations at Saitama than at the other sites. Dicarboxylic acids had high concentrations during the warm seasons because of photochemical activity. Furthermore the dicarboxylic acid compositions were different at each site, suggesting aging of the organic particles. 2-metyltetrols, BSOA markers derived from isoprene, tended to increase during the warm seasons, significantly at the forested site, Akagi. We found that, together with α-pinene BSOA, naturally occurring secondary-generated organic particles exist in non-negligible amounts.

As a result of PMF analysis using a PM$_{2.5}$ component dataset, it was possible to apportion 80-90％ of PM$_{2.5}$ mass concentration among 12 sources. By measuring various organic marker components in addition to the ion components, carbonaceous components and elements, we were able to evaluate the contribution rate of the sources of organic particles such as BPOA, BSOA, biomass burning and cooking. In particular, when we focused our attention on the source contribution rate of OA, we found the following characteristics. At Maebashi in spring, fall and winter, the influence of biomass burning was great, affecting the gain in organic particle concentrations. In spring and summer at Akagi, the contribution of BSOA derived from

isoprene was remarkably high. The influence of local OA in urban areas during the warm seasons at Saitama and biomass burning in the cold season were characteristic. The contribution ratio of sources involved in OA in PM$_{2.5}$ was 39％ at Maebashi, 46％ at Akagi, and 41％ at Saitama. Thus measures against sources of organic particles would be effective for reducing PM$_{2.5}$ concentrations.

We established an organic marker measurement method and receptor modeling that can be applied to monitoring methods already implemented in Japan. Our observations can provide a model case for PM$_{2.5}$ monitoring surveys. These results can serve as basic data for planning future PM$_{2.5}$ reduction measures in Japan.

Acknowledgments

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