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Organic Molecular Tracers in $PM_{2.5}$ at Urban Sites during Spring and Summer in Japan: Impact of Secondary Organic Aerosols on Water-Soluble Organic Carbon

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Abstract: To understand the characteristics of secondary organic aerosols (SOAs) and estimate their impact on water-soluble organic carbon (WSOC) in urban areas in Japan, we measured 17 organic tracers using gas chromatography–mass spectrometry from particulate matter with an aerodynamic diameter smaller than 2.5 μm collected at five urban sites in Japan during spring and summer. Most anthropogenic, monoterpene-derived, and isoprene-derived SOA tracers showed meaningful correlations with potential ozone in both these seasons. These results indicate that oxidants play an important role in SOAs produced during both seasons in urban cities in Japan. WSOC was significantly affected by anthropogenic and monoterpene-derived SOAs during spring and three SOA groups during summer at most of the sites sampled. The total estimated secondary organic carbons (SOCs), including mono-aromatic, di-aromatic, monoterpene-derived, and isoprene-derived SOCs, could explain the WSOC fractions of 39–63% in spring and 46–54% in summer at each site. Notably, monoterpene-derived and mono-aromatic SOCs accounted for most of the total estimated SOCs in both spring (85–93%) and summer (75–82%) at each site. These results indicate that SOAs significantly impact WSOC concentrations during both these seasons at urban sites in Japan.

Keywords: SOA; organic markers; WSOC; potential ozone; SOA-tracer method

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1. Introduction

Atmospheric aerosols, including particulate matter (PM) with an aerodynamic diameter smaller than 2.5 μm ($PM_{2.5}$), possess characteristics, such as light absorptivity, toxicity, and hygroscopicity; therefore, these aerosols impact human health and the global climate directly and indirectly [1,2]. Owing to their toxicity, PMs have been classified as carcinogenic to humans by the World Health Organization [3]. $PM_{2.5}$ consists of various substances, such as carbonaceous components, sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), and metals [4]. Organic components, such as organic carbon (OC) and water-soluble OC (WSOC), account for a large proportion of $PM_{2.5}$, ranging from 10% to 70% [2,4]. Organic compounds in PM play an important role in the PM properties affecting air quality, health, and climate. Therefore, a number of studies have been performed to understand the characteristics of organic aerosols [5]. Organic aerosols are generally categorized into primary organic aerosols (POAs) directly emitted from biomass and fossil fuel combustion, and plant and soil dust, and secondary organic aerosols (SOAs) produced via the oxidation of gas-phase precursors in the atmosphere [6]. SOAs generally have a higher water solubility than their precursors because of oxidation reactions, and their formation is an important factor contributing to the increase in the WSOC concentration. Identifying sources and formation mechanisms is challenging because of the complex sources and atmospheric processing of SOAs.

Recently, specific organic compounds have been proposed as tracers to evaluate the sources and generation processes of organic aerosols. Several tracers of anthropogenic SOA (ASOA) and biogenic SOA have been proposed in laboratory and field studies. 2,3-Dihydroxy-4-oxopentanoic acid (DHOPA), phthalic acid, 4-methylphthalic acid, and some nitroaromatics, such as 3,5-dinitrosalicylic acid, have been proposed as oxidation products from anthropogenic volatile organic compounds (AVOCs) such as toluene and naphthalene [7–10]. Pinonic acid, pinic acid, 3-hydroxyglutaric acid, and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) have been reported as oxidation products from monoterpenes, such as α-pinene [11–13]. Isoprene can be oxidized to 2-methylthreitol and 2-methylerythritol under low-nitrogen oxide (NO_x) conditions and 2,3-dihydroxy-2-methylpropanoic acid (2-methylglyceric acid) under high-NO_x conditions [14,15]. For POA tracers, anhydrous sugars, such as levoglucosan, have been used as tracers for biomass burning [16,17]. In addition, terephthalic acid is a major pyrolysis product of polyethylene terephthalate used in plastic products [18]. Terephthalic acid may also be formed by the secondary formation of aromatic hydrocarbons from traffic emissions in urban areas [19,20]. Arabitol and mannitol are storage substances found in fungal spores and plants [21,22], and glucose is emitted from terrestrial plant fruits and vascular plants [23]. These sugars are known tracers of primary biogenic emissions. These organic tracers are widely used to analyze the sources and formation processes of organic aerosols worldwide.

In Japan, the $PM_{2.5}$ environmental standard was set in 2009 to 15 $\mu g/m^3$ for the annual average concentration and to 35 $\mu g/m^3$ for the 98th percentile value of the daily average [24]. Focusing on carbonaceous aerosols, elemental carbon (EC) concentrations have gradually decreased in urban areas, such as Tokyo [25–27] and Nagoya [28], because of motor vehicle emission controls [29]. Conversely, OC concentrations demonstrated insignificant variations from 2004 to 2014 in Tokyo [27]. Regarding the sources of carbonaceous aerosols, Miyazaki et al. [30] used time-resolved field observations to demonstrate that the hourly WSOC concentration is highly correlated with the secondary organic carbon (SOC) concentration as estimated using the EC-tracer method. To prevent secondary air pollution, such as SOAs and oxidants, regulations controlling VOC emissions were implemented in 2006 in Japan. The goal of this regulation was a 30% reduction of the 2000-emission level by 2010. As a result, a reduction of more than 42% in VOC emissions from stationary sources in Japan was achieved from 2000 to 2009 [29]. To understand the effectiveness of VOC regulations, it is essential to understand the actual status of ASOAs. According to radiocarbon measurements, fossil sources contributed to the high daytime SOA concentration in Maebashi, a suburban city located downwind of Tokyo [31,32]. Ikemori et al. [33] also demonstrated that SOA-produced fossil VOCs contributed to the periods of high fossil-carbon concentration during summer in Nagoya, an urban city in Japan. However, in Japan, the concentrations, formation processes, and contributions of SOA have not been examined in detail. In particular, field studies using organic tracers are limited, especially at urban sites where there are multiple anthropogenic emission sources [9]. In this study, we measured 17 organic tracer compounds of SOAs and POAs using gas chromatography–mass spectrometry (GC–MS) to reveal the characteristics of these tracers during spring and summer when oxidants tend to be highly concentrated. We focused on SOAs and estimated their impact on WSOC in $PM_{2.5}$ at urban sites in Japan.

2. Materials and Methods

2.1. Sampling and Measurements

$PM_{2.5}$ was collected for 24 h on quartz filters to quantify water-soluble ionic species, OC, EC, and organic tracer compounds during spring and summer in 2015 at five urban cities in Japan (Figure 1, Table S1 of Supplementary Material). Detailed information concerning the sampling sites and the $PM_{2.5}$ collection, including the samplers, is given in Table 1.

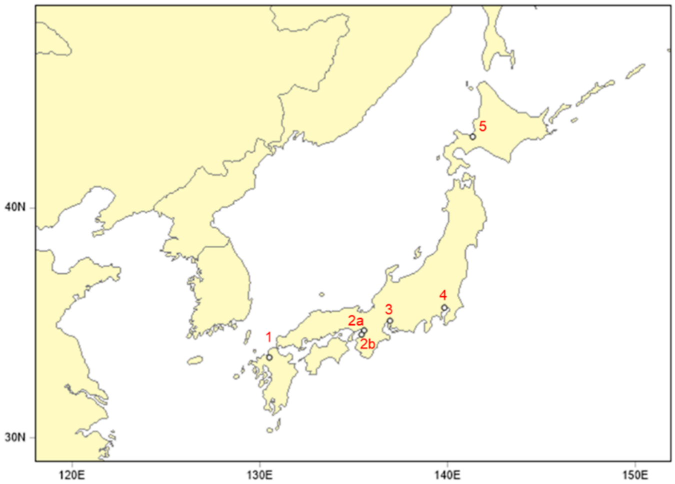


Figure 1. Locations of the $PM_{2.5}$ observation sites.

Table 1. Location and sampler type used at the filter-based monitoring sites.

No.	Site	Prefecture	Latitude (°N)	Longitude (°E)	Sampler		
					Type	Impactor	Flowrate
1	Dazaifu	Fukuoka	33.51	130.50	HV-1000 F (Sibata)	$HVI_{2.5}$	740 L/min
2a	Osaka	Osaka	34.68	135.54	Partisol Plus 2025 (Thermo)	WINS impactor	16.7 L/min
2b	Izumiotsu	Osaka	34.50	135.41	Partisol Plus 2025 (Thermo)	WINS impactor	16.7 L/min
3	Nagoya	Nagoya	35.10	136.92	LV-250 (Sibata)	WINS impactor	16.7 L/min
4	Tokyo	Tokyo	35.67	139.82	FRM2000 (Thermo)	WINS impactor	16.7 L/min
5	Sapporo	Hokkaido	43.08	141.33	FRM2000 (Thermo)	WINS impactor	16.7 L/min

Measurements of ions and carbonaceous components (OC, EC, and WSOC) were conducted according to the standard $PM_{2.5}$ measuring method based on the Ministry of the Environment Air Pollution Control Law in Japan [34]. In brief, the water-soluble ionic species and WSOC were extracted via ultrapure water and determined using ion chromatography (ICS-5000, Thermo Fisher Scientific) and a total organic carbon analyzer (TOC-V CPH, Shimadzu), respectively. OC and EC were analyzed using an OC/EC analyzer (Desert Research Institute Model 2001) according to the Interagency Monitoring of Protected Visual Environments protocol (IMPROVE)/thermal, optical reflectance method. Organic tracer compounds were determined via GC–MS (GC: Agilent 7890, MS: Agilent 5975) following the method reported in our previous studies [35,36]. In brief, a quartz filter aliquot (filter area of 4.3 cm^2 in Dazaifu and 3 cm^2 at the other sites) was spiked with internal recovery standards (succinic acid-d_4, glutaric acid-d_6, levoglucosan-$^{13}C_6$, and mannitol-d_8); organic tracers were then extracted using dichloromethane/methanol (2:1, v/v, 5 mL, Wako Pure Chemical Industries) under ultrasonication for 20 min [35]. The solvent extracts were concentrated using pure nitrogen gas. Then, the dried extracts were reacted with 40 µL N,O-bis(trimethylsilyl)trifluoroacetamide containing 1% trimethylsilyl chloride (BSTFA; GL-sciences) and 10 µL pyridine (Wako Pure Chemical Industries) at 70 °C for 1.5 h to convert the compounds into trimethylsilyl derivatives. Then, the obtained derivatives were diluted with 100 µL isooctane containing the recovery standard (n-pentacosan-d_{52}; C/D/N Isotopes) and measurements of organic tracers were conducted via GC–MS. The GC was equipped with a splitless injector and an InertCap 5MS fused-silica capillary column (30 m + 5 m × 0.25 mm internal diameter, 0.25 mm film thickness; GL-sciences). The MS was operated in electron ionization mode at 70 eV and in selected ion monitoring (SIM)/scan mode, measuring the target mass within a scanning range of 50–650 Da. Quantification of the organic tracer compounds was performed using authentic standards, except for 2-methylthreitol and 2-methylerythritol, estimated using meso-erythritol and threitol, respectively. The SIM results were normalized to the corresponding internal standards and quantified using a linear calibration curve ($R^2 > 0.995$). Recoveries of the quantified organic tracer compounds ranged from 95% to 112% [36].

We used the $PM_{2.5}$ mass and gaseous compound data, including nitric oxide (NO), nitrogen dioxide (NO_2), nitrogen oxide (NO_x), and oxidants (O_x), measured by the local and national governments in Japan at residential monitoring sites within 2.5 km of each $PM_{2.5}$ sampling site. The potential ozone (PO) was calculated as:

$$\mathrm{PO} = \mathrm{O_x} + \mathrm{NO_2} - 0.1 \times \mathrm{NO}, \quad (1)$$

based on the report by Itano et al. [37]. In addition, we used meteorological data measured by the Japanese Meteorological Agency. These data have been published by the National Institute for Environmental Studies [38] and the Japanese Meteorological Agency [39].

2.2. Estimation of Secondary Organic Carbon Using an Organic Tracer-Based Method

SOA (or SOC) originating from biogenic VOC (BVOC) and AVOC was estimated using a tracer-based method (SOA-tracer method). The fraction of SOC (f_{soc}) is defined as:

$$f_{\mathrm{soc}} = \Sigma_i[\mathrm{tr}_i]/[\mathrm{SOC}], \quad (2)$$

where $[\mathrm{tr}_i]$ is the concentration of each organic tracer i in ng/m^3 and (SOC) is the organic carbon concentration of the SOA. Tracer mass fraction factors (f_{soc}) based on chamber experiments have been proposed in previous studies [7,40–43]. We adopted 0.00307, 0.0367, 0.059 and 0.155 as the f_{soc} values for the mono-aromatics estimated by DHOPA [7]; di-aromatic SOCs estimated by naphthalene [7]; monoterpene-derived SOCs estimated by pinonic acid, pinic acid, 3-hydroxyglutaric acid, MBTCA, and 3-hydroxy-4,4-dimethylglutaric acid [43]; and isoprene-derived SOCs estimated by 2-methylthreitol, 2-methylerythritol, and 2-methylglyceric acid [41], respectively. The factor for monoterpene-derived SOCs proposed by Kleindienst et al. [41] has been used in multiple studies. However, this factor was estimated using nine compounds, including pinonic acid, pinic acid, and 3-hydroxyglutaric acid, detected in PM in monoterpene oxidation chamber experiments. Only three of these nine components could be quantified in this study. In addition, MBTCA, which showed a high concentration in this study, was not used to calculate f_{soc} reported in Kleindienst et al. [41]. These factors may cause large errors in estimations of monoterpene-derived SOCs when using the f_{soc} value reported by Kleindienst et al. [41]. Conversely, four of the five tracer compounds used to calculate the factor proposed by Zhang et al. [43] were quantifiable in this study. Therefore, the f_{soc} value reported by Zhang et al. [43] will likely lead to smaller errors than that reported by Kleindienst et al. [41]. Accordingly, we adopted the f_{soc} value proposed by Zhang et al. [43].

3. Results and Discussion

3.1. $PM_{2.5}$ Mass and Major Component Concentrations

Seasonal averages of the $PM_{2.5}$ mass, OC, WSOC, EC, ions, gaseous components, and meteorological data during spring and summer at all sites are shown in Table 2. The component with the highest averaged concentration is sulfate, followed by OC or ammonium, at all sites during both seasons. The seasonal mean concentrations of sulfate in Dazaifu were 1.9–2.8 and 1.4–2.7 times higher than those at other sites during spring and summer. Sulfate is a significant contributing component to long-range $PM_{2.5}$ transported to Japan from the Asian continent. Accordingly, the sulfate concentration is higher in western regions than in eastern regions of Japan [44,45]. The OC concentrations were comparable at all sites during spring but were lower in Sapporo than that at other sites during summer. This concentration trend for OC indicates that OC is not as strongly affected by transboundary pollution as is sulfate. The averaged WSOC fractions of OC at each observation site were large at 68.0–74.6% in spring and 77.1–88.1% in summer. In addition, strong correlations between WSOC and OC at each site were shown in spring ($r = 0.95$–0.98) and summer ($r = 0.94$–0.97), except at Sapporo ($r = 0.59$ and 0.43, respectively), as shown in Table S2 of Supplementary Material. The WSOC was also weakly correlated with the PO in Sapporo in summer ($r = 0.51$) and strongly correlated with the PO in spring ($r = 0.77$–0.88) and summer ($r = 0.78$–0.93) in other cities in both these seasons, as is also shown in Table S2.

WSOC is mainly produced from biomass burning (direct emission) and via secondary reactions of VOC (e.g., [46]). Using an EC-tracer method in the Tokyo urban area, Miyazaki et al. [30] demonstrated that the hourly WSOC is highly correlated with the SOC estimate. Ueno et al. [47] also reported that secondary generation from VOCs, rather than biomass combustion, primarily contributes to WSOC production in Tokyo based on the correlation between WSOC and both potassium ions and PO. Based on a radiocarbon analysis at an urban site in Nagoya, Ikemori et al. [33] suggested that high values of total carbon in summer are associated with secondary formation from AVOC and BVOC. Moreover, the contribution of biomass burning is lower in spring and summer–early fall than in late fall and winter. Our results indicate the possibility that secondary generation from VOC is a significant contributor to WSOC at urban sites during spring and summer; however, the trends observed in Sapporo are different. Using organic tracers, we discuss in detail the origin of WSOCs, especially secondary generation, in Section 3.2.

3.2. Organic Tracers

Seventeen organic tracer compounds were measured and categorized into six groups according to their origins (ASOA, biogenic SOAs from monoterpene and isoprene, biomass burning, plastic burning, and primary biogenic organic aerosols). The seasonal means of the organic tracers in spring and summer are shown in Table 3. The seasonal averages of the total organic tracer components at each site are shown in Figure 2. During spring, the lowest seasonal average was observed in Tokyo; Dazaifu had the highest average among all sites, which can be attributed to the higher concentration of BPOA. In Dazaifu, $PM_{2.5}$ impactor for a high-volume ($HVI_{2.5}$, Tokyo dylec) was used to sample $PM_{2.5}$; however, others have reported that calcium ions contained in the soil (coarse particles) are collected when sampling $PM_{2.5}$ [48]. Similar behavior has been reported when using other high-volume $PM_{2.5}$ impactors [49]. Therefore, tracers for fungal spores and plants, which are abundant in coarse particles, showed high value at Dazaifu. In summer, the seasonal averages across the sites were comparable, although that at Sapporo was the lowest. Isoprene-derived SOA tracers were higher in summer than in spring; meanwhile, biomass burning tracers were clearly higher in spring than in summer. The detailed characteristics of each categorized group and the WSOC relationships are discussed in the following subsections.

Table 2. Seasonal OC, WSOC, EC, and ion averages by filter-based measurements and $PM_{2.5}$ mass, meteorological data, gaseous components, and potential ozone (PO) by online-based measurements during spring and summer at all sites.

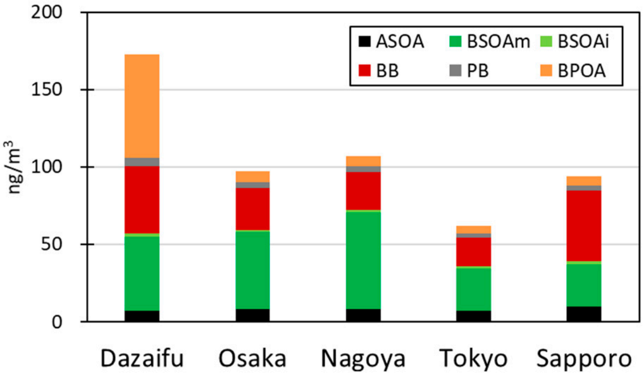
	Spring					**Summer**				
	Dazaifu	**Osaka**	**Nagoya**	**Tokyo**	**Sapporo**	**Dazaifu**	**Izumiotsu**	**Nagoya**	**Tokyo**	**Sapporo**
	***n* = 10**	***n* = 10**	***n* = 10**	***n* = 10**	***n* = 7**	***n* = 16**	***n* = 16**	***n* = 15**	***n* = 16**	***n* = 16**
Filter based measurement, μg/m^3										
OC	4.2 ± 1.5	4.4 ± 1.4	4.1 ± 1.7	3.8 ± 1.3	3.6 ± 0.69	2.5 ± 0.95	3.1 ± 1.3	3.4 ± 1.3	3.3 ± 1.4	1.9 ± 0.67
WSOC	3.0 ± 1.1	3.0 ± 1.0	2.9 ± 1.3	2.7 ± 0.90	2.6 ± 0.43	1.9 ± 0.66	2.9 ± 1.6	2.9 ± 1.3	2.6 ± 1.2	1.4 ± 0.30
EC	1.8 ± 0.63	1.3 ± 0.51	1.2 ± 0.53	1.2 ± 0.44	1.4 ± 0.39	1.2 ± 0.4	1.3 ± 0.72	1.4 ± 0.48	1.5 ± 0.41	0.99 ± 0.25
Na^+	0.22 ± 0.18	0.13 ± 0.08	0.21 ± 0.11	0.19 ± 0.19	0.25 ± 0.19	0.31 ± 0.19	0.16 ± 0.071	0.12 ± 0.054	0.24 ± 0.16	0.073 ± 0.083
NH_4^+	6.1 ± 3.8	2.7 ± 1.9	2.3 ± 1.4	2.2 ± 1.7	2.2 ± 0.94	4.7 ± 3.4	3.5 ± 2.4	2.7 ± 2.0	2.7 ± 1.7	2.1 ± 1.0
K^+	0.36 ± 0.23	0.11 ± 0.070	0.094 ± 0.061	0.10 ± 0.059	0.11 ± 0.027	0.19 ± 0.091	0.17 ± 0.097	0.14 ± 0.15	0.12 ± 0.068	0.052 ± 0.033
Mg^{2+}	0.031 ± 0.018	0.0076 ± 0.0056	0.011 ± 0.0050	0.0099 ± 0.011	0.022 ± 0.016	0.021 ± 0.012	0.0048 ± 0.0021	0.0070 ± 0.0053	0.011 ± 0.0082	0.0019 ± 0.0025
Ca^{2+}	0.35 ± 0.19	0.059 ± 0.056	0.079 ± 0.050	0.080 ± 0.069	0.047 ± 0.017	0.17 ± 0.14	0.038 ± 0.029	0.058 ± 0.047	0.084 ± 0.053	0.0071 ± 0.0038
Cl^-	0.18 ± 0.10	0.097 ± 0.082	0.047 ± 0.016	0.13 ± 0.16	0.087 ± 0.077	0.037 ± 0.014	0.038 ± 0.084	0.027 ± 0.011	0.040 ± 0.062	0.017 ± 0.029
NO_3^-	3.9 ± 3.9	1.5 ± 1.2	1.1 ± 0.62	2.4 ± 1.9	0.87 ± 0.49	0.36 ± 0.18	0.11 ± 0.028	0.096 ± 0.029	0.24 ± 0.15	0.037 ± 0.024
SO_4^{2-}	12.5 ± 7.7	6.5 ± 5.0	5.9 ± 3.8	4.9 ± 4.3	4.5 ± 2.2	14.2 ± 9.8	10.0 ± 6.9	7.5 ± 5.6	7.7 ± 4.8	5.2 ± 3.0
Oxalate	0.48 ± 0.32	0.26 ± 0.14	0.26 ± 0.16	0.23 ± 0.14	0.17 ± 0.036	0.35 ± 0.18	0.27 ± 0.18	0.20 ± 0.099	0.15 ± 0.096	0.12 ± 0.048
Online-based measurement										
$PM_{2.5}$, μg/m^3	23.1 ± 10.4	25.7 ± 10.8	22.5 ± 9.8	21.8 ± 10.5	17.4 ± 13.2	18.6 ± 8.9	24.3 ± 14.1	22.4 ± 11.8	24.1 ± 11.0	13.1 ± 5.1
Wind speed, m/s	2.0 ± 0.39	2.3 ± 0.38	2.8 ± 0.38	2.9 ± 0.59	3.0 ± 1.3	1.9 ± 0.33	1.4 ± 0.40	2.7 ± 0.69	3.0 ± 1.1	2.7 ± 0.71
Daily radiation, MJ/m^2	22.5 ± 5.4	22.8 ± 5.0	24.1 ± 2.3	20.4 ± 4.4	21.7 ± 1.3	22.8 ± 6.3	21.2 ± 5.6	20.3 ± 6.1	21.1 ± 4.6	14.9 ± 5.1
Temperature, °C	17.6 ± 2.4	18.8 ± 2.3	18.9 ± 1.6	18.3 ± 1.8	13.0 ± 2.3	28.9 ± 1.4	29.2 ± 1.9	29.8 ± 1.9	29.6 ± 1.0	24.6 ± 1.5
Relative humidity,%	56.5 ± 15.3	54.5 ± 12.1	56.7 ± 9.9	63.5 ± 7.9	53.6 ± 10.2	72.7 ± 6.6	70.0 ± 8.0	68.2 ± 9.6	72.3 ± 5.2	78.4 ± 6.6
NO, ppb	1.3 ± 0.72	3.1 ± 2.3	4.4 ± 2.0	2.5 ± 2.0	0.91 ± 0.47	2.3 ± 1.1	3.1 ± 3.2	4.9 ± 3.9	5.8 ± 4.7	2.0 ± 0.96
NO_2, ppb	16.9 ± 4.8	22.2 ± 7.4	21.1 ± 6.7	22.2 ± 8.6	11.3 ± 4.0	9.4 ± 2.7	12.1 ± 3.6	15.7 ± 5.0	22.6 ± 7.0	7.8 ± 2.3
NO_x, ppb	18.1 ± 5.2	25.3 ± 9.6	25.5 ± 8.3	24.8 ± 10.3	12.2 ± 4.4	11.7 ± 3.6	15.3 ± 5.3	20.6 ± 7.8	28.4 ± 8.0	9.8 ± 3.1
Ox, ppb	47.2 ± 8.3	44.5 ± 8.8	43.6 ± 7.0	38.6 ± 6.4	45.5 ± 10.1	26.8 ± 7.1	31.5 ± 18.8	28.9 ± 15.8	25.6 ± 16.0	21.0 ± 6.8
PO, ppb	62.3 ± 11.0	64.2 ± 9.8	62.2 ± 7.9	58.4 ± 5.1	55.5 ± 7.2	35.0 ± 8.0	42.0 ± 20.1	42.6 ± 15.7	45.3 ± 18.3	27.8 ± 6.0

Table 3. Organic tracer concentrations (ng/m^3) in $PM_{2.5}$ during spring and summer at each site.

	Spring					**Summer**					**Abbreviation**
	Dazaifu	**Osaka**	**Nagoya**	**Tokyo**	**Sapporo**	**Dazaifu**	**Izumiotsu**	**Nagoya**	**Tokyo**	**Sapporo**	
	***n* = 10**	***n* = 10**	***n* = 10**	***n* = 10**	***n* = 7**	***n* = 16**	***n* = 16**	***n* = 15**	***n* = 16**	***n* = 16**	
ASOA tracers											
DHOPA [1]	1.8 ± 1.4	1.7 ± 0.97	2.2 ± 1.7	1.5 ± 1.3	1.9 ± 0.4	0.96 ± 0.50	1.5 ± 1.1	1.2 ± 0.80	1.2 ± 1.5	0.61 ± 0.33	DHOPA
Phthalic acid	4.6 ± 1.8	5.3 ± 2.8	5.0 ± 2.6	4.9 ± 2.3	6.9 ± 1.2	4.5 ± 2.1	5.9 ± 3.7	6.8 ± 2.9	7.9 ± 5.2	2.7 ± 1.2	PhA
4-Methylphthalic acid	0.71 ± 0.21	1.3 ± 0.67	1.0 ± 0.50	0.95 ± 0.36	1.0 ± 0.95	1.0 ± 0.55	1.5 ± 0.85	1.9 ± 0.98	1.8 ± 1.1	0.53 ± 0.25	4MPhA
Subtotal	7.1 ± 3.1	8.2 ± 4.3	8.2 ± 4.5	7.3 ± 3.8	9.8 ± 2.3	6.5 ± 3.0	8.9 ± 5.6	10.0 ± 4.2	10.9 ± 7.5	3.8 ± 1.7	
Monoterpene-derived SOA tracers											
cis-Pinonic acid	20.5 ± 13.6	27.8 ± 15.7	36.6 ± 19.9	12.4 ± 4.1	5.7 ± 1.9	1.9 ± 1.2	9.4 ± 3.5	5.2 ± 3.1	9.1 ± 2.4	6.1 ± 0.87	PNOA
Pinic acid	8.7 ± 4.2	5.1 ± 1.6	7.7 ± 4.7	2.2 ± 0.9	3.6 ± 1.9	4.9 ± 2.7	8.5 ± 7.5	6.5 ± 4.9	4.3 ± 3.2	3.0 ± 1.4	PA
3-Hydroxyglutaric acid	13.6 ± 8.1	11.9 ± 5.7	12.7 ± 8.0	9.9 ± 5.6	14.8 ± 6.7	13.4 ± 7.2	23.4 ± 20.1	19.5 ± 13.4	17.0 ± 16.0	10.5 ± 5.8	3HGA
MBTCA [2]	5.0 ± 2.5	4.9 ± 2.3	5.3 ± 3.7	2.4 ± 1.5	3.2 ± 2.1	8.9 ± 5.8	14.6 ± 11.5	11.9 ± 8.0	9.5 ± 9.5	4.2 ± 2.8	MBTCA
Subtotal	47.8 ± 18.9	49.7 ± 18.5	62.4 ± 32.4	27.0 ± 8.4	27.3 ± 11.6	29.1 ± 15.8	55.9 ± 40.1	43.2 ± 25.2	40.0 ± 28.8	23.8 ± 9.5	
Isoprene-derived SOA tracers											
2-Methylthreitol	0.20 ± 0.10	0.24 ± 0.12	0.23 ± 0.13	0.18 ± 0.082	0.14 ± 0.032	4.7 ± 3.8	5.7 ± 4.0	1.9 ± 1.1	2.5 ± 1.3	3.1 ± 2.6	2MTT
2-Methylerythritol	0.59 ± 0.30	0.58 ± 0.24	0.55 ± 0.40	0.40 ± 0.16	0.36 ± 0.096	18.4 ± 14.3	17.3 ± 13.5	8.1 ± 5.9	8.7 ± 6.1	10.5 ± 10.0	2MET
2-Methylglyceric acid	1.4 ± 0.45	0.73 ± 0.29	1.0 ± 0.72	0.83 ± 0.35	1.4 ± 0.34	1.5 ± 0.76	1.8 ± 1.3	1.5 ± 0.93	1.6 ± 0.99	1.8 ± 1.4	2MGA
Subtotal	2.1 ± 0.63	1.5 ± 0.42	1.8 ± 1.2	1.4 ± 0.51	1.9 ± 0.44	24.6 ± 18.7	24.8 ± 18.7	11.5 ± 7.7	12.9 ± 8.4	15.3 ± 13.8	
Biomass-burning tracers											
Levoglucosan	37.7 ± 13.4	22.8 ± 18.0	20.8 ± 14.2	16.1 ± 16.5	39.9 ± 24.1	12.1 ± 5.4	9.2 ± 4.5	7.2 ± 3.2	5.8 ± 5.0	3.2 ± 1.7	LEV
Mannosan	4.0 ± 1.3	2.7 ± 2.5	2.5 ± 1.8	1.8 ± 1.8	3.7 ± 2.1	1.1 ± 0.41	1.0 ± 0.52	0.71 ± 0.34	0.69 ± 0.48	0.42 ± 0.20	MAN
Galactosan	2.0 ± 0.78	1.3 ± 0.97	1.2 ± 0.84	0.98 ± 0.82	1.9 ± 1.1	0.52 ± 0.22	0.57 ± 0.22	0.30 ± 0.10	0.41 ± 0.23	0.19 ± 0.072	GAL
Subtotal	43.7 ± 15.4	26.8 ± 21.4	24.4 ± 16.8	18.9 ± 19.1	45.5 ± 27.1	13.7 ± 6.0	10.8 ± 5.2	8.2 ± 3.6	6.9 ± 5.7	3.8 ± 2.0	
Plastic-burning tracer											
Terephthalic acid	5.5 ± 3.0	4.2 ± 3.4	3.7 ± 2.0	2.5 ± 1.2	3.6 ± 2.2	3.5 ± 1.4	3.0 ± 1.9	3.8 ± 2.1	3.2 ± 2.4	0.99 ± 0.52	tPhA
BPOA tracers											
Arabitol	2.6 ± 0.92	1.1 ± 0.66	0.97 ± 0.42	0.61 ± 0.38	0.81 ± 0.20	3.2 ± 1.9	1.7 ± 0.70	2.3 ± 1.2	1.5 ± 0.86	0.64 ± 0.33	ARA
Mannitol	2.1 ± 0.63	0.89 ± 0.58	0.98 ± 0.46	0.55 ± 0.32	0.53 ± 0.18	5.3 ± 1.8	3.1 ± 1.7	4.2 ± 2.5	2.6 ± 1.6	1.2 ± 0.62	MAT
Glucose	61.8 ± 22.3	4.9 ± 3.0	4.9 ± 2.3	3.6 ± 1.9	4.3 ± 1.2	9.7 ± 4.8	4.6 ± 1.7	6.9 ± 3.4	5.2 ± 3.1	2.5 ± 1.3	GLU
Subtotal	66.5 ± 22.8	7.0 ± 4.3	6.8 ± 3.1	4.7 ± 2.4	5.7 ± 1.4	18.2 ± 7.3	9.4 ± 4.0	13.4 ± 7.0	9.3 ± 5.3	4.3 ± 2.1	

[1] DHOPA: 2,3-dihydroxy-4-oxopentanoic acid, [2] MBTCA: 3-methylbutane1,2,3-tricarboxylic acid. Unit: ng/m^3.

(a) Spring



(b) Summer

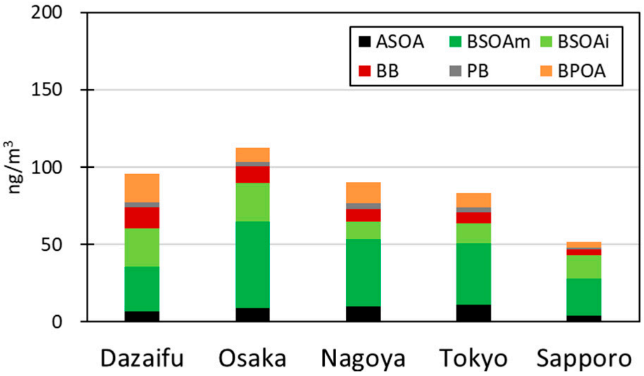


Figure 2. Chemical composition of the organic tracers detected in the $PM_{2.5}$ collected at each site. Six categorized groups are shown (anthropogenic secondary aerosol (ASOA), monoterpene-derived SOA (BSOAm), isoprene-derived SOA (BSOAi), biomass burning (BB), plastic burning (PB), and primary biogenic organic aerosol (BPOA)).

3.2.1. ASOA Tracers

Three organics, DHOPA, phthalic acid, and 4-methylphthalic acid, were quantified as ASOA tracers (Table 3). The seasonally averaged subtotals of the ASOA tracers at each site were comparable in spring and summer; however, those at Sapporo were more than twice as high in spring than in summer. In Sapporo, the highest values were observed in spring, whereas the lowest values were observed in summer. Phthalic acid showed the highest concentrations of the ASOA tracers during both spring and summer at all sites. Seasonally averaged concentrations of DHOPA in spring were higher than those of 4-methylphthalic acid at all sites, whereas the seasonally averaged concentrations of DHOPA in summer were comparable or lower than those of 4-methylphthalic acid. Moderately or highly positive correlations were shown for the three organics during spring (r = 0.69–0.92) and summer (r = 0.56–0.94), excepting absent correlations between 4-methyphthalic acid and both phthalic acid and DHOPA in Sapporo during spring and 4-methylphthalic acid and DHOPA in Nagoya during both these seasons (Table S3 of Supplementary Material).

DHOPA is an aromatic ring-opening SOA product from toluene and is known to be a useful tracer of toluene-derived SOAs [41]. Recently, DHOPA was also detected in SOAs generated from other mono-aromatic VOCs, such as xylenes, ethylbenzene, and trimethylbenzenes, in chamber experiments; therefore, it is a common SOA product for mono-aromatic VOCs [7]. Phthalic and 4-methylphthalic acids have been detected during the photooxidation of naphthalene and methylnaphthalene in chamber experiments [7,42]. Furthermore, it has been reported that ASOA tracers, OC, and anthropogenic sulfate, are often transported from Northeast China to western Japan in spring [36,45,50]. For each sampling day and at each sampling site, 72 h backward trajectories were calculated at 12:00 Japan

Standard Time at an altitude of 1000 m using NOAA Hysprit; the results are presented in Figure S1 of Supplementary Material. Air masses came from China, particularly during the entire sampling period at Sapporo and the first half of the sampling period at other sites. The ASOA tracers also tended to be abundant during this period, as presented in Figure S2 of Supplementary Material. Therefore, it is possible that, in spring, ASOAs are a mixture of regional and transboundary pollution. These factors may suggest a possible reason why the subtotals of the ASOA tracers were equivalent in spring and summer, even though SOA generation is generally more active in summer.

3.2.2. Monoterpene-Derived SOA Tracers

Four monoterpene-derived SOA tracers, pinonic, pinic, and 3-hydroxyglutaric acids and MBTCA, were identified in the $PM_{2.5}$ collected at all sites (Table 3). With respect to the generation mechanism of the tracers, it is proposed that pinonic and pinic acids are first-generation products and that 3-hydroxyglutaric acid and MBTCA are later-generation products [13,51]. The seasonally averaged subtotals of these tracers in Osaka/Izumiotsu and Sapporo were comparable for both seasons. Those in Tokyo were higher in summer than in spring, while those in Dazaifu and Nagoya were higher in spring than in summer. Pinonic acid showed the highest seasonal concentration in spring, followed by 3-hydroxyglutaric acid; however, the reverse order was observed in Sapporo. In summer, the seasonal mean concentration of 3-hydroxyglutaric acid was the highest of the monoterpene-derived SOA tracers at all sites, followed by MBTCA, except in Sapporo. At four sites, except Sapporo, the seasonal mean concentrations of pinonic acid were higher in spring than in summer, whereas those of MBTCA were higher in summer than in spring at all sites. Correlations of pinonic acid with pinic acid were significant in spring ($r = 0.75$–0.90), except in Tokyo and Sapporo; meanwhile, pinonic acid showed insignificant correlations with the other monoterpene-derived SOA tracers in summer at all sites, excluding that with MBTCA in Dazaifu (Table S3). In addition, the pinic and 3-hydroxyglutaric acids and MBTCA were strongly correlated in summer ($r = 0.83$–0.98) at all sites (Table S3). Therefore, pinonic acid exhibited different behavior than the other monoterpene-derived SOA tracers. By comparing measurements of pinonic acid in $PM_{2.5}$ collected on both quartz and polytetrafluoroethylene filters, Ikemori et al. [35] found that pinonic acid in $PM_{2.5}$ collected on quartz filters is gas adsorbed. Therefore, one possible explanation is that pinonic acid varies from the other monoterpene-derived SOA tracers because of its volatility.

These SOA tracers are produced by the photooxidation of α/β-pinene via reactions with O_3 and OH radicals [13,52]. To evaluate the aging level of monoterpene-derived SOAs, the ratio of the first-generation products (pinic acid) to the later-generation products (MBTCA) (P/M ratio) was used in this study. The seasonal averages of the P/M ratio at five sampling sites ranged from 1.2 to 2.3 during spring and from 0.55 to 0.91 during summer. These results indicate that monoterpene-derived SOAs were more aged during summer than during spring.

3.2.3. Isoprene-Derived SOA Tracers

Three isoprene-derived SOA tracers were detected in $PM_{2.5}$ collected at all sites: 2-methylthreitol, 2-methylerythritol, and 2-methylglyceric acid (Table 3). Seasonal mean concentrations of their subtotals were nearly 10 times higher in summer than in spring at all sites. 2-Methylglyceric acid showed the highest seasonal concentration in spring, followed by 2-methylerythritol and 2-methylthreitol. Conversely, 2-methylglyceric acid showed the lowest seasonal concentration in summer. Furthermore, compared with 2-methylthreitol and 2-methylerythritol, the seasonal differences in concentrations of 2-methylglyceric acid between spring and summer were smaller at each site. 2-Methylerythritol was strongly correlated with 2-methylthreitol in both spring and summer ($r = 0.93$–0.99) at all sites (Table S3). 2-Methylglyceric acid was also strongly correlated with 2-methylthreitol and 2-methylerythritol at all sites in summer ($r = 0.78$–0.98); however, these correlations were only significant in Nagoya and Sapporo in spring (Table S3).

Isoprene-derived SOAs form via the oxidation of isoprene by oxidants, such as OH radicals, NO_3 radicals, and O_3 in the atmosphere. Organic tracers of isoprene-derived SOAs are also strongly affected by NO_x [53]. 2-Methylthreitol and 2-methylerythritol are produced by the oxidation of isoprene under low-NO_x conditions. Conversely, 2-methylglyceric acid is produced by the oxidation of isoprene under high-NO_x conditions. Therefore, the ratio of 2-methylglyceric acid to the sum of 2-methylthreitol and 2-methylerythritol (2MGA/2MTLs) will increase as the ratio of NO_x/isoprene increases [14,54,55]. According to field observations, a higher concentration of isoprene was observed in summer than in spring in Nagoya [56]. During our measurement periods, the seasonal mean values of NO_x were comparable in spring and summer at each site. The seasonal mean values of 2MGA/2MTLs were higher in spring (1.1–2.9) than in summer (0.085–0.17) at all sites. This indicates that the differences in the seasonal concentrations of 2-methylthreitol and 2-methylerythritol in this study were related to the isoprene emission amount.

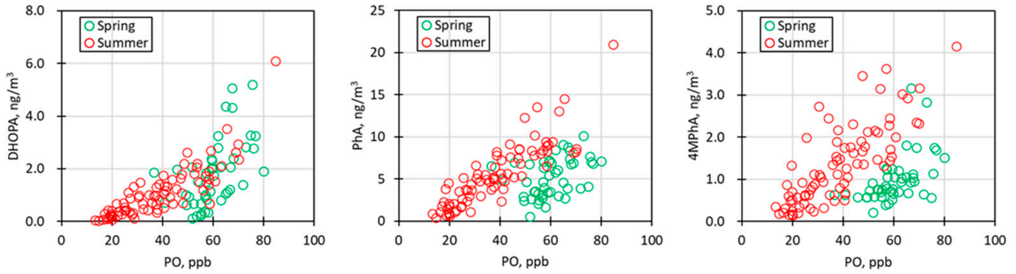
3.2.4. Primary Emission Tracers

Three biomass.burning tracers (levoglucosan, mannosan, and galactosan, [16,17]), one plastic.burning tracer (terephthalic acid, [18]), and three biogenic primary emission tracers (arabitol, mannitol, and glucose, [21–23]) were observed in the $PM_{2.5}$ collected at all sites (Table 3). All biomass-burning tracers had higher concentrations in spring than in summer. Terephthalic acid also had higher concentrations in Dazaifu, Osaka/Izumiotsu, and Sapporo in spring than in summer, with comparable concentrations in Nagoya. Seasonal mean concentrations of arabitol and mannitol were higher in summer than in spring, excepting arabitol in Sapporo. Seasonal mean values of glucose were higher in Dazaifu and Sapporo during spring than during summer but were comparable during both seasons in Osaka/Izumiotsu. The correlations between the tracer compounds were significant in each tracer group, except in some cases between glucose and arabitol and/or mannitol (Table S3). Interestingly, in spring, terephthalic acid was strongly correlated with sulfate at all sites (r = 0.80–0.81), except in Tokyo (r = 0.17). Ikemori et al. [36] proposed that $PM_{2.5}$ emitted from plastic combustion was transported from Northeast Asia downwind to Japan in spring, resulting in the relationship between terephthalic acid and sulfate. This may support the theory that transboundary plastic-burning aerosols are transported to central Japan.

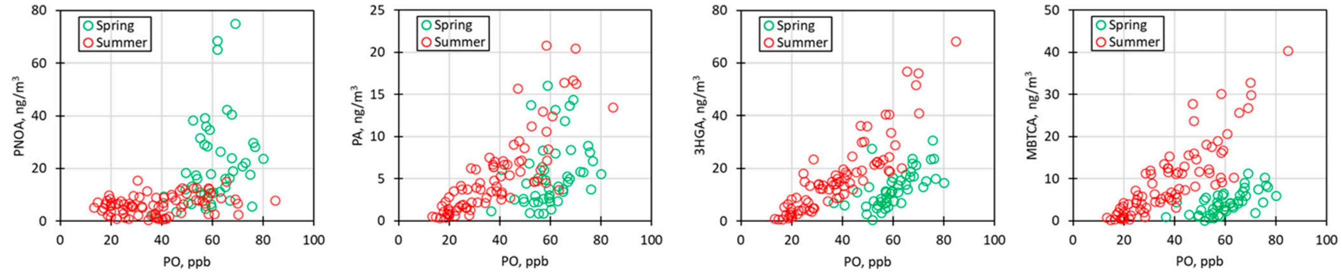
3.2.5. Relationship between PO and SOA Tracers

The correlations between PO and the organic tracers are shown in Table 4. The correlations between PO and the three ASOA tracers were significant during spring in Osaka, Nagoya, and Tokyo, except for DHOPA in Osaka (Table 4). Conversely, PO was only correlated with DHOPA in Dazaifu and was insignificantly correlated with the ASOA tracers in Sapporo. In summer, the correlations of PO with the ASOA tracers were significant at all sites, except in Sapporo. For the monoterpene-derived SOA tracers, PO was significantly correlated with 3-hdroxyglutraic acid and MBTCA in Osaka, Nagoya, and Tokyo in spring and was significantly correlated with pinic acid, 3-hdroxyglutraic acid, and MBTCA in summer at four sites, excepting Sapporo. PO was also significantly correlated with 2-methylglyceric acid in Dazaifu, Nagoya, and Tokyo but was insignificantly correlated with 2-methylthreitol and 2-methyerythritol in spring. In summer, PO showed significant correlations with the isoprene-derived SOA tracers at all sites, except for 2-methylthreitol and 2-methyerythritol in Sapporo. The scatter plots of PO concerning the SOAs at all sites during spring and summer are shown in Figure 3. Most SOA tracers were strongly or moderately correlated with PO in summer; however, they were weakly or insignificantly correlated with PO in spring (Table S4 of Supplementary Material). This result supports the theory that there are similar or common factors increasing the concentrations of these SOA tracers and PO during summer at all sites. Moreover, some tracers show a trend of a higher ratio of tracers to PO in summer than in spring. One possible explanation for this is that the background PO was higher than the background SOA tracers due to transboundary transport. Another possible explanation is that, during summer, there were several factors enhancing the production of SOA, even at low PO concentrations. Notably, pinonic and pinic acids as first-generation products from monoterpene did not show such a trend, while 3-hyroxyglutaric acid and MBTCA as later-generation products demonstrated higher ratios in summer than in spring. Further studies are required to reveal the differences in the relationships between PO and these SOA tracers, including the cause of the differences at the oxidation stage for the monoterpene-derived SOA tracers during spring and summer. Notably, terephthalic acid was moderately or strongly correlated with PO in Dazaifu, Nagoya, and Tokyo in both springs (r = 0.70–0.78) and summer (r = 0.64–0.95). Matos et al. [20] reported that terephthalic acid might be formed by the secondary formation of aromatic hydrocarbons from traffic emissions in urban areas. Although terephthalic acid is commonly used as a plastic combustion marker [57,58], this correlation may imply that terephthalic acid generated from secondary formation can affect its concentration in the atmospheric aerosols in urban areas. Time-resolved observations should be performed to clarify the sources of terephthalic acid and their relationship with PO and ASOA tracers.

(a) ASOA tracers



(b) Monoterpene-derived SOA tracers



(c) Isoprene-derived SOA tracers

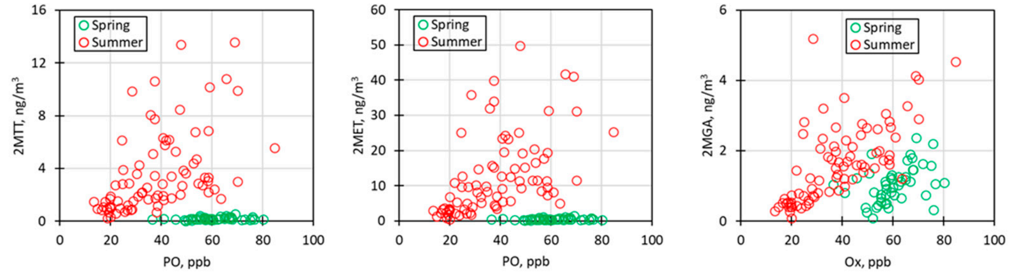


Figure 3. Scatter plots between potential ozone (PO) and SOA tracers with data from all sampling sites during spring (green) and summer (red): (**a**) ASOA tracers (DHOPA, phthalic acid (PhA), and 4-methylphthalic acid (4MPhA)) (**b**) monoterpene-derived SOA tracers (pinonic acid (PNOA), pinic acid (PA), 3-hydroxyglutaric acid (3HGA), and MBTCA), (**c**) isoprene-derived SOA tracers (2-methylthreitol (2MTT), 2-methylerythritol (2MET), and 2-methylglyceric acid (2MGA)).

3.2.6. Relationship between WSOC and Organic Tracers

The correlations between WSOC and the SOA tracers are shown in Table 5. Most ASOA tracers showed significant correlations with WSOC in spring and summer. The monoterpene-derived SOA tracers, except for pinonic acid, were also strongly correlated with WSOC during summer, while the later-generation products, MBTCA and 3-hydroxyglutaric acid, showed a significant correlation with WSOC at all sites even during spring, except for both in Sapporo and MBTCA in Dazaifu. Remarkably, limited correlations of pinonic acid with WSOC were shown during spring in Nagoya and during summer in Dazaifu, indicating different behavior than the other monoterpene-derived SOA tracers. WSOC showed strong or moderate correlations with 2-methylgyceric acid in Tokyo and Dazaifu and with three isoprene-derived SOA tracers in Nagoya in spring. WSOC also showed strong or moderate correlations with the isoprene-derived SOA tracers in summer at all sites. Of the primary emission tracers, the biomass-burning tracers showed weak or moderate correlations with WSOC during spring in Osaka and Nagoya and during summer at all sites; however, these tracers were lower in summer than in spring (Table 3). Although biomass burning is one of the most important sources of WSOC [46,59], it has been reported that emissions from biomass burning are not high in the spring and summer in urban areas in Japan, based on seasonal variations of levoglucosan concentrations [9,35,60]. Specifically, Ikemori et al. [35] reported that levoglucosan concentrations during winter were three and six times higher than those during spring and summer, respectively. Conversely, SOA tracers, such as DHOPA, 3-hydroxyglutaric acid, MBTCA, 2-methyltraitol, and 2-methylglyceric acid, showed higher concentrations during spring and summer than during winter. Hoshi and Saito et al. [60] also reported that similar seasonal levoglucosan trends had been observed in Tokyo. Moreover, they estimated the contributions of biomass burning to OC from the levoglucosan concentrations as 13–31% in the autumn-winter, 4.7–12% in spring, and 2.6–6.2% in the summer in Tokyo. In addition, levoglucosan and WSOC concentrations were moderately correlated during the autumn (r = 0.70) and winter (r = 0.69), but were weakly or insignificantly correlated during the spring (r = 0.40) and summer (r = 0.26). According to Ikemori et al. [9], the concentration of nitrocatechols as tracers of secondary aerosols from biomass burning during autumn was one order higher than those during summer. These studies support our findings of a limited contribution of biomass burning to WSOC during the spring and summer in urban areas of Japan. The primary biogenic emission tracers showed strong correlations with WSOC in Nagoya in spring; however, most of these tracers were insignificantly or weakly correlated with WSOC during spring and summer at the other sites. These results indicate that WSOC was significantly affected by ASOA and monoterpene-derived SOAs during spring at all sites except Sapporo and by the three SOA groups during summer at all sites. In addition, WSOC may be affected by biomass burning and primary biogenic sources at some sites.

Table 4. Correlations between PO and organic tracers during (**a**) spring and (**b**) summer at each sampling site.

(**a**) Spring

PO	DHOPA	PhA	4MPhA	PNOA	PA	3HGA	MBTCA	2MTT	2MET	2MGA	LEV	MAN	GLA	tPhA	ARA	MAT	GLU
Dazaifu	0.73 *	0.29	0.42	−0.02	0.03	0.82 **	0.29	−0.06	−0.20	0.88 **	0.16	0.19	0.21	0.78 **	−0.46	−0.38	−0.04
Osaka	0.58	0.68 *	0.72 *	0.03	0.18	0.81 **	0.78 **	0.03	0.05	0.33	0.23	0.16	0.17	0.62	0.31	0.29	0.32
Nagoya	0.76 *	0.83 **	0.77 **	0.37	0.54	0.82 **	0.83 **	0.45	0.50	0.73 *	0.40	0.31	0.34	0.78 **	0.79 **	0.68 *	0.86 **
Tokyo	0.70 *	0.68 *	0.67 *	−0.22	0.50	0.86 **	0.87 **	0.50	0.40	0.92 **	−0.04	0.05	0.14	0.70 *	0.19	0.25	0.35
Sapporo	0.30	0.64	0.75	0.83 *	0.41	0.46	0.82 *	0.36	0.13	0.63	−0.39	−0.53	−0.49	0.70	0.10	0.22	0.16

(**b**) Summer

PO	DHOPA	PhA	4MPhA	PNOA	PA	3HGA	MBTCA	2MTT	2MET	2MGA	LEV	MAN	GLA	tPhA	ARA	MAT	GLU
Dazaifu	0.85 **	0.86 **	0.78 **	0.27	0.91 **	0.92 **	0.75 **	0.69 **	0.69 **	0.87 **	0.32	0.44	0.60 *	0.64 **	0.22	0.12	0.42
Izumiotsu	0.96 **	0.87 **	0.76 **	0.43	0.88 **	0.94 **	0.92 **	0.93 **	0.91 **	0.93 **	0.51 *	0.49	0.78 **	0.95 **	0.52 *	0.17	0.52 *
Nagoya	0.84 **	0.76 **	0.71 **	−0.12	0.94 **	0.91 **	0.92 **	0.77 **	0.69 **	0.90 **	0.26	0.29	0.73 **	0.50	0.44	0.36	0.45
Tokyo	0.82 **	0.94 **	0.85 **	0.34	0.87 **	0.88 **	0.84 **	0.80 **	0.79 **	0.82 **	0.57 *	0.63 **	0.76 **	0.69 **	0.35	0.39	0.39
Sapporo	0.42	0.44	0.27	−0.23	0.32	0.42	0.32	0.45	0.38	0.57 *	0.06	0.04	−0.04	0.53 *	−0.54 *	−0.45	−0.21

(* $p < 0.05$, ** $p < 0.01$).

Table 5. Correlations between WSOC and organic tracers during (**a**) spring and (**b**) summer in each sampling site.

(**a**) Spring

WSOC	DHOPA	PhA	4MPhA	PNOA	PA	3HGA	MBTCA	2MTT	2MET	2MGA	LEV	MAN	GLA	tPhA	ARA	MAT	GLU
Dazaifu	0.86 **	0.54	0.78 **	0.00	0.20	0.93 **	0.63	−0.07	−0.26	0.85 **	0.50	0.53	0.52	0.90 **	−0.48	−0.24	0.12
Osaka	0.82 **	0.90 **	0.81 **	0.28	0.39	0.83 **	0.77 **	−0.17	−0.07	0.32	0.65 *	0.59	0.59	0.75 *	0.59	0.59	0.61
Nagoya	0.85 **	0.92 **	0.73 *	0.66 *	0.81 **	0.94 **	0.90 **	0.64 *	0.72 *	0.92 **	0.67 *	0.58	0.64 *	0.96 **	0.82 **	0.71 *	0.92 **
Tokyo	0.78 **	0.89 **	0.79 **	−0.44	0.23	0.67 *	0.67 *	0.31	0.17	0.90 **	0.45	0.53	0.63	0.86 **	0.45	0.42	0.77 **
Sapporo	0.50	0.83 *	0.63	0.37	0.10	0.33	0.58	0.50	0.27	0.49	−0.15	−0.27	−0.23	0.48	−0.18	−0.21	0.20

(**b**) Summer

WSOC	DHOPA	PhA	4MPhA	PNOA	PA	3HGA	MBTCA	2MTT	2MET	2MGA	LEV	MAN	GLA	tPhA	ARA	MAT	GLU
Dazaifu	0.67 **	0.77 **	0.85 **	0.65 **	0.88 **	0.85 **	0.96 **	0.78 **	0.80 **	0.83 **	0.73 **	0.72 **	0.74 **	0.47	0.45	0.50 *	0.70 **
Izumiotsu	0.85 **	0.79 **	0.79 **	0.49	0.99 **	0.95 **	0.99 **	0.86 **	0.84 **	0.90 **	0.42	0.42	0.65 **	0.93 **	0.60 *	0.25	0.58 *
Nagoya	0.64 *	0.70 **	0.89 **	−0.37	0.95 **	0.84 **	0.97 **	0.60 *	0.59 *	0.85 **	0.48	0.48	0.69 **	0.45	0.60 *	0.52 *	0.57 *
Tokyo	0.93 **	0.95 **	0.86 **	0.19	0.93 **	0.97 **	0.98 **	0.85 **	0.90 **	0.93 **	0.64 **	0.69 **	0.74 **	0.80 **	0.56 *	0.61 *	0.51 *
Sapporo	0.75 **	0.73 **	0.75 **	−0.31	0.88 **	0.88 **	0.88 **	0.75 **	0.71 **	0.77 **	0.63 **	0.69 **	0.63 **	0.88 **	−0.07	−0.01	0.24

(* $p < 0.05$, ** $p < 0.01$).

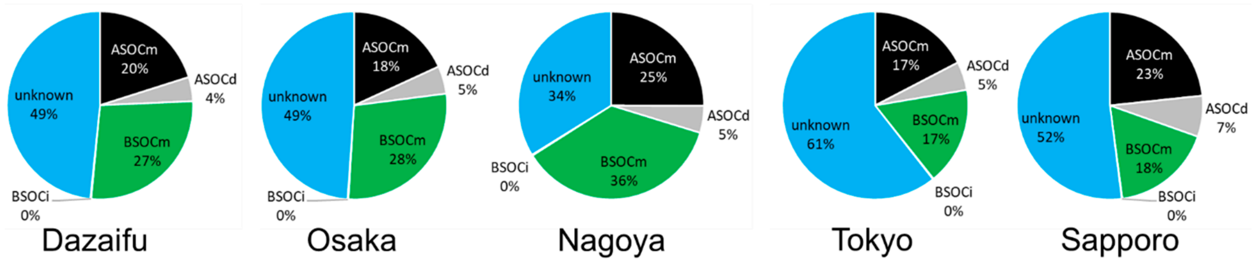
3.3. Source Apportionment of SOCs Using an Organic SOA-Tracer Method

Total mono-aromatic, di-aromatic, monoterpene-derived, and isoprene-derived SOCs were estimated using the SOA-tracer method, as detailed in Table 6 and broken down by fraction in Figure 4. During spring, the seasonal mean concentration of monoterpene-derived SOCs was at its highest, followed using mono-aromatic SOCs in Dazaifu, Osaka, and Nagoya; meanwhile, Sapporo exhibited the opposite trend. In Tokyo, the means of the monoterpene-derived SOCs and mono-aromatic SOCs were comparable. The seasonal means of di-aromatic SOCs followed the two higher SOC means, and the mean concentrations of the isoprene-derived SOCs were the lowest at all sites. During summer, the seasonal mean concentration of the monoterpene-derived SOCs was the highest, followed using the mono-aromatic SOCs at all sites. The seasonal means of the di-aromatic SOCs were higher than those of the isoprene-derived SOCs in Nagoya and Tokyo but were comparable at the other three sites. The isoprene-derived SOCs were more than 10 times higher in summer than in spring; however, their contributions to the total estimated SOCs were insignificant at all sites. The total seasonal means of the estimated SOCs at each site ranged from 1.1 μg/m^3 to 1.9 μg/m^3 in spring and from 0.76 μg/m^3 to 1.7 μg/m^3 in summer. The total estimated SOCs could explain the variation in the WSOC fraction shown in Figure 4 from 39% to 63% in spring and from 46% to 54% in summer at each site. Notably, monoterpene-derived and mono-aromatic hydrocarbon SOCs occupied a high fraction of the total estimated SOCs in both spring (85–93%) and summer (75–82%) at each site. These results indicate that SOCs, especially monoterpene-derived and mono-aromatic SOCs, have a significant impact on the WSOC concentrations during both seasons in urban areas in Japan.

Table 6. Estimated SOC concentrations (ng/m^3) during spring and summer presented herein and those presented by [61–64] in China.

Site	Country	Year	ASOCm	ASOCd	BSOCm	BSOCi	ASOC/BSOC	Reference
				Spring				
Dazaifu	Japan	2015	600	124	809	5.1	0.89	This study
Osaka		2015	548	144	843	5.3	0.82	This study
Nagoya		2015	728	135	1057	5.0	0.81	This study
Tokyo		2015	473	133	458	3.8	1.3	This study
Sapporo		2015	618	187	463	3.3	1.7	This study
Fuzhou	China	2017	749	na	306	39	2.2	[63]
				Summer				
Dazaifu	Japan	2015	313	122	493	149	0.68	This study
Izumiotsu		2015	482	161	947	148	0.59	This study
Nagoya		2015	391	186	733	65	0.72	This study
Tokyo		2015	394	214	678	73	0.81	This study
Sapporo		2015	199	73	403	87	0.56	This study
Beijing	China	2012	1700	na	149	647	2.1	[61]
Taiyuan		2012	988	na	71	306	2.6	[61]
Dunhuang		2012	687	na	59	574	1.1	[61]
Hefei		2012	854	na	291	1513	0.47	[61]
Kunming		2012	783	na	73	655	1.1	[61]
Tianjin		2016	697	185	208	115	2.7	[62]
Tianjin		2016	544	96	234	96	1.9	[62]
Beijing		2017	280	na	303	26	0.85	[64]
Fuzhou		2017	951	na	439	118	1.7	[63]

(a) Spring



(b) Summer

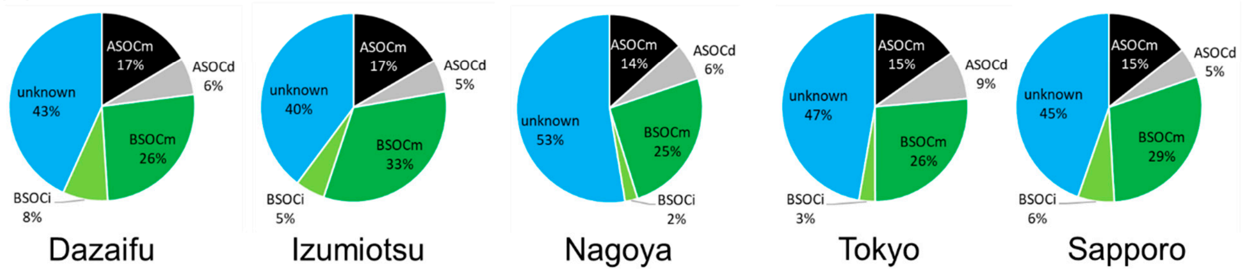


Figure 4. Fractions of mono-aromatic, di-aromatic, monoterpene-derived, and isoprene-derived SOCs (ASOCm, ASOCd, BSOCm, and BSOCi, respectively) in WSOC during (**a**) spring and (**b**) summer at each site.

SOCs estimated from previous studies using the same BSOA tracers used herein at urban sites in China [61–64] are also shown in Table 6. The SOCs in China listed in Table 6 were recalculated using the same method used in this study; the factors and organic tracers in the calculations were used as described in Section 2.2. In summer, the mono-aromatic and isoprene-derived SOCs were higher in China than in Japan, whereas the monoterpene-derived SOCs exhibited higher values in Japan than in China. Even though the di-aromatic SOC values were not available because phthalic acid has not been measured in many studies in China, the ratio of ASOC (sum of mono-aromatic and di-aromatic SOCs) to BSOC (sum of monoterpene-derived and isoprene-derived SOCs) (A/B) was higher in China than in Japan. The annual average concentration of atmospheric toluene in the 2015 fiscal year was 7.2 μg/m^3 in Japan. In Izumiotsu, Nagoya, and Tokyo, the concentrations were 9.5 μg/m^3, 9.1 μg/m^3, and 9.7 μg/m^3, respectively [65–67]. The sum of benzene, toluene, ethylbenzene, and xylenes, which are representative precursors of ASOA, was 15 μg/m^3 in Tokyo in 2015 [67] and was 38.94 ± 27.83 μg/m^3 (range: 6.40–132.09 μg/m^3) in urban areas in China [68]. These values support the notion that the A/B ratio was higher in China than in Japan because of the differences in the precursor VOC concentrations between Japan and China. To reveal the SOA characteristics in detail, simultaneous observations of organic tracers with their precursor VOCs need to be conducted.

4. Conclusions

To evaluate the characteristics of organic tracers and the impact of SOAs on WSOC in PM$_{2.5}$ at urban sites in Japan, we measured 17 organic tracer compounds using GC–MS. Within each category, SOA tracers were often significantly correlated in spring and summer, except pinonic acid in monoterpene-derived SOA tracers. Moreover, most anthropogenic, monoterpene-derived, and isoprene-derived SOA tracers showed meaningful correlations with PO in spring and summer. WSOC was also significantly correlated with ASOA and monoterpene-derived SOAs during spring and with the three SOA groups during summer. These results indicate that the WSOC concentrations were meaningfully influenced by the generation of SOAs, such as ASOAs and monoterpene-derived SOAs during spring and the three SOA groups during summer. The seasonal means of the P/M ratio demonstrate that the monoterpene-derived SOAs were more aged in summer. In addition, the relationship of the seasonal mean values of the 2MGA/MTs ratio with NO$_x$ indicates that the higher seasonal concentrations of 2-methylthreitol and 2-methylerythritol during summer were due to increasing emission amounts of isoprene. The total estimated SOCs, including mono-aromatic, di-aromatic, monoterpene-derived, and isoprene-derived SOCs, according to the SOA-tracer method, could explain the seasonal WSOC fractions at each site of from 39% to 63% in spring and from 46% to 54% in summer. Remarkably, monoterpene-derived and mono-aromatic SOCs accounted for most of the total estimated SOCs in both spring (85–93%) and summer (75–82%) at each site. These results indicate that SOAs have a significant impact on WSOC concentrations at urban sites in Japan.

When considering plans to reduce the $PM_{2.5}$ concentration, it is necessary to investigate the anthropogenic precursor VOCs that have a large impact on anthropogenic SOA formation and to determine their formation mechanisms. Recently, new secondary organic products of ASOAs and biomass-burning-derived SOAs, such as nitroaromatic hydrocarbons, have been detected and quantified in $PM_{2.5}$ [7,9,10,69]. Nitroaromatic hydrocarbons are produced in the presence of NO_x via the insertion of a nitro group into aromatic VOCs. To understand SOAs in urban areas where NO_x emissions are abundant, further detailed studies using these compounds as useful tracers to quantify SOAs are necessary. Furthermore, future works should aim to compare and refine the SOC estimated using other methods, such as the OC/EC tracer method and the receptor model.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/atmos12050579/s1, Table S1. Sampling dates during spring and summer at each sampling site. Table S2. Correlations among OC, WSOC, and PO during (a) spring and (b) summer at each sampling site. Table S3. Correlations among organic tracers during (a) spring and (b) summer at each sampling site. Table S4. Correlations between PO and SOA tracers from all sampling sites during (a) spring and (b) summer. Figure S1. 72 h backward trajectories at (a) Dazaifu, (b) Osaka, (c) Nagoya, (d) Tokyo, and (e) Sapporo from 21 April to 30 April 2014. Figure S2. Variations in ASOA tracers (DHOPA, phthalic acid (PhA), and 4-methylphthalic acid (4MPhA)) at (a) Dazaifu, (b) Osaka, (c) Nagoya, (d) Tokyo, and (e) Sapporo from 21 April to 30 April 2015.

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