

**Seasonal variations
of WSOC in a
deciduous forest**

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Seasonal variations of stable carbon isotopic ratios and biogenic tracer compounds of water-soluble organic aerosols in a deciduous forest

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Abstract

To investigate the seasonal changes in biogenic water-soluble organic carbon (WSOC) aerosols in a boreal forest, aerosol samples were collected continuously in the canopy of a deciduous forest in Northern Japan during 2009–2010. Stable carbon isotopic ratios of WSOC ($\delta^{13}\text{C}_{\text{WSOC}}$) in aerosols exhibited a distinct seasonal cycle, with lower values from June through September ($-25.5 \pm 0.5\%$). This cycle follows the net CO_2 exchange between the forest ecosystem and the atmosphere, indicating that $\delta^{13}\text{C}_{\text{WSOC}}$ likely reflects the biological activity at the forest site. WSOC concentrations showed the highest values in early summer and autumn. Positive matrix factorization (PMF) analysis indicated that the factor in which biogenic secondary organic aerosols (BSOAs) dominated accounted for $\sim 40\%$ of the highest concentrations of WSOC, where BSOAs mostly consisted of α -/ β -pinene SOA. In addition, primary biological aerosol particles (PBAPs) made similar contributions ($\sim 57\%$) to the WSOC near the canopy floor in early summer. This finding indicates that the production of both primary and secondary WSOC aerosols is important during the growing season in a deciduous forest. The methanesulfonic acid (MSA) maximum was also found in early summer and had a distinct vertical gradient with larger concentrations near the canopy floor. Together with the similar vertical gradients found for WSOC and $\delta^{13}\text{C}_{\text{WSOC}}$ as well as the α -/ β -pinene SOA tracers, our results indicate that the forest floor, including ground vegetation and soil, acts as a significant source of the WSOC within a forest canopy at the study site.

1 Introduction

Forest ecosystems act as a major sink of atmospheric CO_2 and a source of atmospheric organic aerosols. Forest vegetation contributes substantially to emissions of a variety of biogenic volatile organic compounds (BVOCs) via processes that are closely linked to photosynthesis. In boreal forests, photosynthesis is inhibited in winter

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and occurs predominantly in sunlight during the growing season. Although forest–atmosphere interactions are potentially important for climate change assessments, such interactions are complex and poorly represented in current global models.

Newly formed particles in forested areas constitute a large fraction of water-soluble organic carbon (WSOC) (e.g., Cavalli et al., 2006; Hallquist et al., 2009), which can significantly alter the hygroscopic property of aerosols and act as cloud condensation nuclei (CCN). Nucleation events were frequently observed in a European boreal forest, and investigation of these events demonstrate a straightforward relation between monoterpene emissions and gas-to-particle formation (Tunved et al., 2006). However, previous observations have often been made in limited periods during intensive campaign studies. Long-term continuous measurements in forested regions are lacking and simultaneous ecosystem-scale measurements of WSOC and CO₂ fluxes over several months to years are particularly scarce. Clarifying the seasonal evolution of WSOC in relation to forest biological activity is crucial for a better understanding of the WSOC formation processes in forests. Besides biogenic secondary organic aerosol (BSOA) fractions, primary biological aerosol particles (PBAPs) (Medeiros et al., 2006; Rogge et al., 2007; Jia et al., 2010) contribute to the budget of WSOC in aerosols, although this budget is still poorly characterized. In addition, the relative importance of the canopy floor within forests is not well understood in terms of WSOC formation.

In this paper, we present seasonal changes in biogenic WSOC within the canopy of a broadleaf deciduous forest over an 18-month period. We provide measurements of WSOC and the stable carbon isotopic ratios of the WSOC ($\delta^{13}\text{C}_{\text{WSOC}}$) in relation to the net CO₂ exchange between the forest ecosystem and the atmosphere. We also present the relative contributions of potential sources to WSOC formation in the forest canopy using $\delta^{13}\text{C}_{\text{WSOC}}$, BSOA tracers, and PBAP tracers. On the basis of these data sets, we discuss the relative importance of the canopy floor in WSOC formation at a deciduous forest site.

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2 Experimental

2.1 Aerosol sampling

Aerosol sampling was conducted at the Sapporo forest meteorology research site (42°59' N, 141°23' E, 182 m a.s.l.), which is a secondary hardwood forest site located in the western part of Hokkaido, the northernmost major island of Japan. The experimental site is covered with broadleaf deciduous trees in a transitional stage from mature birch (*Betula platyphylla*) to climax species, mainly Mizunara oak (*Quercus crispula*). Needle-leaf evergreen trees are also found in the surrounding area. The understory consists of evergreen Sasa bamboo (*Sasa kurilensis* and *Sasa senanensis*), which widely covers the ground surface. Nakai et al. (2003) examined the seasonal variations in the leaf area index (LAI) at this forest site, showing that the initial foliating period is completed by the end of June, after which the LAI remains almost constant until September. They also reported that the evolution pattern of the LAI at this site is similar to that at other temperate deciduous forests (e.g., Greco and Baldocchi, 1996). The soil is loamy, originating from volcanic ash. The mean canopy height at the site is approximately 20 m (Nakai et al., 2003). Snow cover reaches approximately 1 m in depth and continues for more than 120 days per year, from December to mid-April.

Total suspended particulate (TSP) samplings were conducted continuously using high-volume air samplers. The samples were collected using prebaked quartz fiber filters (25 × 20 cm) at a flow rate of 40 m³ h⁻¹ at two levels above the canopy floor: ~ 2 m (June 2009–December 2010) and ~ 15 m (June 2010–December 2010). Each aerosol sample was integrated usually over a 1-week period, corresponding to a sampled air volume of approximately 6700 m³. Local meteorological parameters were measured every 10 min by a weather transmitter (WXT-510, Vaisala, Helsinki, Finland).

Figure 1 shows the location of the sampling site and the surrounding area, as well as the observed frequencies of local wind directions with wind speed greater than 0.5 m s⁻¹ at the sampling site. The predominant local wind direction in summer and autumn (May–October) was from the south to southwest, corresponding to the forested

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area. Moreover, the meteorological data show that the 68 % of the local wind speed was $< 0.5 \text{ m s}^{-1}$. Consequently, the majority of aerosol sampled during this period was likely influenced by emissions from forested areas. In contrast, fractions of air transported from the northwest (sea and urban region) were larger in winter and spring (November–April), with 64 % of the local wind speed $> 0.5 \text{ m s}^{-1}$.

2.2 Chemical analysis

To determine the WSOC, a filter cut of 1.54 cm^2 was extracted with ultrapure Milli-Q water using an ultrasonic bath. The total extracts were then filtrated with a disc filter (Millex-GV, $0.22 \mu\text{m}$, Millipore, Billerica, MA, USA) followed by injection of dissolved OC in the extracts into a total organic carbon analyzer (Model TOC-Vcsh, Shimadzu, Kyoto, Japan) (Miyazaki et al., 2011).

The stable carbon isotopic ratio ($\delta^{13}\text{C}$) is a powerful tool for source determination based on the distinctive signals of different aerosol carbon fractions. The most common carbon isotopic application for aerosol is for total carbon (TC) (e.g., Cachier et al., 1986; Turekian et al., 2003). In contrast, very few studies have used the $\delta^{13}\text{C}$ of WSOC for source apportionment (Fisseha et al., 2009; Kirillova et al., 2010). For the determination of $\delta^{13}\text{C}_{\text{WSOC}}$, a filter (14.13 cm^2) for each sample was acidified to pH 2 with hydrochloric acid (HCl) to remove inorganic carbon prior to extraction. The samples were then dried with a nitrogen stream for approximately 2 h. WSOC was extracted from the decarbonated filters in 20 ml of Milli-Q water using the same method as described above for measuring the WSOC concentration. The extracted samples were concentrated, and $40 \mu\text{l}$ of each sample was transferred to be absorbed onto 10 mg of pre-combusted Chromosorb in a pre-cleaned tin cup. The $\delta^{13}\text{C}_{\text{WSOC}}$ was then measured using an elemental analyzer (EA) (NA 1500, Carlo Erba, Milan, Italy) interfaced to an isotope ratio mass spectrometer (Finnigan MAT Delta Plus, Thermo Finnigan, San Jose, CA, USA) (Kawamura et al., 2004). The recoveries of WSOC using chemical standards (oxalic acid and Suwannee River fulvic acid) and ambient aerosols after the analytical steps were 90 % and 82 %, respectively.

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We also determined the concentrations of BSOA tracers for α -/ β -pinene (3-methyl-1,2,3-butanetricarboxylic acid; 3-MBTCA, 3-hydroxyglutaric acid; 3-HGA, pinic acid, and pinonic acid) and those for isoprene (2-methylerythritol and 2-methylthreitol). In addition, sucrose and trehalose were identified as possible tracers for PBAPs. Briefly, a filter cut was extracted with dichloromethane/methanol and the –COOH and –OH functional groups in the extracted samples were converted to TMS esters and TMS ethers, respectively. The TMS derivatives were then analyzed for the above compounds using a capillary gas chromatograph (HP GC6890N, Hewlett-Packard, Palo Alto, CA, USA) coupled to a mass spectrometer (5973 MSD, Agilent, Santa Clara, CA, USA) (Fu et al., 2009).

For inorganic ions, another filter cut was extracted with Milli-Q water, followed by filtration to determine the major ions by ion chromatography.

2.3 Net ecosystem exchange of CO₂

Besides the aerosol measurements, we derived the net CO₂ exchange between the forest ecosystem and the atmosphere (NEE) to characterize the carbon content in the aerosols in terms of forest biological activity. NEE is defined as the sum of the eddy covariance fluxes at 28.5 m height above the canopy and the change in CO₂ storage in the volume from the ground to the height of the eddy covariance system. Negative values of NEE indicate net uptake of CO₂ by the forest ecosystem. Further details of the NEE derived here are given elsewhere (Nakai et al., 2003).

3 Results and discussion

3.1 Temporal variations of WSOC and $\delta^{13}\text{C}_{\text{WSOC}}$

Figure 2a and b shows the time series of WSOC concentrations and $\delta^{13}\text{C}_{\text{WSOC}}$ near the canopy floor over an 18-month period. The WSOC concentrations peaked

in early summer (May–June) and autumn (September–October), with averages of $2.9 \pm 1.5 \mu\text{g C m}^{-3}$ and $1.7 \pm 0.6 \mu\text{g C m}^{-3}$, respectively. To our knowledge, this is the first report on a full annual cycle of WSOC and $\delta^{13}\text{C}_{\text{WSOC}}$ in forest aerosols. The $\delta^{13}\text{C}_{\text{WSOC}}$ exhibited a pronounced seasonal cycle, with higher ratios during
5 December–April and lower ratios during June–September. The average $\delta^{13}\text{C}_{\text{WSOC}}$ in summer was $-25.6 \pm 0.7\%$, which is within the range (between -25 and -27%) of standard compounds for biogenic tracers (*cis*-pinonic acid and sucrose) and of ambient WSOC aerosols mostly of contemporary biogenic C3 plant origin (Kirillova et al., 2010). The $\delta^{13}\text{C}_{\text{WSOC}}$ value is also similar to those of plant wax *n*-alcohols and *n*-acids
10 in aerosols largely influenced by the temperate North American biosphere (Conte and Weber, 2002). Our results indicate a dominant input of precursor molecules from C3 plants to WSOC from May to October, as generally expected in boreal forest. On the basis of the seasonal cycle of the $\delta^{13}\text{C}_{\text{WSOC}}$, the period during which the highest WSOC concentrations were obtained can be characterized as the growing season for
15 forest vegetation at this site.

Figure 2b also presents the time series of NEE and $\delta^{13}\text{C}_{\text{WSOC}}$. In 2010, uptake of CO_2 due to photosynthesis by the forest ecosystem began in May and increased (corresponding to negative values of NEE) rapidly to a maximum from late June through July. The estimated respiration increased after the disappearance of snow cover in
20 April (data not shown). The seasonal cycle of $\delta^{13}\text{C}_{\text{WSOC}}$ closely followed that of NEE ($r^2 = 0.44$). Even though NEE can be interpreted as whole-ecosystem CO_2 uptake and may not be fully comparable to our $\delta^{13}\text{C}_{\text{WSOC}}$, the covariant temporal trends of $\delta^{13}\text{C}_{\text{WSOC}}$ and NEE suggest that $\delta^{13}\text{C}_{\text{WSOC}}$ was closely linked to the CO_2 uptake by forest biological activity at this site. This indicates that the aerosols collected here may
25 be representative of the studied forest area.

Notably, the seasonal variation of methanesulfonic acid (MSA) also showed a maximum during May and July (Fig. 2c). Possible sources of this MSA maximum will be discussed later in Sect. 3.3.

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3.2 Source apportionment of WSOC using positive matrix factorization

3.2.1 Source profiles

To better understand the seasonal changes in the contribution of possible sources to the observed WSOC, positive matrix factorization (PMF) (Paatero and Tapper, 1994) was applied. PMF can be used to identify underlying covariance among chemical parameters. The PMF analysis was performed for the collected samples using tracer compounds for BSOA, PBAP, and other biologically derived tracer compounds as well as inorganic species.

The analysis resulted in five interpretable factors, which were characterized by the enrichment of each tracer compound and reproduced more than 92 % of the measured WSOC. Figure 3 shows composition profiles for the five factors resolved by PMF. Factor 1 was dominated by 2-methylerythritol (i.e. 86 % of 2-methylerythritol is in factor 1) and 2-methylthreitol (87 %), both of which are isoprene-SOA tracers. Factor 2 was characterized by 3-HGA (49 %), pinic acid (38 %), and 3-MBTCA (34 %), indicating that WSOC was significantly influenced by α -/ β -pinene SOA. On the basis of these characteristics of each source profile, factors 1 and 2 are referred to here as “isoprene-SOA-rich WSOC” and “ α -/ β -pinene-SOA-rich WSOC”, respectively.

Factor 3 was dominated by sucrose (89 %), whereas factor 4 was characterized by trehalose (57 %). Saccharides have recently been proposed as unique molecular tracers for PBAPs such as spores, pollens, and fungi (e.g., Medeiros et al., 2006). Sucrose is an important primary saccharide of pollen grains (Pacini, 2000). On the other hand, trehalose is known to be a fungal metabolite as well as a stress protectant for the soil microbial community, and has been proposed as a marker compound for fungitive dust from biologically active surface soils (Rogge et al., 2007). Factors 3 and 4 are difficult to convincingly attribute to a specific source, given the possibility that these saccharides originated from either PBAPs or other biologically derived sources such as resuspended soil dust and associated biota (e.g., Graham et al., 2003). However, each factor showed different contributions to WSOC in terms of seasonal characteristics, as

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discussed below. Thus, these two source factors are labeled here as “sucrose-rich WSOC” and “trehalose-rich WSOC,” respectively. Factor 5 showed enhanced contributions of both Na^+ and anthropogenic tracers (e.g., hopanes), which could be a mixture of sea salt and anthropogenic aerosols transported from upwind regions.

3.2.2 Relative contributions of each factor to WSOC

Figure 4 shows the seasonal changes in the contribution of each factor to WSOC as resolved by PMF. Average concentrations and ratios of each parameter are also summarized in Table 1. In early summer, α -/ β -pinene-SOA-rich factor 2 accounted for 36% of WSOC, whereas isoprene-SOA-rich factor 1 contributed only 4%. Factor 2 was also a significant contributor to WSOC in autumn (35%), as expected from the peaks of α -/ β -pinene SOA tracers in the two seasonal categories (Table 1). Among the measured α -/ β -pinene SOA tracers, 3-HGA showed the highest concentrations (2.1–9.3 ng m^{-3}) throughout the study period, followed by pinic acid. Conversely, factor 3 contributed 35% of WSOC in early spring but was not apparent in autumn. The sucrose peak obtained in early summer (Table 1) is generally in good agreement with previous reports of the spring/early summer maxima of sucrose at boreal forests and rural sites (e.g., Medeiros et al., 2006; Jia et al., 2010). The large fraction of sucrose-rich factor 3 suggests that pollen or pollen fragment sources contributed significantly to WSOC in this season. Furthermore, trehalose-rich factor 4 accounted for 24% and 50% of WSOC in early summer and autumn, respectively. This implies that biologically derived sources such as resuspended soil dust and associated biota contributed to WSOC in early summer and autumn. The relative enhancement of WSOC in autumn was likely due to enhanced contributions from microbially degraded materials during the period of leaf senescence and decay in this season (Nakai et al., 2003). Given that factors 3 and 4 are both associated with the PBAPs fractions of WSOC, PBAPs can account for 57% and 50% of the WSOC peaks in the two seasons, respectively. In summary, the present results indicate that at this forest site, the SOA formations associated mainly with α -/ β -pinene oxidation and the primary emissions from biological

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sources contribute almost equally to the peak of WSOC in the growing season of early summer as well as in autumn.

The isoprene-SOA-rich factor (factor 1) had different seasonality, with peaks in mid-summer (July–August) accounting for 40 % of WSOC. This seasonal pattern is mainly attributable to the fact that isoprene originates only from photosynthetic tissues (i.e., shoots of ground vegetation) (Guenther et al., 2006); emissions are typically highest in midsummer (Aaltonen et al., 2011), when photosynthesis becomes most active. Note that the average WSOC was relatively low in July both in 2009 and 2010, even though the $\delta^{13}\text{C}_{\text{WSOC}}$ values indicate a dominant contribution of precursor molecules from C3 plants and intense photochemical activity. This may have been partly caused by an enhanced scavenging of aerosols because relatively large amounts of rainfall ($> 200 \text{ mm month}^{-1}$) were recorded (Fig. 2d). Nevertheless, the PMF analysis indicates that biogenic SOA production (46 % from isoprene SOA and 54 % from α -/ β -pinene SOA) was the dominant source of WSOC in the midsummer period.

3.3 Possible sources of MSA

As described in Sect. 3.1, MSA exhibited a distinct seasonal variation with maximum values during May and July as shown in Fig. 2c. The concentrations of MSA ($9\text{--}95 \text{ ng m}^{-3}$) are similar to the ranges reported in previous studies ($\sim 10\text{--}100 \text{ ng m}^{-3}$) in marine aerosols (e.g., Ayers and Gras, 1991). MSA is formed by the photooxidation of dimethylsulfide (DMS), which is abundantly found in the marine atmosphere, although measurements of MSA in terrestrial regions are very limited (e.g., Lukács et al., 2009).

The increase in the MSA concentrations may have been due to either enhanced contributions of marine air masses advectively transported from the sea or the oxidation of terrestrial biogenic DMS (Lamb et al., 1987). In fact, emissions of sulfur gases (DMS, H_2S , and CS_2) have been reported for plant canopies (deciduous trees and pines) (Andreae et al., 1990) and mollisol and histisol soil (Lamb et al., 1987). Figure 5 shows vertical profiles of several parameters within the forest canopy in summer, autumn, and winter. The difference in the MSA at two heights is statistically

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significant in summer and autumn (Fig. 5a): the concentration was higher near the canopy floor ($42 \pm 16 \text{ ng m}^{-3}$) than at the 15-m level ($30 \pm 15 \text{ ng m}^{-3}$) throughout these seasons. The vertical gradient of MSA indicates an upward mass flux. Similar vertical profiles were also found for WSOC in summer and autumn (Fig. 5b). In contrast, MSA showed an anti-correlation with Na^+ during summer and autumn, with enhanced concentrations occurring in the two seasons when $\delta^{13}\text{C}_{\text{WSOC}}$ decreased (Fig. 5c) near the ground. Moreover, according to the analysis of the local wind analysis, the majority of the observed aerosols in summer and autumn were likely influenced by emissions from major forested regions rather than marine sources, as shown in Fig. 1. In combination, these findings indicate that the enhanced concentrations of MSA in summer were most likely due to production from DMS that originated from the forest floor rather than transport of MSA from oceanic regions.

3.4 Implications for WSOC production near the forest floor

Negative vertical gradients were also found for the α -/ β -pinene SOA tracers determined here (e.g., 3-HGA shown in Fig. 5d) both in summer and autumn. The average concentrations of 3-HGA were about two times higher near the canopy floor than at the 15-m level in the two seasons. Aaltonen et al. (2011) recently reported that BVOC emissions from a boreal forest, mostly consisting of monoterpenes, also peaked in early summer and autumn. They attributed the seasonal variations to changes in the amount and types of litter, soil microbial activity, and physiological stages of plants, pointing out that the boreal forest floor can be a significant source of BVOC. Furthermore, MSA showed a statistically significant correlation with 3-HGA ($r^2 = 0.50$) and 3-MBTCA ($r^2 = 0.55$) in our data. The result indicates that the canopy floor in a boreal forest is likely a significant source of WSOC in summer and autumn. It should be noted that turbulent exchange of air between the forest and the atmosphere above can partly cause the lower concentrations of WSOC and the other tracers at the 15-m level. However, the vertical gradient of $\delta^{13}\text{C}_{\text{WSOC}}$ was insignificant (Fig. 5c) in the two seasons as well as in winter. Moreover, several samples taken only at night, when the forest

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and the air above the canopy would be decoupled, also showed the significant vertical gradient of WSOC (data not shown). These results support possible sources near the canopy floor.

In addition to the source strength, photochemical activity is also an important factor to control the concentrations of secondarily formed WSOC. Zhang et al. (2010) recently found an Arrhenius-type correlation between the 3-MBTCA concentration and inverse temperature with a temperature range of 275–300 K based on ambient aerosol samples in Central Europe. They suggested that the temperature dependence of 3-MBTCA is largely due to enhanced photochemical production by hydroxyl radicals (OH), indicating that 3-MBTCA can be used as a tracer for chemical aging of BSOA by OH. Considering that 3-MBTCA is formed by OH-initiated oxidation of *cis*-pinonic acid (PA) (Szmigielski et al., 2007), the 3-MBTCA/PA ratio can be an indicator of photochemical aging of BSOA. In our samples, the 3-MBTCA/PA ratio was highest in early summer (2.59) compared with other seasons (0.72–2.38) (Table 1). This result implies that photochemical activity as well as intense emissions of BVOC from the canopy floor can contribute to an increase in WSOC concentrations in early summer.

3.5 Possible sources of WSOC in winter

In winter, a factor in which a mixture of sea salt and anthropogenic aerosols dominated was a major contributor to WSOC (~56–83%). This is consistent with the $\delta^{13}\text{C}_{\text{WSOC}}$, which exhibited higher values ($-21.9 \pm 0.7\text{‰}$) from December through April, similar to a typical range of marine sources (-20‰ to -22‰) (Miyazaki et al., 2011). Additionally, the local wind direction supports that the air mass was influenced by the upwind marine region during this period (Fig. 1). These results indicate a predominant contribution of marine aerosols from an upwind oceanic region during this period. Note that some minor isotopic fractionation processes for $\delta^{13}\text{C}$ cannot be ruled out a priori. However, reported isotopic effects on $\delta^{13}\text{C}$ during aerosol formation and reactions relevant to $\delta^{13}\text{C}_{\text{WSOC}}$ are on the order of 0–2‰ (Rudolph et al., 2003), which is lower than the difference in the $\delta^{13}\text{C}_{\text{WSOC}}$ between summer and winter ($\Delta \sim 4\text{‰}$). Therefore,

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such processes would not have significantly affected the source apportionment ability of $\delta^{13}\text{C}_{\text{WSOC}}$ in this study.

The vertical gradients of WSOC in winter were fairly weak compared to those in other seasons, likely due to the snow coverage from mid-December until March at the site. In boreal forest soils, lower temperature and snow cover in winter may suppress, but not completely halt, microbial activity (Kähkönen et al., 2001). The current results imply that the forest floor (ground vegetation and/or soil) acts as a significant source of WSOC within the forest canopy.

4 Conclusions

This paper presents the seasonal changes in biogenic WSOC in the canopy of a deciduous forest based on the aerosol samples collected in 2009–2010. The $\delta^{13}\text{C}_{\text{WSOC}}$ in aerosols exhibited a distinct seasonal cycle, with depleted ratios from June through September ($-25.5 \pm 0.5\%$). The $\delta^{13}\text{C}_{\text{WSOC}}$ in summer and autumn is within that reported for contemporary biogenic C3 plant origin, indicating a dominant input of precursor molecules from C3 plant ecosystems to WSOC. The seasonal cycle of $\delta^{13}\text{C}_{\text{WSOC}}$ corresponds to that of the CO_2 uptake by the forest ecosystem from the atmosphere, indicating that $\delta^{13}\text{C}_{\text{WSOC}}$ reflected the degree of biological activity at this forest site.

The WSOC concentrations showed peaks in early summer and autumn. PMF analysis indicated that factors in which BSOA (mostly α -/ β -pinene SOA) dominated ($\sim 40\%$) and PBAPs dominated ($\sim 57\%$) made similar contributions to the maximum WSOC near the canopy floor in early summer. The findings suggest that the growing season of forest vegetation is important for both primary and secondary formation of WSOC in a deciduous forest. In contrast, the PMF analysis indicated that biogenic SOA production was the dominant source of WSOC in midsummer. We found that MSA concentrations were also highest in early summer, with a distinct vertical gradient. Together with the similar vertical gradients of WSOC and $\delta^{13}\text{C}_{\text{WSOC}}$ as well as the α -/ β -pinene SOA tracers, our results imply that the forest floor, including ground vegetation and soil, is

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a significant source of the WSOC within a forest canopy.

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Table 1. Averages with standard deviations of each parameter near the forest floor in each season during 2010.

	Jan–Apr (Winter–Spring)	May–Jun (Early Summer)	Jul–Aug (Summer)	Sep–Oct (Autumn)	Nov–Dec (Winter)
WSOC ($\mu\text{g C m}^{-3}$)	1.0 ± 0.3	2.9 ± 1.5	1.5 ± 0.4	1.7 ± 0.6	1.2 ± 0.4
$\delta^{13}\text{C}_{\text{WSOC}}$ (‰)	−21.9 ± 0.7	−24.0 ± 0.8	−25.6 ± 0.7	−24.7 ± 0.8	−22.6 ± 0.1
MSA (ng m^{-3})	30 ± 8	64 ± 15	52 ± 23	30 ± 7	27 ± 12
α -/ β -Pinene SOA (ng m^{-3})					
3-HGA ^a	2.1 ± 0.9	9.3 ± 2.0	8.7 ± 2.8	9.1 ± 4.9	3.4 ± 2.8
pinic acid	1.6 ± 0.5	4.4 ± 1.2	4.0 ± 1.0	5.2 ± 1.8	2.6 ± 1.3
3-MBTCA ^b	0.1 ± 0.2	1.1 ± 0.3	1.3 ± 0.5	1.3 ± 0.7	0.4 ± 0.4
pinonic acid	0.2 ± 0.1	0.4 ± 0.2	0.6 ± 0.2	0.6 ± 0.2	0.5 ± 0.4
Isoprene SOA (ng m^{-3})					
2-methylerythritol	0.1 ± 0.1	3.9 ± 3.8	24.8 ± 14.1	16.2 ± 12.3	0.2 ± 0.1
2-methylthreitol	0.1 ± 0.1	1.6 ± 1.4	6.7 ± 3.1	4.0 ± 4.3	0.1 ± 0.1
Sucrose (ng m^{-3})	25.0 ± 53.9	176.5 ± 220.1	2.8 ± 2.1	3.2 ± 1.6	1.0 ± 0.4
Trehalose (ng m^{-3})	0.7 ± 0.3	173.4 ± 84	128.5 ± 93.0	188.3 ± 122.0	1.7 ± 1.2
nss-SO ₄ ²⁻ ($\mu\text{g m}^{-3}$)	3.3 ± 1.2	4.6 ± 2.0	3.8 ± 2.0	2.5 ± 1.6	3.0 ± 0.6
Ambient Temperature (°C)	−1.7 ± 4.4	14.1 ± 4.7	21.8 ± 2.0	14.0 ± 5.5	1.5 ± 4.6

^a 3-HGA: 3-hydroxyglutaric acid.

^b 3-MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid.

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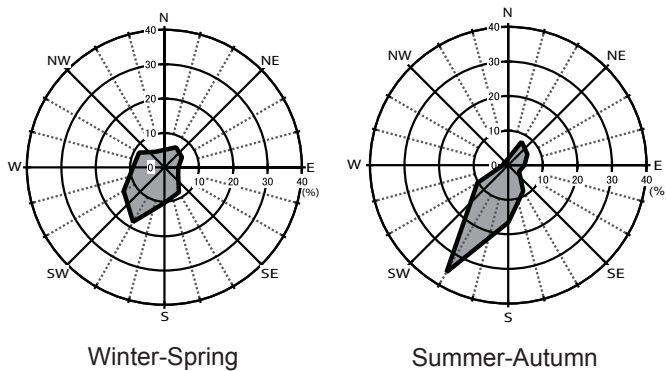
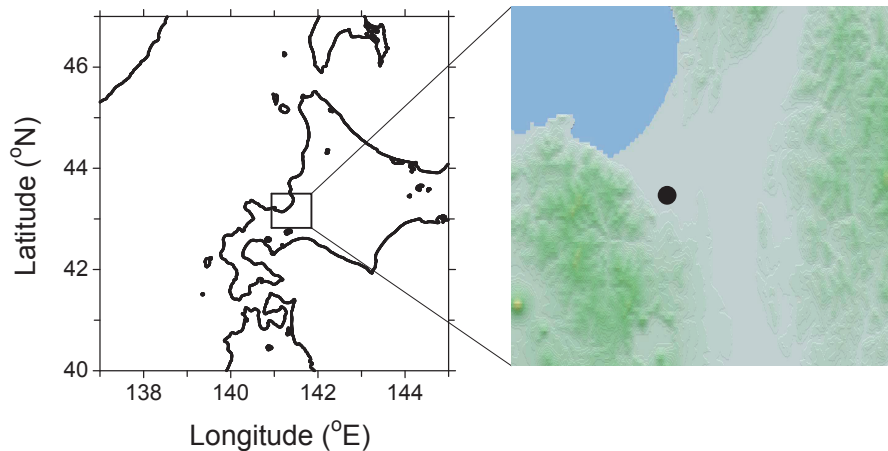


Fig. 1. Location of the sampling site (the Sapporo forest meteorology research site). Also shown is the observed frequency of local wind directions with wind speed $> 0.5 \text{ m s}^{-1}$ in winter–spring (November–April) and summer–autumn (May–October).

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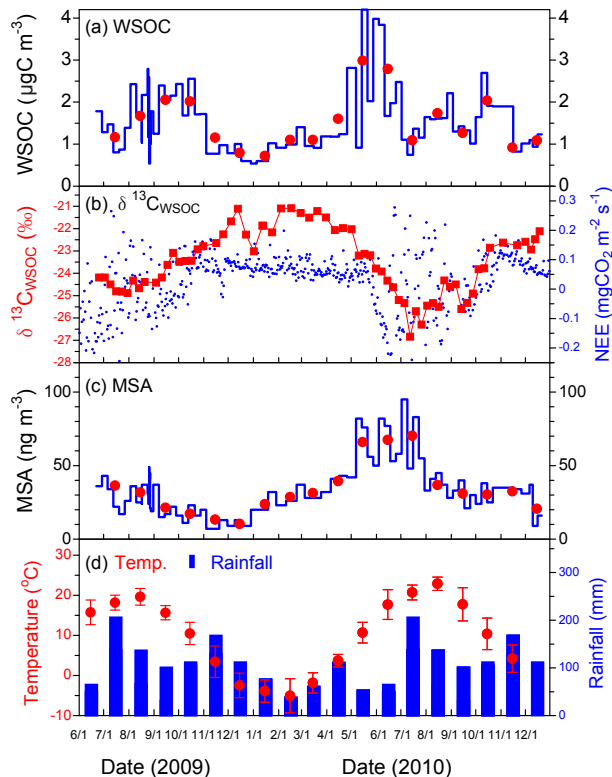


Fig. 2. Temporal variations of **(a)** WSOC, **(b)** $\delta^{13}\text{C}_{\text{WSOC}}$ (red solid squares) and NEE (blue dots), **(c)** MSA, and **(d)** ambient temperature and rainfall near the ground surface at a boreal forest site during the period June 2009–December 2010. The red solid circles in **(a)**, **(c)**, and **(d)** indicate average monthly values. Negative values of NEE in **(b)** indicate uptake of CO_2 by the forest ecosystem.

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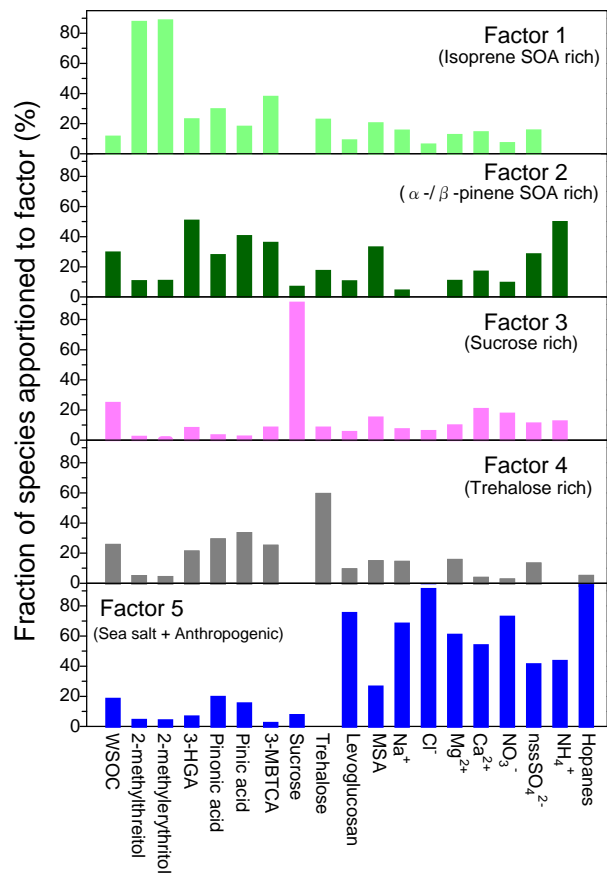


Fig. 3. Five compositional WSOC source factors isolated by PMF.

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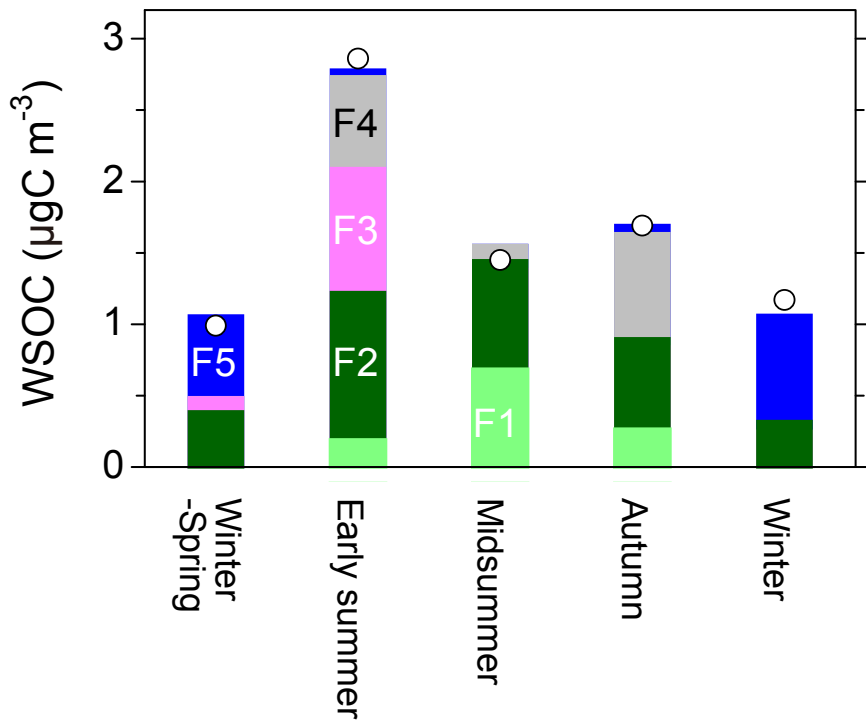


Fig. 4. Estimated relative contributions of different sources to WSOC concentrations resolved by PMF in each season. Open circles indicate the average concentrations of the measured WSOC.

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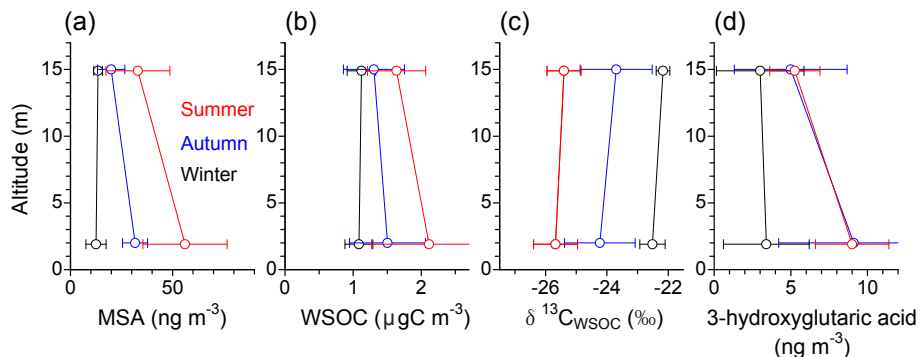


Fig. 5. Vertical profiles of (a) MSA, (b) WSOC, (c) $\delta^{13}\text{C}_{\text{WSOC}}$, and (d) 3-hydroxyglutaric acid (HGA) in summer (June–August 2010), autumn (September–November 2010), and winter (December 2010) at the study site. Values shown are averages with standard deviations at two heights.

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