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Key Points:

- Seasonal cycles of WSON aerosol in a forest were studied for possible sources
- Formation of WSON in the forest is linked to biogenic sources
- Multiple sources of WSON in the forest dominate over others in summer and autumn

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Seasonal cycles of water-soluble organic nitrogen aerosols in a deciduous broadleaf forest in northern Japan

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Abstract The seasonal variations in aerosol water-soluble organic nitrogen (WSON) concentrations measured in a deciduous forest canopy over an approximately 30 month period were investigated for possible sources in the forest. The WSON concentrations (average $157 \pm 127 \text{ ng N m}^{-3}$) and WSON/water-soluble total nitrogen mass fractions (average $20 \pm 11\%$) in the total suspended particulate matter exhibited a clear seasonal cycle with maxima in early summer. The WSON mass was found to reside mostly in the fine-mode size range ($D_p < 1.9 \mu\text{m}$) during the summer months. WSON was positively correlated with oxidation products of α -pinene and isoprene with similar size distributions, suggesting that secondary formation from biogenic hydrocarbon precursors is a plausible source for WSON in summer. In contrast, the majority of WSON in autumn was associated with coarse fraction ($D_p > 1.9 \mu\text{m}$), which was similar to the size distributions of sugar compounds, indicating that the major WSON sources in autumn are associated with primary biological emissions. The vertical differences in WSON concentrations suggest that the water-soluble organic aerosol is enriched with nitrogen below the canopy level relative to the forest floor. The WSON concentration increased with enhanced hydrogen ion concentrations in aerosol in the early summer, indicating that aerosol acidity associated with anthropogenic sources outside the forest likely plays an important role in the formation of WSON in that season. The study suggests that multiple sources of WSON within the forest canopy may dominate over others in specific seasons, providing insights into WSON formation processes in forest environments.

1. Introduction

Organic nitrogen (ON) in aerosols affects the formation, chemical transformations, hygroscopicity, and acidity of organic aerosols (OA) as well as global biogeochemical cycles of nitrogen. ON composition ranges from small semivolatile molecules through oligomers to proteins and other macromolecules [e.g., Cornell *et al.*, 2001; Mace *et al.*, 2003; Wang *et al.*, 2010; Cape *et al.*, 2011]. Besides anthropogenic sources, ON from terrestrial biological sources has been poorly characterized and largely unknown [Kanakidou *et al.*, 2012]. Aerosol ON from terrestrial vegetation sources includes biological particles directly emitted from soil, vegetation, pollen, and bacteria. The other candidate for ON source is secondary production, such as reaction of the nitrate radical (NO_3) with biogenic volatile organic compounds (VOCs). ON produced from NO_3 oxidation of isoprene and monoterpenes has been suggested as a substantial source of biogenic secondary OA (SOA) [Ng *et al.*, 2008; Fry *et al.*, 2009].

Recent estimates with regard to nitrated and sulfated (i.e., nitrooxy organosulfates) derivatives of isoprene suggest that isoprene oxidation may be an important contributor to total organic particulate mass, particularly during the summer [e.g., Kleindienst *et al.*, 2007]. It is suggested that the nitrogen oxides (NO_x) level plays a crucial role in SOA formation from α -pinene and isoprene [Perraud *et al.*, 2012; Surratt *et al.*, 2010]. Additionally, recent laboratory studies suggest that reactions of SOA components with ammonia (NH_3) or ammonium (NH_4^+) salts can produce light-absorbing nitrogen-containing compounds, which may contribute to aerosol optical properties [Updyke *et al.*, 2012]. However, little is known about the origin, including the relative contributions of primary emissions and secondary ON sources, because of a lack of ambient measurements.

As an example of the available measurements of ON in the terrestrial environment, Lin *et al.* [2010] estimated that 33% of the total nitrogen in particulate matter 2.5 ($\text{PM}_{2.5}$) was organic at the Duke Forest site in North Carolina, U.S. They suggested that elevated concentrations of ON were associated with a variety of “continental” origins, although the main source was not quantified. Fry *et al.* [2009] reported environmental chamber measurements of SOA formation in the reactions of NO_3 + β -pinene and proposed monohydroxynitrates and

dihydroxynitrates as possible structures of the aerosol organic nitrate. More recently, based on ambient measurements in California, *Rollins et al.* [2012] demonstrated that the nighttime formation of particulate organic nitrates increases with NO_x and is suppressed by high concentrations of organic molecules that rapidly react with NO_3 .

Water-soluble fraction of ON is important in this context assuming that solubility, hygroscopicity, and bio-availability of ON are linked. The water-soluble ON (WSON) can be estimated as the difference between water-soluble total nitrogen (WSTN) and inorganic nitrogen. The method can quantify an upper limit of ambient particulate WSON. Previous studies reported that WSON constituted a significant proportion (typically around 30%) of the WSTN in precipitation and atmospheric aerosols [*Zhang et al.*, 2002; *Cornell et al.*, 2003; *Mace et al.*, 2003; *Cape et al.*, 2011; *Zamora et al.*, 2011]. WSON may exist across a wide range of particulate sizes depending on its sources. For example, *Smith et al.* [2010] identified amines in ultrafine particles, which may play a key role in nucleation [*Kurten et al.*, 2008]. *Chen et al.* [2010] reported size-fractionated measurements of WSON in a coastal environment. They found that WSON in fine particles (particle diameter $< 1 \mu\text{m}$) may originate from combustion processes, whereas WSON in coarse particles (particle diameter $> 1 \mu\text{m}$) may be generated from continental soil dust and sea spray. WSON such as proteins and peptides are expected to reside in the coarse-mode size ranges. Therefore, size segregation of WSON can provide information on the origins and evolution of WSON aerosols.

Here we investigate possible sources of WSON aerosols in a mixed forest in northern Japan based on aerosol samples collected over a period of ~ 30 months. Seasonal patterns in the concentrations of ON in a forest environment provide insight into potential sources and formation processes for aerosol ON from biogenic origins. Our approach to investigating WSON sources in the forest is to examine the relation between WSON concentration and molecular markers of biogenic emission sources and atmospheric processing. In this paper, we focus on the seasonal changes and mass size distributions of the WSON concentration and oxidation products of VOCs. Some of our previously presented data on water-soluble organic carbon (WSOC) in total suspended particulate (TSP) at the same site [*Miyazaki et al.*, 2012a] are included here to allow more coherent discussion on seasonal variations and size distributions of WSON and major biogenic organic marker compounds.

2. Experiments

2.1. Forest Site Description

Aerosol samplings were continuously made at the Sapporo Hitsujigaoka Experimental Forest ($42^\circ 59' \text{N}$, $141^\circ 23' \text{E}$, 180 m above sea level) site in northern Japan [*Miyazaki et al.*, 2012a, 2012b]. The experimental site is covered with a broadleaf forest, which consists of Mizunara oak and other species. In the forest, the snow cover reaches ~ 1 m in depth and remains more than 120 d/yr, from December to mid-April. The mean canopy height at the forest site is approximately 20 m [*Kitamura et al.*, 2012]. The length of the foliated period, as estimated by seasonal changes in the leaf area index, was about 6 months from May to early November [*Kitamura et al.*, 2012].

The predominant local wind direction and wind speed in summer and autumn (May–October) at this forest site indicated that the majority of aerosols sampled during the summer and autumn periods (May–November) were likely influenced by emissions from forested areas [*Miyazaki et al.*, 2012a], with occasional inflow of polluted air masses from urban areas [*Jung et al.*, 2013]. In contrast, fractions of air masses transported from the sea and urban regions are more evident in winter and spring (December–April).

2.2. Aerosol Sampling

The total suspended particulate (TSP) samples were collected continuously using high-volume air samplers (HVASs) at two altitude levels (2 m and ~ 15 m above the forest floor) at the research site from 22 June 2009 to 30 December 2011. The sampling was conducted using precombusted (at 450°C for 6 h) quartz fiber filters (25×20 cm) with a flow rate of 1200 L min^{-1} . The sampling duration of each aerosol sample was approximately 1 week.

To obtain mass size distributions of aerosol WSON, WSOC, and related compounds, size-segregated aerosol samplings were also performed with a cascade impactor (CI) running in parallel to the HVASs. The size-segregated sampling was made with each sampling period lasting around 1 week. The sampling was made according

to the 50% equivalent aerodynamic cutoff diameters between 0.39 and 10.0 μm [Miyazaki *et al.*, 2010]. The ambient samples were collected on precombusted quartz filters (8 cm ID). The impactor was set at the 2 m level above the canopy floor. Ambient air was drawn at a flow rate of 120 L min^{-1} per sample without temperature and humidity control. In this study, we show size-segregated aerosol data obtained during 18–25 June 2010, 13–20 August 2010, and 13–21 October 2009, which are representative for early summer, midsummer, and autumn, respectively.

2.3. Chemical Analysis of Water-Extracted Samples

A total organic carbon (TOC)/total nitrogen (TN) analyzer (Model TOC-Vcsh, Shimadzu) was used to determine the total aerosol carbon and nitrogen dissolved in water [Miyazaki *et al.*, 2011]. A filter cut of 3.14 cm^2 was extracted with 20 mL of ultrapure water using an ultrasonic bath. The ultrapure water ($>18 \text{ M}\Omega \text{ cm}^{-1}$) was generated by Sartorius Stedim Biotech Arium Pro purifiers (Model 611). The extracts were then filtered with a disc filter (Millex-GV, 0.22 μm , Millipore, Billerica, MA, U.S.), followed by injection of the extracts into the analyzer for the measurements of OC and TN. The nitrogen content was determined by measuring nitrogen monoxide with an ozone chemiluminescence detector. Because the instrument measured the TN in a liquid sample, we use the term water-soluble total nitrogen (WSTN) when referring to the concentrations measured with this instrument.

Recovery of several nitrogen-containing organic species was tested with our instrument using authentic standards in our previous study [Miyazaki *et al.*, 2011]. Briefly, the laboratory experiments indicated that most of the dissolved organic nitrogen compounds can be detected by the analyzer with efficiencies of nearly $\sim 100\%$ (L-alanine, diethylamine, anthranilamide, and Suwannee River fulvic acid). In contrast, compounds that have nitrogen atoms in adjacent positions in their molecular structure (e.g., 4-imidazole carboxylic acid and imidazole-2-carboxaldehyde) may not be quantitatively detected under the operating conditions of the instrument. The field blanks for WSOC and WSTN dissolved in water were $40 \pm 7 \mu\text{g C L}^{-1}$ and $12 \pm 5 \mu\text{g N L}^{-1}$, respectively. These values represent 2% and 1% of the average WSOC and WSTN concentrations in ambient aerosols, respectively. The data presented in this study were corrected for blanks. The total uncertainties in the WSOC and WSTN concentrations were estimated to be 11% and 10%, respectively.

Another filter cut of 1.54 cm^2 was extracted with ultrapure water. The extracts (10 mL) were then filtered using a membrane disc filter to determine major anions and cations using a Metrohm ion chromatograph (Model 761 compact IC). The blank levels of the major ions were below 4% of the measured concentrations.

The WSON concentration was determined by subtracting the inorganic nitrogen (IN) concentration from the WSTN concentration. Here IN is defined as the sum of nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+)-nitrogen measured with the IC ($\text{WSON} = \text{WSTN} - \text{IN}$). We examined the variations due to analytical errors and homogeneity of the filters by analyzing different sections of the same filter sample repeatedly, and the deviation coefficients were found to be less than 6% for WSON. Using the propagating errors of each parameter, the measurement uncertainty of WSON was estimated to be 14%.

For the analysis of biogenic molecular marker compounds, a filter portion was extracted with dichloromethane/methanol. The $-\text{COOH}$ and $-\text{OH}$ functional groups in the extracts were reacted with N, O-bis-(trimethylsilyl) trifluoroacetamide to form trimethylsilyl (TMS) esters and TMS ethers, respectively. The TMS derivatives were then analyzed for the above compounds using a capillary gas chromatograph (HP GC6890, Hewlett-Packard, Palo Alto, California, U.S.) coupled to a mass spectrometer (5973 Mass Selective Detector, Agilent, Santa Clara, California, U.S.) [Fu *et al.*, 2009]. We measured 3-methyl-1,2,3-butanetricarboxylic acid (3-MBTCA), pinic acid, and pinonic acid as oxidation products of α - and β -pinene [Yu *et al.*, 1999; Claeys *et al.*, 2007; Szmigielski *et al.*, 2007]. As oxidation products of isoprene, we determined the concentrations of the two diastereoisomeric 2-methyltetrols (2-methylerythritol and 2-methylthreitol) [Claeys *et al.*, 2004]. Additionally, we quantified sucrose, trehalose, arabinol, and mannitol as possible tracers for primary biological aerosol particles (PBAPs) [Simoneit *et al.*, 2004; Elbert *et al.*, 2007].

To measure nitrogen isotope ratios ($\delta^{15}\text{N}$) of WSTN ($\delta^{15}\text{N}_{\text{WSTN}}$), WSTN was extracted from a filter (14.13 cm^2) for each sample in 20 mL of ultrapure water. The extracted samples were concentrated by rotary evaporation, and 40 μL of the concentrated samples were transferred onto 10 mg of precombusted Chromosorb to be absorbed in a precleaned tin cup [Miyazaki *et al.*, 2012a]. The $\delta^{15}\text{N}_{\text{WSTN}}$ value was then measured using an elemental analyzer (NA 1500, Carlo Erba, Milan, Italy) interfaced to an isotope ratio mass spectrometer

Table 1. Quantitative Comparison Between Size-Segregated (SS) and TSP Samplings ($n = 4$)

Species/Components	[SS]/[TSP] (Average $\pm$ SD)
SO_4^{2-}	0.96 ± 0.13
NO_3^-	1.16 ± 0.19
NH_4^+	1.06 ± 0.05
WSOC	1.18 ± 0.14
2-methylerythritol	0.76 ± 0.21
2-methylthreitol	0.95 ± 0.03
Pinic acid	0.79 ± 0.22
3-MBTCA	0.66 ± 0.29

(Finnigan MAT Delta Plus, Thermo Finnigan, San Jose, CA, U.S.). The uncertainty of the $\delta^{15}\text{N}_{\text{WSTN}}$ measurement was approximately 0.5‰.

The quartz fiber filters collected using the HVAS were also used to determine the hydrogen ion concentration in water-soluble aerosols, denoted as $[\text{H}^+]_{\text{aerosol}}$. Because of the absence of any available techniques for directly measuring the pH of aqueous aerosols, $[\text{H}^+]_{\text{aerosol}}$ was determined here as follows. A filter cut of 3.14 cm^2 was extracted with 20 mL ultrapure water. The pH of the water extracts was measured with a

Horiba D-21 pH meter using an electrode. The $[\text{H}^+]_{\text{aerosol}}$ in nanomoles per cubic meters was then calculated using the resulting aqueous hydrogen ion concentration.

2.4. Comparison of TSP and Size-Segregated Samples

For quality control, concentrations of chemical species or components obtained from the CI were integrated for all stages and compared with the concentrations in TSP collected using the HVAS. Table 1 summarizes the ratios of the mass concentrations of chemical species/components measured using the CI to that using the HVAS. In general, the ratios for inorganic species, WSON, and WSOC were close to unity with some variations ($< \pm 18\%$), which indicates proper agreement between the two data sets. For biogenic species, concentrations obtained by the CI were generally lower than those by the HVAS ($\sim 5\text{--}34\%$). Volatilization from particles deposited onto the CI quartz filters and more adsorption of gas-phase organics onto the HVAS filters might contribute to this discrepancy.

3. Results and Discussion

3.1. Seasonal Variations in the WSTN Budget

Figure 1 shows time series of WSTN concentrations and relative abundances of WSTN species from individual samples at the forest site over an approximately 30 month period (July 2009 to December 2011). Average

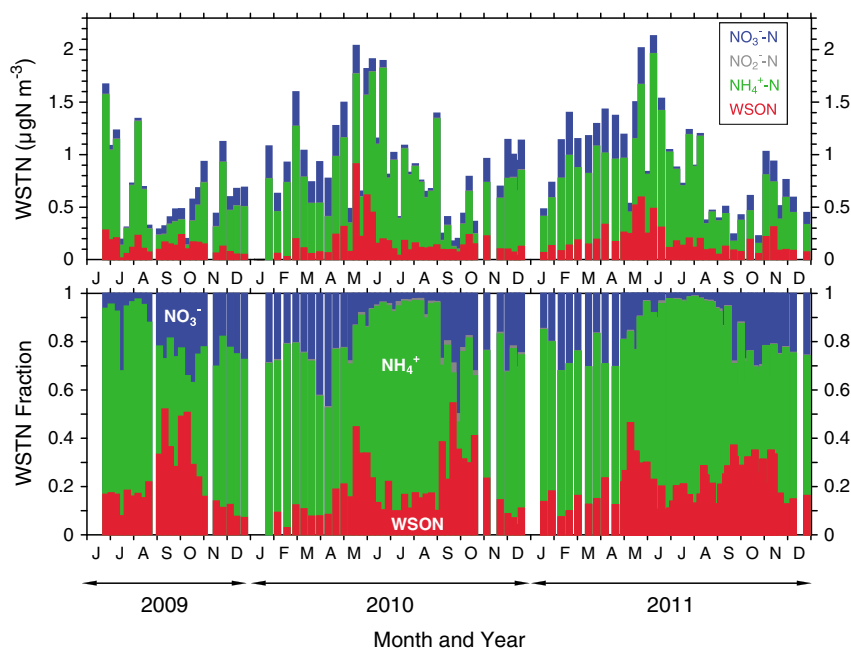


Figure 1. Time series of (top) nitrogen mass concentrations of NO_3^- -N, NO_2^- -N, NH_4^+ -N, and WSON and (bottom) relative contributions of each compound to WSTN in 2009–2011.

Table 2. Median Values of N Concentrations in Aerosols Sampled at the Forest Site^a

	WSON (ng N m ⁻³)	NH ₄ ⁺ (ng m ⁻³)	NO ₃ ⁻ (ng m ⁻³)	NO ₂ ⁻ (ng m ⁻³)
Mar–Apr (spring)				
2010	112	735	1449	15
(n = 7)	(144 ± 108)	(690 ± 209)	(1334 ± 209)	(15 ± 2)
2011	190	893	1404	7
(n = 6)	(212 ± 84)	(969 ± 130)	(1559 ± 427)	(8 ± 3)
May–Jun (early summer)				
2010	208	1152	420	23
(n = 8)	(375 ± 287)	(1112 ± 591)	(546 ± 287)	(24 ± 2)
2011	308	1165	512	12
(n = 7)	(381 ± 148)	(1055 ± 543)	(806 ± 561)	(11 ± 2)
Jul–Aug (midsummer)				
2009	111	733	163	24
(n = 9)	(132 ± 89)	(819 ± 505)	(160 ± 106)	(24 ± 1)
2010	115	912	100	25
(n = 9)	(114 ± 43)	(901 ± 325)	(115 ± 89)	(25 ± 2)
2011	126	801	102	13
(n = 8)	(147 ± 47)	(838 ± 367)	(109 ± 53)	(12 ± 2)
Sep–Nov (autumn)				
2009	142	243	489	26
(n = 12)	(131 ± 56)	(320 ± 273)	(534 ± 252)	(28 ± 11)
2010	100	271	472	24
(n = 10)	(132 ± 55)	(290 ± 249)	(489 ± 227)	(21 ± 6)
2011	127	380	567	10
(n = 9)	(131 ± 84)	(407 ± 84)	(508 ± 297)	(10 ± 2)
Dec–Feb (winter)				
2009	56	508	792	14
(n = 8)	(55 ± 16)	(581 ± 162)	(793 ± 147)	(15 ± 3)
2010	84	780	968	10
(n = 7)	(94 ± 36)	(769 ± 207)	(1011 ± 207)	(20 ± 13)
2011	88	461	644	7
(n = 3)	(80 ± 10)	(397 ± 10)	(577 ± 96)	(6 ± 2)

^aNumbers in parenthesis are averages with standard deviations.

concentrations of WSTN species in each season are also summarized in Table 2. The WSTN concentrations exhibited a clear seasonal cycle with distinct peaks in early summer (May–June), in both 2010 and 2011. The WSON concentrations ranged from 24 to 911 ng N m⁻³, with a median value of 123 ng N m⁻³ (average 157 ± 127 ng N m⁻³). The average mass contributions of WSON to WSTN were 20 ± 11%, which were within the range of ~10–30% reported in previous studies [e.g., González Benítez *et al.*, 2010; Lin *et al.*, 2010; Cape *et al.*, 2011]. The mass fractions of WSON to WSTN showed great season-to-season variability, with peaks in the early summer and autumn (September–November) in each year. On average, NH₄⁺ was the most abundant WSTN species, accounting for 62 ± 19% of WSTN in nitrogen mass. The average contribution of NO₃⁻ to WSTN in nitrogen mass was highest in spring (29%) followed by winter (25%), whereas it became lowest in midsummer (July–August) (<5%). The seasonal difference in the NO₃⁻ fraction can be explained by the difference in the observed frequencies of air masses transported from the urban regions, which were more evident in winter and spring [Miyazaki *et al.*, 2012a] as well as the phase partitioning of nitrate into the particle phase in the colder seasons. NO₂⁻ had negligible contributions to WSTN (<2% in nitrogen mass) throughout the study period.

Figure 2 shows annual cycles of the WSON and WSOC concentrations during 2009–2011. To our knowledge, this is the first study reporting a full annual cycle and characteristic changes in the seasonal variation in WSON within a forest canopy. The WSON concentrations showed a maximum in early summer. This seasonal cycle is closely associated with that of WSOC, the details of which are discussed in our previous study [Miyazaki *et al.*, 2012a]. Additionally, the seasonal trend was observed to be similar each year. The average concentration of WSON in the early summer was 378 ± 260 ng N m⁻³ (Table 2). This value accounted for 27 ± 11% of WSTN.

The mass ratio between ON and OC in water-soluble aerosol provides an insight into the origin and chemical properties of aerosol WSON. The average WSON/WSOC mass ratio was 0.09 ± 0.03 at a level of 2 m height

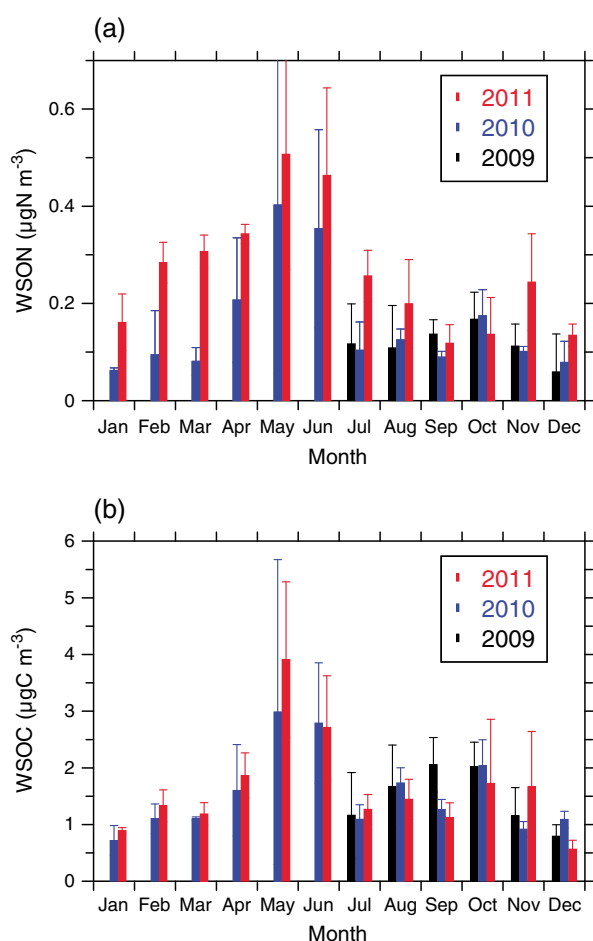


Figure 2. Annual cycles of the WSON and WSOC concentrations in 2009–2011.

of 2-methyltetrols (Figure 3b) also closely followed the trend of temperature, showing its consistency with the highest isoprene emission rates and photochemical activity expected during the summer months. It is well known that emissions of monoterpene and isoprene from terrestrial vegetation depend strongly on temperature [e.g., Guenther *et al.*, 1993; Fowler *et al.*, 2009]. Therefore, an increase in temperature is expected to increase the concentrations of biogenic SOA compounds that resulted from the photooxidation of α -pinene and isoprene. Moreover, SOA yields via aqueous-phase reactions are expected to increase at high RH ($> 75\%$) (Figure 3c) together with increased emissions of biogenic VOCs during the summer months [e.g., Ervens *et al.*, 2011].

Based on positive matrix factorization analyses, Miyazaki *et al.* [2012a] estimated that biogenic SOA production accounted for 90% of WSOC in TSP (50% from α -pinene SOA and 40% from isoprene SOA) in midsummer at the same forest site. Meanwhile, the analysis also suggests that biogenic SOA ($\sim 40\%$) and PBAPs ($\sim 57\%$) made similar contributions to the maximum WSOC concentration in TSP in early summer. They also reported that during the summer months, the stable carbon isotopic composition of WSOC ($\delta^{13}\text{C}_{\text{WSOC}}$) in TSP at the sampling site showed values ($-25.5 \pm 0.5\text{‰}$) that are similar to those of C3 plants, indicating that the dominant source of WSOC is closely linked to forest biological activity in this season. In section 3.2, we discuss the mass size distributions of WSON and compare them with those of biogenic molecular markers and major inorganic species with regard to possible sources of the observed WSON.

3.2. Mass Size Distributions of WSON

3.2.1. Comparison With WSOC and Major Inorganic Species

Figures 4a–4c present typical mass size distributions of WSON and WSOC in three seasonal categories. These samples were obtained in June 2010, August 2010, and October 2009, which are representative for the early

during the entire study period. In general, the ratio observed in this study was higher than ON/OC ratios in aerosols reported elsewhere. The WSON/WSOC ratio was higher than the ON/OC ratios reported for forest and mountain sites (0.03–0.05) [Lin *et al.*, 2010; Sun *et al.*, 2009] and for submicrometer aerosols observed in urban environments (0.01–0.02) [Aiken *et al.*, 2008; Sun *et al.*, 2011]. In particular, the WSON/WSOC ratio in June was as high as 0.15 ± 0.03 in our data. This is due to the relative increase in the nitrogen content compared to the carbon content in water-soluble fractions of organic aerosols in the early summer at this site (Figure 2).

To discuss possible contributions of biogenic sources to the observed WSON, Figure 3 presents the seasonal changes in molecular marker compounds of oxidation products of α -pinene and isoprene along with ambient temperature and relative humidity (RH) at the sampling site. Pinonic acid and 3-MBTCA are major oxidation products of the α -pinene ozonolysis [Yu *et al.*, 1999; Szmigielski *et al.*, 2007], whereas 2-methyltetrols (= 2-methylerythritol + 2-methylthreitol) is a photooxidation product of isoprene [Claeys *et al.*, 2004]. The monthly averages of pinonic acid and 3-MBTCA started to increase in April, peaking in August (Figure 3a). They generally followed the trend of ambient temperature (Figure 3c). The seasonal trend

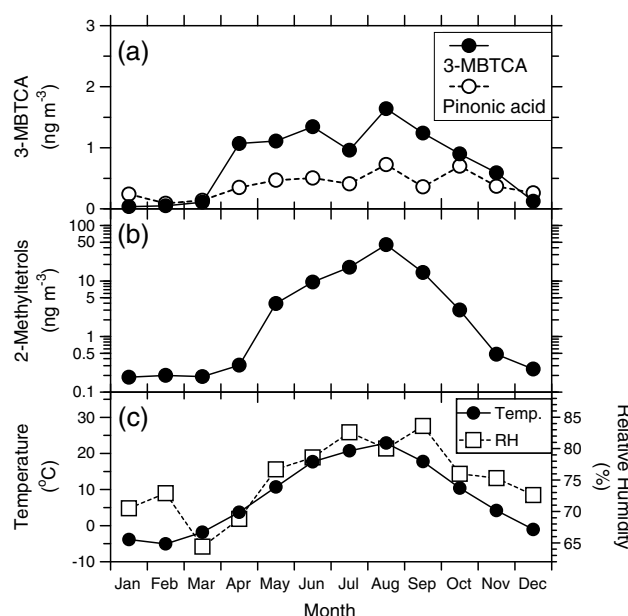


Figure 3. Monthly averages of (a) 3-MBTCA (solid circle) and pinonic acid (open circle) concentrations, (b) 2-methyltetrols concentrations, (c) ambient temperature, and relative humidity (RH) in 2010. The y axis in Figure 3b is plotted on a log scale.

summer, midsummer, and autumn (September–November) periods, respectively. Within the same seasons, the absolute values of size-integrated mass concentrations varied within a factor of 4. However, the patterns of the mass size distributions, such as peak diameter ranges, were similar within each seasonal category for our size-segregated data. Therefore we chose “typical” profiles of the mass size distributions to represent those in each season. The WSOC exhibits bimodal size distributions, with peaks in the submicrometer and supermicrometer ranges, regardless of the seasonal categories. However, the mass size distributions of WSON are distinctly different between summer and autumn. The majority of the WSON mass during the early summer and midsummer was observed in fine particles with aerodynamic diameter $<1.9 \mu\text{m}$, peaking at $1.0\text{--}1.9 \mu\text{m}$ (Figures 4a and 4b). On average, the mass fraction of WSON in the fine particles was $\sim 95\%$ in the early summer and midsummer (Table 3). In contrast, a substantial fraction of the WSON mass (70%) was found to reside in the coarse-mode size range (aerodynamic diameter $>1.9 \mu\text{m}$) in autumn (Figure 4c).

Mass size distributions of major inorganic species (SO_4^{2-} , NH_4^+ , and NO_3^-) in the three seasons are shown in Figures 4d–4f. It should be noted that the concentrations of non-sea-salt (nss) SO_4^{2-} were estimated assuming that all of the observed Na^+ at the sampling site originated from NaCl in sea salt. On average, the fraction of nss- SO_4^{2-} was $95\% \pm 5\%$ of the total SO_4^{2-} in TSP between early summer and autumn, indicating that ss- SO_4^{2-} was a minor contributor to the total SO_4^{2-} . Therefore, we use the term SO_4^{2-} instead of nss- SO_4^{2-} in this paper. SO_4^{2-} and NH_4^+ showed similar mass size distributions in all seasons. They were concentrated in the fine fractions, particularly in the size range between 0.4 and $1.9 \mu\text{m}$. The concentrations of these species were highest in the early summer (Figure 4d). As we have reported in our previous study [Miyazaki *et al.*, 2012a], the average SO_4^{2-} concentration in TSP in the early summer was $4.6 \pm 2.0 \mu\text{g m}^{-3}$, whereas they were $3.8 \pm 2.0 \mu\text{g m}^{-3}$ and $2.5 \pm 1.6 \mu\text{g m}^{-3}$ during the midsummer and autumn periods, respectively. Jung *et al.* [2013] reported that the measured SO_2 concentrations (and calculated H_2SO_4 concentrations) at the same site increased when air masses were transported from a nearby urban area. They also showed that these air masses typically caused new particle formation within the forest canopy. In the current study, the seasonal patterns and peak diameters of WSON and SO_4^{2-} are generally similar in the summer season. The size-segregated data showed linear correlations between WSON and SO_4^{2-} concentrations in early summer ($r^2 = 0.74$) and midsummer ($r^2 = 0.85$), indicating that formation processes for WSON are closely linked with those for SO_4^{2-} during the summer period. In contrast, no significant correlation was observed between WSON and SO_4^{2-} in autumn ($r^2 = 0.07$). NO_3^- exhibited a size distribution with substantial mass fraction in the coarse mode, suggesting that the primary coarse particles such as alkaline elements promote the adsorption of nitric acid onto coarse fraction of the observed aerosol.

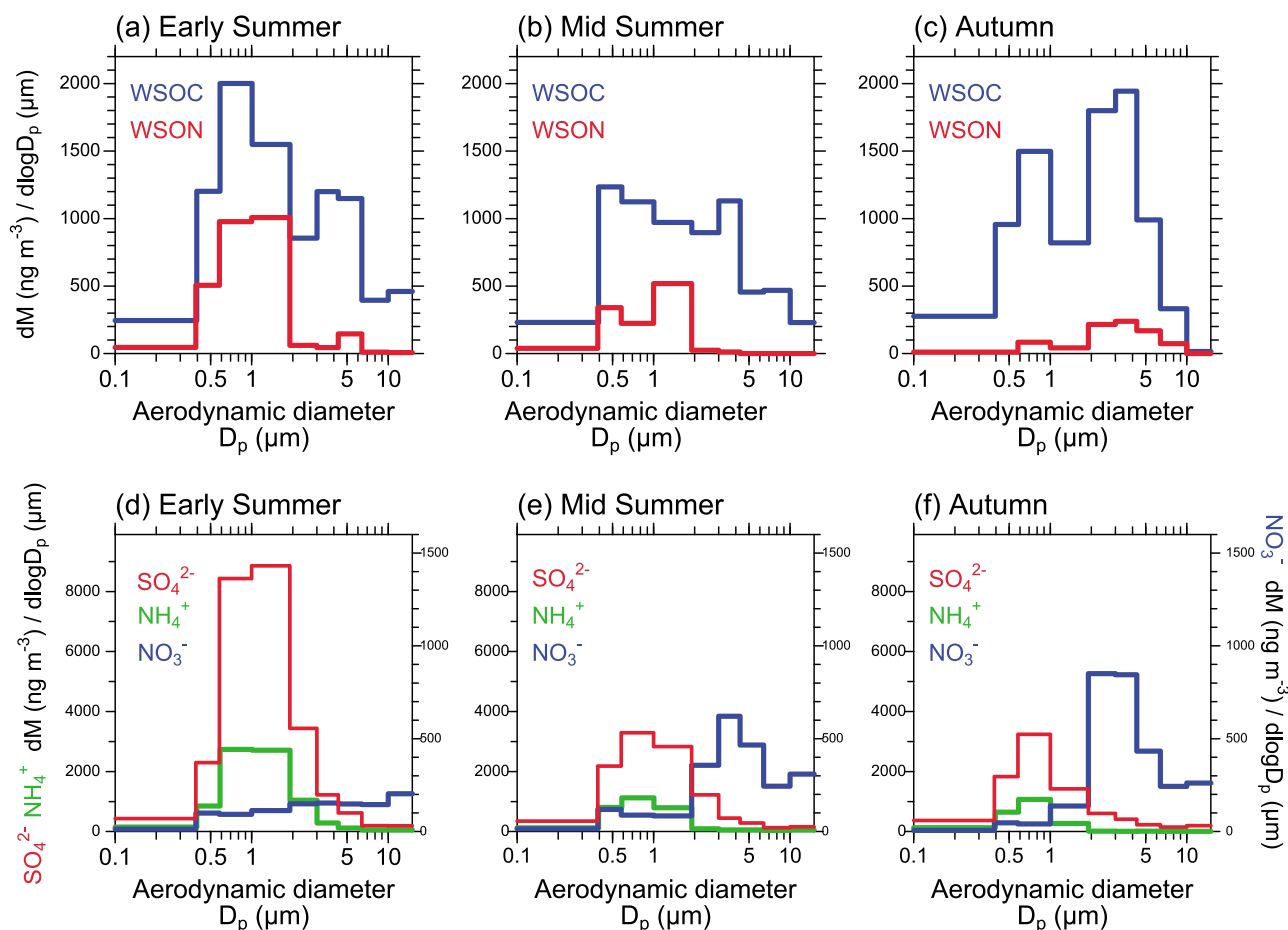


Figure 4. Typical mass size distributions of WSON, WSOC, SO_4^{2-} , NH_4^+ , and NO_3^- : (a and d) early summer (18–25 June 2010), (b and e) midsummer (13–20 August 2010), and (c and f) autumn (13–21 October 2009).

3.2.2. Comparison With Oxidation Products of Biogenic VOCs

To investigate the link between WSON and biogenic sources within the forest canopy, Figure 5 compares the mass size distributions of WSON with those of molecular marker compounds for biogenic SOA in each season.

Table 3. Concentrations in the Fine- ($D_p < 1.9 \mu\text{m}$) and Coarse-Mode ($D_p > 1.9 \mu\text{m}$) Size Ranges in Three Seasonal Categories

	Early Summer (18–25 Jun 2010)		Midsummer (13–20 Aug 2010)		Autumn (13–21 Oct 2009)	
	Fine	Coarse	Fine	Coarse	Fine	Coarse
WSON (ng N m^{-3})	672	48	317	7.0	52	124
WSOC (ng C m^{-3})	1503	731	1118	573	1188	900
SO_4^{2-} ^a	5542	1059	2497	421	2060	296
NH_4^+ ^a	1791	294	819	54	639	8.6
NO_3^- ^a	91	151	88	362	66	479
Pinic acid ^a	2.5	0.5	1.9	0.4	2.9	0.7
Pinonic acid ^a	0.9	1.1	0.6	0.8	0.6	1.3
3-MBTCA ^a	1.0	0.1	0.8	0.1	2.5	0.1
2-methylerythritol ^a	1.7	1.0	12	3.9	0.2	0.1
2-methylthreitol ^a	0.6	0.5	4.0	1.8	0.1	0.1
Trehalose ^a	1.1	49	3.2	76	13	81
Sucrose ^a	0.1	0.9	0.2	0.8	0.2	0.4
Mannitol ^a	1.7	73	5.7	141	8.6	107
Arabitol ^a	1.1	73	3.2	68	5.1	65

^aUnits are nanograms per cubic meters.

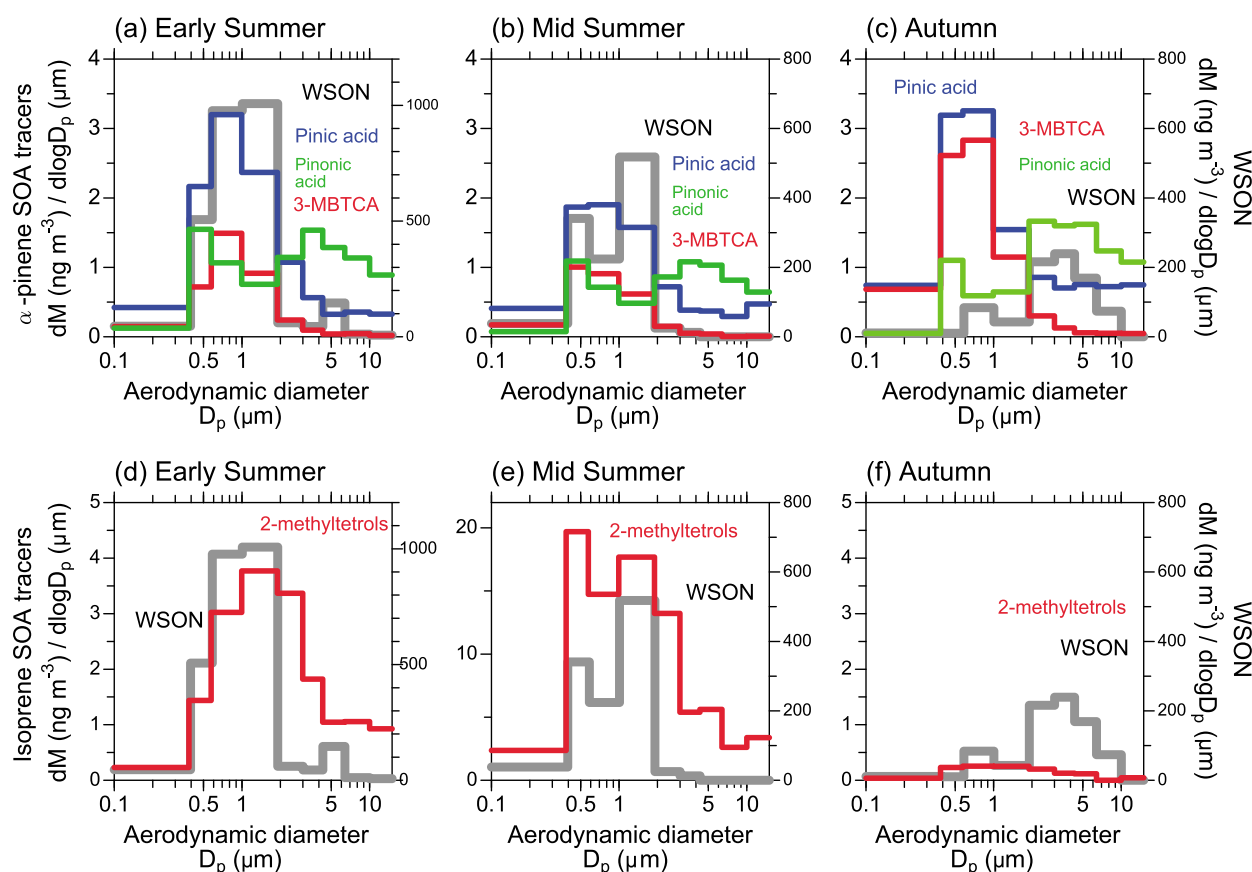


Figure 5. Typical mass size distributions of WSON in comparison with those of organic molecular oxidation products of (a–c) α -pinene and (d–f) isoprene: (Figures 5a and 5d) early summer, (Figures 5b and 5e) midsummer, and (Figures 5c and 5f) autumn.

The mass size distributions of pinic acid and 3-MBTCA showed that they were mostly in the fine mode regardless of the season (Figures 5a–5c). The mass concentrations of WSON showed a positive correlation with those of pinic acid in early summer ($r^2 = 0.72$) and midsummer ($r^2 = 0.57$). Similarly, WSON was positively correlated with 3-MBTCA in early summer ($r^2 = 0.78$) and midsummer ($r^2 = 0.55$). The similarity in the size distributions together with the positive correlations of WSON with pinic acid and 3-MBTCA indicate that the observed WSON in the early summer and midsummer was associated with oxidation of α -pinene in the forest canopy.

The size distributions of 2-methyltetrols (Figures 5d–5f) exhibited broader size distributions, with peaks in the fine mode, showing a tail into the coarse mode. It has been suggested that 2-methyltetrols can be formed by acid-catalyzed degradation of C_5 -epoxydiols [Paulot *et al.*, 2009] and C_5 -trihydroxyhydroperoxides [Kleindienst *et al.*, 2009] in a heterogeneous process. WSON exhibited a positive correlation with 2-methyltetrols in midsummer with r^2 of 0.80 ($n = 9$), which is higher than that (0.64) in early summer ($n = 9$). This result indicates that besides oxidation of α -pinene, the WSON mass was also associated with oxidation of isoprene, the contribution of which is likely more significant in midsummer than in early summer. In addition to the photochemistry of isoprene, Nozière *et al.* [2011] suggested that some fraction of 2-methyltetrols is likely primary biological origin, which may be associated with its production by plants, algae, and other living organisms. Moreover, a recent field study indicated that a significant fraction of methyltetrols exists in the gas phase [Isaacman *et al.*, 2013]. It is therefore likely that volatilization of methyltetrols from the fine particles occurred followed by gas-particle repartitioning. The broader size distributions of 2-methyltetrols found in this study, particularly in the coarse-mode fraction, can be partly attributed to the primary organic source and/or gas-particle repartitioning of 2-methyltetrols.

It is noted that pinonic acid showed bimodal mass size distributions in the three seasonal categories, with peaks at 0.39–0.58 μm and 1.9–3.0 μm (Figures 5a–5c). The mass fractions of pinonic acid were similar in the fine- (~43–46%) and coarse-mode (~54–57%) fractions in the early summer and midsummer, but larger in the coarse-mode (~70%) fractions in autumn (Table 3). The difference in the size distributions between pinonic acid and the

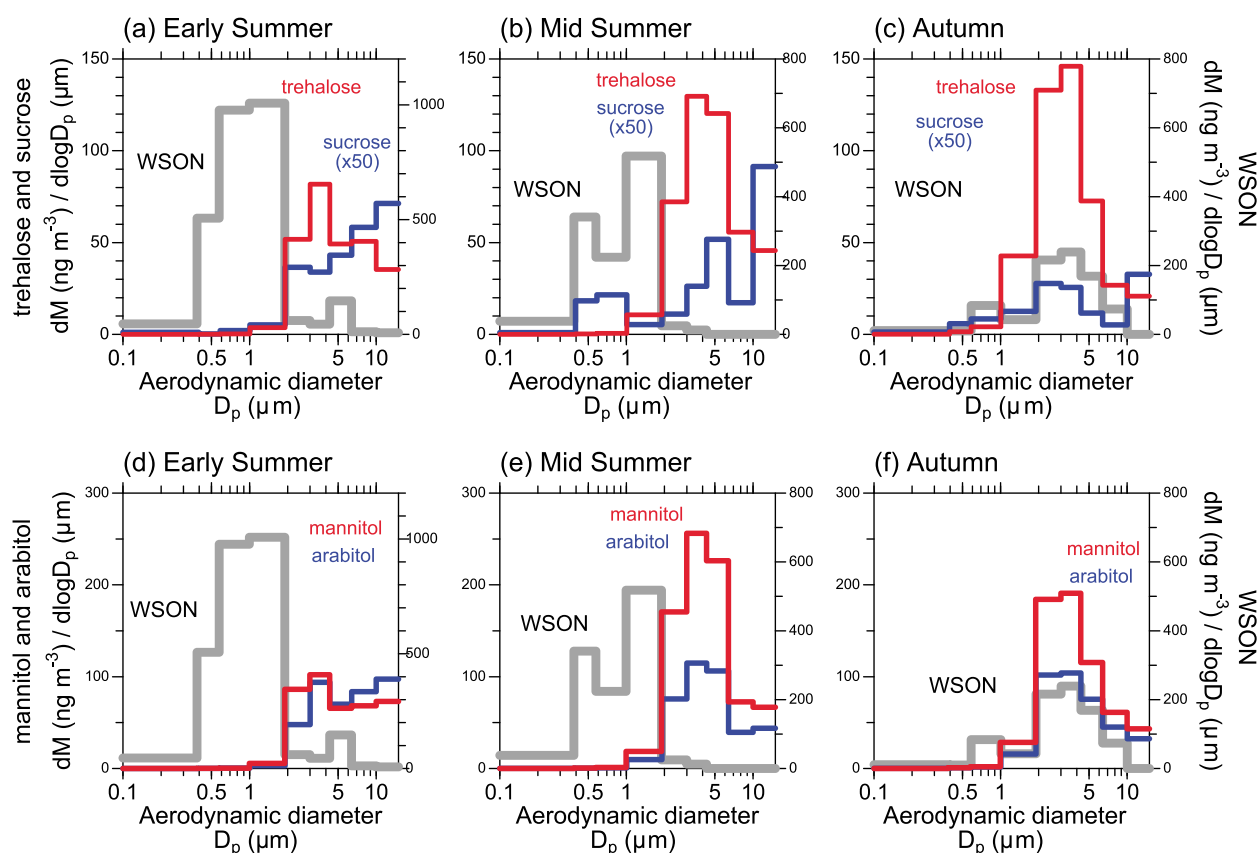


Figure 6. Typical mass size distributions of WSON in comparison with those of (a–c) trehalose and sucrose and (d–f) mannitol and arabitol: (Figures 6a and 6d) early summer, (Figures 6b and 6e) midsummer, and (Figures 6c and 6f) autumn.

other oxidation products of α -pinene is attributable to the difference in their volatilities: pinonic acid is highly volatile/semivolatile, whereas the volatilities of 3-MBTCA and pinic acid are relatively low [Zhang *et al.*, 2010]. Zhang *et al.* [2010] also reported similar mass concentrations of pinonic acid in fine (aerodynamic diameter $< 3 \mu\text{m}$) and coarse fractions during summer and autumn in Mainz, Germany. The minor fractions of WSON in the coarse-mode size range during the early summer and midsummer indicate the formation of WSON having low vapor pressures due to a partition toward the particle phase. This finding also indicates that adsorption of semivolatile WSON in the gas phase onto the coarse-mode fraction (e.g., processes similar to adsorption of HNO_3 onto alkaline coarse particles) is a minor production process for WSON during the summer season.

3.2.3. Comparison With Molecular Markers for PBAPs

The contribution of PBAPs such as bacteria and spores to the WSON mass is poorly understood [Elbert *et al.*, 2007]. Here we compare the mass size distributions of WSON with those of several molecular markers for PBAPs (Figure 6). Saccharides enter the aerosol phase by direct emission from the biota [Graham *et al.*, 2003] or by the resuspension of organic-rich soil particles [Simoneit *et al.*, 2004]. Hence, they have 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 in pollen grains [Pacini, 2000]. Trehalose is known to be a fungal metabolite and a stress protectant for the soil microbial community. It has also been proposed as a marker compound for fugitive dust from biologically active surface soils [Rogge *et al.*, 2007]. The mass size distributions of sucrose and trehalose in this study showed that they were dominated by the coarse-mode fractions in the entire seasonal category (Figures 6a–6c), which is consistent with their primary source origin.

Mannitol and arabitol also exhibited mass size distributions with a single mode in the coarse-mode size range in all the periods (Figures 6d–6f). These sugar compounds, along with sucrose and trehalose, likely contributed to the observed WSOC in the coarse mode in all the seasons (Figures 4a–4c) [Miyazaki *et al.*, 2012a]. However, the minor fractions of these sugar compounds in the fine mode suggest that the contributions of the source materials for these sugars to the WSON in the fine mode are likely insignificant in early summer and midsummer.

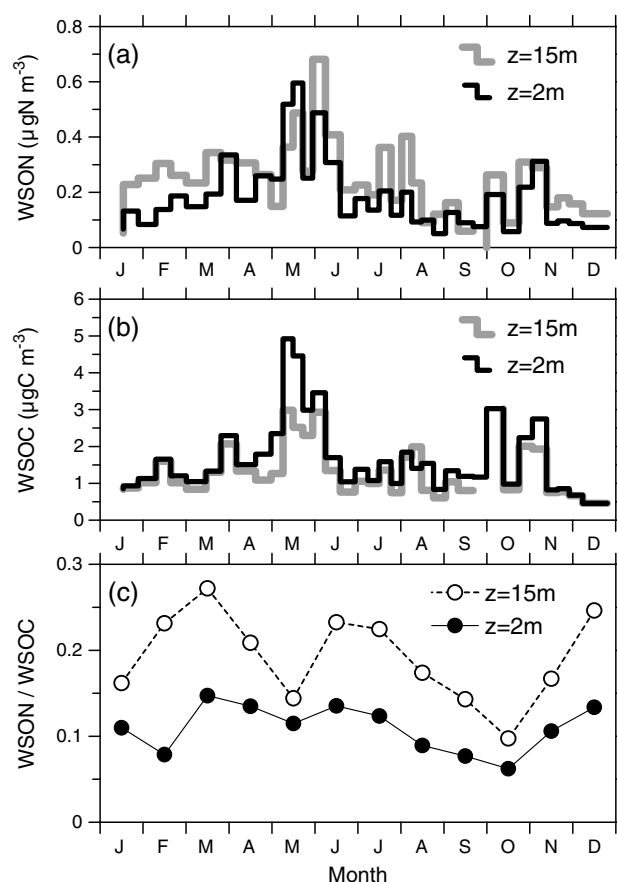


Figure 7. Time series of the mass concentrations of (a) WSON, (b) WSOC and (c) the monthly averages of the WSON/WSOC mass ratio at 15 m (open circle) and 2 m (solid circle) above the forest floor at the sampling site. The data are averaged over 2010 and 2011.

The size distribution of WSON in autumn is similar to those of trehalose, mannitol, and arabitol, with peaks in the range 3.0–4.3 μm . This is within the size range for spores of airborne fungal strains [e.g., Bauer *et al.*, 2002]. Indeed, the size-segregated WSON showed statistically significant correlation with trehalose ($r^2 = 0.71$), mannitol ($r^2 = 0.83$), and arabitol ($r^2 = 0.75$) in the autumn season ($n = 9$). Our data suggest that the major fractions of WSON in autumn are likely associated with primary biological products, which are different from the secondary production as plausible sources of WSON in early summer and midsummer.

The coarse-mode WSON from primary biological origins is also reported by Huffman *et al.* [2012]. In the rainforest of central Amazon, they observed PBAPs liquid-coated with mixed organic-inorganic materials including nitrogen, which could be primary liquids emitted with fungal spores from their sources. In the current study, the reason for the minor fractions of WSON in the coarse mode in the summer season is not clear, although our data imply that primary sources specific to autumn can contribute to the WSON at the forest site. In this study, the minor fractions of the WSON

mass in the fine-mode size range in autumn can be explained by lower photochemical activity as indicated by the lower concentrations of SO_4^{2-} (Figure 4f), which resulted in lower oxidation of precursors to form WSON.

3.3. Potential Processes for WSON Formation and Aerosol Acidity

In this section, we give a particular focus on the role of biological sources and possible oxidation processes to form the peak concentrations of WSON observed in early summer. Figures 7a and 7b present the time series of the WSON and WSOC concentrations at two heights within the forest canopy. The WSON concentrations at the 15 m level were generally larger than those at the 2 m level (Figure 7a). In contrast, the WSOC concentrations generally showed larger values at the 2 m level (Figure 7b), suggesting strong sources of aerosol OC near the forest floor [Miyazaki *et al.*, 2012a]. The difference in the vertical profiles of WSON and WSOC resulted in higher WSON/WSOC ratios at the 15 m (0.19 ± 0.05) than at the 2 m level (0.09 ± 0.03) (Figure 7c). This result indicates that water-soluble OA is enriched with nitrogen just below the canopy height compared with near the forest floor.

Possible reasons for the higher WSON/WSOC ratios at the 15 m level are higher production rate of WSON near the forest canopy and/or strong downward transport of WSON from outside the forest. Because the vertical profiles of biogenic SOA compounds (i.e., emissions of biogenic hydrocarbon) were generally similar to those of WSOC [Miyazaki *et al.*, 2012a], formation processes for WSON related to nitrogen might contribute to the higher WSON/WSOC ratios near the forest canopy. Previous studies documented the effect of acidity on SOA formation through heterogeneous reactions [Jang *et al.*, 2002; Gao *et al.*, 2004; Kleindienst *et al.*, 2006; Surratt *et al.*, 2007, 2010]. For example, Kourtchev *et al.* [2008] showed $\text{PM}_{2.5}$ sampled at a boreal forest site had a greater fraction of 2-methyltetrols during an episode of elevated SO_2

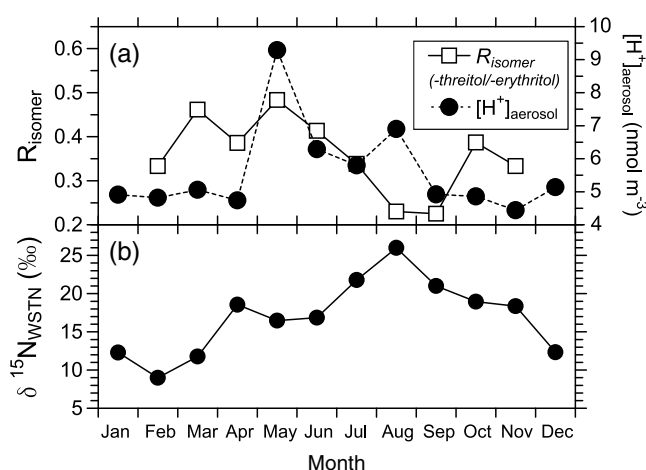


Figure 8. Monthly averages of (a) 2-methylthreitol/2-methylerythritol ratios (R_{isomers} , open square) and hydrogen ion concentration in water-soluble aerosols ($[H^+]_{\text{aerosol}}$) (solid circle) and (b) $\delta^{15}\text{N}$ of WSTN ($\delta^{15}\text{N}_{\text{WSTN}}$). The data are averaged over 2010 and 2011. The R_{isomers} in January and December are not shown because the average mass concentrations of both 2-methylthreitol and 2-methylerythritol were low ($< \sim 0.1 \text{ ng m}^{-3}$) in these months.

levels, which is likely resulted in the increased aerosol acidity. Wang *et al.* [2010] observed high molecular weight nitrogen-containing organic salts in urban aerosols and proposed that their formation is associated with acid-catalyzed reactions among amines, formaldehyde, and carbonyls. In this context, the ratio between 2-methylthreitol and 2-methylerythritol, which are isomers of 2-methyltetrols, can indicate the difference in the aerosol acidity [Claeys *et al.*, 2010]. Additionally, we also consider the measured $[H^+]_{\text{aerosol}}$ which offers insights into the aerosol acidity.

Figure 8a shows monthly averages of the 2-methylthreitol/2-methylerythritol ratio, denoted as R_{isomers} , and $[H^+]_{\text{aerosol}}$ in the observed aerosols. The monthly

averaged R_{isomers} ranged from 0.23 to 0.48, with an average of 0.36 ± 0.09 . This compares well to the R_{isomers} ranging from 0.30 to 0.58 found for aerosols collected at other forested sites [e.g., Ion *et al.*, 2005; Xia and Hopke, 2006; Clements and Seinfeld, 2007; Kourtchev *et al.*, 2008; Claeys *et al.*, 2010; Fu and Kawamura, 2011]. The $[H^+]_{\text{aerosol}}$ ranged from 4.4 to 9.3 nmol m^{-3} , with an average of $5.6 \pm 1.4 \text{ nmol m}^{-3}$. The $[H^+]_{\text{aerosol}}$ values in this study are comparable to the lower limit of prior field measurements [e.g., Surratt *et al.*, 2007], although relatively long duration of aerosol sampling (~ 1 week) may underestimate hydrogen concentration of shorter duration (e.g., 6–24 h) [Liu *et al.*, 1996]. Overall, the seasonal variation in the R_{isomers} tracked well with that in the $[H^+]_{\text{aerosol}}$. This shows a consistency between the two parameters, both of which can indicate differences in the observed aerosol acidity.

Both the R_{isomers} and $[H^+]_{\text{aerosol}}$ showed the highest values in early summer (Figure 8a), indicating that the aerosol acidity was relatively high in this season. The higher R_{isomers} (> 0.4) in the early summer could be explained by the elevated SO_4^{2-} concentration (average $4.6 \pm 2.0 \mu\text{g m}^{-3}$) transported from an urban area near the forest, which are discussed in detail by Miyazaki *et al.* [2012a]. In the early summer, the WSON concentration is linearly correlated with the R_{isomers} (average 0.45 ± 0.05) ($r^2 = 0.86$) in data obtained from individual samples. Moreover, the WSON showed a linear correlation with $[H^+]_{\text{aerosol}}$ ($r^2 = 0.75$). These positive correlations together with the increased concentrations of biogenic oxidation products associated with the forest biological activity (Figure 3) indicate that aerosol acidity likely plays an important role in the formation of WSON via acid-catalyzed reactions in early summer at the forest site. This is supported by the similarity in the mass size distributions of WSON and SO_4^{2-} in the early summer (Figure 4a) as discussed previously.

To examine the origin of water-soluble nitrogen in aerosols, monthly averages of the $\delta^{15}\text{N}$ of WSTN ($\delta^{15}\text{N}_{\text{WSTN}}$) in aerosols are plotted in Figure 8b. The average $\delta^{15}\text{N}_{\text{WSTN}}$ in aerosols ranged from $+9.0\text{‰}$ to $+26.0\text{‰}$. These values are similar to the typical $\delta^{15}\text{N}$ range of anthropogenic nitrogen [e.g., Kundu *et al.*, 2010; Cape *et al.*, 2011], which are substantially higher than those of soil-released nitric oxide, vegetation tissues, and biogenic soil organic matter ($< -20\text{‰}$) [e.g., Li and Wang, 2008; Felix *et al.*, 2012]. This result implies that the majority of nitrogen in WSTN was likely anthropogenic rather than originating from the forest (i.e., biogenic soils). The nitrogen in WSTN that originated from anthropogenic sources may have reacted with biogenic hydrocarbons to form WSON in the forest atmosphere.

In midsummer, the oxidation products of α -pinene and isoprene showed the maximum concentrations (Figures 3a–3b). However, the SO_4^{2-} concentrations in midsummer were relatively low (Figure 4e), which can be explained by the fact that the inflow of polluted air mass from outside the forest was less frequent than in the early summer. Moreover, the rainfall was frequent in this season (100–200 mm per month) [Miyazaki *et al.*, 2012a], which could result in the removal of WSON aerosols by wet deposition. These factors could explain

relatively lower concentrations of WSON in the midsummer than in the early summer. In summary, this study provides an evidence for secondary production of aerosol WSON from biogenic hydrocarbons in the forest.

4. Conclusions

This study investigated contribution of WSON to the WSTN budget in aerosol and possible sources of aerosol WSON in a temperate mixed forest. The analysis is based on seasonal changes in the concentrations of WSON and organic molecular markers and their mass size distributions. On average, the WSON concentrations and WSON/WSTN mass fractions in TSP were $157 \pm 127 \text{ ng N m}^{-3}$ and $20 \pm 11\%$, respectively. A clear seasonal cycle with distinct peaks in the early summer was observed for both WSON concentrations ($378 \pm 260 \text{ ng N m}^{-3}$) and WSON/WSTN ratios ($27 \pm 11\%$).

Contrasting examples of size distributions of WSON in the different seasons were shown. The WSON mass mostly resided in the fine-mode size range ($D_p < 1.9 \mu\text{m}$) in the early summer and midsummer. On the other hand, WSOC exhibited a bimodal mass size distribution, with peaks in submicrometer and supermicrometer size ranges regardless of the season. The positive correlation of WSON with oxidation products of α -pinene and isoprene and the similarity in their mass size distributions in early summer and midsummer suggest that oxidation of biogenic hydrocarbons emitted from the forest is plausible sources for the majority of the observed WSON in those seasons. In contrast, the majority of the WSON mass was associated with the coarse-mode fraction ($D_p > 1.9 \mu\text{m}$) in autumn. The mass size distributions of WSON in this season were similar to those of trehalose, mannitol, and arabitol, indicating that the major source of WSON in autumn are likely associated with primary emissions of biological products in the forest.

The vertical differences in the concentrations of WSON and WSOC within the forest canopy suggest that water-soluble organic aerosol is enriched with nitrogen below the canopy level relative to near the forest floor. The WSON concentration increased with enhanced concentrations of aqueous hydrogen ion and oxidation products of monoterpene/isoprene in aerosols in the early summer. The result indicates that aerosol acidity associated with anthropogenic sources outside the forest may play an important role in the formation of WSON in that season. This study suggests the importance of multiple sources of WSON within the forest canopy that may dominate others in specific seasons. The result provides insights into the processes for and relative importance of WSON formation in forest environments.

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