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TELLUS

Diurnal variations and vertical gradients of biogenic volatile and semi-volatile organic compounds at the Tomakomai larch forest station in Japan

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ABSTRACT

Volatile and semi-volatile organic compounds (VOCs and SVOCs) in the atmosphere control oxidative capacity of the air and formation of organic aerosols. To investigate sources, variations and fluxes of VOCs and SVOCs in the forest atmosphere, samples were collected in a larch forest at different heights in Tomakomai, Japan, from 3 to 5 September 2003 and were analyzed for VOCs (isoprene and α-pinene) and SVOCs (n-nonanal, n-decanal, glycolaldehyde, hydroxyacetone, glyoxal and methylglyoxal) using GC-FID and GC-MS. Isoprene (8–851 pptv) showed a diurnal variation with a maximum in daytime, whereas diurnal pattern was indistinct for α-pinene (6–145 pptv). SVOCs showed diurnal variations similar to isoprene, suggesting their origin to be biogenic. Denuder samplings of SVOCs demonstrated that up to 60% of SVOCs were present in aerosol particles. n-Nonanal and n-decanal were more abundant at lower altitude, suggesting their primary emissions from vegetations. In contrast, other four SVOCs showed an opposite or no trend and are considered as oxidation products of biogenic precursors such as isoprene. The averaged upward fluxes of isoprene and α-pinene were obtained to be 34.8 and 9.8 ng m^{-2} s^{-1}, respectively. Magnitudes of SVOC fluxes were comparable to those of α-pinene, indicating that SVOCs affect budgets of organic gases/aerosols over the forest.

1. Introduction

In the troposphere, volatile organic compounds (VOCs) play an important role in a number of chemical processes including formation/decomposition of O_3 and other oxidants (Fehsenfeld et al., 1992) as well as secondary formation of organic aerosols. Emissions of biogenic VOCs are suggested to be one order of magnitude larger than those of anthropogenic VOCs on global scale. Forest can act as a major source of biogenic VOCs, being dominated by isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$; e.g. α-pinene). The emissions of VOCs from forests not only control oxidative capacity of ambient air, but also affect air quality of urban and semi-urban environments as well as the remote atmosphere by the transport followed by mixing with anthropogenic nitrogen oxides (NOx).

Some organics that are produced photochemically from biogenic VOCs and/or emitted directly from vegetation and microbial processes have semi-volatile characteristics (Kavouras et al., 1999; Matsunaga et al., 2004). These semi-volatile organic compounds (SVOCs) are oxygenated, bearing carbonyl, hydroxyl and carboxyl groups in their chemical structures. The oxygenated compounds are in many cases less volatile than their precursors and are potentially partitioned in gas phase and aerosol particles. Further, the biogenic SVOCs may participate in new particle formation in the forest atmosphere (Kavouras et al., 1998). Such a process may play an important role in the earth climate system, because organic aerosol particles can act as efficient cloud condensation nuclei (Novakov and Penner, 1993).

To better understand the role of atmospheric organic compounds of biogenic origin, we need to obtain critical information including their emissions and transformation/degradation processes, as well as budgets of the compounds between the forest and the atmosphere. But so far, such studies are limited and temporal variations of biogenic VOCs and SVOCs

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were rarely measured simultaneously over the forest canopy. Moreover, information on the emissions/fluxes of oxygenated SVOCs between the forest and the atmosphere are very scarce, being in contrast to biogenic VOCs. In this study, we conducted 3-day observation to determine the concentrations of two VOC (isoprene and α-pinene) and six SVOC components (n-nonanal, n-decanal, glycolaldehyde, hydroxyacetone, glyoxal and methylglyoxal) at two different heights using a 42 m high research tower in a Japanese larch forest in Hokkaido, Japan. Isoprene and α-pinene are dominant hydrocarbons emitted from forest plants, whereas six SVOCs studied are major bi-functional carbonyls in the forest atmosphere (Matsunaga et al., 2003, 2004). Here we present diurnal variations and vertical profiles of VOCs and SVOCs. Further, fluxes of VOCs and SVOCs were calculated using a modified gradient method. The results are discussed in terms of photochemical degradation and production as well as secondary formation of organic aerosols.

2. Experiment

2.1. Sampling site

VOCs and SVOCs were sampled on a research tower (height, 42 m) of Tomakomai Flux Research Site (42°44′ N, 141°31′E; elevation 140 m) in Japan during September 3–5, 2003. The schematic of the sampling site is presented in Fig. 1. This site is located within a plantation area (117 ha) dominated by a larch species of *Larix kaempferi Sarg* (Hirano et al., 2003). Larch is a dominant species of boreal forests in the northern part of East Asia, including Siberia. This site is characterized by a canopy height of 15 m on average, tree age of 45 years old and a good tree health condition. The fetch and the slope of the ground are 300–800 m and 1–2°, respectively, both of which are suitable for flux measurements. Air samplings for quantification of VOCs and SVOCs were carried out at heights of 22 and 38 m of the tower, which are equivalent to ca. 7 and 23 m above the canopy. During the sampling period, weather condition was fine except for the period after 1 pm on September 5 when rain started. Meteorological data including air temperature, wind speed/direction, humidity and photosynthetically active photon flux density (PPFD) were also collected on the tower. During the sampling period, the air temperature and wind speed at a height of 27 m ranged from 12 to 23 °C and from 0.47 to 6.8 m s^{-1}, respectively.

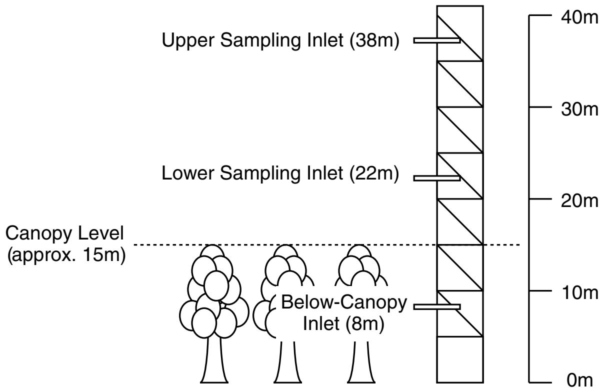

Fig. 1. Schematic representation of the research forest and the tower (sampling site).

2.2. Sampling methods for VOCs and SVOCs

Table 1 presents the sampling schedule of VOCs and SVOCs during this study. VOC samples were collected in 6-liter canisters (Silico Can, Restek) that were pre-cleaned twice in a laboratory by purging helium at about 80 °C and pumped in vacuum prior to use. At heights of 22 and 38 m, sample air was drawn in the canister at a flow rate of 500 ml min^{-1} through a bellows pump (Iwaki air pump type BA) and a thermal mass flow controller (STEC PAC-D2). Silico-steel tubing (GL Science, 1/4 inch) was used for sampling lines to minimize a potential adsorptive loss of VOCs in the lines. At a height of 8 m, on the other hand, air was collected in the canisters instantly without any flow control. A PTFE membrane filter was placed at the sampling inlet to remove aerosol particles. Ozone scrubber was not used because test samplings showed no significant decrease in concentrations of isoprene and α-pinene during the storage of 5 min to 1 week after sample collections.

Annular denuder sampling system was used to collect SVOCs in both gas phase and particles. Details of this method are described elsewhere (Matsunaga et al., 2003, 2004). Briefly, the SVOC sampling system consists of a cyclone-inlet (URG-2000-30EU), a reaction tube, a multi channel front annular denuder (URG-2000-30 × 242-3CSS), a quartz filter, and a back-up

Table 1. Start time of VOC and SVOC samplings

Date	Height	VOCs	SVOCs
3 September	22, 38 m	9:00, 12:15, 16:45, 20:00	8:00, 12:20, 16:30, 22:00
	8 m	13:00	—
4 September	22, 38 m	0:00, 6:10, 9:30, 13:00, 16:30, 19:00	5:30, 9:00, 12:30, 16:00, 22:00
	8 m	0:00, 13:15	—
5 September	22, 38 m	6:00, 10:00, 13:00	5:30, 9:00, 12:30
	8 m	0:00, 13:15	—

denuder and a diaphragm pump. Based on the difference in diffusion rates of gas and particles, the front denuder collects volatile compounds and the filter and backup denuder collect particulate compounds. The inner walls of the denuders were coated with a collection reagent of 5% O-benzylhydroxylamine hydrochloride ($C_6H_5CH_2ONH_2 \cdot HCl$; BHA-HCl) and 3% XAD-7. Gas phase carbonyls that contact with the reagents and immediately react with them are retained on the denuder walls in the form of BHA-oximes. To remove oxidants in sample air, nitrogen monooxide (NO) was mixed with the sample air at the inlet, resulting in the NO concentration in the air to be 2 ppmv. A model calculation of gas-phase chemical reactions has shown that this method effectively removes OH and NO_3, as well as O_3 (Mochida et al., 2003). Pump exhaust was passed through a NO trap (Nitta Corporation) to avoid contamination of ambient air with high NOx. Sample air was sucked at a constant flow rate of 10 liter min^{-1} for 3 hours. After sampling, SVOCs collected on denuders were immediately extracted with 10 ml methanol and the extracts were stored in centrifugal tubes at −20 °C prior to analysis. Particulate SVOCs collected on filters were also stored at −20 °C in clean glass vials (50 ml) with Teflon-lined caps.

2.3. *Analytical methods for VOCs and SVOCs*

VOCs were analyzed by GC-MS and all the analyses were completed within 2 weeks after the sample collection. Using an automated concentration system (DKK GAS-30) and a diaphragm pump, VOC sample air in the canister was transferred to an absorption column (1/8 inch) containing 150 mg of Tenax TA at 45 ml min^{-1} for 10 min at room temperature. The Tenax TA column was heated to 280 °C for 15 min and the VOCs trapped were transferred to a capillary GC column. Desorbed VOCs were then trapped at the inlet of capillary column at −150 °C using a cryofocusing unit (DKK GAS-2BCF) and then heated to 180 °C to transfer VOCs to a GC-MS system (GC: Hewlett Packard HP 6890, MS: HP 5973). A CP-Sill 8CB column (60 m × 0.25 mm i.d. × 0.25 μm film thickness) was used with the GC oven temperature programmed from 30 °C (5 min) to 250 °C (10 min) at 20 °C min^{-1}. Post-run was conducted at 320 °C for 5 min to clean up the GC column. Helium was used as a carrier gas at a flow rate of 2 ml min^{-1}. Stainless steel tubes of the sampling lines were heated to 100 °C to reduce absorption of VOCs on lines.

The mass spectrometer with an electron impact ionization source was operated at a selective-ion monitoring mode. Monitoring ions of m/z 67 and 72 were used for quantification of isoprene and m/z 93, 121 and 136 were for α-pinene. A standard VOC mixture (Taiyotoyosanso Corp.) containing 10 hydrocarbon species of 20 ppbv was analyzed by the GC-MS at different dilution ratios, and a linearity of the GC-MS response to the sample amount was confirmed ($R^2 \geq 0.99$). This standard was analyzed once a day for calibration before the atmospheric sample analysis.

SVOCs were analyzed as follows. First, the methanol extracts from the denuder were centrifuged to remove remaining XAD-7 particles. The filter samples were extracted with methanol and were combined to the extracts from the backup denuders, which contain BHA-HCl reagent. This allows the carbonyls on the filter to be derivatized to BHA-oximes. The extracts were concentrated in a pear shaped flask (50 ml) using a rotary evaporator down to 0.5 ml, to which 10 ml of ethyl acetate, 7 ml of pure water and 1 ml of 8 N hydrochloric acid were added. After the shaking of the pear shape flask, the aqueous layer was removed. The ethyl acetate layer was concentrated to ca. 0.5 ml and transferred to a 1.5 ml glass vial, to which 50 μl of Sylon BFT (BSTFA:TMCS = 99:1, Supelco Corporation) was added after dryness. The vial was heated at 60 °C for 60 min for derivatization. The solvents were then evaporated under a gentle Argon stream and the derivatives were dissolved in 50 μl of n-hexane. By the procedure above, carbonyl groups of compounds to be quantified are derivatized to oximes whereas hydroxyl and carboxyl groups are derivatized to trimethylsilyl ethers and esters, respectively (Fig. 2).

SVOC-derivatives were quantified using a capillary GC-FID (Carlo Erba HRGC MEGA 2 series, column; DB-1701, 60 m × 0.32mm(i.d.) × 0.25 μm). The GC oven temperature was programmed from 70 to 150 °C at 20 °C min^{-1} and then to 280 °C (10 min) at 4 °C min^{-1}. More details of SVOC analysis were described elsewhere (Matsunaga and Kawamura, 2000; Matsunaga et al., 2004).

As described above, concentrations of six SVOCs (n-nonanal, n-decanal, glycolaldehyde, hydroxyacetone, glyoxal and methylglyoxal), which have been found in high concentrations in the forest (Matsunaga et al., 2003, 2004), are presented in this paper. As an oxidation product of α-pinene, pinonic acid was quantified by this method, but its concentration was in most cases below the detection limit (4 ng m^{-3}). Although dimmers of α-pinene oxidation products have recently been reported (Tolocka et al., 2004), identification/quantification of such compounds were not attempted in this study. Field blanks of SVOCs correspond to 1.3–30 ng m^{-3} depending on compounds. They were used to correct SVOC concentrations. In the case of VOCs, blanks levels were low enough and thus neglected for calculations of VOC concentrations. Precisions (reproducibility) of SVOC analysis ranged from 2 to 14%, whereas those of VOCs were from 6 to 8%.

2.4. *Calculations of vertical fluxes of VOCs and SVOCs*

VOC and SVOC fluxes were calculated by a modified gradient method. Briefly, the VOC flux F_s (ng m^{-2} s^{-1}) was calculated from the following equation:

$$F_S = -K \frac{\Delta c}{\Delta z}, \qquad (1)$$

where K (m^{-2} s^{-1}) is the eddy diffusion coefficient. Δc (ng m^{-3}) is the difference in the VOC and SVOC concentrations between

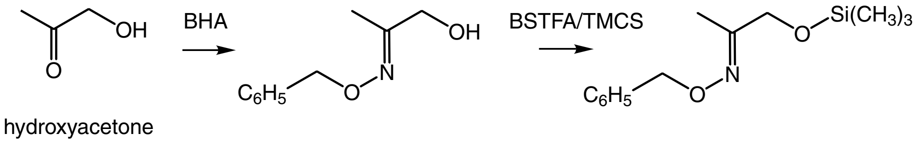

Fig. 2. Two-step derivatization of bi-functional carbonyl compounds used in this study. An example for hydroxyacetone is presented.

two sampling heights of 22 and 38 m. Δz (m) is the difference in sampling heights ($38 - 22 = 16$ m). Eddy diffusion coefficient K was obtained from the following equation assuming that eddy diffusion coefficients for heat and mass are identical:

$$\rho C_p \overline{w'T'} = \rho C_p \times K \times \frac{\Delta T}{\Delta z_T}, \qquad (2)$$

where $\rho C_p \overline{w'T'}$ is a sensible heat flux (W m^{-2}), which was obtained by the eddy covariance method using the data measured by a three-dimensional sonic anemometer-thermometer at 27 m of the tower (Hirano et al., 2003). ρ and C_p are the density (g m^{-3}) and the isopiestic specific heat (J g^{-1} K^{-1}) of air, respectively. ΔT is the difference in air temperature (K) at heights of 22 and 32 m, and Δz_T is 10 m. K was not obtained accurately when ΔT was so small. Such situation occasionally happened at night and early morning, and the K values were eliminated for such cases from the analysis of data.

3. Results and discussion

3.1. Diurnal variations of VOCs

Mixing ratios of isoprene and α-pinene at heights of 8, 22 and 38 m are presented in Fig. 3 together with air temperature and PPFD. Mixing ratios of isoprene both at 22 m and 38 m increased with an increase in PPFD and air temperature, showing a maximum in midday. The maximum concentrations of isoprene during the sampling periods were 851 and 700 pptv at heights of 22 and 38 m, respectively. Its nighttime concentrations were on the other hand very low, down to 23 and 13 pptv at heights of 22 and 38 m, respectively. Concentrations of isoprene positively correlated with PPFD ($R^2 = 0.75$ at 22 m) and air temperature ($R^2 = 0.52$ at 22 m), being consistent with the theory that biogenic isoprene emission is mainly controlled by leaf temperature and light intensity (Guenther et al., 1993). Concentrations of α-pinene were approximately one order of magnitude lower than those of isoprene, and the maximum concentrations of α-pinene at heights of 22 and 38 m were 145 and 94 pptv, respectively. In the case of α-pinene, the diurnal variations at both heights were less clear than those of isoprene. This may be related to the difference in the emission mechanism between isoprene and α-pinene; α-pinene emission is not so sensitive as isoprene to PPFD (Kesselmeier and Staudt, 1999).

At a height of 8 m, concentrations of VOCs were obtained twice a day (see Table 1). Being similar to the cases of 22 and 38 m, diurnal patterns of isoprene (range: 8–503 pptv) and α-pinene (range: 33–93 pptv) at the 8 m height were also different; isoprene showed a clear diurnal pattern whereas α-pinene stayed almost unchanged throughout day and night.

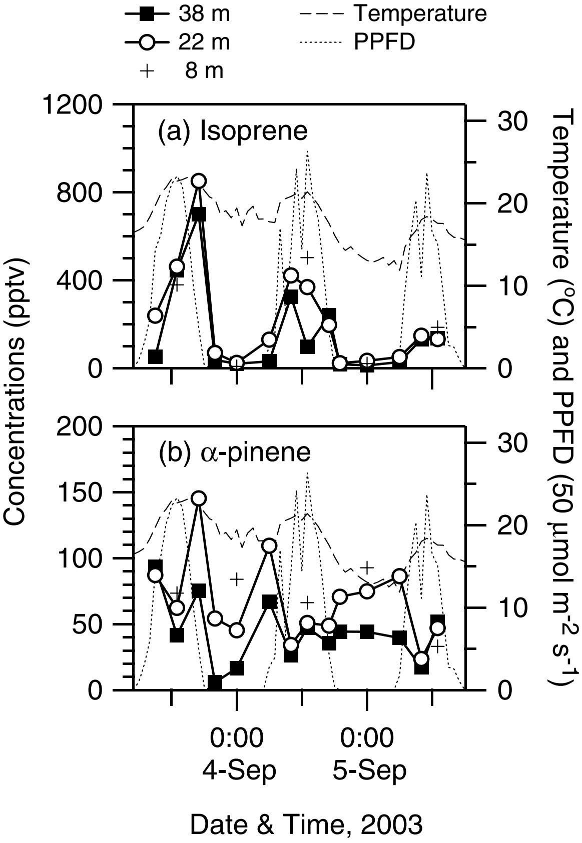

Fig. 3. Concentrations of VOCs (isoprene and α-pinene) at heights of 8 m (cross), 22 m (open circle) and 38 m (solid square) above the ground level. Air temperature (dashed line) and PPFD (dotted line) at a height of 27 m are superimposed on the figure.

3.2. Diurnal variations of SVOCs

Concentrations of six SVOCs (gas + particle) at heights of 22 and 38 m are presented in Fig. 4. All the SVOCs showed diurnal variations with maxima in daytime. If SVOCs are directly emitted from the forest, it is reasonable that they show diurnal patterns with maxima in daytime, because their emission may positively correlate to ambient temperature and/or PPFD like isoprene. On the other hand, if the SVOCs are secondarily formed, they may also show daytime maxima because photochemical processes and emissions of biogenic precursors are enhanced in daytime. Therefore, the diurnal variations of SVOCs are consistent with

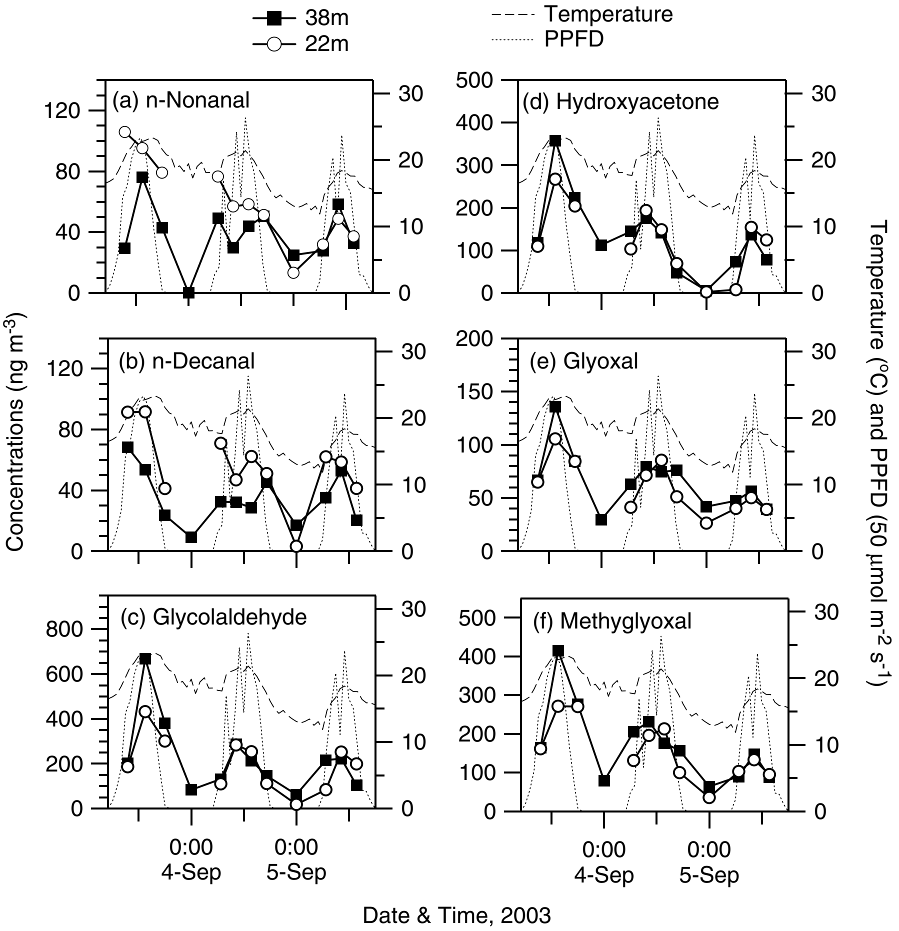

Fig. 4. Concentrations of six SVOCs (n-nonanal, n-decanal, glycolaldehyde, hydroxyacetone, glyoxal and methylglyoxal,) at heights of 22 m (open circle) and 38 m (solid square) above the ground level. Air temperature and PPFD at 27 m are superimposed on the figure.

the characteristic of VOCs of biogenic origin. Because glycolaldehyde and hydroxyacetone (Figs. 4c and 4d) are known as two major oxidation products of isoprene with methylvinylketone and methacrolein being as intermediates (Finlayson-Pitts and Pitts, 2000), our results suggest that isoprene oxidation significantly controls the abundances of SVOCs at the sampling site. Actually, glycolaldehyde and hydroxyacetone (Figs. 4c and 4d) showed co-variation with isoprene (Fig. 3a), suggesting that isoprene oxidation is a significant process to control the SVOC distributions. Glyoxal and methylglyoxal (Figs. 4e and 4f) are also known to be oxidation products of isoprene. They showed a similar temporal variation with isoprene, implying the contribution of isoprene oxidation to their abundance. Glyoxal and methylglyoxal may also be produced in part from other biogenic precursors because their carbon structures are simple and they bear only carbonyl groups, which are the most typical functional groups being introduced as a result of atmospheric oxidation.

As presented in Fig. 4, significant differences in concentrations of SVOCs at two sampling heights were shown for some samples. For instance, concentrations of n-nonanal and n-decanal (Figs. 4a and 4b) at 22 m were generally significantly higher than those at 38 m. On the other hand, the differences are less significant for other four carbonyls, glycolaldehyde, hydroxyacetone, glyoxal and methylglyoxal. This point is discussed in more detail below.

Table 2 summarizes concentration ranges and means of SVOCs, as well as those of VOCs.

3.3. Gas/particle partitioning of SVOCs

Attributing the SVOCs collected by the front denuder to be originally in gas phase and those on the filter and backup denuder to be in particles, the gas/particle partitioning of SVOCs can be obtained. As reported previously (Matsunaga et al., 2003; 2004), results from denuder sampling suggests the presence of SVOCs in aerosol particles. Ranges and means of the ratios of [particle]/[gas + particle] during the sampling period are calculated with a correction of measured collection efficiency of denuders for SVOCs. The results are summarized in Table 3. The mean ratios ranged from 0.4 to 24% for six SVOCs, which are within the range reported in previous studies (Matsunaga et al., 2003; 2004).

Table 2. Concentrations of VOCs and SVOCs at heights of 22, 38 and 8 m

		22 m			38 m			8 m		
		n[a]	Range	Mean	n[a]	Range	Mean	n[a]	Range	Mean
VOCs (pptv)	Isoprene	14	23–851	225	14	13–700	163	5	8–503	219
	α-pinene	14	24–145	67	14	6–94	43	5	33–93	70
SVOCs (ng m^{-3})	n-nonanal	11	13–106	60	12	$\leq$7–76	37	—	—	—
	n-decanal	11	$\leq$9–92	56	12	9–68	35	—	—	—
	Glycolaldehyde	11	18–432	203	12	62–668	226	—	—	—
	Hydroxyacetone	11	$\leq$13–267	126	12	$\leq$13–358	134	—	—	—
	Glyoxal	11	26–106	60	12	30–136	66	—	—	—
	Methylglyoxal	11	36–271	155	12	64–415	174	—	—	—

[a] Number of samples.

Table 3. Collection efficiency of denuders and ratios of particle/(gas + particle) (%) determined from the denuder and filter analysis

		22 m			38 m		
Compounds	CE[a]	n[b]	Range[c]	Mean[c]	n[b]	Range[c]	Mean[c]
n-nonanal	0.95 ± 0.07	11	0–57	21	11	0–32	16
n-decanal	0.91 ± 0.12	10	0–55	23	12	0–57	24
Glycolaldehyde	1.00 ± 0.00	11	0–45	15	12	2–38	17
Hydroxyacetone	0.85 ± 0.12	9	0–27	7	11	0–51	15
Glyoxal	0.81 ± 0.03	11	0–43	10	12	0–18	8
Methylglyoxal	0.71 ± 0.20	11	0–42	5	12	0–4	0.4

[a] Collection efficiency (CE) of denuders that was calculated by $1 - (C_1/C_2)$, where C_1 and C_2 are concentrations of SVOCs collected by first and second denuders, respectively, in the absence of filters. Averages of two experiments are presented. Potential artifacts by attachment of particles on denuders are not considered.

[b] Number of samples. Samples whose concentrations (gas + particles) were less than blank levels were omitted.

[c] Ratios of gas/(gas + particle) after a correction of CE. The zero value means that the SVOC concentration in particles after the correction of CE is calculated to be ≤ 0.

Such high abundances of particulate carbonyls are surprising, taking into account the fact that boiling points of some carbonyls compounds (e.g. glyoxal) are even lower than that of water. However, recent laboratory studies have suggested unexpected enhancement of particle formation due to volatile carbonyl compounds (Jang et al., 2002). They attributed the presence of carbonyl in particles to be originated from chemical reactions in particles, such as formation of acetals. Further, reactions of semi-volatile carbonyl compounds to form aerosol particles via polymerization have been observed by chamber studies (Kalberer et al., 2004; Liggio et al., 2005). These mechanisms possibly explain the unexpectedly large abundance of SVOCs in aerosol particles as observed in this study. But so far, it is not known whether the carbonyls as a unit of polymers in aerosol particles can be detected by the method used in this study. Polymerization is potentially an important process for the formation of biogenic aerosols, and further studies are required to better understand the gas/particle partitioning of SVOCs.

3.4. *Vertical gradients of VOCs and SVOCs and their implications for the emission and formation processes*

In addition to the diurnal variation of VOCs and SVOCs, their vertical gradients may provide information on their origins. Figure 5 presents differences in VOC and SVOC concentrations at two heights of 22 and 38 m by:

$$L = \log_{10} \frac{[C_{38}]}{[C_{22}]}, \tag{3}$$

where C_{38} and C_{22} are the concentrations of compounds at heights of 38 and 22 m, respectively. If there is no vertical gradient observed, L is equal to zero. Apparently, in the cases of isoprene, α-pinene, n-nonanal and n-decanal, negative L values are more frequently observed than positive L values (Fig. 5). In contrast, frequency of positive L values is similar to or more than that of negative L values for glycolaldehyde, hydroxyacetone, glyoxal and methylglyoxal.

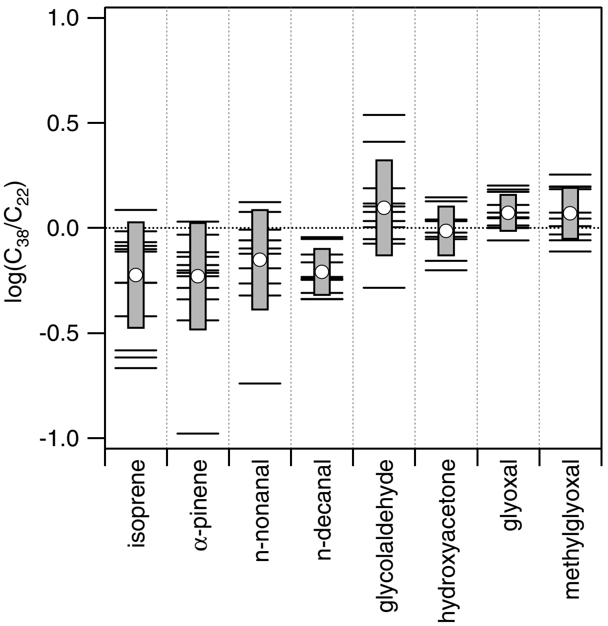

Fig. 5. Vertical gradients of VOCs and SVOCs represented by $L = \log_{10}$ ([Concentrations at 38 m]/[Concentrations at 22 m]). The raw data points, means and one-standard deviations are presented by horizontal lines, open circles and solid vertical bars, respectively. The values whose concentrations at one of two heights were lower than their errors originating from blank subtractions are not included here because of a large uncertainty in L.

To evaluate whether or not the averaged L values are significantly different from zero and have systematic trends, t-test was applied for eight organic compounds studied (Table 4). By 10% two-sided t-test, averages of the ratios for the first four compounds, isoprene, α-pinene, n-nonanal and n-decanal, are confirmed to be significantly lower than zero. This indicates that their main sources are present in the forest below the canopy level. It has been well known that isoprene and α-pinene are major biogenic VOCs emitted from vegetations. Significant emissions of nonanal and decanal from vegetation and microbial processes have been suggested (Kesselmeier and Staudt, 1999), being consistent with the vertical gradients of these two aldehydes measured in this study. This also indicates that possible secondary formations of n-nonanal and n-decanal (e.g. oxidation of aliphatic compounds) are relatively minor compared to the direct emissions from vegetations. It should be noted that concentrations of n-nonanal obtained in this study are potentially biased because omega-9 unsaturated fatty acids attached to filters and denuders during the atmospheric sampling possibly decompose to form n-nonanal via ozonolysis (Fruekilde et al., 1998). On the other hand, this is not the case for n-decanal because of the absence of biological unsaturated fatty acids containing a double bond at omega-10 position.

On the other hand, different trends were observed in the vertical distributions of glycolaldehyde, hydroxyacetone, glyoxal and methylglyoxal (Fig. 5). In the case of glyoxal and methylglyoxal, downward flux was significant on average basis. On the other hand, mean fluxes of glycolaldehyde and hydroxyacetone were not significantly different from zero. This result suggests that possible primary emissions of these four carbonyls from vegetations were, even if present, less important than other sources. Since diurnal variations of these compounds were similar to that of biogenic isoprene, secondary formation from biogenic precursors by photochemical oxidation are the most likely sources for the oxygenated organic compounds. Isoprene is known to produce glycolaldehyde, hydroxyacetone, glyoxal and methylglyoxal via O_3 and OH radical reactions (Finlayson-Pitts and Pitts, 2000). Hence isoprene may contribute substantially to the concentrations of these four carbonyls.

To confirm that secondary formation from isoprene does not lead to negative L values, time scales for the production of these four compounds from isoprene were calculated using a box model. In this model, both 1st oxidation products (i.e. methacrolein and methylvinylketone) and 2nd oxidation

Table 4. Results of two-sided t-test for the null hypothesis $\log(C_{38}/C_{22}) = 0$

Compounds		n[a]	t[b]	$P(T < \lvert t \rvert)$[c]	10% two-sided t-test[d]
VOCs	Isoprene	14	−3.34	0.53%	Rejected
	α-pinene	14	−3.39	0.48%	Rejected
SVOCs	n-nonanal	11	−2.12	6.0%	Rejected
	n-decanal	11	−6.06	0.019%	Rejected
	Glycolaldehyde	11	1.41	19%	Not rejected
	Hydroxyacetone	10	−0.37	72%	Not rejected
	Glyoxal	11	2.79	1.9%	Rejected
	Methylglyoxal	9	1.90	8.6%	Rejected

[a] Number of samples subjected to the t-test.

[b] $t = (\bar{L} - 0)/\sqrt{V/n}$, where $\bar{L}$ and V are mean and variance of $\log(C_{38}/C_{22})$, respectively.

[c] Limit of probability that null hypothesis is rejected by 10% two-sided t-test.

[d] “Rejected” means that the $\log(C_{38}/C_{22})$ is significantly different from zero by 10% two-sided t-test.

products (i.e. glycolaldehyde, hydroxyacetone, glyoxal and methylglyoxal) were included. Concentrations of isoprene-reaction products with O_3 and OH were calculated using the maximum O_3 concentration measured at the site (ca. 40 ppbv), and OH concentration fixed to be 1×10^7 molecules cm^{-3}, and reaction rate constants for O_3 and OH (Paulson et al., 1992; Paulson and Seinfeld, 1992). Photolysis rates were calculated based on the latitude at the site and the solar zenith angle at noon. Time evolutions of the concentrations of carbonyls were obtained by solving the differential equations numerically with a 4th-order Runge-Kutta scheme (Jain, 1984).

Calculated temporal evolution of the concentrations of isoprene and the degradation products, and their formation rates, are presented in Fig. 6. The results indicate that at least several tens of minutes are necessary in order that glyoxal, methylglyoxal, glycolaldehyde and hydroxyacetone can be produced from isoprene. On the other hand, a residence time of air below the sampling tower in daytime was calculated to be on the order of minutes from the diffusion coefficients as well as air volume below the sampling heights. Thus, SVOCs (glyoxal, methylglyoxal, glycolaldehyde and hydroxyacetone) are produced not only below the sampling height (22–38 m) in the forest, but also above it. This results in a uniform vertical distribution of SVOCs. The reasons of positive L values observed for glyoxal and methylglyoxal may be caused by dry deposition on leaves, enhanced photochemical formation above the canopy due to enhanced light intensity and oxidant concentrations, or their transport into the forest from the outside. From the dataset in this study, however, it is difficult to specify which process is responsible for vertical gradients of glyoxal and methylglyoxal.

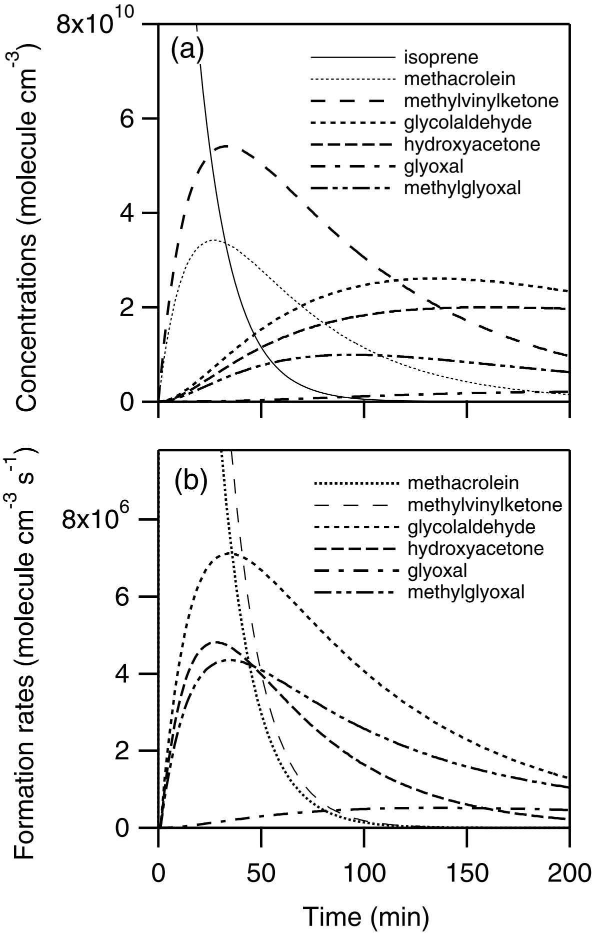

Fig. 6. Result from a box model calculation of photochemical oxidation of isoprene. Initial concentration of isoprene is 2.5×10^{11} molecule cm^{-3}. (a) Time profiles of VOC and SVOC concentrations after introduction of isoprene to the system. (b) Formation rates of VOCs and SVOCs as a function of time.

3.5. *Fluxes of VOCs and SVOCs over the forest*

Based on the modified gradient method described in the experimental section, vertical fluxes of VOCs and SVOCs were calculated from the differences in the concentrations at heights of 22 and 38 m. Table 5 summarizes mean fluxes of VOCs and SVOCs obtained in this study. The mean fluxes of isoprene and α-pinene during the sampling were 34.8 and 9.8 ng m^{-2} s^{-1}, respectively. To our knowledge, no flux measurements of VOCs over a larch forest has been conducted. However, for instance, the magnitudes of our isoprene fluxes are comparable to the values 40.5–183 ng m^{-2} s^{-1} reported over a sitka spruce forest in southwestern Scotland (Beverland et al., 1996) with similar daytime maximum air temperature (<15–19 °C). On the other hand, α-pinene fluxes obtained in our study are much lower than those reported in the southwestern Scotland (24.7–156 ng m^{-2} s^{-1}).

Being similar to the vertical profiles of SVOCs shown in Fig. 5, SVOC fluxes can be separated into two groups. Mean fluxes of n-nonanal and n-decanal are positive (upward) on average (Table 5). In contrast, fluxes of other SVOCs, that is, glycolaldehyde, hydroxyacetone, glyoxal and methylglyoxal, are rather unclear if their uncertainty (one standard deviation) was considered. As discussed above, these SVOCs may not be

Table 5. Mean vertical fluxes (ng m^{-2} s^{-1}) of VOCs and SVOCs studied

Compounds	Mean ($\pm 1\sigma$)[a]
VOCs	
Isoprene	34.8 ± 80.8
α-pinene	9.8 ± 9.0
SVOCs	
n-nonanal	3.8 ± 7.1
n-decanal	4.4 ± 4.0
Glycolaldehyde	−6.9 ± 22.1
Hydroxyacetone	1.1 ± 11.0
Glyoxal	−3.5 ± 8.8
Methylglyoxal	−9.0 ± 22.7

[a] Positive values correspond to upward flux.

emitted from the forests significantly, rather they are likely produced above/below the canopy by the photochemical oxidation of their precursors such as isoprene and, to a lesser extent, α-pinene. The sum of the mean fluxes of n-nonanal and n-decanal is 8.3 ng m^{-2} s^{-1}, whereas that of glycolaldehyde, hydroxyacetone, glyoxal and methylglyoxal fluxes was -18.4 ng m^{-2} s^{-1}. The summed flux of n-nonanal and n-decanal was nearly equal to the α-pinene flux, meaning that supply of n-nonanal and n-decanal from vegetation to the atmosphere is significant at this site.

The large positive (upward) and negative (downward) fluxes of SVOCs imply its potential importance to the budget of organic gases and aerosols in the interface between the forest and the atmosphere. As SVOCs are more polar and thus are stickier than VOCs, adsorptive loss on leaves and stems and their re-evaporation in daytime may control, at least in part, their vertical fluxes. This adsorption/evaporation process possibly enhances the diurnal behavior of the SVOCs, in particular bi-functional carbonyls that are produced by the oxidation of isoprene. Further studies are required to better understand the atmospheric behavior of SVOCs and the importance of their fluxes, particularly in terms of the formation of biogenic aerosols.

4. Summary and conclusions

Diurnal distributions and vertical gradients of two VOCs (isoprene and α-pinene) and six SVOCs (n-nonanal, n-decanal, glyoxal, methylglyoxal, glycolaldehyde and hydroxyacetone) were studied over the larch forest in Hokkaido, Japan. Diurnal patterns of six SVOCs with a maximum in daytime suggest that they are mainly of biogenic origin. Substantial presence of SVOCs in aerosol particles is suggested by denuder samplings, being consistent with previous studies. A significant decrease in the concentrations at higher altitude was observed for n-nonanal and n-decanal, suggesting that they are mainly released directly from the vegetations. On the other hand, other four SVOCs (glyoxal, methylglyoxal, glycolaldehyde and hydroxyacetone) that are known as oxidation products of isoprene showed on average no- or opposite trends in vertical distributions. This indicates that direct emissions of these four carbonyls from vegetations are minor and that bi-functional carbonyls are mainly produced by photochemical oxidation of biogenic organic compounds emitted to the air. Calculations of the VOC and SVOC fluxes have revealed that emissions of SVOCs are substantial in comparison to VOCs, suggesting that SVOCs are important components to better understand the budget of organic gases and aerosols in the forest atmosphere.

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References

Beverland, I. J., Milne, R., Boissard, C., ÓNéill, D. H., Moncrieff, J. B. and Hewitt, C. N. 1996. Measurement of carbon dioxide and hydrocarbon fluxes from a sitka spruce forest using micrometeorological techniques. *J. Geophys. Res.* **101**, 22 807–22 815.

Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A. B., Hewitt, C. N., Lamb, B., Liu, S., Trainer, M., Westberg, H. and Zimmerman, P. 1992. Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry. *Global Biogiochem. Cycles* **6**, 389–430.

Finlayson-Pitts, B. J. and Pitts Jr., J. N. 2000. *Chemistry of the Upper and Lower Atmosphere*. Academic Press, San Diego, CA, 969 pp.

Fruekilde, P., Hjorth, J., Jensen, N. R., Kotzais, D. and Larsen, B. 1998. Ozonolysis at vegetation surfaces: A source of acetone, 4-oxopentanal, 6-methyl-5-hepten-2-one, and geranyl acetone in the troposphere. *Atmos. Environ.* **32**, 1893–1902.

Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K. and Fall, R. 1993. Isoprene and monoterpene emission rate variability—model evaluations and sensitivity analysis. *J. Geophys. Res.* **98**, 12 609–12 617.

Hirano, T., Hirata, R., Fujinuma, Y., Saigusa, N., Yamamoto, S., Harazono, Y., Takada, M., Inukai, K. and Inoue, G. 2003. CO_2 and water vapor exchange of a larch forest in northern Japan. *Tellus* **55B**, 244–257.

Jain, M. K. 1984. *Numerical Solution of Differential Equations*, 2nd Edition. Wiley, New York, NY, 698 pp.

Jang, M., Czoschke, N. M., Lee, S. and Kamens, R. M. 2002. Heterogeneous atmospheric aerosol producition by acid-catalyzed particle-phase reactions. *Science* **298**, 814–817.

Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A. S. H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R. and Baltensperger, U. 2004. Identification of polymers as major components of atmospheric organic aerosols. *Science* **303**, 1659–1662.

Kavouras, I. G., Mihalopoulos, N. and Stephanou, E. G. 1998. Formation of atmospheric particles from organic acids produced by forests. *Nature* **395**, 683–686.

Kavouras, I. G., Mihalopoulos, N. and Stephanou, E. G. 1999. Formation of gas/particle partitioning of monoterpenes photo-oxidation products over forests. *Geophys. Res. Lett.* **26**, 55–58.

Kesselmeier, J. and Staudt, M. 1999. Biogenic volatile organic compounds (VOC): an overview on emission, physiology end ecology. *J. Atoms. Chem.* **33**, 23–88.

Liggio, J., Li, S.-H. and McLaren, R. 2005. Heterogeneous reactions of glyoxal on particulate matter: Identification of acetals and sulfate esters. *Environ. Sci. Technol.* **39**, 1532–1541.

Matsunaga, S. and Kawamura, K. 2000. Determination of α- and β- hydroxycarbonyls and dicarbonyls in snow and rain samples by GC/FID and GC/MS employing benzyl hydroxyl oxime derivatization. *Anal. Chem.* **72**, 4742–4746.

Matsunaga, S., Mochida, M. and Kawamura, K. 2003. Growth of organic aerosols by biogenic semi-volatile carbonyls in the forestal atmosphere. *Atmos. Environ.* **37**, 2045–2050.

Matsunaga, S., Mochida, M. and Kawamura, K. 2004. Variation on the atmospheric concentrations of biogenic carbonyl compounds and their removal processes in the northern forest at Moshiri, Hokkaido Island in Japan. *J. Geophys. Res.* **109**, D04302, doi:10.1029/2003JD004100.

Mochida, M., Matsunaga, S. and Kawamura, K. 2003. A model evaluation of the NO titration technique to remove atmospheric oxidants for the determination of atmospheric organic compounds. *Environ. Sci. Technol.* **37**, 1589–1597.

Novakov, T. and Penner, J. E. 1993. Large contribution of organic aerosols to cloud-condensation-nuclei concentrations. *Nature* **365**, 823–826.

Paulson, S. E., Flagan, R. C. and Seinfeld, J. H. 1992. Atmospheric photooxidation of isoprene part II: The ozone-isoprene reaction. *Int. J. Chem. Kinet.* **24**, 103–125.

Paulson, S. E. and Seinfeld, J. H. 1992. Development and evaluation of a photooxidation mechanism for isoprene. *J. Geophys. Res.* **97**, 20 703–20 715.

Tolocka, M. P., Jang, M., Ginter, J. M., Cox, F. J., Kamens, R. M. and Johnston, M. V. 2004. Formation of oligomers in secondary organic aerosol. *Environ. Sci. Technol.* **38**, 1428–1434.