**Atmospheric
Chemistry
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Discussions**

**VOC concentrations
and emissions in
early spring**

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Boundary layer concentrations and landscape scale emissions of volatile organic compounds in early spring

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Abstract

Boundary layer concenrations of several volatile organic compounds (VOC) were measured during two campaigns in springs of 2003 and 2006. Measurements were conducted over boreal forests near SMEAR II measurement station in Hyytiälä, Southern Finland. In 2003 the measuremens were performed using light aircraft and in 2006 using hot air ballon. Isoprene concentrarions were low, usually below detection limit. This is explained by low biogenic production due to cold weather. Monoterpenes were observed frequently. Average total monoterpene concentration in the boundary layer was 33 ppt$_v$. Many anthropogenic compounds e.g. benzene, xylene and toluene, were observed in high amounts. Ecosystem scale surface emissions were estimated using simple mixed box budget methodology. Total monoterpene fluxes varied up to 80 μg m^{-2} h^{-1}, α-pinene contributing typically more than two thirds of that. Highest fluxes of anthropogenic compounds were those of p/m xylene.

1 Introduction

Atmospheric aerosol particles are important for the global radiation budget (Seinfeld and Pandis, 1998; Twomey, 1991; Ramanathan et al., 2001; Cess et al., 1995; Kurten et al., 2003; Kulmala et al., 2004a). In addition to anthropogenic sources, biogenic activities increase significantly aerosol load (e.g. Tunved et al., 2006). Substantial production of aerosol particles is observed over forests of boreal areas (Mäkelä et al., 1997; Kulmala et al., 2004b). The maximum of new aerosol particle formation over boreal forests occurs in the spring (Dal Maso et al., 2005). Aerosol formation and especially the growth in rural areas are expected to be caused mainly by terpenoid compounds and their oxidation products (O'Dowd et al., 2002; Tunved et al., 2006). To understand the details of these formation and growth processes, it is important to know the distribution of condensable vapors in the atmosphere.

Surface- and boundary layer concentrations of volatile organic compounds (VOC)

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have been measured by various investigators (e.g. Hakola et al., 2003). Atmospheric concentration of each compound is dependent on surface emission and atmospheric lifetime of that compound. Surface emissions can be estimated in different scales. Branch scale VOC emissions of typical tree species in the boreal areas are measured by e.g. Hakola et al. (1998), Tarvainen et al. (2005) and Hakola et al. (2006a). Less disturbance to the plants are caused by ecosystem scale measurements which are conducted above boreal forests by e.g. Rinne et al. (1999, 2000) and Spanke et al. (2001). These studies prove boreal vegetation to be strong monoterpene emitters, with some sesquiterpene and isoprene emissions as well.

Surface emissions in the landscape scale can be estimated using boundary layer concentrations. Davis et al. (1994) performed first measurements of landscape scale hydrocarbon emissions using mixed-layer gradient technique. They measured isoprene and monoterpene concentrations in the lower part of the boundary layer in the areas of Amazon rainforest and Alabama, USA. Spirig et al. (2004) measured boundary layer concentrations of isoprene and monoterpenes using tethered balloon in the Southern Finland. They used both mixed-layer gradient and mixed box budget methods and estimated the surface fluxes of monoterpenes to be between 180 and 300 μg m^{-2} h^{-1} in August 2001. However, no previous measurements over boreal forests in early spring exist.

In the present study, we measured concentrations of several non-methane hydrocarbons throughout mixed boundary layer. Among these, there are compounds that are typically of biogenic or anthropogenic origin. There is not much information on the boundary layer concentrations of the anthropogenic compounds in rural areas. In addition, we calculated estimates for the landscape scale surface emissions of these compounds. Our measurements were conducted early spring when events of new aerosol particle formation are often observed in boreal areas. Extensive aerosol measurements were performed simultaneously.

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2 Materials and methods

The measurements were performed during QUEST II (Quantification of Aerosol Nucleation in the European Boundary Layer) measurement campaign in 2003 and LABACET (LAgrangian Balloon-borne Aerosol Characterization ExperimenT) experiment in 2006. In 2003 the measurements were carried out between 21 March 2003 and 2 April 2003 using a light aircraft. In 2006 the measurements were conducted between 10 March 2006 and 17 March 2006 using a hot air balloon as a measurement platform.

The measurements took place near SMEAR II measurement station, located in Southern Finland (61°51′ N, 24°17′ E, 170 m a.s.l.). The area belongs to the southern boreal zone. Vegetation consists mainly of coniferous trees, dominated by Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*). Figure 1 shows the different land use categories around SMEAR II station. In Table 1 the proportional abundances of different categories are given. The land use data is derived from satellite photographs and forest inventories by National Land Survey of Finland. It has a resolution of 25×25 m.

The annual mean temperature in the area is 3°C. The warmest month is July with mean temperature of 16°C and the coldest is February with mean temperature of –8°C. The annual mean precipitation is 700 mm (data from Juupajoki meteorological station, Drebs et al., 2002).

At the SMEAR II measurement station many environmental parameters are measured routinely (Hari and Kulmala, 2005). These include various aerosol measurements, concentrations and surface fluxes of H_2O, CO_2 and O_3 as well as ordinary meteorological parameters. In Fig. 2 air temperature and relative humidity measured at 8 m height and photosynthetic photon flux density measured above forest during springs 2003 and 2006 are shown. Spring 2003, with mean temperature around zero, was clearly warmer than spring 2006.

Both aircraft and hot air balloon were equipped with temperature and humidity sensors. These data were used to find the top of the boundary layer. Boundary layer height was approximated subjectively from the potential temperature and water vapour mixing

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ratio data. The top of the boundary layer was assumed to be at the height where water vapour mixing ratio has a strong change or potential temperature gradient changes to positive. In Fig. 3, one typical case (13 March 2006) is shown.

The measurement platform at QUEST II flights was a DHC-6/300 Twin Otter STOL fixed-wind, twin engine aircraft OH-KOG. The airflow for VOC samples was taken in through a pitot tube located at the roof of the aircraft, in front of the engines. Dynamic pressure of the pitot tube generated a flow through 3 m Teflon tubing that had outlet below the aircraft. Sampler devices were connected to this line. The total airflow at the sample inlet was much higher than required for VOC sampling devices. For more details, see O'Dowd et al. (2006).

The burner in the hot air balloon produces contamination, including unburned hydrocarbons. To avoid these, the measurements were performed only during descend of the balloon, when there is strong flow of unaffected air from down under and when the usage of burner is minimal. In addition, the samples were collected about two meters below gondola base. From the data of aerosol particle number concentration, temperature and humidity it was confirmed that these procedures were adequate to guarantee contamination free measurements.

Light C_2-C_6 hydrocarbons were sampled into 0.85 l electro polished stainless steel canisters. The canisters were evacuated beforehand and pressurized during sampling using Teflon coated pump. The duration of one canister filling was 0–200 s. Chemical analysis was performed using a gas chromatograph (HP-6890) with a flame ionization detector (FID).

Heavier C_5-C_{10} hydrocarbons were trapped into cartridges filled with Tenax-TA and Carbopack-B adsorbents. The samples were taken using 10-min sampling time and constant flow of about 0.26 l per minute in the QUEST II campaign. During the LABACET experiment only 1- to 4-min sampling times were possible. Therefore we had to use quite high sampling flow of about 0.45 l per minute. At this high flow rate breakthrough is a significant problem and hence we used two cartridges in series. The analysed concentrations from these two cartridges were summed to yield the total con-

centration. The adsorbent samples were analyzed using automatic thermodesorption device (Perkin-Elmer ATD-400) connected to a gas chromatograph (HP-5890) and a mass-selective detector (HP-5972).

In addition to the airborne measurements, surface layer monoterpene concentrations were measured at the top of the SMEAR II tower, above the forest canopy, during the QUEST II campaign. The samples were collected on Tenax-TA at 50 ml min^{-1} for 2 h per sample. A sampler system with timers and solenoid valves was used to enable sampling around the clock for the duration of the campaign. Samples were analysed in the laboratory by ATD-GC-MS. For more details of the sampling and analysis system, see Janson et al. (2001).

In order to estimate the magnitude of the surface emission, we used simple mixed box budget methodology. In this method, the mixed boundary layer is treated as a closed and well mixed box where sources (surface emission) and sinks (chemical loss and entrainment) are in balance. Here we assume that these processes are constant in time and space, causing the mean concentrations of the compounds to be constant as well. Entrainment flux at the top of the boundary layer is neglected, as Spirig et al. (2004) showed that this would lead to less than 20% underestimation in the surface flux. After these assumptions we can write

$$F = zS, \tag{1}$$

where F is the surface flux, z is the height of the boundary layer and S is the chemical loss rate.

The chemical loss rates for different hydrocarbons were estimated from their reactions with ozone (O_3) and hydroxyl radical (OH). Ozone concentrations were measured at the top of the SMEAR II mast, 67 m above ground level. Typical daytime concentrations of OH were obtained from photochemical model calculations (Hakola et al., 2003). Reactions with nitrate radical (NO_3) were ignored because they are important only during nighttime. Loss rates were calculated from

$$S = c_{VOC} \left(c_{O_3} k_{O_3} + c_{OH} k_{OH} \right), \tag{2}$$

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where c_{VOC} is the concentration of a particular VOC compound, c_{O_3} and c_{OH} are the concentrations of O_3 and OH, respectively, and k_{O_3} and k_{OH} are the corresponding second order rate coefficients.

Average boundary layer concentrations were obtained by trapezoid integrals. Integration was done from the lowest measured point up to top of the boundary layer. The uppermost concentration measurement was extrapolated to represent the concentration at the top of the boundary layer. Concentrations that were below the detection limit of the chemical analysis were converted to value detection limit divided by two.

3 Results and discussion

3.1 Boundary layer concentrations of volatile organic compounds

Statistics of the VOC concentrations are presented in Table 2. Isoprene concentration exceeded the detection limit ($10\,ppt_v$) only in two samples. This is explained by early time of year and cold weather at the time of the measurements. Isoprene is known to be emitted by many boreal plant species (e.g. Hakola et al., 1998; Hellén et al., 2006; Haapanala et al., 2006) directly from synthesis which is light and temperature dependent (Guenther et al., 1993).

Monoterpenes were observed frequently throughout the boundary layer. Figure 4 shows relative abundances of different monoterpenes in the surface air and in the air upper within the boundary layer. In this comparison only data from QUEST II was used. The most abundant monoterpene was α-pinene with average daytime surface concentration of $37\,ppt_v$ and boundary layer concentration of $18\,ppt_v$. The second most abundant monoterpene was Δ^3-carene. Contribution of camphene was strongly increased upwards. This is, at least partly, explained by the differences in reactivates of different monoterpenes. Camphene has lowest reactivity against OH and O_3 of the monoterpenes analyzed (Atkinson, 1994). Hakola et al. (2003) measured total ambient concentrations of monoterpenes to be about $80\,ppt_v$ in March 2001 at SMEAR II. This

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value as well as the monoterpene distribution is quite similar compared to our results. Higher in the boundary layer the average total monoterpene concentration was 33 ppt_V. Spirig et al. (2004) measured average monoterpene concentration to be 37 ppt_V within mixed layer in August 2001 above Hyytiälä. Also the monoterpene distribution was quite close to our results except for the significant limonene concentrations measured by Spirig et al. (2004). The measurements of Spirig et al. (2004) were conducted in August and also Hakola et al. (2003) found out that limonene concentrations have seasonal variation with higher concentrations during summer and fall.

In Fig. 5 there are examples of vertical gradients of monoterpene concentrations. The gradients are seldom well behaving although clear decreasing trend upwards can be seen. Figure 5b shows how monoterpene concentrations suddenly dropped at nearly constant altitude. Some of these variations in the gradients can be explained by changes of vegetation inside measurement footprint during movement of the measurement platform. Some of the variation is explained by analytical uncertainties of 17% up to 61% for different monoterpenes. The magnitudes of analytical uncertainties are calculated as mean relative standard deviation of parallel samples taken regularly at the SMEAR II station. Due to short sampling times in the present study, real uncertainties are likely to be even higher.

In addition to biogenic compounds, the concentration data of four VOCs of mainly anthropogenic origin are given in Table 2. The highest concentrations are those of benzene, being 179 ppt and 148 ppt during QUEST II and LABACET, respectively. Figure 6 shows some vertical gradients of benzene. For comparison, Hakola et al. (2006b) observed average benzene concentrations of 211 ppt_V and 28 ppt_V in the winter and summer, respectively. Those surface air measurements were done at a rural site in the Northern Finland. Xylene concentrations varied a lot, average concentration being close to that of benzene.

3.2 Estimates of surface emissions

The total flux of monoterpenes varied between 5±4 and 39±11 μg m^{-2} h^{-1} during QUEST II and between 0±10 and 79±17 μg m^{-2} h^{-1} during LABACET, α-pinene being the dominant compound (see Fig. 7). Emission did not show clear dependence on the surface temperature (see Fig. 8) which can be due to very low temperatures and resulting low concentrations as compared to analytical uncertainties. For comparison we calculated the average landscape scale emission using the land use data presented in Table 1 and emission potentials and foliar biomass densities used by Lindfors and Laurila (2000). The resulting landscape scale emission potential of monoterpenes was 575 μg m^{-2} h^{-1}, which leads to considerably higher emissions than those derived in this paper. Also Spirig et al. (2004) reported landscape scale emissions to be lower than ecosystem scale emissions measured before at the same place.

4 Conclusions

Boundary layer concentrations of volatile organic compounds were measured over boreal forests during early springs of 2003 and 2006. Despite of cold weather, boundary layer concentrations of monoterpenes were at same level than those measured in August during earlier studies. Isoprene, however, was almost absent.

Landscape scale surface emissions were estimated using simple mixed box method. Vertical profiles were seldom enough well-behaving for gradient methods. In the summer, boundary layer might be better mixed and thus allow use of these methods. Emissions of monoterpenes were low, lower than predicted by ecosystem scale measurement data. The highest monoterpene emissions were those of α-pinene and Δ^3-carene.

Due to short sampling times in LABACET experiment 2006, those results are more uncertain. Because of the ability to maintain stable flight altitude, aircraft seems to be better measurement platform than hot air balloon for this kind of work.

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Table 1. The proportions of different land use categories in the area of 1600 m^2 around SMEAR II station.

Land use type	Proportion [%]
built areas	0.3
wetlands	0.7
clear cut	1.7
deciduous forest	2.0
open land	2.9
agriculture	10.2
water bodies	13.0
mixed forest	20.9
pine dominated forest	22.7
spruce dominated forest	25.5

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Table 2. Statistics of the average VOC concentrations in ppt_v.

	DL	2003 surface layer				2003 boundary layer				2006 boundary layer			
		mean	stdev	min	max	mean	stdev	min	max	mean	stdev	min	max
isoprene	10					b.d.l.	b.d.l.	b.d.l.	b.d.l.	6	2	b.d.l.	10
α-pinene	14	37	21	b.d.l.	62	15	9	b.d.l.	37	20	10	14	37
β-pinene	2	3	5	b.d.l.	12	4	2	b.d.l.	9	1	2	b.d.l.	4
Δ^3-carene	4	21	19	b.d.l.	50	8	4	b.d.l.	18	10	9	4	25
camphene	4	2	5	b.d.l.	15	7	4	b.d.l.	21	1	2	b.d.l.	5
Σmonot.		63				34				32			
benzene	4					179	39	101	257	148	46	81	199
toluene	46					108	72	38	285	61	27	46	108
p/m xylene	68					123	94	26	329	81	27	68	130
o xylene	85					48	36	11	123	102	36	85	166

DL = typical detection limit, b.d.l. = below detection limit.

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Table 3. Statistics of the VOC emissions in μg m^{-2} h^{-1}.

	2003				2006			
	mean	stdev	min	max	mean	stdev	min	max
isoprene	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.7	0.6	b.d.l.	2.8
α-pinene	13.1	8.2	3.3	24.7	27.4	16.2	16.1	55.5
β-pinene	1.7	1.4	0.3	4.3	0.4	1.0	b.d.l.	2.2
Δ^3-carene	3.9	3.2	b.d.l.	8.6	8.6	8.0	2.4	22.2
camphene	1.5	1.7	b.d.l.	4.9	0.3	0.5	b.d.l.	1.1
Σmonot.	20.2				38.4			
benzene	1,1	0,6	0,3	2,0	0.4	0.2	0.2	0.6
toluene	1,0	0,4	0,3	1,7	0.9	0.5	0.6	1.7
p/m xylene	3,3	2,4	1,5	8,7	4.6	1.7	3.3	7.7
o xylene	0,9	0,6	0,1	2,3	4.2	1.6	3.0	7.0

b.d.l. = below detection limit
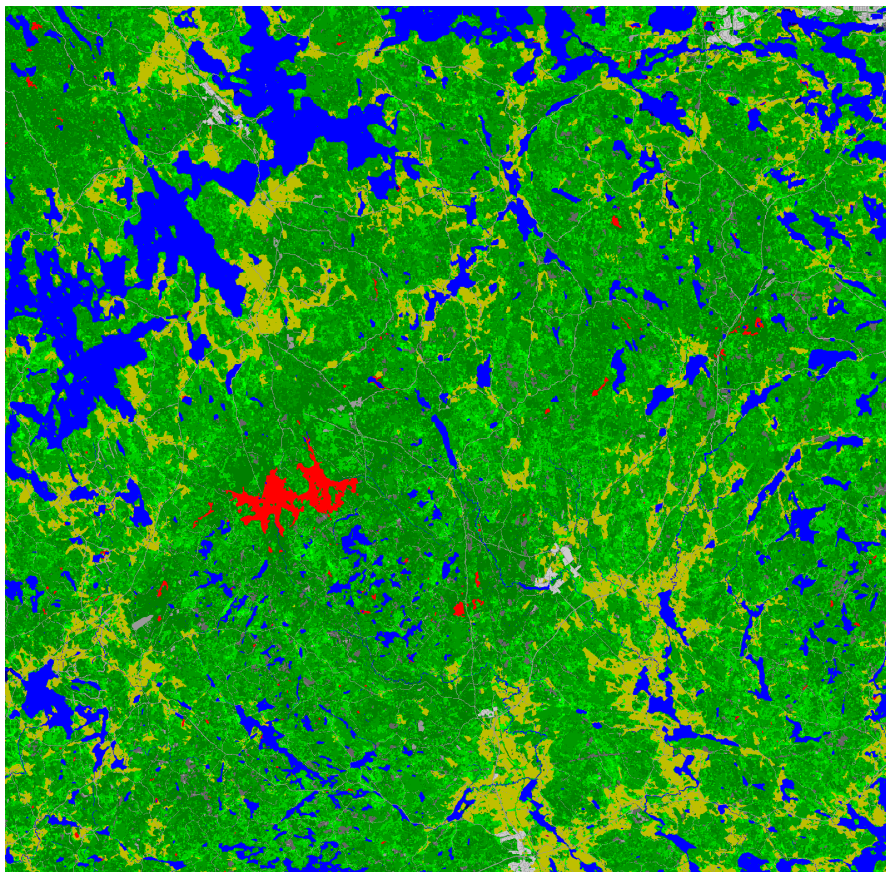
Fig. 1. A map of the land use around SMEAR II station. The area shown is 40×40 km^2. Shades of green are forests, yellow are agricultural lands, red are wetlands and blue are water bodies. Copyright National Land Survey of Finland 2002.

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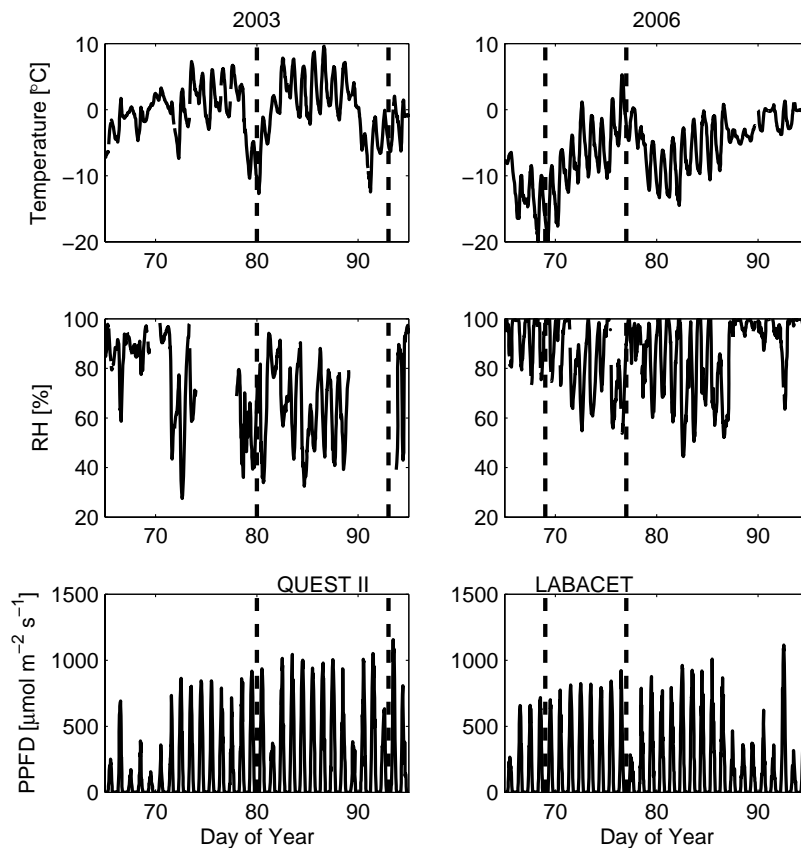
Fig. 2. Air temperature and relative humidity at 8 m height and photosynthetic photon flux density (PPFD) above forest canopy during springs 2003 and 2006. Time periods of the measurement campaigns are marked in the figures.
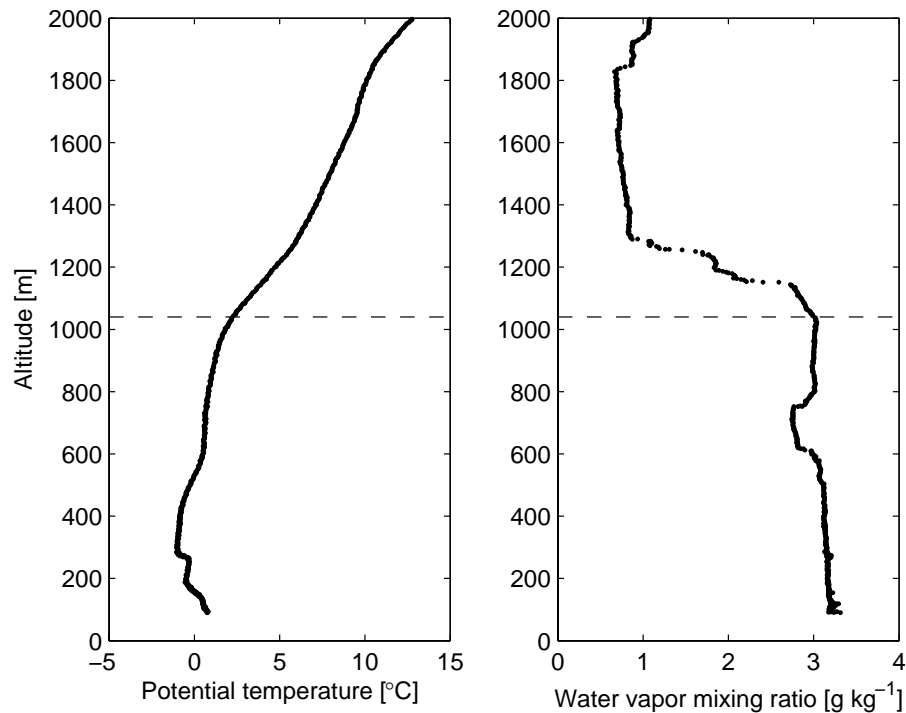
Fig. 3. Vertical profiles of potential temperature (left panel) and water vapor mixing ratio (right panel) on 13 March 2006. The dashed line shows subjectively approximated height of the boundary layer top.

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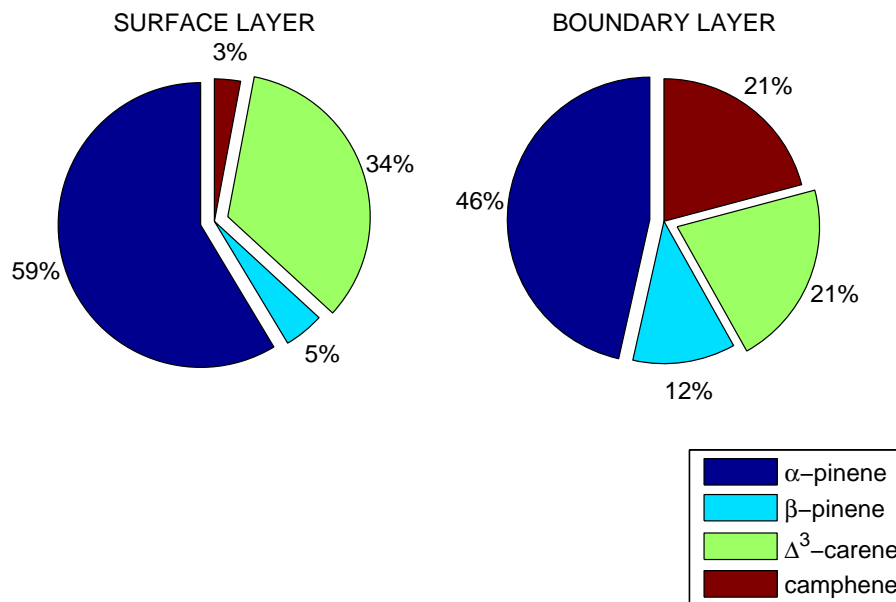
Fig. 4. Relative abundances of different monoterpenes during QUEST II in the surface air (left panel) and upper in the boundary layer (right panel).

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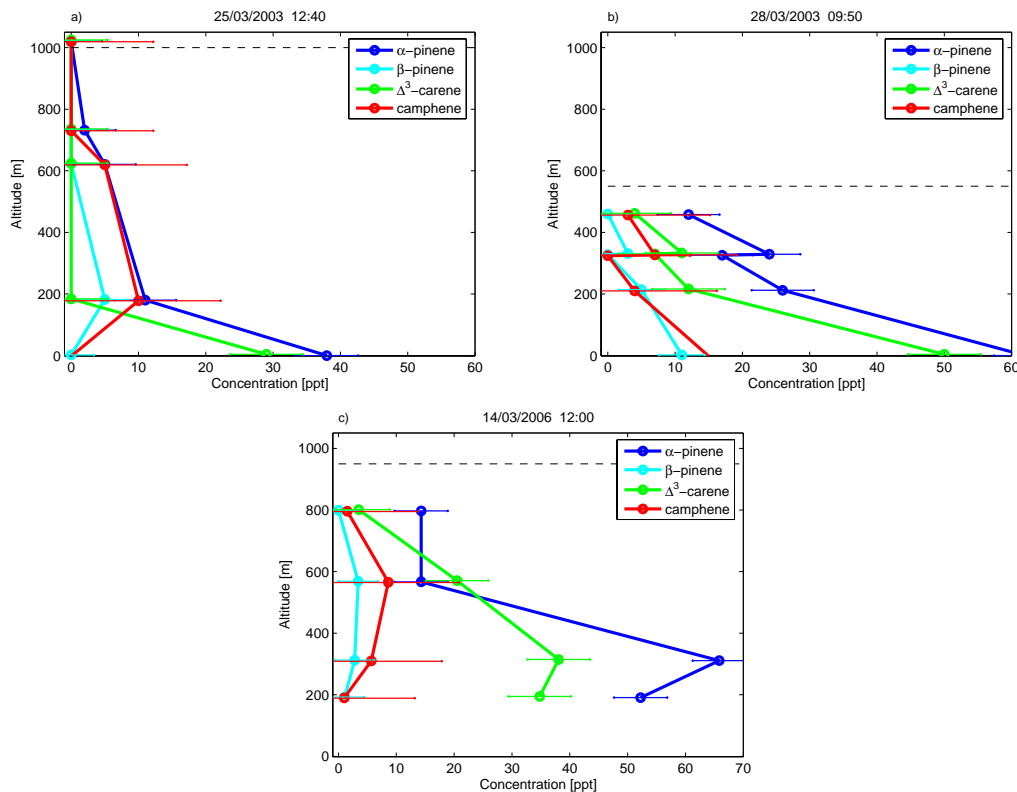
Fig. 5. Examples of vertical gradients of different monoterpene species. Dashed line indicates the height of boundary layer.
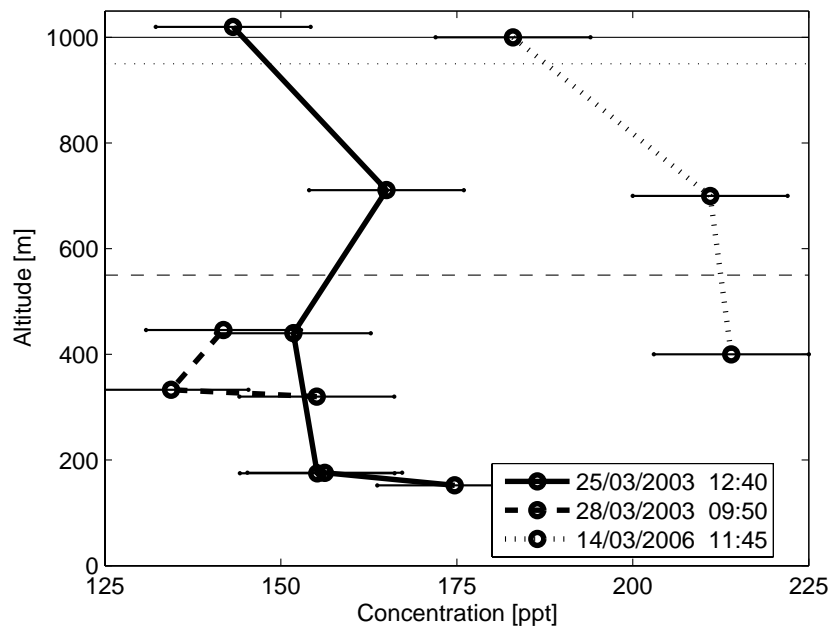
Fig. 6. Concentrations of benzene in the boundary layer on three days and corresponding boundary layer heights.

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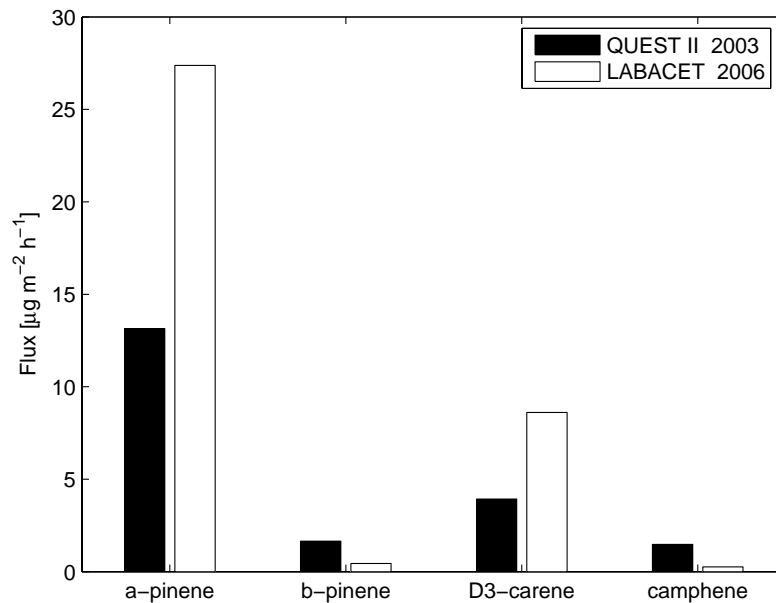
Fig. 7. Average fluxes of different monoterpene species during the two experiments.
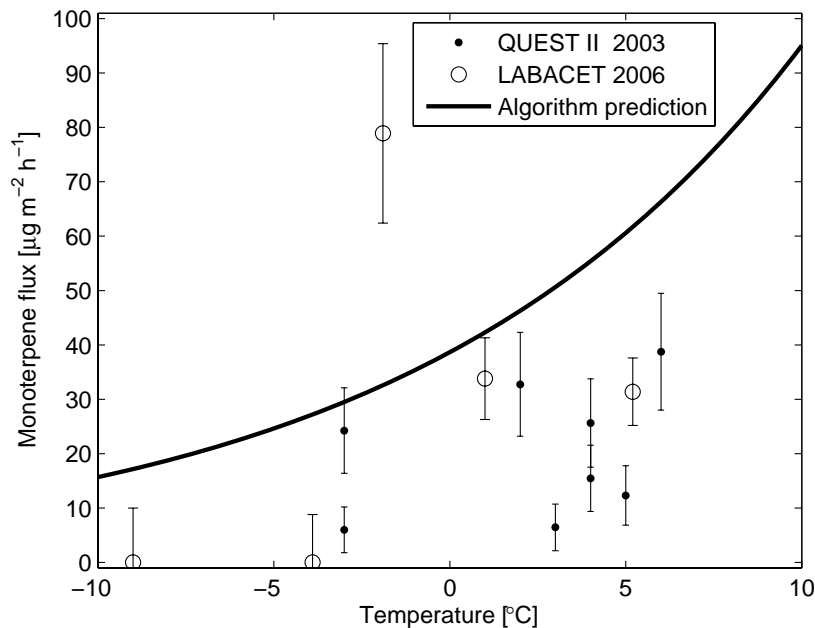
Fig. 8. Sum flux of monoterpenes versus surface temperature. Blue line shows algorithm prediction.

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