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measurements of
biogenic VOCs**

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Tethered balloon measurements of biogenic volatile organic compounds at a Boreal forest site

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Abstract

Measurements of biogenic volatile organic compounds (VOCs) were performed at Hyytiälä, a Boreal forest site in Southern Finland as part of the project OSOA (origin and formation of secondary organic aerosol) in August 2001. At this site, frequent formation of new particles has been observed and the role of biogenic VOCs in this process is still unclear. Tethered balloons served as platforms to collect VOC samples within the planetary boundary layer at heights up to 1.2 km above ground during daytime. Mean mixed layer concentrations of total monoterpenes varied between 10 and 170 pptv, with α -pinene, limonene and Δ^3 -carene as major compounds, isoprene was detected at levels of 2–35 pptv. A mixed layer gradient technique and a budget approach are applied to derive surface fluxes representative for areas of tens to hundreds of square kilometres. Effects of spatial heterogeneity in surface emissions are examined with a footprint analysis. Depending on the source area considered, mean afternoon emissions of the sum of terpenes range between 180 and 300 $\mu\text{g m}^{-2} \text{h}^{-1}$ for the period of 2 to 12 August 2001. Surface fluxes close to Hyytiälä were higher than the regional average, and agree well with mean emissions predicted by a biogenic VOC emission model. Total rates of monoterpene oxidation were calculated with a photochemical model. The rates did not correlate with the occurrence of new particle formation, but the ozone pathway was of more importance on days with particle formation. Condensable vapour production from the oxidation of monoterpenes throughout the mixed layer can only account for a fraction of the increase in aerosol mass observed at the surface.

1. Introduction

The biosphere and plants in particular release a variety of reactive volatile organic compounds (VOCs) that are of importance for atmospheric chemistry. Among the major biogenic emissions are those of monoterpenes, C_{10} -compounds that are readily

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oxidized in the atmosphere by OH-, NO₃-radicals or ozone. Several products of these reactions are of low volatility and partition between gas and particulate phases and accordingly may contribute to organic aerosol mass. Through this pathway of secondary organic aerosol (SOA) formation, biogenic VOCs are estimated to significantly add to the load of aerosols on a global scale (Griffin et al., 1999).

Various smog chamber studies have proven the potential of monoterpenes to form aerosols upon oxidation (Hoffmann et al., 1997; Kamens et al., 1999). Several field studies have also indicated the links between the oxidation of biogenic VOCs and formation of organic aerosol under environmental conditions (Kavouras et al., 1998; Kavouras et al., 1999; Leaitch et al., 1999). While it seems clear that biogenic VOC contribute to organic aerosol mass, their role in the process of new particle formation is still uncertain, however. There is also evidence from observations that monoterpene oxidation products are rather linked to growth than to new formation of particles (Janson et al., 2001).

At Hyytiälä, a Boreal forest site in Southern Finland, extensive particle measurements have been carried out in recent years and formation of new particles has been observed on a regular basis (Kulmala et al., 2001; Mäkelä et al., 1997). These nucleation events are postulated to occur on a large horizontal scale in the order of hundreds of km, as they were detected simultaneously at sites in distances of more than one hundred km (Nilsson et al., 2001).

In summer 2001, we participated in a field campaign at Hyytiälä as part of the EU project OSOA (origin and formation of secondary organic aerosol formation). The aim of this project was to quantitatively understand the sources and formation mechanisms of secondary organic aerosols with both laboratory and field experiments.

In order to judge the impact of biogenic VOCs during particle formation events, one important piece of information is the quantification of their surface flux. Past measurement efforts at the site confirmed the emission of various biogenic VOCs, terpenes in particular, with the use of chamber and micrometeorological gradient techniques (Janson et al., 2001; Rinne et al., 2000; Spanke et al., 2001). As a result of these studies,

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monoterpene emissions close to the SMEAR II site could be characterized. However, it is desirable to verify larger scale fluxes with measurements as well. This is of particular interest for biogenic VOC fluxes at the Hyytiälä site since the particle formation events are believed to occur on large spatial scale. This work aims to determine if the VOC fluxes on a larger scale are consistent with those near the tower. For this purpose, we performed VOC measurements throughout the atmospheric boundary layer (up to about 1km above ground) using a tethered balloon sampling platform. From these measurements we derive surface flux estimates representative for areas of tens to hundreds of square kilometres by means of a gradient method and a boundary layer budget approach.

2. Experimental

2.1. Site description

The experiment took place in Southern Finland at Hyytiälä (61°51′ N, 24°17′ E, 181 m a.s.l.), a research site operated by University of Helsinki (SMEAR II, Station for Measuring Forest Ecosystem-Atmosphere Relations). The station is surrounded by Boreal coniferous forest, dominated by Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*). According to landuse data encompassing 20 × 20 km around the station, 72% of the surface is covered with forest (Fig. 1). Water bodies (12%), open fields (10%) and clear cuts account for most of the remainder. Of the forest area, 37% are pine dominated, 16% by spruce, 18% is covered by deciduous forest, the remainder is mixed coniferous and broadleaf forest (29%). There is no major source of anthropogenic trace gases nearby; the nearest city is Tampere, located 60 km in South-western direction. The terrain around the site exhibits only modest terrain height variation, with 95% of the area within 20 × 20 km between 100 and 220 m a.s.l.

At SMEAR II, aerosols size distribution, gaseous pollutants (SO₂, O₃ and NO_x) and (micro) meteorological parameters have been measured on a routine basis for several

years. The sensors are installed at several levels on a 67 m high tower, located 0.8 km northeast of the research site buildings. The tethered balloons were launched from a soccer field next to these buildings, about 100 m east of a lake (Fig. 1).

2.2. Measurements by tethered balloons

5 Two 9 m³ helium balloons (Blimp Works, Statesville, NC) served as platforms to collect VOC samples and meteorological data at heights between 100 m and 1.3 km above ground. Three tether lines and winch systems were employed during the campaign. Two were commercially available electric winches (model TS-3-AW, Air Instrumentation Res. Inc., now Vaisala, Boulder CO) that can either be operated with a 12 V DC car
10 battery or on AC-power. The lines on these winches were of 700 m and 800 m length, respectively. A third system, with a 1500 m line, was a custom built spool driven by an electric drill.

2.2.1. Sample collection and temperature measurements

15 VOCs were collected using miniaturized sampling packages that were attached at several different points on the tether line (for a detailed description, see Greenberg et al., 1999a). They are operated by timers and provide flow controlled air sampling onto adsorbent cartridges (adsorbent was a two-stage combination of Carbotrap®, and Carbosieve S-III® by Supelco, Inc., Bellefonte, Pennsylvania). The flow rates were 200 ml/min yielding sampling volumes between 6 and 10 l for pumping times between
20 30 and 50 min. In addition to collecting trace gases on cartridges, the packages also record pressure, temperature and humidity, all of them logged at 0.5 Hz. In front of the cartridge, glass wool filters (Acrodisc, Pall Corp., Ann Arbor, MI) soaked with potassium iodide were installed in order to remove ambient ozone and avoid VOC losses through ozone (Helmig, 1997). Cartridges were conditioned in the week before the
25 experiment and stored at ~-30°C. At Hyytiälä, cartridges were in a freezer at ~-10°C, during transport to and from Finland (approximately 20 h) cartridges were kept in an

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ice chest (0–5°C). All samples were stored at –30°C and analyzed within 30 days after the experiment.

The sampling packages were attached to the tether line in two configurations. (1) Setup for integrative VOC measurement with one package right below (1–2 m) the balloon, operating during ascent and descent. This arrangement delivers temperature and humidity profiles (vertical resolution usually 1–2 m) and an integrative VOC measurement from ground to the maximum height reached.

(2) Profile setup, three VOC sampling packages are attached to the tether line at heights of about 120 m, 250 m and 500–600 m. The packages sampled air at those heights during 30 min, delivering a mean VOC profile of the lowest 500–600 m.

Altitudes were determined from pressure data recorded during sampling. Pressure and temperature readings of the different sampler packages were referenced daily against the official pressure measurement in the SMEAR II station. Considering the precision of pressure sensors and variability due to up and downdrafts of the balloon during sampling, height accuracy is estimated to be within 20 m.

2.2.2. Analysis of VOC samples

The contents of the adsorbent cartridges were analysed by a gas chromatograph with a mass spectrometry detector (GC-MS, Hewlett Packard model HP5890/5972). Transfer of the samples onto the chromatographic column (30 m × 0.32 mm I.D., 1 μm-film DB1-column, J&W Scientific, Folsom, CA) was achieved by an automated inlet system described in detail by Greenberg et al. (1996; 1999a). The key steps can be summarized as follows: Water trapped during sampling is first removed by purging with helium at 40°C. VOCs are then desorbed from the cartridge at 325° (purge flow of 20-30 ml He for 30 min), and focused in a cryogenic freeze-out loop (2 mm ID × 100 mm length stainless steel tubing packed with 60/80 mesh glass beads). Finally, the cryotrap is rapidly heated to 150°C and the sample is transferred onto the column, which is held at –50° for 2 min after injection, then heated to 200°C at 4°C min⁻¹. In regard to the low VOC concentrations encountered in the experiment, the detector was operated in

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selective ion mode. Isoprene was quantified from m/z 67 and monoterpenes from m/z 93.

Response factors were determined by calibration against pressurized gas standards. Primary standard was a cylinder with 201 ppb 2,2-dimethylbutane from the National Institute of Standards and Technology (Boulder, CO), a cylinder with 10 ppb camphene and 11 ppb isoprene (custom made by E. Apel, NCAR, Boulder, CO) was used as secondary standard. Runs with the secondary standard were performed daily, by collecting volumes of 500–1000 ml onto identical cartridges as used in the field experiment. Several halogenated hydro-carbons were introduced into each sample as internal standards, to allow for the estimation of any variations in mass spectrometer sensitivity: chloropropane, which eluted just after isoprene, and 3-fluorotoluene and decahydro-naphthalene (decalin), which elute before and after monoterpenes, respectively. Considering these uncertainties and including errors during sampling and storage as mentioned above, accuracy and precision are estimated to be approximately 20 ppt for isoprene at 50 ppt and for monoterpenes at 100 ppt.

2.3. Flux calculation methods

Concentration measurements of monoterpenes and isoprene at different heights within the boundary layer are used to derive corresponding surface fluxes. We applied two methods, a technique deducing surface fluxes of a scalar from its mixed layer gradient and a boundary layer budget approach.

2.4. Mixed layer gradient technique (MLG)

Gradient methods have widely been applied to determine fluxes from measurements within the surface layer. The flux is described in analogy to molecular diffusion by the product of a gradient and a diffusion coefficient, whereas it is a turbulent exchange coefficient rather than a diffusion coefficient in case of the surface layer gradient theory. In similar genre, Wyngaard and Brost (1984) proposed a flux gradient relationship for

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the mixed layer, whereas the mixed layer encompasses that part of the convective boundary layer (CBL) dominated by convective eddies whose scales are comparable to the depth of the entire CBL:

$$\frac{\partial C}{\partial z} = -g_b \left(\frac{z}{z_i} \right) \frac{\overline{wC_0}}{z_i w^*} - g_t \left(\frac{z}{z_i} \right) \frac{\overline{wC_{z_i}}}{z_i w^*}, \quad (1)$$

5 with w^* denoting the convective velocity scale within the CBL ($w^* = (g(\overline{w\theta_v})_0 z_i / \theta_{v0})^{1/3}$), $(\overline{w\theta_v})_0$ is the surface virtual temperature flux, z_i the depth of the CBL, $\overline{wC_0}$ and $\overline{wC_{z_i}}$ are the turbulent scalar surface and entrainment fluxes, respectively, z is the altitude above ground, C is the mean scalar mixing ratio, and g_b and g_t are dimensionless bottom-up and top-down gradient functions of height within the
10 CBL.

Moeng and Wyngaard (1984; 1989) determined the gradient functions from large eddy simulations of scalar transport within the CBL. From the results of these simulations, Davis (1992) derived following fits for the gradient functions:

$$g_b = 0.4 \cdot \left(\frac{z}{z_i} \right)^{-3/2} \quad \text{and} \quad g_t = 0.7 \cdot \left(1 - \frac{z}{z_i} \right)^{-2}. \quad (2)$$

15 Given these gradient functions g_b and g_t , and measurements of CBL depth z_i and the convective velocity scale, two unknowns remain in Eq. (1), the surface and entrainment flux. Being interested in the surface flux, one can integrate and resolve the equation if the concentration gradients over two height intervals are known, or, alternatively if only one value for $\partial C / \partial z$ and the entrainment flux are known. The latter can be estimated
20 by a simple jump model, describing the entrainment as the product of the concentration difference (“jump”) across the boundary layer top and the entrainment rate:

$$\overline{wC_{z_i}} = -w_e (C_{ML} - C_F). \quad (3)$$

C_{ML} and C_F are the mean concentrations of the scalar in the upper mixed layer (ML) and the atmosphere above the ML, respectively. The entrainment velocity (w_e) is the

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rate at which air is drawn into the ML from above, and can be determined from observations of mixed layer depth growth.

The calculation of scalar surface fluxes by the MLG technique therefore requires the scalar concentrations at two or more heights within the CBL, information about the strength of convective mixing (w^*), and the CBL depth. Measurements with the tethered balloon provide mixed layer concentrations and the height of the convective boundary layer. Values for w^* are calculated from measurements of potential temperature fluxes at the SMEAR II tower. Finally, surface fluxes for single VOC profiles collected at Hyytiälä are obtained by fitting the MLG equation to the measured concentrations with a least square method.

When applying the MLG technique for flux estimates, the validity of the MLG assumptions needs careful evaluation (Davis et al., 1994; Guenther et al., 1996; Helmig et al., 1998). In short, the critical requirements are 1) Sufficiently rapid convective mixing for maintaining a quasi-steady profile, i.e. convective turnover time (z_i/w^*) is smaller than variations in surface heat flux and convective layer growth. 2) Lifetime of species is large compared to the timescale of vertical mixing. 3) Sufficient integration time of concentration measurements in order to average over at least a few eddies. Finally, MLG theory assumes a horizontally homogenous system, implying spatial homogeneity in emissions and vertical mixing.

In typical midday conditions at Hyytiälä, convective turnover times were about 10–15 min ($z_i = 1200 - 1600$ m, $w^* = 1.5 - 2$ ms⁻¹). This turnover time is sufficiently short compared to the timescale of midday variations in mixed layer depth, as well as to the lifetime of most biogenic VOCs. During the increase of the CBL in the morning, however, the changes in surface heat flux may occur on a comparable time scale as z_i/w^* and profiles during these times may not be suitable for MLG calculations. The sampling time of 30 min in the profile measurements is long enough to represent a mean mixed layer gradient and should be sufficient to encompass the average over several eddies.

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2.4.1. Mixed box technique (MB)

In this budget approach, the convective boundary layer is treated as a well-mixed box. A simplified conservation equation for the mean scalar in this box can be written as

$$\frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} + \frac{\overline{wC_0} - \overline{wC_{z_i}}}{z_i} + S. \quad (4)$$

C is the mean scalar mixing ratio, U is the mean horizontal wind, $\partial C/\partial x$ is the local concentration gradient along the mean horizontal wind direction, $\overline{wC_0}$ and $\overline{wC_{z_i}}$ are the turbulent fluxes at the surface and at the top of the mixed layer (z_i), respectively. The term S denotes either a sink or source of the scalar in the mixed box. This representation neglects turbulent horizontal advection and mean vertical advection, and premises a linear vertical flux profile in the mixed layer. All these assumptions are commonly satisfied in the well-mixed convective boundary layer (Guenther et al., 1996). Resolving this equation for the surface flux yields

$$\overline{wC_0} = \overline{wC_{z_i}} + z_i \left(\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} - S \right). \quad (5)$$

To calculate the surface flux of biogenic VOCs, we assume their concentration has reached a steady state ($\partial C/\partial t = 0$), is homogenous in space ($\partial C/\partial x = 0$), and that entrainment can be neglected. The surface flux is then given by the product of $z_i \cdot S$, whereas S is the total loss rate due to chemical reactions in this case.

We briefly address the relevance of these mixed box assumptions here, a more detailed discussion is provided by Guenther et al. (1996). Neglecting entrainment results in an underestimate of the actual surface flux, whereas the effect of omitting horizontal advection cannot be uniquely qualified. However, the magnitude of both terms can usually be estimated from the balloon profiles. Entrainment fluxes can be assessed with help of the jump model (Eq. 3), and the temporal variations in mean mixed layer concentrations throughout the day provide an estimate for the importance of horizontal advection.

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The overall uncertainty of box model flux estimates is usually dominated by the uncertainty in quantifying the chemical sink term. For biogenic VOCs, the total loss rate during daytime can be approximated by the sum of their reactions with OH-, NO₃-radicals and ozone (O₃).

5 The final equation for calculating the flux of a particular VOC is then

$$\overline{wC_0} = z_i \cdot [\text{VOC}] \cdot \left(k_{\text{OH}} \cdot [\text{OH}] + k_{\text{O}_3} \cdot [\text{O}_3] + k_{\text{NO}_3} \cdot [\text{NO}_3] \right) \quad (6)$$

with k_{OH} , k_{O_3} and k_{NO_3} being the second order rate coefficients of the VOC with OH, O₃, and NO₃, respectively. The surface flux calculation by the MB method therefore requires measurements of the boundary layer depth and the mean concentration in the mixed layer, as well as estimates for the total chemical loss rates of VOCs.

2.5. Photochemical model

Chemical VOC degradation within the mixed layer was quantified with a photochemical box model. The chemical mechanism of the model consists of about 3340 gas phase reactions among 1200 species, as described by Aumont et al. (1999) and Hauglustaine et al. (1999). Photolysis rates are calculated with the tropospheric ultraviolet-visible (TUV 4.1) model (Madronich and Flocke, 1999). An albedo of 10% was assumed for these calculations and total ozone columns (310–340 Dobson Units) were taken according to data of the NASA Earth Probe TOMS satellite.

As in previous applications of the model for planetary boundary layer (PBL) cases (Greenberg et al., 1999b; Karl et al., 2002), entrainment of air during the growth of the PBL was represented as a first-order source or sink for chemical species in the PBL, depending on the concentration difference between background and PBL

$$\frac{dX_{\text{PBL}}}{dt}_{\text{entrainment}} = -K_{\text{entrainment}} (X_{\text{PBL}} - X_{bg}) \quad (7)$$

X_{PBL} is the concentration of the species in the PBL, X_{bg} is the concentration above the PBL (background), first-order rate constants $K_{\text{entrainment}}$ (> 0 during growth of the

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PBL and zero at all other times) were chosen specifically for each day, derived from maximum PBL heights and duration of PBL growth. Background concentrations X_{bg} were kept constant with time and set to zero for all VOCs with tropospheric lifetimes shorter than 5 h (corresponding to simple dilution during PBL growth).

5 Measurements of O_3 , NO_x , VOCs, and radiation are used to constrain the box model. For this purpose, biogenic VOC concentrations are taken from the balloon measurements, anthropogenic VOCs are set to mean concentrations as measured on the tower during the second week of the experiment or as reported in earlier campaigns at this site (Janson et al., 2001; Spanke et al., 2001); total non-methane VOC levels measured were below 5 ppb. Ozone and NO_x levels are constrained to the half hourly
10 measurements at 67 m above ground on the SMEAR II mast. Finally, the clear sky photolysis rates calculated by the model were scaled with help of UVA-measurements taken above the forest canopy.

2.6. Footprint modelling

15 Deriving fluxes from boundary layer measurements has the advantage of delivering estimates representative for large areas. Each of the methods we apply has its own area of influence. For concentration measurements, this area can be estimated from the footprint function. It can be understood as a probability function that describes how strongly an emission from a given elemental source downwind affects the measurement point (Fig. 1). The footprint of the MLG technique corresponds to the actual
20 footprint of the profile measurements. Under strongly convective conditions with mean wind speeds up to 5 ms^{-1} , it typically encompasses an upwind range of 0.2 to 10 km, yielding footprint areas in the order of tens of square km. The fluxes derived by the MB technique are representative for even larger areas. For a given VOC, the upwind
25 range of the footprint is approximately mean wind speed multiplied by the time until this compound has reached a steady state concentration. For terpenes with usual lifetimes between 2–3 h, this results in a footprint in the order of hundreds of square kilometres.

Spatial variation in surface emissions violates the assumptions of horizontal homo-

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geneity in the boundary layer flux calculation methods. For the Hyytiälä site this may be an issue as the balloon launch site was located close to a lake. We therefore model the footprints of our profile measurements, for the purpose of determining the impact of heterogeneous surface emissions on the results of our flux estimates. The footprint model is described in detail by Kljun et al. (2002) and is based on a three-dimensional Lagrangian stochastic particle dispersion model (De Haan and Rotach, 1998). The model has been shown to produce valid footprint predictions under a wide range of stratifications and for receptors at heights from the surface to the mixed layer (Kljun et al., 2003).

3. Results and discussion

3.1. Balloon measurements

From 2 till 12 August 2001, we collected a total of 80 VOC samples from tethered balloons. Weather conditions were variable during this period, 3, 7, and 8 August were mostly sunny, other days were often cloudy and rainy. Operation of the balloon had to be interrupted several times by rain and high wind speeds that resulted in unsafe tethered balloon operating conditions.

Temperature and humidity profiles obtained from flights with continuous sampling during ascent and descent were used to determine boundary layer depths. Part of the flights did not exceed the top of the boundary layer and their depths were estimated. In these cases, they were approximated with the flux-ratio method (Stull, 2000), based on continuous measurements of the surface heat flux on the tower and potential temperature differences across the boundary layer top as derived from balloon profiles early in the day.

Figure 2 gives an overview on the meteorological conditions and averaged VOC concentrations in the mixed layer. The integrative VOC measurement during the ascent and descent of the balloon is considered as a representative sample of the mean

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boundary layer concentration. From three-level-profiles, mean concentrations are derived by fitting the MLG profile to the three measurements and building the average over the whole profile. With our choice of heights for the three samplers, these mixed layer averages did not significantly differ from the arithmetic means of the measurements. Total monoterpene concentrations in the mixed layer during OSOA 2001 were of the order of 10–100 ppt, with α -pinene (38%), limonene (23%), Δ^3 -carene (20%) and camphene (9%) as the major compounds. Isoprene was also found in all samples, although at lower concentrations than the sum of monoterpenes.

Highest concentrations of biogenic VOCs were recorded on days with reduced radiation, apparently as a consequence of reduced vertical mixing and shallower boundary layer heights. Note however, that a day-by-day comparison of these concentrations is problematic as data coverage on single days varied significantly due to weather conditions. Winds were from a sector between 120 and 300° during the balloon flights, at speeds up to 7 ms⁻¹ (wind measurements at 50.9 m height on the tower). Maximum mixed layer heights varied between 1 and 2.2 km and were in agreement with results from earlier studies at Hyytiälä (Nilsson et al., 2001).

The concentration dependence with height above ground showed the expected behaviour for gases with a source at the surface. In general, concentrations decrease with height (Fig. 3). The maximum height of the uppermost samplers in our profile measurement was 600–750 m, wherefore sample collection above the mixed layer was limited to situations with a shallow mixed layer, usually early in the day. Comparing the concentrations within and above the mixed layer from these flights (total of 7 profiles), the ratio of concentrations within the mixed layer (ML) and above the mixed layer (AML) was greater than one in nearly all cases for terpenes (Table 1). For isoprene, this trend was still observed in average, however with several inverse cases. Myrcene, tricyclene and sabinene were also detected in several samples, with greater concentrations in the mixed layer than above. The comparison of absolute concentrations within and above the mixed layer is more ambiguous, apparently as a consequence of large variations between concentrations of individual profiles.

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Earlier VOC studies in the area found α -pinene, Δ^3 -carene and β -pinene as the dominating monoterpenes, limonene proportions were significantly lower than in our measurements. Based on leaf-level measurements of the dominating tree species in the area, Scots Pine and Norway Spruce (Komenda and Koppmann, 2002), limonene in such high proportions is surprising.

We considered the possibility of an analytical artefact in our VOC measurements. A general background problem is unlikely, as limonene concentrations correlated with those of the other terpenes. The use of KI traps for removal of ozone prior to sampling is known to produce artefacts (iodine-containing VOCs, though none shown to be derived from monoterpenes), but they can easily be distinguished from terpenes based on the EI-mass spectrum (Helmig and Greenberg, 1995). Finally, two VOC samples taken in parallel to our measurements, using different adsorbent media were analysed at CNR laboratories in Rome, Italy. The limonene concentrations determined there are consistent with the results of our measurements (Ciccioli et al., 2002). Limonene has also been detected in earlier measurements at this and other Boreal forests sites in Finland (Hakola et al., 2000; Rinne et al., 2000). It has been shown that the composition of terpenes emitted by Scots Pine exhibits significant plant to plant variation and can also vary with season (Janson et al., 2001; Komenda and Koppmann, 2002). Results of a recent study (Hakola et al., 2003) on seasonal variations of monoterpene concentrations at Hyytiälä indicate that the proportions of limonene in emissions of Norway Spruce increase from early to late summer. Limonene has also been measured as a major compound emitted from soils (Hayward et al., 2001), and during decomposing of coniferous needles (Kainulainen and Holopainen, 2002). Finally, limonene concentrations are low enough to be caused by emissions from single plant species that may not be accounted for in the regional vegetation database. Given the lack of evidence for analytical artefacts and the above possibilities for the higher than expected limonene concentrations, we proceed with the measured concentrations in the following analyses.

3.2. Flux estimates from mixed layer gradients

As pointed out in Sect. 2.3.1, several conditions need to be fulfilled in order to derive fluxes from a gradient within the mixed layer. For compliance with sufficiently strong convective conditions, morning profiles before 1100 local time were excluded. From the remaining data set we also removed profiles with measurements exclusively above heights of $z/z_i = 0.3$. The MLG equation predicts only small concentration differences in dependence of the surface flux at these heights. As a consequence, concentration gradients above this height do not contain sufficient information about the surface flux. After this screening, 12 profiles comprised of 32 individual VOC samples remained for flux calculations with the mixed layer gradient method.

The MLG equation was then fitted to the measured profiles, both with and without assumptions for entrainment fluxes. In all cases, varying assumptions of entrainment fluxes did not result in significant differences of the surface fluxes (less than 10%). This is not surprising, as we chose the concentration measurements at heights where gradients are influenced by the surface flux rather than the entrainment flux. Furthermore, our data selection includes midday to afternoon profiles exclusively, without cases of strong mixed layer growth, and concentration jumps across the boundary layer height were too small to result in significant entrainment fluxes. For simplicity, only results with entrainment fluxes set to zero are presented.

Figure 4 shows the median fluxes of those VOC that were detected in every single measurement within the profiles. The median of the sum of monoterpene fluxes is $278 \mu\text{g m}^{-2} \text{h}^{-1}$. If the median terpene flux is calculated from the gradients of total terpene concentrations of individual profiles, the resulting median flux of terpenes is $312 \mu\text{g m}^{-2} \text{h}^{-1}$. The higher number in the latter case is attributed to the very low concentrations of terpenes that could often be detected at the lowest altitude only and consequently pronounced the gradients of total terpenes. For isoprene, the MLG method derives a median deposition flux for this selection of profiles, while the average shows a small emission of $15 \mu\text{g m}^{-2} \text{h}^{-1}$.

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As biogenic VOC emissions depend strongly on temperature, it is useful to normalize emission rates to a standard temperature. The temperature dependency of monoterpene emissions can be described by the equation

$$E = E_{30} \cdot \exp[\beta(T - 30^{\circ}\text{C})], \quad (8)$$

5 where E_{30} is the emission rate normalized to 30°C , β is an empirical coefficient ($= 0.09$) and T is temperature in degrees Celsius (Guenther et al., 1993). Normalizing the monoterpene fluxes to 30°C according to this algorithm yields an emission potential of $832\text{--}927 \mu\text{g m}^{-2} \text{h}^{-1}$. As documented by the large interquartile ranges, the variation of fluxes between individual profiles is considerable in spite of the preceding data
10 selection. The following section addresses uncertainties and the effects of potential violations of the MLG assumptions in our flux calculations.

3.2.1. Error and footprint discussion

MLG estimates heavily rely on accurate measurements of mixing ratio differences. With the small VOC levels encountered at Hyytiälä, the differences for single terpene concentrations were close to the detection limit. The uncertainty of terpene measurements
15 at these levels is estimated to be $\pm 30\%$, propagating into large uncertainties of the flux estimates.

Non-homogeneity in surface emissions is one of the most common violations of the MLG assumptions in practice. Our balloon launch site was located close to a lake (Fig. 1) and often downwind of this lake during the measurement period. This severe inhomogeneity in surface emissions may influence our profiles. With the help of a footprint analysis, we evaluate how strongly the lake affects the flux estimates. The footprints of individual profile measurements are calculated with a footprint model (Sect. 2.5). By combining them with detailed land use data of $20 \times 20 \text{ km}$ around the
20 site, we assess differences in the source areas of individual profile measurements. The footprint model is run under the assumption of an infinite homogenous forest surface and a homogenous mean wind field. This implies that potential stratification effects due

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to the lake cannot be represented. In cases with the receptor downwind of the lake, the modelled footprint function may therefore overemphasize the surface elements close to the receptor, as stratification has the tendency to shift the footprint farther upwind. In our effort to assess the impact of the nearby lake as a non-emitting spot within the source area, the model result therefore will reflect an upper limit estimate of its influence.

As an example for the model results, Fig. 1 illustrates the footprint of the measurement at 150 m on 3 August, 13:00 local time. Fetches for the profile measurements were calculated as the distance upwind where the crosswind-integrated footprint accumulates to 95%. Typical fetches in the afternoon were 7 to 12 km, yielding footprint areas in the order of 20 to 40 km². With increasing measurement altitude, the fetches get larger and the maximum of the crosswind-integrated footprint function shifts further upwind. For measurements at 150 m above ground, the function peaks between 0.4 and 0.8 km upwind, the corresponding maxima for receptor heights around 600 m are less pronounced and occur at about 5 km. As a consequence, the proportion of the nearby lake within the footprints is most pronounced for measurements at lower levels. Figure 5 is a box plot (medians, quartiles and extremes) showing the proportions of forested area within the footprints for the three sampling altitudes. The forest proportion is systematically smaller at the lowest measurement level. However, the variation of forest areas between different heights is within 15% of the average, a range considerably smaller than the error range due to the uncertainties in the concentration measurements.

A systematic error in the MLG calculations is introduced by neglecting chemical degradation. For very reactive VOCs like limonene and isoprene, chemical sinks are large enough to pronounce the vertical profile and the surface flux may be overestimated. In order to assess how strongly this accentuation of the gradient may influence the fluxes, we adjusted the profile concentrations to correct for chemical degradation. The concentration decrease at a certain height is approximated by the typical duration of vertical transport (w^* × height of measurement) times the total chemical loss rate

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of the VOC. The later was obtained from the photochemical model results (3.3). Flux estimates from such modified profiles resulted in 5–15% lower fluxes in the median. Effects were most pronounced for limonene and only minor for other terpenes. The uncertainty associated with neglecting chemical sinks is therefore well within the overall uncertainties. Furthermore, this overestimate due to neglecting chemistry approximately compensates for the potential underestimate due to the spatial inhomogeneities in emissions.

Some variability is introduced by calculating mean fluxes from individual profiles that were collected at differing temperatures and wind directions. Examining the rotation of selected footprints around the launch site, we conclude that the proportions of the forested surface do not vary by more than 15% for wind directions as observed during the campaign. Varying wind directions can therefore not explain the observed differences in fluxes. Surface temperatures during the selected profile measurements were also in a narrow range. With the exception of two profiles at 14°C, surface temperatures were between 17.5 and 21.4°C. As there is no evident correlation between fluxes from single profiles and corresponding temperatures, we acknowledge that other influences must dominate the overall variation.

An important issue violating the MLG assumption of a horizontally homogenous boundary layer is partial cloud cover. Most of the days within the OSOA campaign exhibited partly cloudy weather. It is impossible to quantify the error associated to variability in cloudiness, but it can be qualified as non-systematic.

Summarising this analysis, we conclude that systematic errors like the uncertainties as a consequence of footprint anomalies within single profiles or due to negligence of chemical degradation are small compared to non-systematic errors. These are dominated by uncertainties in the concentration measurements and by violations of the assumption of a horizontally homogenous boundary layer. Given these errors are random in nature, the averaged terpene flux derived from the ensemble of profiles can be considered meaningful. On the other hand it is problematic to interpret fluxes from single profiles. The MLG method is not sensitive enough to determine the surface flux

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of isoprene or the emissions of single terpenes at this site, with the exception of that of α -pinene. A plot of the MLG concentration profile for α -pinene as predicted for the median flux from all individual profiles illustrates the large overall variation, but also the plausibility of the median flux as the fit lies within the observed concentrations of individual profiles (Fig. 6).

3.3. Fluxes from mixed box calculations

While the MLG technique relies on theoretically firmer assumptions, flux estimates by the mass balance approach have the advantage of being based on the more robust measurement of mean mixed layer concentrations as compared to concentration differences from profile measurements. The balloon flights during OSOA delivered 40 mean mixed layer concentrations suitable for flux calculations with the mixed box technique. The median flux of total terpenes derived from these data is 100 and 186 $\mu\text{g}/\text{m}^2/\text{h}$ for all measurements and the selection of afternoon data, respectively (Fig. 7). Normalized to 30°C (Eq. 8) the total monoterpene emissions are 575 $\mu\text{g}/\text{m}^2/\text{h}$.

We first evaluate the magnitude of errors due to neglecting entrainment and horizontal advection in the MB approach. Mixed layer growth rates during the day were up to 0.05 ms^{-1} , and the concentration difference of short-lived VOCs across the boundary layer top corresponds to the mean mixed layer concentrations, at most. This translates (Eq. 3) into a maximum entrainment rate of 35 $\mu\text{g}/\text{m}^2/\text{h}$ for typical monoterpene concentrations ($0.19 \mu\text{g}/\text{m}^3$) at Hyytiälä. While this may be a substantial fraction of the calculated surface flux during mixed layer growth before noon, the afternoon flux calculations are only slightly affected. The underestimate of MB fluxes due to the neglect of entrainment is therefore 20%, at most.

Typical changes of mean monoterpene concentrations with time were $0 \pm 0.03 \mu\text{g}/\text{h}$. The random nature of these changes indicates that advection is dominating, but also supports that neglecting advection in average is reasonable (Eq. 4). From observed time changes of concentration and with typical mixed layer heights of 1500 m, the uncertainty in box model surface flux estimates due to negligence of advection becomes

$\pm 30 \mu\text{g m}^{-2} \text{h}^{-1}$.

The uncertainty in quantifying the chemical sink term in Eq. (6) usually dominates the overall uncertainty of box model flux estimates (Greenberg et al., 1999a). However, with the measurements of NO_x , O_3 , VOCs and radiation available at Hyytiälä, it was possible to reasonably constrain the photochemical box model. The constraint of a box model representing the mixed layer with O_3 and NO_x measurements taken at the surface may be problematic in areas with strong local emissions of NO_x (Spirig et al., 2002). At Hyytiälä however, there are no major NO_x emissions upwind within several turnover times of the mixed layer, measurements were taken at 67 m above ground, reducing any influence of near-surface gradients.

Among the input data used for the photochemical box model, we consider the concentrations of VOCs other than biogenic compounds as those with the highest uncertainty. The sensitivity of the radical levels on anthropogenic VOC concentrations was evaluated by running the model with double and half anthropogenic VOC levels. The resulting maximum changes in OH levels at daytime were -18% and $+13\%$, for doubled and half anthropogenic VOC concentrations, respectively. This limited sensitivity is a consequence of the severe constraints with measurements, but also of the general characteristics of this rural site, which was not affected by significant pollution events during our measurements. We estimate the overall uncertainty for the quantification of the chemical loss rate for terpenes as $\pm 30\%$. The determination of mixed layer heights from balloon profiles or estimates is associated with a 20% error. Assuming standard propagation of these errors in mixed layer depth and loss rate yields an uncertainty of $\pm 36\%$.

Overall, the error range of the MB calculations is estimated to $\pm 50\%$ for the averaged fluxes, and even higher for fluxes from single profiles, as a consequence of the influence of horizontal advection that accounts for an additional uncertainty of 20–30%.

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3.4. Comparison of flux estimates

The surface flux derived by the mixed box (MB) technique is lower in average than that calculated by the mixed layer gradient (MLG) method, even when the selection of MB fluxes is reduced to an ensemble comparable to that of the MLG estimates (encompassing fluxes after 11:00 local time, exclusively).

The two techniques yield flux estimates representative for different areas. As calculated with the footprint model, fetches for the profile measurements and the MLG method were 7 to 12 km, and footprints in the order of 30 to 50 km². For comparison, the fetch of the MB technique can be estimated from the mean wind speed in the PBL times the lifetime of the substances. MB fetches for monoterpenes were between 50 and 100 km, resulting in footprint areas of 200 to 500 km² (assuming the same ratio of lateral and longitudinal dimension of the footprint as in the case of the modelled footprint functions). The different flux estimates from the two methods therefore indicate that monoterpene emissions close to the site are higher than the regional average.

Previous measurement efforts at Hyytiälä include the determination of fluxes with the surface layer gradient technique. Emissions derived from those measurements, representing the immediate surroundings of the SMEAR II tower, were between 200 and 450 µg/m²/h for comparable temperature conditions in August 1998 (Rinne et al., 2000; Spanke et al., 2001). The fluxes derived by the MLG technique are in the same range, whereas the MB method with its significantly larger footprint observes a lower emission, again supporting our conclusion of lower emissions on regional scale.

Such a trend should also be reflected in the landcover data, so it is useful to look at modelled biogenic emissions for the Hyytiälä site. Lindfors et al. (2000) calculated biogenic emissions for European Boreal forests based on land cover information from satellite data and meteorological observations. Using the same emission model, terpene and isoprene emission rates were calculated for the areas 1 × 1 km and 10 × 10 km around the SMEAR II site. Figure 8 shows model emissions and the flux estimates from our balloon measurements. The selection of model data includes the emissions

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between 11:00 and 18:00 local time for 2–12 August. The larger of the model areas is comparable to the footprint size of the MLG technique, while the MB method estimates surface fluxes for even a larger area. On average, modelled and observationally derived emissions agree well. Furthermore, the trend of higher monoterpene emissions close to the site is also predicted in the emissions model. The trend of higher emissions near SMEAR II as compared to the regional average is therefore in agreement with the landuse data around Hyytiälä.

Model and observations also agree for emissions of isoprene. As noted earlier, the MLG method proved not sensitive enough for the relatively low fluxes of isoprene, possibly because of rather inhomogeneous distribution of isoprene emissions within the mostly coniferous forest. For the budget technique with its larger footprint, this effect would be of less importance. The isoprene fluxes from this method are similar to the model results.

3.5. Production of condensable vapours

The results of the photochemical modelling are also used to look at the monoterpene oxidation rates on different days. As terpene oxidation is considered as an important source of condensable vapours, this analysis attempts to look at the links between monoterpene emissions and particle formation. Figure 9 shows the oxidation rates representing mean mixed layer conditions from 2 to 12 August for the days with VOC measurements from tethered balloons. Total oxidation rates (terpene + OH-, O₃-, and NO₃-reactions) were between 1 – 8 · 10⁵ molecules cm⁻³ s⁻¹. The days with particle formation events (highlighted yellow in Fig. 9) exhibit rates of 2 · 10⁵ molecules cm⁻³ s⁻¹ or lower.

The oxidation products of monoterpene are expected to partition between the gas and aerosol phase according to gas/particle partitioning theory (Odum et al., 1996). For the conditions at Hyytiälä with rather low amounts of pre-existing organic aerosol mass, an upper aerosol yield from terpene oxidation of 5% can be assumed. Using

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this fraction as an estimate for the amount of condensable products formed upon oxidation, the degradation of monoterpenes produces condensable compounds at a rate of $1 \cdot 10^4$ molecules $\text{cm}^{-3} \text{s}^{-1}$ or less on days when particle formations were observed. This rate is close to those derived in a similar way from VOC measurements in August 1998 on the tower, which were $1.2 \cdot 10^4$ molecules $\text{cm}^{-3} \text{s}^{-1}$ in average (Spanke et al., 2001). This production of condensables is too low to explain the observed aerosol growth during those days. From aerosol size distribution measurements, the production of condensable vapours necessary to explain the observed growth of particles can be derived. For the period of interest here, these source rates were between $1 - 2.6 \cdot 10^5$ molecules $\text{cm}^{-3} \text{s}^{-1}$ on days with particle formation (Boy et al., 2003). Comparing these results with our calculations, at most 10% of the condensable vapours necessary to account for the newly formed aerosol could be explained by oxidation of monoterpenes.

However, our oxidation rates are representative for conditions within the mixed layer, whereas the amounts of condensable vapours were calculated from aerosol measurements at two metres above ground. Monoterpene concentrations and oxidation rates close to the surface may be significantly higher than the average in the mixed layer. This was observed during a field campaign in 1998, where terpene oxidation rates derived from measurements at two metres height were found high enough to explain most of the observed aerosol growth (Janson et al., 2001). One might now speculate that particle production occurs mainly close to the surface. On the other hand, from all measurements carried out at Hyytiälä in 2001, including particle measurements throughout the mixed layer, there are no indications that particle formation would occur close to the surface exclusively. A definite answer can therefore not be given at this point, but these findings indicate that it would be valuable to have more vertically resolved measurements of particle distributions in future.

Another aspect of biogenic VOC and particle formation is the question, if monoterpene oxidation products play a role in the nucleation process. In this perspective, we looked at the different oxidation pathways. Hoffmann et al. (1997), and Jang and

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Kamens (1999) showed that oxidation by ozone yields higher amounts of low volatile products than the reaction with OH, and ozonolysis is considered as the only pathway to generate nucleating species from terpene oxidation under atmospheric conditions (Bonn and Moortgat, 2002). The upper panel in Fig. 9 shows the relative contribution of the O₃-pathway to the total oxidation rate. Because OH sources are of photolytical origin mainly, the relative importance of O₃-oxidation exhibits a strong diurnal variation in opposite to radiation. For the purpose of the day-to-day comparison in Fig. 9, data points prior to 11:00 and later than 17:00 local time were therefore excluded. It can be seen that the relative importance of the O₃ channel tends to be higher on the days when new particle formations were observed. The same trend cannot be seen in the absolute amount of monoterpenes oxidized by O₃, though, as a consequence of the lower concentrations of terpenes on event days. The trend of pronounced O₃ oxidation on event days in a relative but not in an absolute way may be an indication that ozone-oxidation of VOCs not considered here could play an important role. Possible compounds could be sesquiterpenes, biogenically emitted VOCs that are especially reactive with ozone and have very high yields of condensable vapours.

4. Conclusions

Observations from tethered balloon platforms were used to derive monoterpene and isoprene fluxes on landscape scales around Hyytiälä for the period of 2 to 12 August 2001. The analysis of error sources in both methods revealed that the averaged surface fluxes derived from a number of profiles represent a robust order of magnitude estimate for regional emissions. On the other hand, flux estimates from single profiles are heavily influenced by non-systematic errors, especially for the low to moderate emission levels of single compounds encountered at Hyytiälä. For these conditions, the methods are not useful for providing temporal resolution, but can characterize regionally averaged emissions.

Total monoterpene fluxes representative for areas of tens and hundreds square kilo-

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metres around Hyytiälä were 278 and 186 $\mu\text{g m}^{-2} \text{h}^{-1}$, respectively, at a mean surface temperature of 17.5°C. The mean level of biogenic VOC fluxes and the tendency of higher emissions close to the site are in agreement with the results of a biogenic VOC emission model. It gives confidence in the approaches of biogenic emission models combining experimental information about single plants emissions and landuse data to derive surface fluxes of larger areas.

The links between biogenic VOC emissions and particle formation events remain ambiguous. Chemical analyses of aerosols clearly show a contribution of monoterpene oxidation products (Boy et al., 2003). On the other hand, our modelled oxidation rates of monoterpenes in the mixed layer are too low to account for the observed aerosol growth during the nucleation days alone, a significant fraction of condensing vapours needs to arise from a different source. One possibility could be components directly emitted from conifer leaf epicuticular wax, as recent analyses of organic aerosol matter in forested areas have shown significant contributions of such primary compounds (Kavouras and Stephanou, 2002).

Insufficient information about the vertical distribution of aerosols made it difficult to relate VOC measurements within the boundary layer to aerosol observations close to the surface. It would therefore be interesting to collect more information about the temporal evolution and the differences in aerosol and gas concentrations within the forest canopy and the layers above.

Future work on biogenic VOCs and aerosols should also include measurements of sesquiterpenes and oxygenated VOCs. However, the methods applied in this work cannot be used to estimate sesquiterpene fluxes from boundary layer measurements because of their short atmospheric lifetimes in the range of a few minutes.

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Table 1. Average concentrations of biogenic VOCs at Hyytiälä and the ratios of their concentrations within (ML) and above the mixed layer (AML)

	isoprene	α -pinene	limonene	Δ^3 -carene	camphene	β -pinene	Σ terp.
Average concentrations in mixed layer, μgm^{-3} (40 flights)							
Average	0.041	0.079	0.049	0.041	0.02	0.015	0.26
proportion of total terpenes		38%	23%	20%	9%	7%	
Concentration ratios within and above the mixed layer (ML/AML) (7 flights)							
mean	1.75	2.30	2.30	2.10	1.47	3.28	2.01
median	0.93	1.57	1.87	1.98	1.29	1.45	1.77
interquartile range	0.73–1.8	1.39–2.97	1.67–2.25	1.69–2.52	0.90–1.65	0.93–2.67	1.55–2.11

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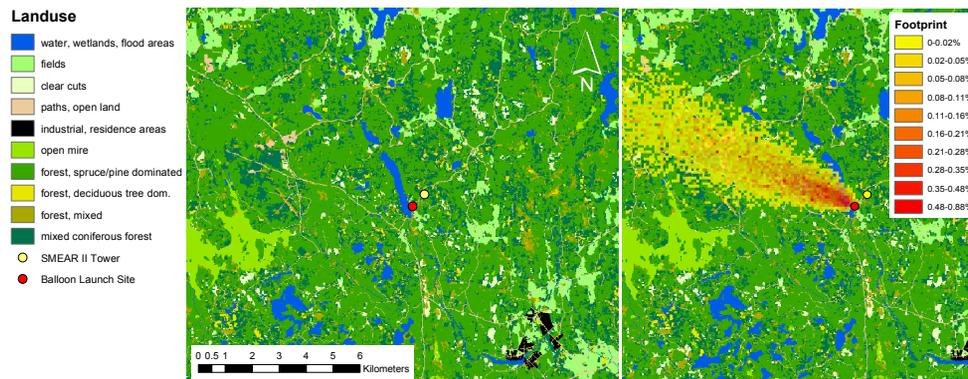


Fig. 1. Land cover around the SMEAR II site at Hyytiälä and visualization of a typical footprint for a 30 min measurement on the tethered balloon (3 August 2001, 13:00, at 150 m above ground level).

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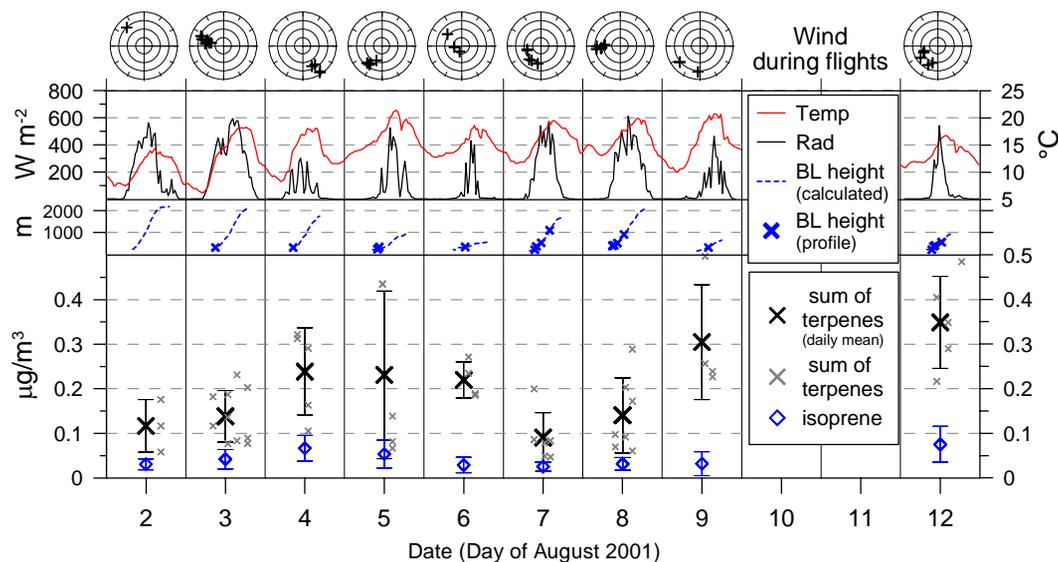


Fig. 2. Overview of mean mixed layer concentrations of biogenic VOCs and meteorological conditions during the OSOA campaign at Hyytiälä. The angles of the polar plots correspond to wind directions, the radii to speeds (scale from 0 to $8\ ms^{-1}$, spacing of concentric circles is $2\ ms^{-1}$).

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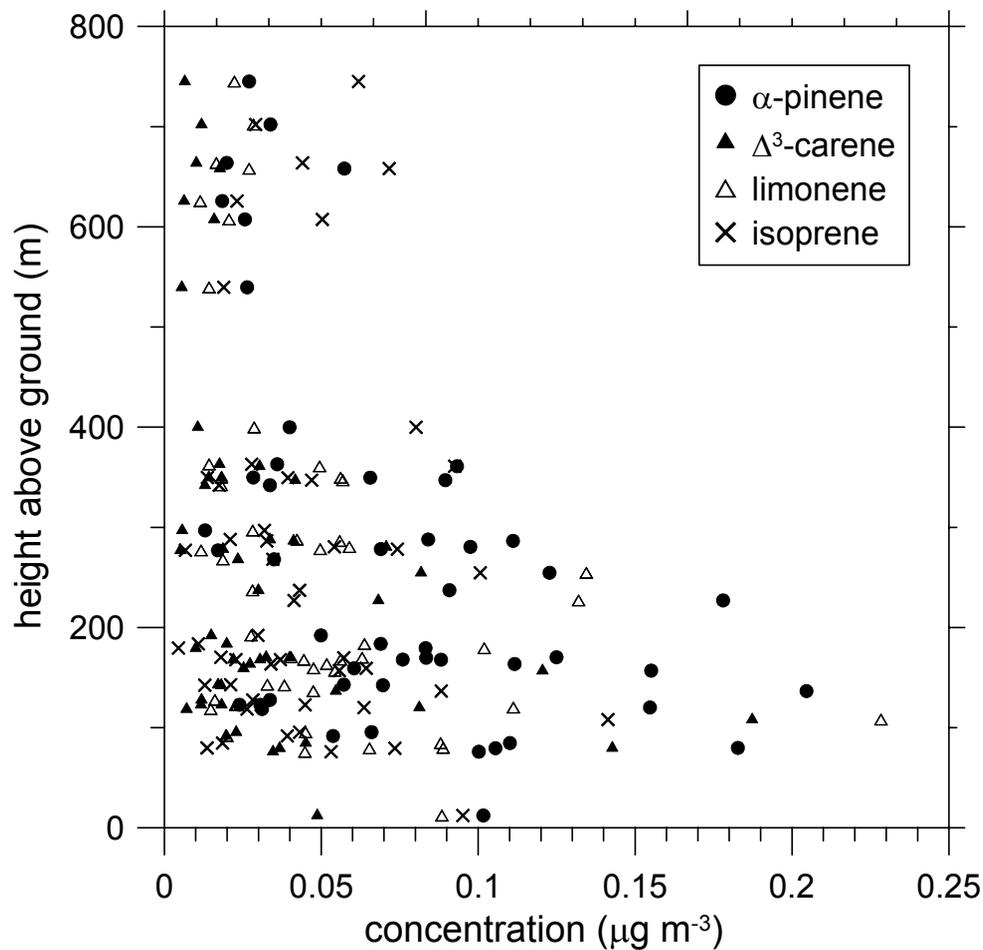


Fig. 3. Concentrations of major biogenic VOCs from 20 balloon profile measurements.

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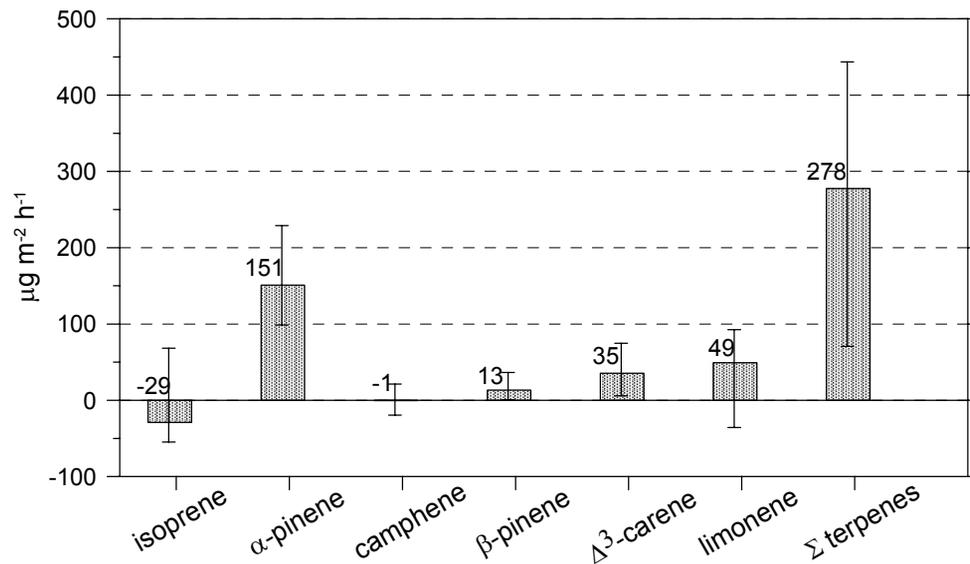


Fig. 4. Flux estimates from balloon profiles by the mixed layer gradient technique (medians, error bars are interquartile ranges).

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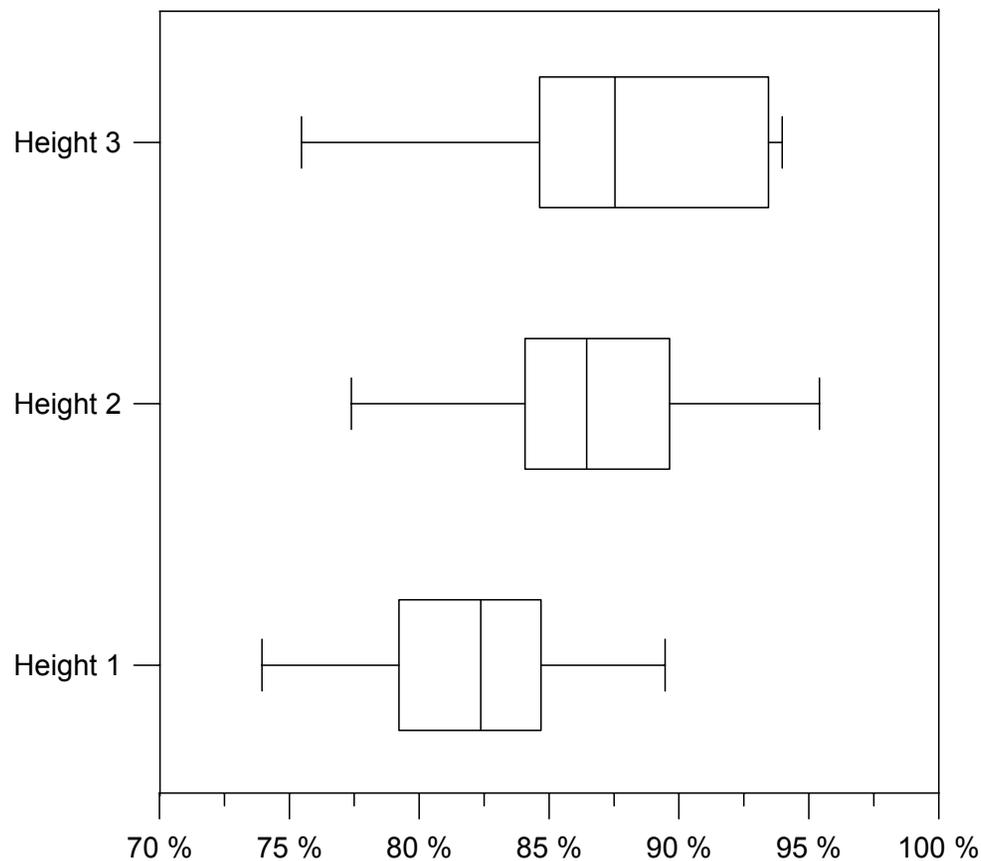


Fig. 5. Forest proportions in footprints of the balloon profiles, categorized by sampling levels (Height 1 = 100–150 m above ground, Height 2 = 250–350 m, Height 3 = 450–750 m).

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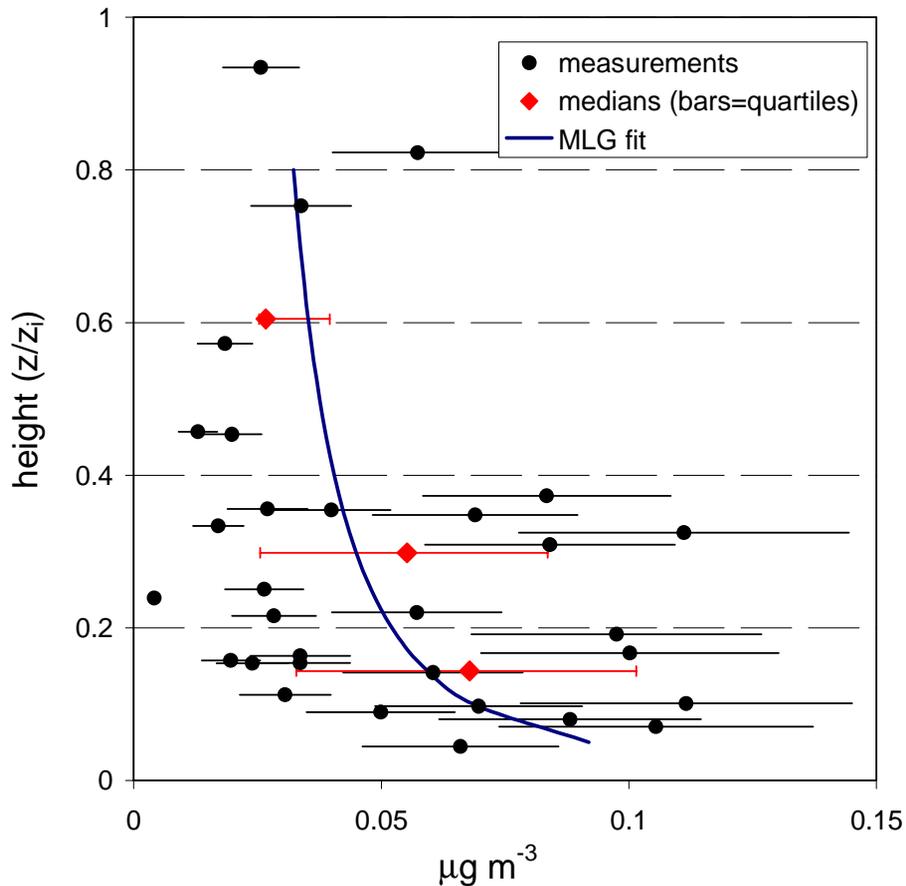


Fig. 6. Measurements of α -pinene mixing ratios and predicted profile by the MLG equation for an α -pinene surface emission of $130 \mu\text{g m}^{-2} \text{h}^{-1}$ and the median vertical mixing velocity (1.7 ms^{-1}) of all profiles.

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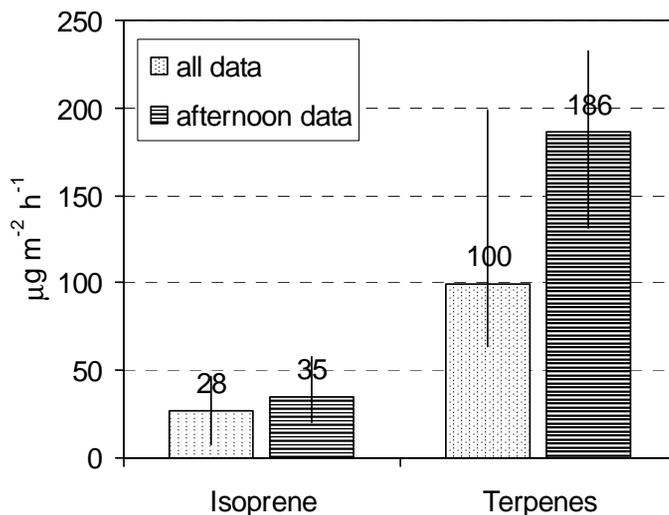


Fig. 7. Medians of surface fluxes as calculated by the MB technique during 2–12 August 2001, representing 40 individual data points. Error bars denote interquartile ranges.

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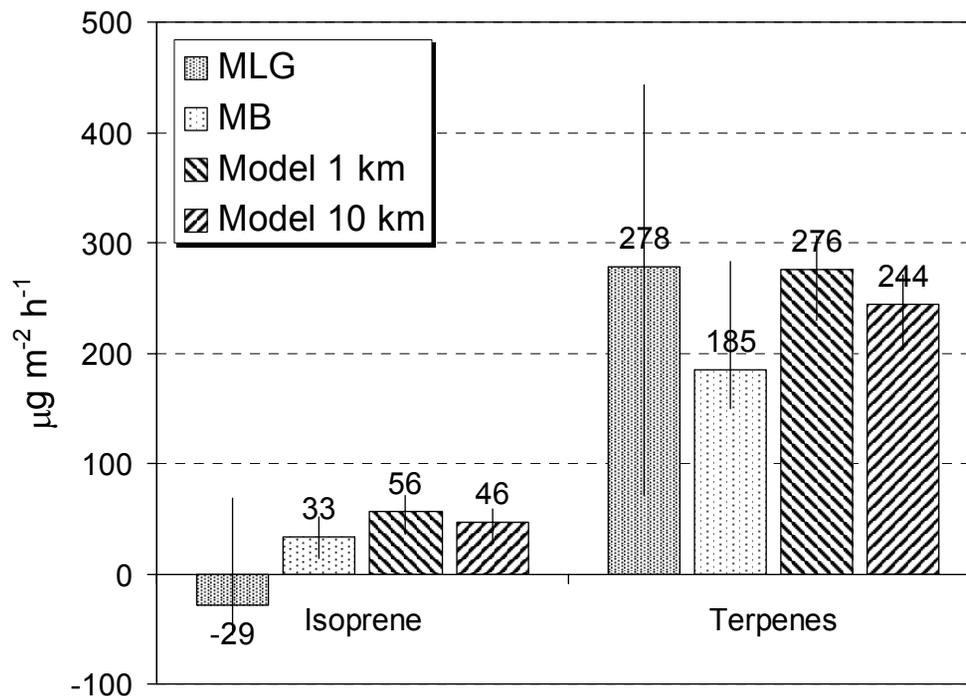


Fig. 8. Afternoon surface fluxes (medians) at Hyytiälä as derived from balloon profiles (MLG- and MB-technique) for 2–12 August 2001 and modelled biogenic VOC emissions (Lindfors et al., 2000) for areas of 1 × 1 km and 10 × 10 km around the site during the same period. Error bars are interquartile ranges.

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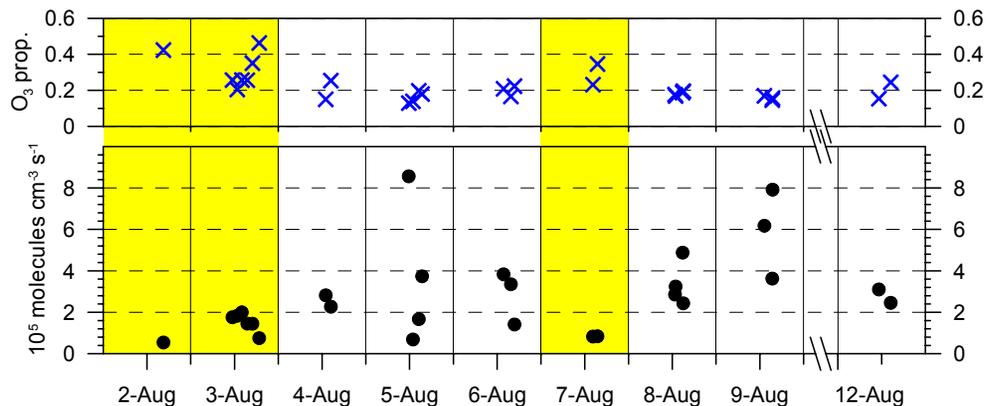


Fig. 9. Terpene oxidation rates, total oxidation rate (lower panel) and fraction of O_3 -pathway (upper panel) relative to the total rate. Days with observations of new particle formation are highlighted in yellow.

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