Emission fluxes and atmospheric degradation of monoterpenes above a boreal forest: field measurements and modelling

By JÖRG SPANKE[1], ÜLLAR RANNIK[2], RENATE FORKEL[3], WALTER NIGGE[1] and THORSTEN HOFFMANN[1]*, [1]*Institute of Spectrochemistry and Applied Spectroscopy (ISAS), PO Box 101352, D-44013 Dortmund, Germany;* [2]*University of Helsinki, Department of Physics, PO Box 9, FIN-00014 University of Helsinki, Finland;* [3]*Fraunhofer-Institute for Atmospheric Environmental Research (IFU), Kreuzeckbahnstrasse 19, D-82467 Garmisch-Partenkirchen, Germany*

ABSTRACT

The contribution of monoterpenes to aerosol formation processes within and above forests is not well understood. This is also true for the particle formation events observed during the BIOFOR campaigns in Hyytiälä, Finland. Therefore, the diurnal variation of the concentrations of several biogenic volatile organic compounds (BVOCs) and selected oxidation products in the gas and particle phase were measured on selected days during the campaigns in Hyytiälä, Finland. α-pinene and Δ^3-carene were found to represent the most important monoterpenes above the boreal forest. A clear vertical gradient of their concentrations was observed together with a change of the relative monoterpene composition with height. Based on concentration profile measurements of monoterpenes, their fluxes above the forest canopy were calculated using the gradient approach. Most of the time, the BVOC fluxes show a clear diurnal variation with a maximum around noon. The highest fluxes were observed for α-pinene with values up to $20 \text{ ng m}^{-2} \text{ s}^{-1}$ in summer time and almost $100 \text{ ng m}^{-2} \text{ s}^{-1}$ during the spring campaign. Furthermore, the main oxidation products from α-pinene, pinonaldehyde, and from β-pinene, nopinone, were detected in the atmosphere above the forest. In addition to these more volatile oxidation products, pinic and pinonic acid were identified in the particle phase in a concentration range between 1 and 4 ng m^{-3}. Beside these direct measurement of known oxidation products, the chemical sink term in the flux calculations was used to estimate the amount of product formation of the major terpenes (α-pinene, β-pinene, Δ^3-carene). A production rate of very low volatile oxidation products (e.g., multifunctional carboxylic) from $\cdot$OH- and O_3-reaction of monoterpenes of about $1.3 \cdot 10^4$ molecules $\text{cm}^{-3} \text{ s}^{-1}$ was estimated for daylight conditions during summer time. Additionally, model calculations with the one-dimensional multilayer model CACHE were carried out to investigate the diurnal course of BVOC fluxes and chemical degradation of terpenes.

1. Introduction

Vegetation releases numerous volatile organic compounds (VOCs) into the troposphere, particularly isoprene, monoterpenes, sesquiterpenes, as well as a series of oxygen-containing compounds. The atmospheric chemistry of these biogenic VOCs has received particular attention because of the large quantities emitted globally as compared to anthropogenic VOCs, as well as the high reactivity of the mostly unsaturated biogenic VOCs. For example, there is substantial evidence that biogenic hydrocarbons influence the regional

* Corresponding author.
e-mail: hoffmann@isas-dortmund.de

distribution of ozone (Hagerman et al., 1997). However, one of the major uncertainties of the impact of biogenic hydrocarbons on atmospheric processes is still the lack of quantitative understanding of their ability to form organic aerosols. Their reactions with the principal atmospheric oxidising agents — ozone, hydroxyl and nitrate radicals — result in the formation of low volatile products, which can undergo gas-to-particle conversion. To distinguish this fraction of tropospheric aerosols from the direct input of particulate organics into the atmosphere (e.g., from leaf waxes, combustion sources), it is specified as secondary organic aerosol (SOA).

One aspect of biogenic aerosol formation from VOC oxidation is the question whether the oxidation products just add to the tropospheric aerosol mass by condensation on pre-existing particles or if they also contribute to the aerosol number concentration by homogeneous nucleation of very non-volatile products. Current aerosol climate models mainly focus on sulfur chemistry, especially when the formation of new particles in the troposphere is considered. Nucleation events are usually discussed in terms of sulfuric acid nucleation, either as a binary (H_2SO_4/H_2O) or ternary system ($H_2SO_4/NH_3/H_2O$) (Kulmala et al., 2000). However, recent field studies on the aerosol formation at rural sites indicate a link between new particle formation processes and the oxidation of volatile organic compounds. The observation of nanometer size particles at the SMEAR II station in southern Finland, are examples of particle formation events over boreal pine forests (Makela et al., 1997). Similar observations were made in forested areas in Portugal (Kavouras et al., 1998), Greece (Kavouras et al., 1999), Canada (Leaitch et al., 1999), and the USA (Marti et al., 1997). In all these cases the observation of nucleation events took place in remote forested areas, where the release of highly reactive VOCs from trees, followed by a rapid oxidation to low volatile products, has to be considered as a potential source for nucleating vapours. Unfortunately, the absolute amount of a condensable species needed to form nanometer particles is extremely low and the chemical identification of the actual nucleating species in the field is rather difficult.

Several measurement approaches were applied for the interpretation of the aerosol data received during the BIOFOR (BIOgenic aerosol formation in the boreal FORest) field campaigns in order to get a better understanding of the role of organics during the nucleation events. One important parameter which has to be estimated is the total flux of biogenic VOCs into the boundary layer. In principle two methods are available to measure VOC fluxes, the relaxed eddy accumulation technique (REA) (Christensen et al., 2000; Ciccioli et al., 1999) and the gradient approach (Darmais et al., 2000; Rinne et al., 2000; Schween et al., 1997). In contrast to branch enclosure studies (Janson et al., 2001; Kesselmeier et al., 1998), both methods yield biogenic VOC flux data on a larger scale, averaged over an extended area of forest that consequently includes the released VOCs from all plant species. In this work the gradient approach was used for the flux estimates.

The resulting BVOC flux data can be used as an input parameter for the chemical modelling and, for example, the calculation of production rates of low volatile oxidation products. Furthermore, using a sensitive adsorptive preconcentration-thermodesorption GC/MS technique, the diurnal variation of the concentrations of selected semi-volatile biogenic VOC oxidation products, which can exist in the gas and particle phase and are indicative for atmospheric oxidation processes, can also be measured. Relatively long-living atmospheric species (e.g., nopinone) are especially suitable for this purpose. Finally, detection of tracer compounds for secondary biogenic organic aerosol formation in the particle phase is helpful in order to link the biogenic VOCs and aerosol formation processes. Since SOA formation is known to include dozens of different compounds, these studies were focused on a limited number of substances (tracer compounds) that have been identified in laboratory investigations, e.g., pinic acid from α-pinene oxidation (Christoffersen et al., 1998; Hoffmann et al., 1998). In order to analyse the low-volatile fraction of oxidation products, a different analytical technique has to be used. Here, filter samples were taken at the site and analysed using a μ-LC/MS system with MS/MS capabilities to separate and identify particle phase biogenic oxidation products.

In summary, the motivation of the work presented here was to get a better insight into the possible link between VOC emission from plants and the formation of aerosols at the site, based

on the application of different analytical techniques and interpretation methods. Target compounds for the chemical analysis were both the potential natural aerosol precursors in the gas-phase and their oxidation products in the particle phase. Micro-meteorological calculations based on the measured profiles and model calculations with a canopy/chemistry model were subsequently performed to estimate the amount of low volatile oxidation products formed by the monoterpenes during vertical transport.

2. Experimental section

2.1. Site description

The SMEAR II forest research station is located at Hyytiälä in southern Finland (61°51′N, 24°17′E, 181 m above sea level). Measurements of biogenic and anthropogenic VOCs were made from the 72 m tower at 3 different heights above the forest on 13 days during the three BIOFOR measurement campaigns (April–May and August 1998, April 1999; see Table 1). The coniferous forest surrounding the site has a mean canopy height of 13.3 m, dominated by Scots pine (*Pinus sylvestris*) with some Norway spruce (*Picea abies*) and birch (*Betula sp.*). A more detailed site description and a complete list of measurements performed during the BIOFOR field campaigns, are given by Kulmala et al. (2001) and Haataja and Vesala (1997).

The site was studied in terms of surface layer similarity theory by Rannik (1998), who applied the micro-meteorological profile method for estimation of heat fluxes and obtained good correspondence with the eddy covariance measurements. Therefore the site is considered to be suitable for the profile technique.

2.2. VOC sampling and analysis

The samples were taken by using a newly developed sampling unit, which was able to sample seven samples in a row. While the timer and control unit of the sampling system was placed inside the SMEAR II station, the sampling units (adsorption tubes, MFC, pumps, solenoid values) were placed at three different heights in the tower. The sampling flow was controlled by Mass Flow Controllers (MFC 1159 or MFC 1259, MKS Instruments GmbH, München, Germany; max. flow 200 ml min^{-1}) and the switching between the different lines was done by solenoid valves. To prevent the formation of artifacts through oxidising reactions during sampling, an ozone scrubber was installed upstream of the sampling tubes. The scrubber consisted of three manganese dioxide-coated copper nets (o.d. 24 mm) within a glass housing. The nets were taken out of an ozone analyser, usually used to generate zero air in the calibration cycle of the instrument (Ansyco GmbH, Karlsruhe, Germany) (Hoffmann, 1995). One of the seven lines in each sample unit was used only for purging the ozone scrubber for a period of about 10 min just before the sampling started. The adsorption tubes, filled with a combination of Tenax TA and Carbotrap, were connected with the ozone scrubber and the solenoid valves of the sampling unit with stainless steel Swagelok connections. The sampling flow rate was adjusted to about 130 ml min^{-1} and a sampling time of 40 min was chosen. This resulted in a total sampling volume of 5 to 5.5 l, which proved to be an appropriate amount to allow the detection of minor hydrocarbons and certain oxidation products. In order to synchronise ongoing measurements at the SMEAR II station and subsequent data analysis, the Finnish winter time (UTC + 2) was chosen as the timebase for all measurements.

After sampling, the tubes were sealed with Swagelok end caps and stored in the dark at 4°C

Table 1. *Days at which the sampling took place*

Campaign	Date (samples per stage)
BIOFOR 1	23.04.98 (10); 24.04.98 (10); 25.04.98 (10); 13.05.98 (10); 15.05.98 (8)
BIOFOR 2	11.08.98 (10); 12.08.98 (10); 13.08.98 (10); 15.08.98 (14)
BIOFOR 3	21.04.99 (10); 22.04.99 (5); 26.04.99 (11); 27.04.99 (8)

until they were transported to the laboratory at the ISAS in Dortmund, Germany. There, the compounds of interest were thermally desorbed and automatically focused within a cryotrap (GLT-tube). The cryotrap temperature was maintained below 190 K. Finally, the compounds were injected onto a capillary column (50 m DB-5, 0.32 mm i.d.; SGE GmbH, Weiterstadt, Germany) by computer controlled heating of the trap. The eluted substances were transferred to a mass spectrometric detector (ion trap, ITD 700, Finnigan MAT, Bremen, Germany) and monitored for their typical fragment ions. The comparison of the full scan mass spectra and retention times with those of reference compounds was used to identify the different biogenic hydrocarbons. Experimental details about preparation and analysis of the adsorption tubes can be found in Hoffmann (1995).

2.3. Particle sampling and analysis

For the purpose of identifying BVOC oxidation products in the particle phase, filter samples were taken at the top of the forest canopy, typically two samples during daytime and one during the night. Glass fibre filters with a diameter of 70 mm were used (Type GF 55; Schleicher and Schuell, Dassel, Germany) and a sampling flow rate of 1.8 m³ h⁻¹ was chosen. Certainly, using this sampling technique possible positive or negative artifacts during the sampling step cannot be completely excluded (Lane, 1999). Unfortunately, very few information on possible sampling errors for the target compounds is available. Kavouras et al. (1998) investigated the influence of ozone on the recovery of pinonic acid, a particle phase BVOC oxidation product, and did not observe any degradation of the organic acid. Other possible sampling artifacts, such as losses from the filter during sampling, have not been investigated. However, due to the relatively low sampling flow rate chosen for the studies presented here, potential sampling errors can be expected to be smaller than for high volume sampling, which is typically used for preconcentration of organic aerosol components. After termination of sampling, the glass fibre filters were stored separately at 5°C in glass vessels until analysis at the ISAS in Dortmund, Germany.

The samples were analysed with a preconcentration/μ-LC/MS technique. The analytes were extracted with 2 ml methanol and a 20 μl aliquot was preconcentrated on a μ-column (5 mm, 0.3 mm i.d., Nucleosil SB, 10 μm particle size, 10 nm pore size; GROM, Herrenberg, Germany). Afterwards the analytes were directly injected onto the analytical column (15 cm, 0.1 mm i.d., Gromsil 120 ODS 3 CP, 5 μm particle size; GROM, Herrenberg, Germany). Separation was done by applying a gradient (A: $H_2O + NH_4Ac$ (10 mM, pH 3.6); B: 5% Acetonitrile + 95% A; (t min⁻¹)/% A: 0/98, 5/90, 20/20, 50/50) with a flow rate of 5 μl min⁻¹. The eluted substances were transferred to a mass spectrometric detector (double focusing sector field, MAT 90, Finnigan MAT, Bremen, Germany), equipped with an electrospray ionisation interface, and monitored by their quasi-molecular ions in the negative ion mode.

3. Interpretation methods

3.1. Flux calculations from measured profiles

Generally, in the analysis of fluxes and concentration profiles of reactive chemical species the influence of chemistry has to be accounted for (Galmarini et al., 1997; Vilà-Gerau de Arellano and Duynkerke, 1995). For chemically reactive species the vertical flux, given by $\overline{w'c_i'}$, is not constant with height. Under horizontally homogeneous, stationary conditions the vertical flux divergence is equal to the chemical depletion/production

$$\frac{\mathrm{d}\overline{w'c_i'}}{\mathrm{d}z} = \bar{Q}_i, \tag{1}$$

where $\bar{Q}_i$ is the chemical source/sink term of the compound i and no other sources and sinks are assumed. Then, for the reactive species the vertical concentration profile above the forest can be written as:

$$\bar{C}_i(z) = \bar{C}_i(h) - \frac{\overline{w'c_i'}(h)}{\kappa u_*} \int_h^z \frac{\phi(\zeta)\gamma(z)}{z-d}\,\mathrm{d}z$$
$$- \frac{1}{\kappa u_*} \int_h^z \left(\int_h^z \bar{Q}_i(z)\,\mathrm{d}z \right) \frac{\phi(\zeta)\gamma(z)}{z-d}\,\mathrm{d}z, \tag{2}$$

where the last term accounts for the flux divergence with height. In the above equation d is the displacement height, h is the canopy height and

z is the height from the surface, $\kappa = 0.4$ is the von Kármán constant and u_* the friction velocity. Over low vegetation or at sufficiently high levels in the ASL, the non-dimensional scalar concentration gradient,

$$\phi = -\frac{\kappa u_*(z-d)}{\overline{w'c'}}\frac{dC}{dz}, \tag{3}$$

is the function of non-dimensional height $\zeta = (z-d)/L$. The Obukhov stability length L is determined by momentum and heat fluxes (Kaimal and Finnigan, 1994). For a conservative scalar, the function ϕ is assumed to be equal to the corresponding function for heat. Above high vegetation inside the roughness sublayer (RSL), the eddy diffusivity increases and the non-dimensional gradient decreases compared to what is expected over low vegetation. In (2), the effect of RSL on the non-dimensional gradient was accounted for in accordance with Cellier and Brunet (1992) as

$$\gamma(z) = \frac{z-d}{Z_*-d}, \tag{4}$$

where Z_* is the roughness sublayer height. Above RSL γ is equal to 1.

In flux calculation the zero-plane displacement d was taken to be 2/3 of the forest height. The non-dimensional flux-gradient relationships according to (Högström, 1988) were applied and the RSL was assumed to extend up to twice the forest height. The friction velocity and stability length values were obtained from simultaneous eddy covariance measurements of momentum and heat fluxes performed at the site.

The fluxes $\overline{w'c'(h)}$, and thus $\overline{w'c'(z)}$ following from (1), were estimated similarly to Rannik (1998) from the measured concentration values by obtaining the best fit with theoretical profile (2) in least square sense as

$$\overline{w'c'_h} = \frac{N(\sum \overline{C}_z I_z - \sum \overline{C}_z II_z) - \sum I_z(\sum \overline{C}_z - \sum II_z)}{N\sum I_z^2 - (\sum I_z)^2},$$

$$\overline{C}_h = \frac{1}{N}\left(\sum \overline{C}_z - \overline{w'c'_h}\sum I_z - \sum II_z\right), \tag{5}$$

where I_z and II_z correspond to terms in (2) according to

$$\overline{C}_z = \overline{C}_h + \overline{w'c'_h}I_z + II_z. \tag{6}$$

Subscript denotes here the observation level and the summation is made over all measurement levels ($N \geqslant 2$). In estimation procedure the integrals in I_z and II_z were calculated by numerical integration. In addition, the linear correlation statistics were used to estimate the error (one standard deviation) of the flux.

3.2. Application of a canopy/chemistry model

In addition to the flux and production rate calculations based on measured profiles, a multi-layer canopy/chemistry model was applied to gain insight into BVOC oxidation product formation above the forest. Since the model was initialised by the actual measurements (e.g., BVOC concentrations at noon time) and was than used to follow the daily course of different measured species, its application can be regarded as a model verification exercise. However, due to the fact that after the initialisation step the vertical transport and BVOC chemistry was treated independently from the measurements, its results can also be considered as an additional tool to estimate production rates of condensable species in the vicinity of the forest.

The canopy/chemistry model CACHE (canopy atmospheric chemistry emission model, Forkel et al. (1999)) predicts diurnal courses of temperature and concentrations of water vapour and chemical constituents by solving the prognostic equations for heat and mass. The model accounts for the energy balance at the leaf and the soil surface, turbulent vertical transport of heat, moisture and 45 chemical compounds, deposition, BVOC emission as well as chemical transformation. Chemical transformations were computed with a slightly modified version of the RACM chemistry mechanism (RACM, Stockwell et al., 1997), in which the first step of the monoterpene degradation was treated separately using the rate constants listed in Table 2.

Emissions of monoterpenes and other VOCs by the leaves were modelled according to Steinbrecher et al. (1999), taking into account the predicted leaf temperatures and photosynthetic active radiation (PAR) profiles in the canopy. Steinbrecher et al. shows that the emission of terpenes can be described by considering emission from pools as well as from synthesis:

$$E(T, \text{PAR}) = e_{\text{pool}}f_T + e_{\text{synth}}f_{T,\text{PAR}}, \tag{7}$$

Table 2. *Rate constants k at 298 K and 1013.25 hPa total pressure of air for the reactions of selected terpenes with $\cdot OH$, $\cdot NO_3$, O_3 (Atkinson, 1997)*

	$10^{-12} \times k_{OH}$ (cm³ molecule⁻¹ s⁻¹)	$10^{-12} \times k_{OH_3}$ (cm³ molecule⁻¹ s⁻¹)	$10^{-18} \times k_{O_3}$ (cm³ molecule⁻¹ s⁻¹)
camphene	53	0.66	0.90
Δ^3-carene	88	9.1	37
β-caryophyllene	197	19	11600
limonene	171	12.2	200
longifolene	47	0.68	<0.5
myrcene	215	11	470
β-phellandrene	168	8.0	47
α-pinene	53.7	6.16	86.6
β-pinene	78.9	2.51	15
sabinene	117	10	86

with e_{pool} and e_{synth} being plant specific emission factors at 30°C and standard PAR (i.e., 1000 µE). The temperature correction function for the pool term is the widely used function of the temperature T,

$$f_T = \exp(\beta(T - T_s)), \qquad (8)$$

with $\beta = 0.09°C^{-1}$ and $T_s = 30°C$. The correction factor $f_{T,PAR}$ for the synthesis term follows the description by Guenther et al. (1993) for isoprene

$$f_{T,PAR} = \frac{\exp \dfrac{c_1(T - T_s)}{RT_s T}}{0.96 + \exp \dfrac{c_2(T - T_M)}{RT_s T}}$$
$$\times \frac{\alpha c_3 L}{\sqrt{1 + \alpha^2 L^2}}, \qquad (9)$$

with c_1 (95,000 J mol⁻¹), c_2 (230,000 J mol⁻¹), c_3 (1.066), α (0.0027) and T_M (314 K) being empirical constants, R the gas constant and L the PAR value in µE. NO emissions at the soil surface were taken as temperature and soil water dependent. The deposition of trace gases at the soil and leaf surfaces was described according to Wesley (1989). For the model runs presented here, the canopy and the atmospheric boundary layer up to 3 km were resolved into 40 layers.

4. Results and discussion

4.1. BVOC concentrations

The pie chart in Fig. 1 and Table 3 show the percentage composition of the monoterpenes aver-

aged over all samples during the three measurement campaigns for each sampling height. The number of samples are given in Table 1. First of all, it is obvious that during all three campaigns the monoterpene composition was dominated by α-pinene and Δ^3-carene. The two endocyclic terpenes always contributed to more than 75% of the overall monoterpene concentration. As expected, the highest concentrations of the monoterpenes were measured at the lowest level and generally decreased with increasing measurement height. This concentration gradient was more pronounced during the summer campaign (BIOFOR 2, Fig. 1) than during the two spring campaigns (BIOFOR 1 and 3, Table 3). Also the gradient in the relative composition was slightly different between the BIOFOR 2 and the BIOFOR 1 and 3 campaigns. Whereas the relative composition at the three levels was almost constant during the two spring campaigns, the BIOFOR 2 data show a clear increase of the relative contribution of the nonreactive terpenes (tricyclene, camphene) with increasing height. In principle, the relative composition of the emission from the different forest areas, which serve as footprints for the different monitoring levels, could be responsible for such an observation (Janson et al., 2001). However, the relative composition at different heights might also change because of the chemical reactions during vertical transport. The quantitative contribution of chemical degradation reactions will be discussed later in this paper.

The very reactive compounds myrcene, limonene and β-phellandrene (Table 2) are missing in the pie charts depicted in Fig. 1 and in Table 3,
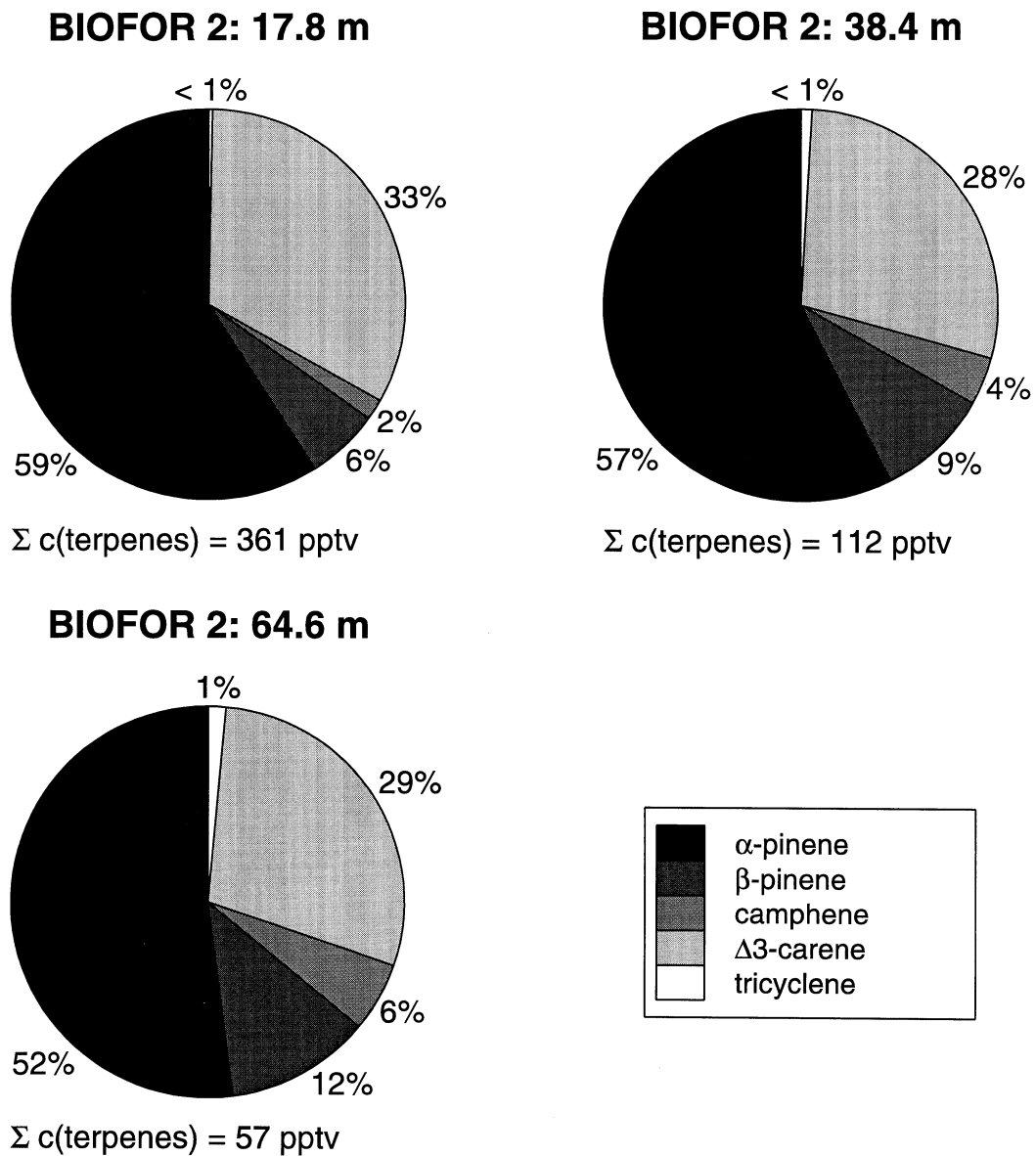
BIOFOR 2: 17.8 m

< 1%

33%

2%

59%   6%

Σ c(terpenes) = 361 pptv

BIOFOR 2: 38.4 m

< 1%

28%

4%

57%   9%

Σ c(terpenes) = 112 pptv

BIOFOR 2: 64.6 m

1%

29%

6%

52%

12%

	α-pinene
	β-pinene
	camphene
	Δ3-carene
	tricyclene

Σ c(terpenes) = 57 pptv

Fig. 1. Percental composition of the monoterpenes during BIOFOR 2 (August 1998).

as compared to the results of emission measurements on selected trees of *pinus sylvestris* (Janson et al., 2001). As indicated above, this can be explained by chemical degradation during vertical transport and mixing with older air parcels in which these reactive monoterpenes have already been oxidised.

The atmospheric concentration of nopinone and pinonaldehyde, the main oxidation products of β-pinene and α-pinene, were mostly below the detection limit during the third measurement campaign, enhanced during BIOFOR 1 and showed the highest values during BIOFOR 2. Although our data base is limited, this can be explained qualitat-

Table 3. *Percental composition of the monoterpenes during the BIOFOR campaigns*

Campaign height (m)	BIOFOR 1			BIOFOR 2			BIOFOR 3		
	17.8	38.4	64.6	17.8	38.4	64.6	17.8	38.4	64.6
α-pinene	55.9%	55.2%	59.2%	59.1%	57.5%	52.1%	74.1%	70.0%	74.4%
β-pinene	9.2%	9.8%	8.0%	6.0%	9.3%	11.9%	5.2%	5.2%	6.0%
camphene	7.2%	10.5%	8.2%	1.7%	3.9%	5.8%	1.1%	3.4%	1.5%
Δ^3-carene	25.4%	20.7%	21.4%	32.8%	28.4%	28.8%	18.8%	19.2%	16.5%
tricyclene	2.4%	3.8%	3.2%	0.3%	0.9%	1.5%	0.8%	2.3%	1.6%
$\sum$ (*terpenes*) (pptv)	150	94	95	361	112	57	102	94	40

ively by the higher temperature during summer, accompanied with higher natural emissions and higher photolysis rates that yield higher ·OH concentrations. Therefore, a more rapid degradation of the more reactive BVOCs should be observable during the summer campaign, which would explain the higher values of the biogenic oxidation products. Nevertheless, the highest concentrations of both compounds were often observed in the early morning hours, most likely a result of the combination of high educt concentration due to low vertical mixing and starting photochemistry. Then, peak concentrations were observed in the range between 30–140 pptv for pinonaldehyde and 10–45 pptv for nopinone. However, if the concentration ratios of oxidation product to parent hydrocarbon are calculated, the strong influence of transport processes can be eliminated. To demonstrate the influence of chemistry on educt and product concentrations during the August campaign, Fig. 2 shows the diurnal variation of these ratios for nopinone and its precursor β-pinene. As can be seen in the figure, the maximum values were observed around noon, strongly indicating that ·OH-chemistry is happening. In fact, the measured diurnal variation of the nopinone/β-pinene ratio perfectly matches the expected daily course of the OH-radical concentration.

4.2. Monoterpene fluxes above forest

The degradation of monoterpenes during daytime occurs through the reactions with ozone and hydroxyl radicals. Generally, these reactions of the monoterpenes are considered to be too slow as compared to the timescale for vertical mixing (τ, see, e.g., Darmais et al., 2000; Rinne et al., 2000)
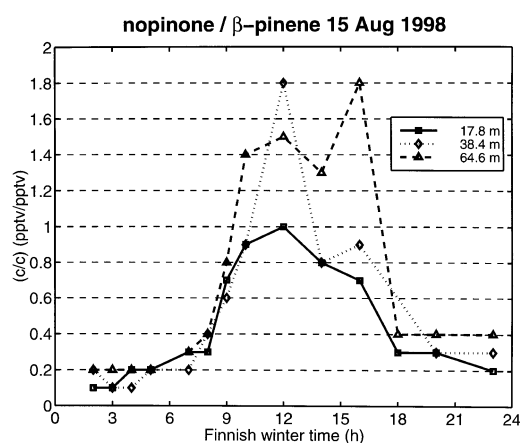

Fig. 2. Nopinone/β-pinene ratio measured at 15 August 1998 (the line through the data points are just meant to lead the eye).

as given by:

$$\tau = \frac{z}{u_*}. \tag{10}$$

However, in order to test this hypothesis, the atmospheric degradation of the most abundant monoterpenes α-pinene, Δ^3-carene and β-pinene were included in the flux calculations, choosing midday on August 11, 1998 as a test case. Fig. 3 shows the diurnal variation of the α-pinene concentration at the three heights on 11 August. This day was sunny with a global radiation of about 500 W m^{-2} and an average midday temperature above the forest of 16°C. The wind was from the northwest (327°), with an extended area of forest upwind at the site (Ranni, 1998). The friction
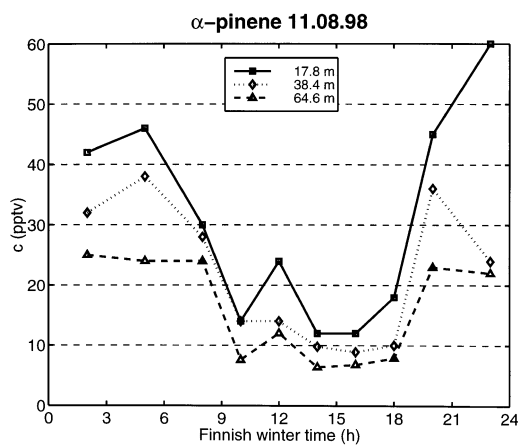
Fig. 3. α-pinene concentration gradient measured at 11 August 1998 (the line through the data points are just meant to lead the eye).

velocity was $u_* = 0.6\,\mathrm{m\,s}^{-1}$ and the Obukhov stability length $L = -85$ m.

The chemical sink term (1) for terpenes, by considering second-order chemical reactions with O_3 and $\cdot OH$, can be written as:

$$\bar{Q}_i = -k_{O_3}\bar{c}_i[O_3] - k_{OH}\bar{c}_i[\cdot OH], \qquad (11)$$

where terms arising from correlation between the concentrations of different species (segregation terms) is neglected as being unimportant in the atmospheric surface layer (Galmarini et al., 1997). The rate coefficients k_{O_3} and k_{OH} for α-pinene, Δ^3-carene and β-pinene (Table 2) were adopted from Atkinson (1997). To estimate the chemical sink term, the O_3 and $\cdot OH$ profiles above the forest need to be known. The $\cdot OH$ concentration profile was obtained from model simulations with the canopy/chemistry model CACHE and the O_3 concentration profile was obtained from the concentration measurements (Vesala et al., 1998) at four heights above the forest. In Figs. 4a,b the fitted profiles follow the theoretical relationship (2) with the parameters estimated according to (5).

Fig. 4a shows the fitted concentration profiles for α-pinene, Δ^3-carene and β-pinene, together with experimental data points. For the monoterpenes, the last term of equation (2) was considered, i.e., chemical depletion of monoterpenes was accounted for. However, the influence of chemistry on non-dimensional gradients of given monoterpenes was observed to be negligible, because the chemistry term in the second-order closure flux equation is much smaller compared to other terms
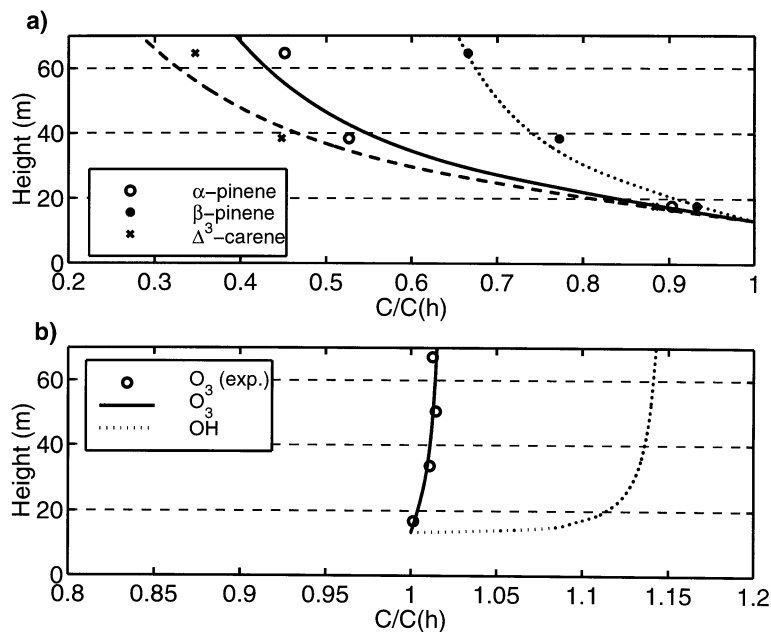

Fig. 4. Vertical profiles of (a) α-pinene, Δ^3-carene and β-pinene, and (b) O_3 and $\cdot OH$ above the forest at midday, 11 August 1998.

(Galmarini et al., 1997). The estimated concentrations and fluxes at the forest top are given in Table 4.

For comparison, the monoterpene fluxes without the chemistry effect were also estimated for this case study. The obtained fluxes were smaller than the values in Table 4 estimated for the forest top by including chemistry effect. The fluxes decrease with height due to chemistry and this results in a lower flux estimation when the chemistry is excluded. However, the difference was smaller than 5% for the given monoterpenes. Therefore, considering other uncertainties in monoterpene flux estimation, the chemistry effect will not be included in further flux analysis.

Fig. 5 shows the estimated monoterpene fluxes together with uncertainty intervals during two days in August, 1998. The fluxes of α-pinene, Δ^3-carene and β-pinene exhibit clear diurnal variations. Two explanations are obvious: The emission of the biogenic VOC has a diurnal cycle, which depends on temperature and light (Kesselmeier and Staudt, 1999). Furthermore, during the night the turbulent transport is inhibited by stable stratification, leading to storage of the emitted BVOC in the low air layers. The nightly storage of monoterpenes results in significantly elevated concentration levels in the vicinity of the canopy as compared to daytime values (Fig. 3). 11 August was a clear day, while on 12 August a rapid variation in global radiation due to clouds was observed especially in the afternoon (not shown). As shown in Fig. 5, an almost identical behaviour was observed for the individual monoterpenes. A similar emission pattern as shown in Fig. 5 was also observed for camphene, limonene and sabinene (data not shown), but the flux estimates for these compounds were more scattered, mainly due to analytical

difficulties in the determination of gradients of very small concentrations.

During the spring campaigns of 1998 and 1999, a reasonable flux estimate could only be made for the most abundant monoterpenes — α-pinene and Δ^3-carene. Fig. 6 shows the corresponding fluxes in 23–25 April 1998. The flux estimates from this period are more scattered, but are occasionally larger by a factor of four compared to the August campaign. This result can be compared with the results from cuvette measurements at the site by Janson et al. (2001), who also found higher maximum BVOC emissions in spring than in the summer time. During 23 April the radiation was more variable due to cloudiness, which might explain the low fluxes during midday at that day.

4.3. Production of condensable species

Although chemical degradation of terpenes was found to be negligible for flux estimates, chemical reactions of BVOCs can still be significant when aerosol formation processes are considered. The monoterpenes emitted by the forest are chemically depleted while transported upwards. Fig. 7a shows the monoterpene flux profiles above the forest. Within the considered height interval, about 4% (Δ^3-carene), 5% (α-pinene) and 10% (β-pinene) of the quantity, emitted by the forest, is chemically converted between the forest top and 67 m level. The differences in the flux profiles for β-pinene, α-pinene, and Δ^3-carene is mainly due to the different shapes of the concentration profiles of the three terpenes. Overall, the concentrations are smaller at 67 m for the given case study by about 35% (β-pinene), 60% (α-pinene) and 70% (Δ^3-carene) compared to their values at the forest top, mainly due to the fact that the source is located below the forest top. Chemical degradation contributes

Table 4. *Concentrations, fluxes and chemical degradation rate at the forest top estimated for midday, 11 August 1998*

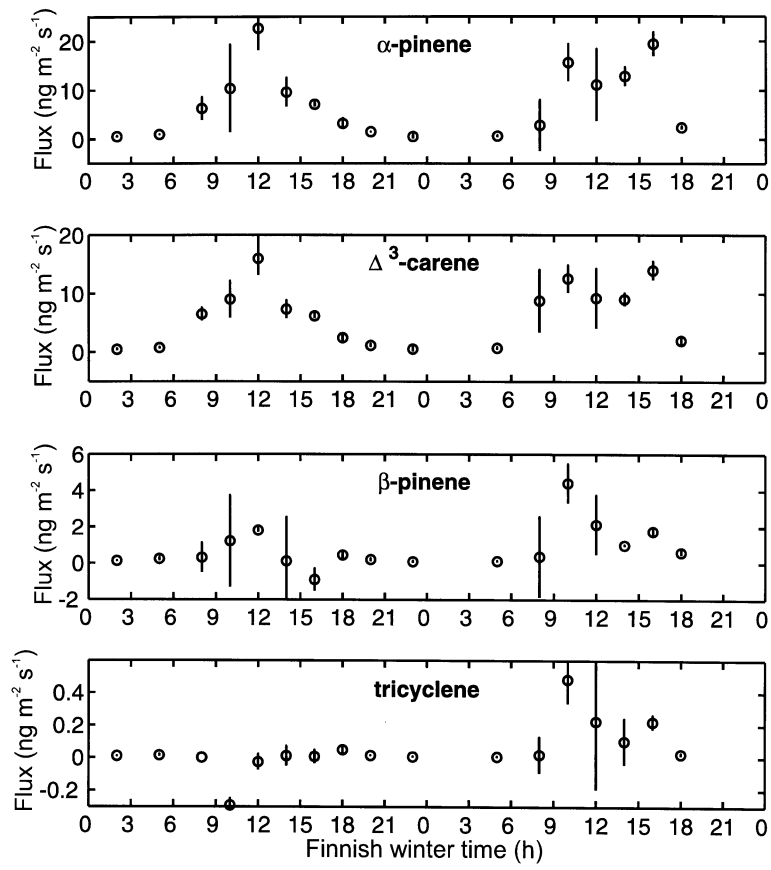|	$\bar{c}(h)$ (ppbv)	$F(h)$ (pptv m s^{-1})	$\bar{Q}_{calc.}(h)$ (ppbv s^{-1})	$\bar{Q}_{model}(h)$ (ppbv s^{-1})
O$_3$	31.3	-110 ± 30		
·OH	8.86×10^{-5}			
α-pinene	2.66×10^{-2}	3.9 ± 0.6	5.2×10^{-6}	4.8×10^{-6}
β-pinene	3.75×10^{-3}	0.31 ± 0.03	7.5×10^{-7}	9.9×10^{-7}
Δ^3-carene	1.58×10^{-2}	2.7 ± 0.3	3.8×10^{-6}	4.9×10^{-6}

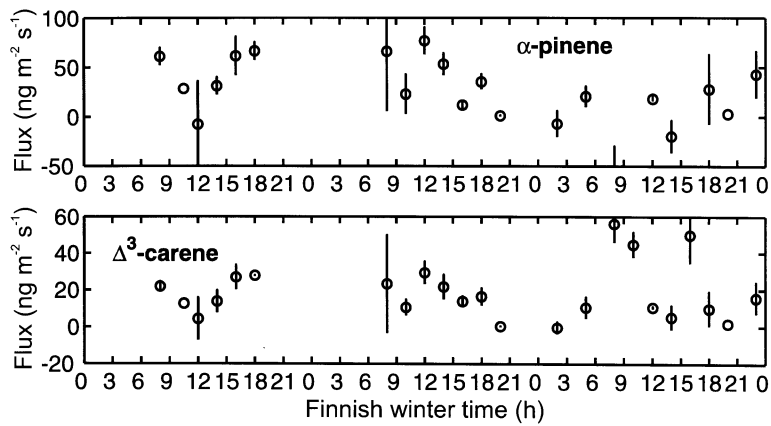Fig. 5. Fluxes of α-pinene, Δ³-carene, β-pinene and tricyclene in 11–12 August 1998.

Fig. 6. Fluxes of α-pinene and Δ³-carene in 23–25 April 1998.

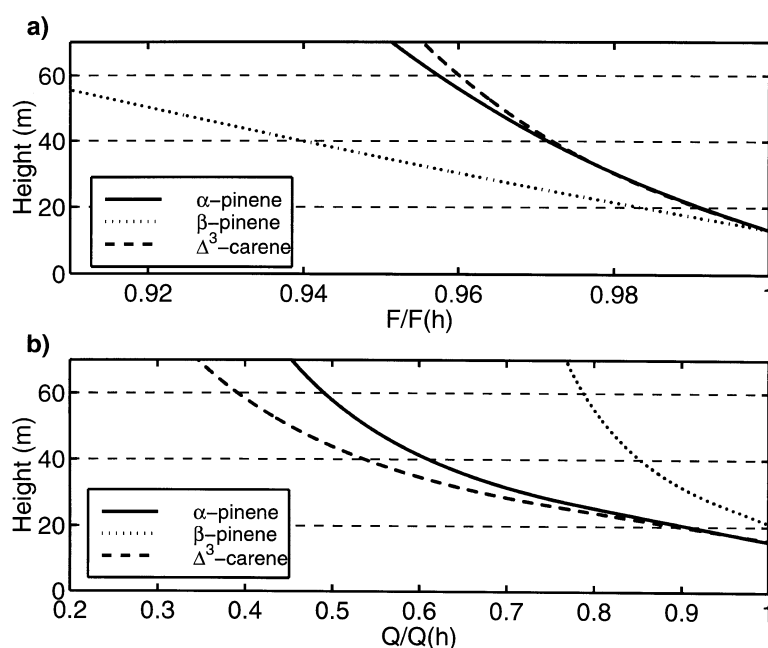*Fig. 7.* Vertical profiles of (a) fluxes of α-pinene, Δ^3-carene and β-pinene, and (b) chemical sink term for the given monoterpenes above the forest at midday, 11 August 1998.

only a little to the gradient in concentration profile (Fig. 4) via last term in (2).

Fig. 7b presents the estimated chemical sink terms of three monoterpenes. The values at the forest top are given in the last column of Table 4. The chemical sink $\bar{Q}$ profiles are similar to concentration profiles because of the direct proportionality to concentrations. The strongest depletion of monoterpenes occurs close to the forest top. During this chemical degradation low volatility organic compounds (e.g., organic acids) are formed which can support particle formation through condensation or nucleation.

Since one major goal of the terpene measurements was to establish a link between biogenic VOC degradation and particle formation, it is useful to assess the production rate of condensable oxidation products due to chemical reactions of the terpenes above the forest. Using the chemical degradation rate $(\bar{Q}_{calc.}(h))$ of the three terpenes given in Table 4 and assuming an average formation yield of low volatile products (e.g., multifunctional carboxylic acids) of 0.05 [from O_3 and ·OH-reactions, see Jang and Kamens, 1999; Yu et al., 1999), a production rate of about $1.2 \cdot 10^4$

molecules $cm^{-3} s^{-1}$ can be calculated. Of course, SOA formation is generally believed to be described by gas/particle partitioning theory and therefore not all product molecules necessarily convert to the particle phase. However, considering the fact that just very low volatile products were accounted for (which possess relatively large partitioning coefficients), the number given above might be used as an upper limit for condensable molecules formed from BVOC oxidation at the site on 11 August 1998. This value can then be compared with results from aerosol growth rate analysis (Kulmala et al., 2001), which showed source rates of condensable vapour of $7.5-11 \cdot 10^4$ molecules $cm^{-3} s^{-1}$. Therefore, chemical degradation of α-pinene, Δ^3-carene and β-pinene can explain about 10 to 16% of the condensable vapour needed to explain the observed particle growth, assuming a yield of condensable products of 0.05.

4.4. Modelling of BVOC fluxes and chemistry

As mentioned before, the application of the CACHE model is composed of two elements, a

model verification component and, after adjusting certain parameters to match the observations, a prognostic component in order to calculate terpene degradation in the vicinity of the forest and production rates of condensable species. Model simulations with CACHE were carried out for 11 August 1998. In this paper, the flux from forest as it would be calculated purely based on cuvette measurements will be referred to as potential flux. In contrast to the potential flux, the flux above the canopy includes the effect of chemical loss of BVOC or storage of terpenes in the canopy. The model is used here to estimate both kind of fluxes.

The model was initialised at midnight using measured temperature, humidity, wind speed, and ozone concentration profiles from the mast up to 67 m and values from the meteorological sounding at Jokioinen, Finland above this height up to 3 km. For this case study, the emissions factors (Steinbrecher et al., 1999) were adjusted by a factor of 0.25 to obtain agreement between measured and modelled concentrations at noon time. It was found that the model could well reproduce the daily course of the measured temperatures with a maximum value of about 18°C at 4 m and about 16°C at 67 m. The modelled ozone concentrations around noon were around 30 ppbv, which is in agreement with the measured values.

To verify the model results, which consider chemistry, they are compared to the measured VOC concentrations. As an example Fig. 8 shows the modelled diurnal variation of the α-pinene
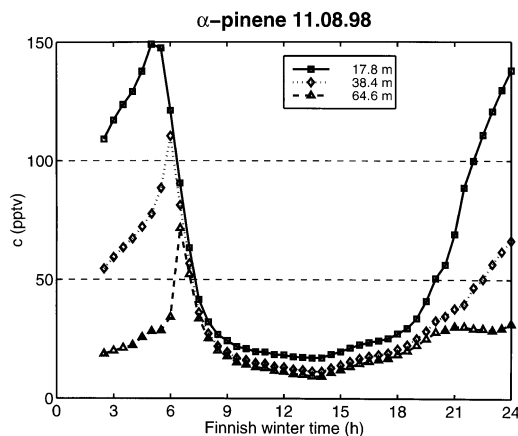

Fig. 8. Modelled concentrations of α-pinene for 11 August 1998, using CACHE.

concentrations at three heights on 11 August 1998, which can be compared with Fig. 3. The modelled concentrations at the two lower levels (17.8, 38.4 m) during the night indicate that the vertical exchange in the vicinity of the canopy top might be overestimated by the model for stable conditions. For unstable conditions during the day, which is the more important period since most BVOC are emitted during this time, a reasonable agreement between measured and modelled concentration profiles was found.

The modelled fluxes at 36 m (Fig. 9) show the same general pattern and order of magnitude as the calculated fluxes from gradient measurements (Fig. 5). In comparison to the fluxes calculated from measured profiles, the modelled fluxes do not display the pronounced peak at noontime and decrease more slowly in the afternoon. Also, the fluxes calculated from the measurements do not show the small peak of the modelled fluxes at about seven o'clock in the morning, which can be attributed to the release of terpenes which were accumulated during the night and which are released into the boundary layer with the slow breakup of the stable layer at the canopy top in the morning. This difference could be due to the low time resolution of the measurements or that the mixing of the different air masses is going on faster than predicted by the model. However, VOC gradient measurements on other days (data not shown) also displayed a pronounced increase of monoterpene concentrations between six and nine o'clock in the morning, which supports the model results. As shown in Fig. 9, the morning peak in the flux above the canopy even exceeds the potential emission flux, i.e., the emission directly from the branches in the morning hours.

Chemical degradation rates at canopy top as predicted by the model show good agreement with the degradation rates derived from the measured profiles (Table 4). A production rate of low volatile oxidation products of the three most abundant monoterpenes (α-pinene, β-pinene and Δ^3-carene) was calculated under utilisation of the modelled $\bar{Q}_{model}(h)$ to posses a value of $1.3 \cdot 10^4$ molecules $cm^{-3} s^{-1}$, which is in very good agreement with the production rate calculated in Subsection 4.3. Similar to the results from Subsection 4.2, the influence of chemistry during vertical transport on the flux estimates is small. The modelled decrease of the fluxes between canopy top and 67 m ranged
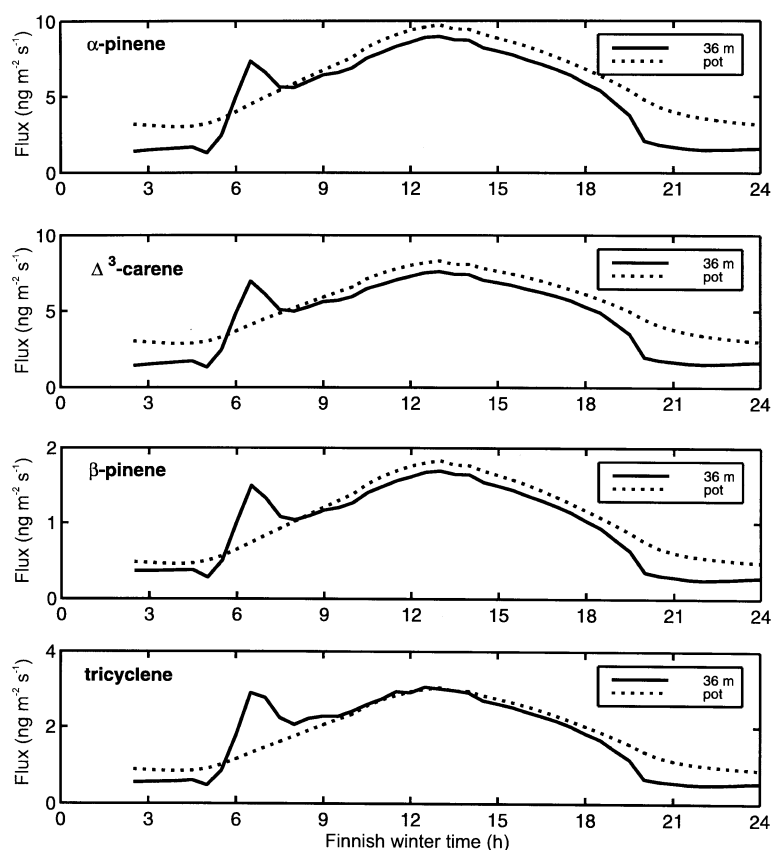
Fig. 9. Modelled fluxes of α-pinene, Δ^3-carene, β-pinene and tricyclene for the height of 36 m and their potential flux at 11 August 1998.

around 10% for the more reactive terpenes like α-pinene or β-pinene and only 1% for tricyclene.

4.5. Particle phase

Because the number of condensable organic species are known to be rather high, we focused on the main oxidation products from the most important biogenic VOCs. Two products could be identified: cis-pinonic acid, a well known ketoacid formed from the oxidation of α-pinene, and cis-pinic acid, a C_9-diacid that was identified only recently as an ozonolysis product of the biogenic VOC (Christoffersen et al., 1998; Hoffmann et al., 1998). Due to the physical-chemical properties of the latter, especially its very low vapour pressure of about $(5.6 \pm 4.0) \cdot 10^{-8}$ Torr (Koch et al., 1999) as well

as its tendency to form stable dimers (Hoffmann et al., 1998), makes it a highly interesting compound when the formation of secondary biogenic aerosol is considered.

Fig. 10 shows the concentrations for the 2 compounds mentioned above. As their parent compounds, they also show higher concentrations during daytime, especially pinonic acid. Most of the time the sum of pinonic acid and pinic acid concentrations was found to lie in the range between 0.8 and 2.4 ng m^{-3}. This can be compared with results of other groups. For example, Kavouras et al. (1999) quantified the two acids in the particle phase above a coniferous forests in Greece and found concentrations in the same range as estimated in this study, whereas they observed pinonic and pinic acid concentrations one order of magnitude higher above an
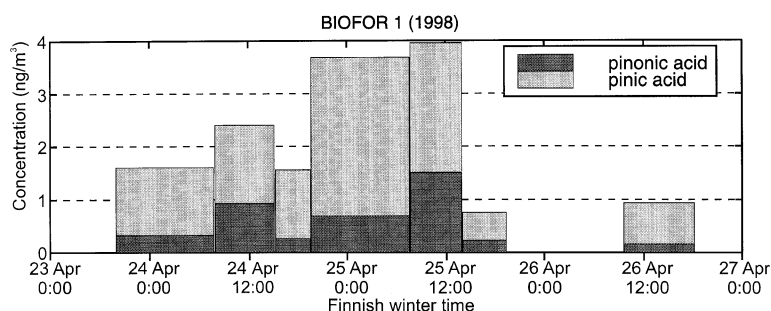
Fig. 10. Organic acids identified on glass fibre filter samples during BIOFOR 1 (April 1998).

Eucalyptus globulus forest in Portugal (Kavouras et al., 1998). On 25 April 1998, a minor nucleation event was observed at the site (a so-called Class 3 event (Kulmala et al., 2001). During this day, the highest concentrations of about 4 ng m^{-3} for the sum of both organic acids were observed. However, due to the low time resolution of the measurements and the question if the applied filter sampling technique yields perfectly reliable concentration data for low volatile biogenic VOC oxidation products (see Subsection 2.3), a direct link of particle phase composition and nucleation or particle growth is difficult to prove. Nevertheless, the compounds measured here are formed in the gas-phase and will undergo gas to particle conversion, a process which will have the largest impact on the growth and composition of submicrometer particles.

5. Conclusions

α-pinene and Δ^3-carene dominate the monoterpene composition above the boreal forest, followed by β-pinene and camphene. The individual concentrations are highly variable (<10 to several hundred pptv), typically reaching the highest concentrations in the night and early morning hours and the lowest during the day. As expected, their concentrations decrease with height, an effect that was more pronounced during the summer campaign (especially in the night) than during the spring campaigns. During the summer campaign, a clear increase of the relative contribution of the nonreactive terpenes (tricyclene, camphene) was observed with increasing height.

The main oxidation products from α-pinene, pinonaldehyde, and from β-pinene, nopinone, were detected in the atmosphere above the boreal forest, showing the highest concentrations during the early morning hours (maximum concentrations; pinonaldehyde 140 ppt, nopinone 45 pptv). The diurnal variation of their concentrations can be used together with the mixing ratios of the parent hydrocarbons to monitor periods when significant VOC oxidation is going on. This information in turn can be used to predict efficient times for the formation of very low-volatile oxidation products that contribute to the particle phase. Furthermore, low volatile oxidation products of biogenic VOCs, pinonic and pinic acid, could be detected in the particle phase just above the canopy top during spring 1998 in Hyytiälä, Finland. The sum of their concentrations in the particle phase were observed to be in the range between 1 and 4 ng m^{-3}.

Based on concentration profile measurements of monoterpenes, their fluxes above the forest canopy were calculated using the gradient approach. Most of the time, the BVOC fluxes show a clear diurnal variation with a maximum around noon. The highest fluxes were observed for α-pinene with values up to 20 ng m^{-2} s^{-1} in summer time and almost 100 ng m^{-2} s^{-1} during the spring campaign. Comparison of the calculated fluxes with modelled fluxes using the CACHE model reveal a reasonable agreement. For both, flux calculations from measured profiles and modelled fluxes from the CACHE model, chemical degradation of terpenes was found to be negligible when compared to other uncertainties in monoterpene flux estimations. Nevertheless, to reproduce measured concentrations with the model and especially to connect the measurements with aerosol formation processes, chemical reactions of BVOCs have to be considered in the data analysis.

The chemical sink term of the flux calculations

was used to calculate the production rate of low volatile oxidation products. For the three most important monoterpenes this production rate was estimated for daylight conditions during summer time at the site, using both flux calculations and model approach, and were found to be highest at the forest top with values of about $1.2–1.3 \cdot 10^4$ molecules $cm^{-3} s^{-1}$ (assuming a yield of low volatile oxidation products of 0.05) and decreasing production rates with increasing height above the forest. This estimated range can account for about 10 to 16% of the condensable vapour needed to explain the observed particle growth at the site.

However, if the formation of low volatile oxidation products from biogenic precursors above and within the forest is also involved in the new particle formation events observed at the site, cannot conclusively be answered based on the results presented here.

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