

# Hydrocarbon fluxes above a Scots pine forest canopy: Measurements and modeling

J. Rinne, R. Taipale, T. Markkanen, T. M. Ruuskanen, H. Hellén, M. K.

Kajos, T. Vesala, M. Kulmala

## ▶ To cite this version:

J. Rinne, R. Taipale, T. Markkanen, T. M. Ruuskanen, H. Hellén, et al.. Hydrocarbon fluxes above a Scots pine forest canopy: Measurements and modeling. Atmospheric Chemistry and Physics Discussions, 2007, 7 (1), pp.2357-2388. hal-00302593

# HAL Id: hal-00302593 https://hal.science/hal-00302593

Submitted on 18 Jun 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés. Atmos. Chem. Phys. Discuss., 7, 2357–2388, 2007 www.atmos-chem-phys-discuss.net/7/2357/2007/ © Author(s) 2007. This work is licensed under a Creative Commons License.



**ACPD** 

7, 2357–2388, 2007

Hydrocarbon fluxes above a Scots pine forest canopy

J. Rinne et al.

## **Title Page** Introduction Abstract Conclusions References **Tables Figures** ►T. Back Close Full Screen / Esc **Printer-friendly Version** Interactive Discussion EGU

# Hydrocarbon fluxes above a Scots pine forest canopy: Measurements and modeling

J. Rinne<sup>1</sup>, R. Taipale<sup>1</sup>, T. Markkanen<sup>1,2</sup>, T. M. Ruuskanen<sup>1</sup>, H. Hellén<sup>3</sup>, M. K. Kajos<sup>1</sup>, T. Vesala<sup>1</sup>, and M. Kulmala<sup>1</sup>

<sup>1</sup>Department of Physical Sciences, PL 68, FI-00014 University of Helsinki, Helsinki, Finland <sup>2</sup>Department of Micrometeorology, Bayreuth University, Bayreuth, Germany <sup>3</sup>Finnish Meteorological Institute, PL 503, FI-00101 Helsinki, Finland

Received: 9 February 2007 - Accepted: 13 February 2007 - Published: 21 February 2007

Correspondence to: J. Rinne (janne.rinne@helsinki.fi)

#### Abstract

We measured the fluxes of several hydrocarbon species above a Scots pine (*Pinus sylvestris*) stand using disjunct eddy covariance technique with proton transfer reaction – mass spectrometry. The measurements were conducted during four days in July at SMEAR II research station in Hyytiälä, Finland. Compounds which showed significant emission fluxes were methanol, acetaldehyde, acetone, and monoterpenes. A stochastic Lagrangian transport model with simple chemical degradation was applied to assess the sensitivity of the above canopy fluxes to chemistry. According to the model, the chemical degradation had a minor effect on the fluxes measured in this study but has a major effect on the vertical flux profiles of more reactive compounds, such as sesquiterpenes. The monoterpene fluxes followed the traditional exponential temperature dependent emission algorithm but were considerably higher than the fluxes measured before at the same site. The normalized emission potential (30°C) was  $2.5 \,\mu g \, g_{dw}^{-1} \, h^{-1}$  obtained using the temperature dependence coefficient of  $0.09^{\circ}C^{-1}$ .

#### 15 **1** Introduction

Reactive hydrocarbons, or volatile organic compounds (VOCs), take part in many chemical processes occurring in the atmospheric boundary layer. Together with nitrogen oxides they are involved in ozone production and destruction processes (Chameides et al., 1992; Fehsenfeld et al., 1992), thus affecting regional ozone pollution. These
compounds are also involved in the formation and growth of atmospheric aerosol particles (Kulmala et al., 2004; Tunved et al., 2006) which affect the transfer of solar radiation in the atmosphere and act as cloud condensation nuclei. In addition VOCs may have an effect on the optical properties of aerosol particles (Nozière and Esteve, 2005). Guenther (2002) and Bortoluzzi et al. (2006) have also discussed the role of
the biogenic hydrocarbon emissions in the carbon balances of various ecosystems.

Globally, Guenther et al. (1995) have estimated vegetation to emit about seven times



more hydrocarbons into the atmosphere than human activity. Also, on a regional scale, in areas with low population density, such as Finland, Simpson et al. (1999) and Lindfors et al. (2000) have estimated that hydrocarbon emissions from vegetation exceed the anthropogenic emissions. About half of the emitted hydrocarbons is comprised of

- terpenoids, mostly isoprene and monoterpenes (Guenther et al., 1995). The majority of the research on VOC emissions has focused on the isoprene and monoterpene emissions, while non-terpenoid hydrocarbons, making up the other half of the emissions, have received considerably less attention. As a result, emission estimates of these compounds remain highly uncertain.
- Recently, both analytical skills and flux measurement methodologies have developed to allow us to measure the emissions of both terpenoid and non-terpenoid hydrocarbons at the canopy scale more directly than in the past. The development and commercialization of the proton transfer reaction – mass spectrometry (PTR-MS) has allowed on-line concentration measurements of hydrocarbons with a reasonably short response time (Lindinger et al., 1998) and the application of the disjunct eddy covariance technique (Rinne et al., 2001; Karl et al., 2002) has enabled us to conduct

simultaneous flux measurements of several hydrocarbon species. As many VOCs have a relatively short lifetime in the atmospheric boundary layer,

the above canopy fluxes do not necessarily fully reflect the surface emission. The emitted compounds may for instance react and be transformed to other compounds before they are transported to the measurement point. The ratio of the above canopy vertical mixing time ( $\tau_{mix} = z/u_*$ ) to the chemical lifetime of a compound, called the Damköhler number,  $Da = \tau_{mix} / \tau_{chem}$ , is often used to assess the importance of the chemical degradation on the measured fluxes. However, for tall canopies the below

<sup>25</sup> canopy sources, chemistry and transport are not well characterized by this approach. In order to assess the possible impact of the chemical degradation on the fluxes, we used a stochastic Lagrangian transport model with simplified chemical degradation similar to that used by Strong et al. (2004).

Experiments conducted on various plant species and ecosystems have indicated



large emissions of such non-terpenoid hydrocarbons as methanol and acetone (Janson et al., 1999; Janson and de Serves, 2001; Warneke et al., 2002; Spirig et al., 2005). However, very little experimental data exist on the emissions of non-terpenoid hydrocarbons from most ecosystems. In Finland, boreal coniferous forests cover about 60%

- of the land area and the dominant tree species are Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* Karst.) (FFRI, 2005). This far, the non-terpenoid emissions from these ecosystems have been measured only at the branch scale (Janson et al., 1999; Janson and de Serves, 2001). Our aim is to determine the magnitude of the emissions of different non-terpenoid, as well as terpenoid, hydrocarbon species at the
   canopy scale from a boreal pine forest ecosystem using the disjunct eddy covariance
- 10 canopy scale from a boreal pine forest ecosystem using the disjunct eddy cova technique combined with proton transfer reaction – mass spectrometry.

#### 2 Methods

#### 2.1 Flux measurements

We applied the disjunct eddy covariance (DEC) technique to measure the fluxes of
 VOCs from the Scots pine forest ecosystem. In the disjunct eddy covariance method the flux is calculated as a covariance of the vertical wind speed and trace gas concentration

$$F = \langle w'c' \rangle = \frac{1}{N} \sum_{i=1}^{N} w'_i c'_i, \qquad (1)$$

where  $w'=w - \langle w \rangle$  is the momentary deviation of the vertical wind velocity w from its average value, and  $c'=c - \langle c \rangle$  is that of the trace gas concentration. The brackets denote averages over the measurement period, typically 30–60 min. Each vertical wind speed and trace gas concentration value must be measured with a fast time response instrument in order to take into account the high frequency contribution to the flux.



Typically instruments with response times shorter than one second are used in eddy covariance flux measurements.

In contrast to the traditional continuously sampling eddy covariance technique, in the disjunct eddy covariance technique the vertical wind speed and trace gas concentration

- <sup>5</sup> values used for the flux calculation have a relatively long time interval between them. The sub-sampling of the continuous time series does increase the random uncertainty of the measured flux value, but does not lead to systematic errors as far as the averaging period is much longer than the integral time-scale of w'c' (Lenschow et al., 1994). The variant of the DEC technique we are utilizing, first used by Karl et al. (2002),
- takes the advantage of the features of the PTR-MS analyzer. The PTR-MS method is based on detecting charged molecules that are selected according to their mass. The response time of the fast response PTR-MS is well below one second making it capable of eddy covariance measurements with continuously sampling. However, PTR-MS is not able to measure more than one mass at a time. In the DEC method which we
- utilize, concentrations of different masses are thus measured cyclically, each mass for less than a second. The whole cycle, with the successive mass measurements, can last anything from a few seconds up to half a minute. A disjunct time series of each mass measured with fast response time is thus formed, which is then correlated with the vertical wind speed.

The DEC techniques have been compared with the traditional continuously sampling eddy covariance method by Ammann et al. (2006) and Rinne et al. (2007). Both observed good correlation with the fluxes measured by the DEC and conventional continuously sampling eddy covariance methods. In the intercomparison experiment by Rinne et al. (2007) grab samplers similar to those used by Rinne et al. (2001), Warneke

et al. (2002) and Grabmer et al. (2004) were utilized. On the other hand, Ammann et al. (2006) utilized the variant of DEC which we are using here and which has previously been used by Karl et al. (2002; 2003; 2004; 2005) and Spirig et al. (2005).

Our measurement system consisted of an acoustic anemometer (Gill Instruments Ltd., Solent HS1199), 8 mm i.d., 32 m long sample line with  $15 L min^{-1}$  flow rate, and a



proton transfer reaction – mass spectrometer (PTR-MS, Ionicon Analytik GmbH). The sonic anemometer and inlet of the sample line were at the height of 22 meters above the ground. The three dimensional wind data was measured continuously at a rate of 10 Hz and recorded on a separate computer. The concentrations of selected VOCs were measured with the PTR-MS by pulling a side flow of 0.1 L min<sup>-1</sup> from the main sample line via 1 m long tubing with inner diameter of 1.6 mm (Fig. 1). The measurement cycle lasted about 5.9 s and consisted of measurements of primary ion and water cluster signals and seven masses associated with VOCs (Table 1).

Due to the residence time of the air sample in the sample tubing, there is a lagtime between the moment when the concentration signal is drawn into the sample line and the time when it is measured by the analyzer. This causes a time lag between the vertical wind velocity and VOC concentration time series. Additional source of uncertainty in the timing of these time series is caused by the use of two separate computers. We determined the time lag between the vertical wind speed time series and the concentration time series by finding the maximum in the covariance function. This is the standard method for determination of the time lag used in the CO<sub>2</sub> flux

measurement networks (Moncrieff et al., 1997; Aubinet et al., 2000). The uncertainty of the flux value is determined using the standard deviation of the

covariance function far from its maximum value (Spirig et al., 2005). If we assume this variance to be normally distributed we obtain 95% confidence interval by multiplying

variance to be normally distributed we obtain 95% confidence interval the standard deviation by 1.96.

#### 2.2 VOC concentration measurements

We calculated the VOC concentrations,  $c_i$ , according to

$$c_{i} = \alpha_{i} \frac{S_{i} - S_{i,\text{zero}}}{\left(\delta_{M21/M19}^{-1} S_{M21} + \delta_{M39/M37}^{-1} S_{M39}\right)}$$



Interactive Discussion

(2)

EGU

where  $\alpha_i$  is the calibration coefficient,  $S_i$  is the signal of the mass in cps, $S_{i,zero}$  is the signal of the mass when hydrocarbon free air is being fed to the analyzer,  $S_{M21}$  and  $S_{M39}$  are signals of M21 and M39 respectively.  $\delta_{M21/M19}$ =0.002 is the ratio of H<sub>3</sub><sup>18</sup>O<sup>+</sup> to H<sub>3</sub><sup>16</sup>O<sup>+</sup>.  $\delta_{M39/M37}$ =0.004 is the ratio of the sum of H<sub>2</sub><sup>18</sup>OH<sub>3</sub><sup>16</sup>O<sup>+</sup> and H<sub>2</sub><sup>16</sup>OH<sub>3</sub><sup>18</sup>O<sup>+</sup> to the H<sub>2</sub><sup>16</sup>OH<sub>3</sub><sup>16</sup>O<sup>+</sup>. We obtained the calibration coefficients by direct calibration with gas

standard and inverting the Eq. (2) to yield  $\alpha_i$ .

The PTR-MS was calibrated weekly using a VOC standard mixture (Apel-Riemer Environmental Inc.) that contained all compounds associated with the measured masses except for hexenal. The concentration of each VOC in the standard was in the range of

<sup>10</sup> 1 ppm per compound. The standard gas was diluted to the range of 50 ppb using VOCfree air that was obtained from ambient air with a zero-air generator (Parker ChromGas, model 1001). The background signal of VOCs was measured every second hour from the zero-air.

2.3 Measurement site

5

<sup>15</sup> The measurement site, SMEAR II station (61°51'N, 24°17'E, 181 m a.s.l.) in Hyytiälä, Finland, is located in south boreal sub-zone (Vesala et al., 1998; Kulmala et al., 2001; Hari and Kulmala, 2005). Vegetation at the site is dominated by 40 yr old Scots pine (*Pinus sylvestris*) trees. The canopy height is approximately 15 m. The ground vegetation consists of lingonberry (*Vaccinium vitis-idaea*), blueberry (*Vaccinium myrtillus*), and mosses (*Pleurozium scheberi*; *Dicranum polysetum*). The dry needle biomass density of Scots pines, obtained by methods described by Ilvesniemi and Liu (2001), was 540 g m<sup>-2</sup> (2005 data, Ilvesniemi, pers. comm.). The total biomass of ground vegetation at the site was 100 g m<sup>-2</sup>, (Launiainen et al., 2005). Previously, Rinne et al. (2000) and Spanke et al. (2001) have conducted canopy scale VOC emission mea<sup>25</sup> surements at the site using gradient techniques. Leaf and branch scale measurements of the VOC emissions from vegetation at the site have been conducted by Janson and de Serves (2001), Ruuskanen et al. (2005), Tarvainen et al. (2005), Hakola et al.



(2006), and Hellén et al. (2006). General overview of long term flux measurements of carbon dioxide, water vapor, ozone and aerosol particles at the site is given by Suni et al. (2003).

The measurements described here were conducted 14–17 July 2005. The air tem-<sup>5</sup> perature, photosynthetical photon flux density (PPFD) and friction velocity (u\*) during the measurement period are shown in Fig. 2.

2.4 Modeling the effect of chemical degradation

20

~ - - - -

We used a stochastic Lagrangian transport model with first order chemical decay (SLTC) to study the effect of the chemical degradation on the fluxes. In the stochastic
Lagrangian transport models air parcels are released from a certain height and transported by both mean wind and turbulent motions. The mean wind is described as a pre-described wind profile. Thus the horizontal transport by mean wind depends on the height of the air parcel at each time step. The transport by turbulence is described as a stochastic process which depends on the turbulence statistics. This random displacement due to the turbulence occurs in both horizontal and vertical direction at each time step. The transport in detail by Markkanen et al. (2003).

In the model with chemical degradation each air parcel is released with the same initial concentration of the trace gas, which is then reduced at each time step due to the chemical degradation. The differential equation describing the degradation of the concentration of a reactive hydrocarbon, [R], in the air parcel can be written as

$$\frac{\partial [R]}{\partial t} = -k_{OH} [OH][R] - k_{O_3} [O_3][R] - k_{NO_3} [NO_3][R] - k_{\text{photolysis}}[R], \qquad (3)$$

where  $k_i$  are rate coefficients and square brackets denote concentrations of the trace gas, *R*, and oxidants (OH: hydroxyl radical, O<sub>3</sub>: ozone, and NO<sub>3</sub>: nitrate radical). Depending on the time of the day different terms in the Eq. (3) can have different importance. For example during night the OH reaction and photolysis are negligible as there

ACPD 7, 2357-2388, 2007 Hydrocarbon fluxes above a Scots pine forest canopy J. Rinne et al. **Title Page** Introduction Abstract Conclusions References **Figures** ►T. Back Close Full Screen / Esc **Printer-friendly Version** Interactive Discussion EGU

is very little OH and no solar short wave radiation available. On the opposite, during the daytime the NO<sub>3</sub> reaction is negligible. In the Eq. (3) only sink terms are taken into account. However, many compounds, such as methanol and acetone, are also generated in the atmosphere by chemical reactions. In principle these chemical sources can <sup>5</sup> also be taken into account in this kind of model.

As our aim was to obtain information on the sensitivity of the measured fluxes on the chemical degradation of measured hydrocarbons, the concentrations of oxidants are taken to be constant. Thus the change of the VOC concentration can be described by a simple first-order differential equation

10 
$$\tau_c \frac{\partial [R]}{\partial t} + [R] = 0$$

where the time constant is

$$\tau = \left(k_{OH}\left[OH\right] + k_{O_3}\left[O_3\right] + k_{NO_3}\left[NO_3\right] + k_{\text{photolysis}}\right)^{-1}.$$
(5)

This leads to exponential behavior of the tracer concentration in the air parcel

$$[R] = [R]_0 \exp\left(-t/\tau_c\right), \qquad (6)$$

where  $[R]_0$  is the initial concentration, which is set to one for each air parcel. Thus, we used Eq. (6) to calculate the concentration at each time step.

The rate constants used to calculate the chemical lifetimes are shown in the Table 2. The daytime concentration of OH was taken to be 0.25 ppt. This was obtained by the model of Boy et al. (2005). Nighttime concentration of  $NO_3$  was taken to be 2.5 ppt (1) to be 2.5 ppt (2) to be 2.5 ppt (1) to be 2.5 ppt (2) to be 2.5 ppt (1) to b

(Hakola et al., 2003). During the measurement period ozone concentrations above the canopy varied between 25 and 50 ppb, with little systematic difference between daytime and nighttime concentrations. Therefore we used a value of 40 ppb in the calculations. The photolysis rates were calculated as described by Hellén et al. (2004).

Even though the transport model we used is commonly used to calculate flux footprints we were not interested in the footprint itself. The asymptotic behavior of the flux

(4)

footprint, however, can be used to estimate the effect of the chemical degradation on the fluxes. While the cumulative footprint function of an inert trace gas approaches unity as the distance from the measurement point increases, the cumulative footprint of a reactive hydrocarbon does not reach this value (Fig. 3). The difference between the asymptotic value of the cumulative footprint and unity thus shows the effect of the chemical degradation.

#### 3 Results and Discussion

5

Of seven masses measured, four showed a more or less clear positive peak in the covariance function (Figure 4) indicating upward fluxes. Masses with the clear flux signals were M33 (methanol), M45 (acetaldehyde), M59 (acetone) and M137 (monoterpenes).

#### 3.1 Effect of chemistry on fluxes

Figure 5 shows the asymptotic values of cumulative footprints at different heights. These express the vertical profiles of fluxes, normalized by the primary emission. Two cases, one with sources in the canopy and the other with sources at the surface, are shown. The fraction of the surface emission which reached the flux measurement height clearly depends on the chemical lifetime. The ratio of the flux to the emission of the more reactive hydrocarbons depends strongly on the height.

The effect of the chemical degradation was very small for the hydrocarbons with chemical lifetimes of about one hour. For a compound with chemical lifetime of about 5 min the effect of the chemical degradation is already significant. However, even for hydrocarbons with this short chemical lifetime, a large part of the surface emission reaches the measurement height. Also the height of the emission had an effect, as the chemistry has a larger effect on the fluxes of hydrocarbons emitted at the forest floor. Interestingly, the compounds with short chemical lifetimes emitted from the canopy showed negative fluxes below canopy. This was due to the chemical degrada-



tion causing flux divergence also below the canopy.

The four compounds with clear emission fluxes during the daytime have daytime lifetimes between slightly less than two hours and several days (Table 3). The results of the SLTC model showed that the effect of the chemical degradation had a minor effect

- on the daytime fluxes of compounds with lifetimes in this range. Thus we can take these above-canopy fluxes to be equal to the surface emission. We can also estimate the magnitude of the sesquiterpene flux at our measurement height by assuming the sesquiterpene emission from the forest to be about 20% of the monoterpene emissions (Hakola et al., 2006). The fraction of the emission of a compound emitted from the canopy, with lifetime in the range of one minute such as most sesquiterpenes, reach-
- ing the measurement height of 22 m, is around 30-40%. This would lead to fluxes of sesquiterpenes to be below 10% of the monoterpene fluxes. Taking into account the fragmentation of sesquiterpenes in the PTR-MS instrument and typical instrument noise, these fluxes are well below detection limit.
- 15 3.2 VOC fluxes

20

The highest fluxes were those of monoterpenes (Figure 6). These fluxes, averaging  $500\mu g m^{-2} h^{-1}$ , are considerably higher than the monoterpene emissions from the same site reported by Rinne et al. (2000) and Spanke et al. (2001). The emissions of methanol and acetone were in the same range of magnitude with each other while the acetaldehyde fluxes were the smallest. The fluxes of all these four hydrocarbons show

a diurnal cycle with higher fluxes during the day and smaller at night. The uncertainties of the fluxes, defined as 95% confidence interval, were relatively large.

The fluxes of non-terpenoid compounds are a significant part of the total VOC emission from the forest, comprising nearly half of the measured total VOC emissions on

the mass basis (Table 4). This is roughly the same as the proportion of the emissions of other (than isoprene and monoterpene) VOCs globally or in the national level as estimated by Guenther et al. (1995) and Lindfors et al. (2000).

Methanol and acetone were the non-terpenoid hydrocarbons emitted in largest quan-



tities, while acetaldehyde made a smaller contribution. Previous studies conducted by enclosure technique with adsorbent and denuder sampling and gas chromatographic analysis have shown Scots pines to emit monoterpenes, acetone and acetaldehyde (Janson 1993, Janson et al., 1999, Janson and de Serves, 2001). No methanol emissions from Scots pine have been reported as their detection has not been possible due to limitations of measurement methods.

Canopy scale emissions of methanol have previously been reported from coniferous forests such as mixed lodgepole pine, subalpine fir, and Engelman spruce forest (Baker et al., 2001; Karl et al., 2002), ponderosa pine plantation (Schade and Goldstein, 2001), and loblolly pine plantation (Karl et al., 2005). Using only canopy scale

flux measurements it is not possible to determine if the methanol was emitted by the canopy or by sub-canopy vegetation. However, Karl et al. (2005) measured significant emissions of methanol from loblolly pine needles. Also ponderosa pine forest floor has been reported to emit methanol, acetone and acetaldehyde (Schade and Goldstein,

10

<sup>15</sup> 2001). Compared to the canopy scale methanol emissions by coniferous forests reported by Baker et al. (2001) and Schade and Goldstein (2001), our measurements showed a relatively low emission. The emissions reported by Karl et al. (2005) are in the same range with the measurements reported here.

In comparison to canopy emissions we measured, the monoterpene emissions from forest floor in summer at Hyytiälä site reported by Hellén et al. (2006) were negligible. Also those measured from a mixed Scots pine – Norway spruce forest floor by Janson et al. (1999) were small compared to the canopy emissions. Thus we may conclude that the monoterpene fluxes we measured originate mainly from the canopy emissions.

The leaf level acetone and acetaldehyde emissions, measured by Janson et al. (1999) and Janson and de Serves (2001), are in the same range with the canopy scale emissions presented here, when multiplied by the needle biomass density of the Hyytiälä site (540  $g_{dw}$  m<sup>-2</sup>). No acetaldehyde or acetone emissions from boreal forest floor were reported by Janson et al. (1999). Therefore it seems that the emissions of these carbonyls originate mainly from the canopy.



However, the carbonyls are also produced in the chemical reactions of e.g. monoand sesquiterpenes. Therefore the chemical reactions may contribute positively to the fluxes of these compounds but this chemical production was not taken into account in our simple model.

#### 5 3.3 Emission potentials

10

Fluxes of all the four compounds, methanol, acetone, acetaldehyde and monoterpenes, had a clear diurnal cycle (Fig. 6), which could be due to diurnal cycles in temperature, solar radiation or some biological factors. Emissions of monoterpenes from evergreen plants having resin ducts, such as Scots pine, have usually been taken to depend only on leaf or needle temperature (Janson, 1993; Komenda and Koppmann, 2002; Tarvainen et al., 2005). The temperature dependence of the monoterpene emission is usually described by the equation

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

where E is the emission, E<sub>30</sub> is the normalized emission potential, and β is the temperature dependence coefficient (Guenther et al., 1993). By fitting an exponential curve to the measured monoterpene fluxes we obtained temperature dependence coefficient of 0.11 °C<sup>-1</sup> and emission rate standardized to 30°C of 1.55 mg m<sup>-2</sup> h<sup>-1</sup> (Fig. 7). The data with friction velocity less than 0.25 m s<sup>-1</sup> were removed from this analysis. This friction velocity limit is a general data quality criterium for fluxes measured at the Hyytiälä site (Markkanen et al., 2001). The temperature dependence is in the range with previous observations (Janson, 1993; Janson and de Serves, 2001; Rinne et al., 1999; 2000; Spanke et al., 2001; Tarvainen et al., 2005; Hakola et al., 2006). By using the temperature dependence coefficient of 0.09 °C<sup>-1</sup>, commonly used in the emission inventory models, we arrived at the normalized emission potential of 1.37 mg m<sup>-2</sup> h<sup>-1</sup> (30°C).

Assuming that all the monoterpenes were emitted by the Scots pine needles and using the needle biomass density of 540  $g_{dw}$  m<sup>-2</sup>, we obtained an emission potential of 2.5  $\mu g g_{dw}^{-1} h^{-1}$ . This is considerably higher than the value of 1.2  $\mu g g_{dw}^{-1} h^{-1}$  obtained



(7)

for the same measurement site by Rinne et al. (2000) using surface layer gradient technique.

There can be several reasons for the differences between normalized emission potentials we obtained and those reported previously. When comparing canopy scale
emission measurements to the emissions measured in the branch scale using enclosure technique (Janson, 1993; Janson and De Serves, 2001; Tarvainen et al., 2005; Hakola et al., 2006), one has to be aware that the canopy scale measurements include emissions from sources which are not measured by the branch enclosure technique. For example emissions from ground vegetation and tree trunks can contribute to
the canopy scale fluxes. The previous canopy scale measurements above Scots pine

- forests (Rinne et al., 1999, 2000; Spanke et al., 2001) have been conducted with surface layer gradient technique. As a rather indirect flux measurement technique it may have more sources of systematic uncertainties than direct disjunct eddy covariance technique. Also in the total monoterpene emissions reported by Rinne et al. (1999;
   2000) limonene was not included. However, limonene contributed only 0.5–1.4% of the
- total monoterpene emission from Scots pine (Tarvainen et al., 2005).

As yet, there exists no emission algorithm for non-terpenoid VOC emissions from vegetation. These compounds have been included into some emission inventories using for example the temperature dependent monoterpene emission algorithm (Guen-

- ther et al., 1995). However, it seems that the daily cycles of ambient concentrations of the main non-terpenoids emitted in Hyytiälä site, methanol, acetone and acetaldehyde, are governed by different processes than the daily cycles of monoterpene concentrations (Rinne et al., 2005). As there are differences also in the chemical degradation of these compounds we can not attribute the difference only to the source behavior.
- <sup>25</sup> Therefore controlled environment leaf or branch level laboratory studies should be conducted in order to reveal the dependencies of emissions of non-terpenoid hydrocarbons on environmental parameters.

# ACPD 7, 2357-2388, 2007 Hydrocarbon fluxes above a Scots pine forest canopy J. Rinne et al. **Title Page** Introduction Abstract Conclusions References Tables **Figures** ►T. Back Close Full Screen / Esc **Printer-friendly Version** Interactive Discussion EGU

#### 4 Conclusions

5

10

15

20

25

We measured fluxes of several hydrocarbon species above a Scots pine (*Pinus sylvestris*) forest canopy by the disjunct eddy covariance method utilizing a proton transfer reaction – mass spectrometer. We also applied a stochastic Lagrangian transport model with simple chemical degradation to study the sensitivity of the fluxes on the degradation.

Significant fluxes of monoterpenes, methanol, acetone and acetaldehyde were detected. The monoterpene fluxes were considerably higher than those measured previously at the same site. Combined, the emission of acetone, acetaldehyde and methanol was of the same magnitude as the monoterpene emission which is in line with the previous emission inventories.

Of the fluxes presented here, the chemical degradation has largest effect, about 10%, to the fluxes of monoterpenes. For acetone, acetaldehyde and methanol the effect is even smaller. Thus we can take the fluxes of these compounds to be equivalent to the surface emission. However, if fluxes of more reactive compounds, such as sesquiterpenes, were measured, the chemical degradation should be taken into account in interpreting the results.

The monoterpene fluxes followed the traditional exponentially temperature dependent emission algorithm. Normalized emission potential (30°C) obtained using the temperature dependence coefficient of 0.09 °C<sup>-1</sup>, was 1.37 mg m<sup>-2</sup> h<sup>-1</sup>, or 2.5  $\mu$ g g<sup>-1</sup><sub>dw</sub>

 $h^{-1}$ . This is also considerably higher than the values obtained previously.

Acknowledgements. We thank M. Boy at the University of Helsinki for the hydroxyl radical data and Hannu Ilvesniemi at the University of Helsinki for the needle dry biomass density. We acknowledge Academy of Finland (209216, 109601) Environmental Research Center of the University of Helsinki (URPO) and Kone foundation for financial support.

# **ACPD** 7, 2357–2388, 2007

#### Hydrocarbon fluxes above a Scots pine forest canopy



#### References

5

20

- Ammann, C., Brunner, A., Spirig, C. and Neftel, A.: Technical note: Water vapour concentration and flux measurements with PTR-MS, Atmos. Chem. Phys., 6, 4643–4651, 2006.
- Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds, Journal of Physical and Chemical Reference Data, Monograph 2, 216 p, 1994.
- Atkinson, R.; Aschmann, S. M.; Winer, A. M., and Pitts, J. N., Jr.: Rate Constants for the Gas-Phase Reactions of O3 with a Series of Carbonyls at 296 K, Int. J. Chem. Kinet., 13, 1981.

Atkinson, R., Baulch, D. L., Cox, R. A, Crowley, J. N., Hampson, R. F. Jr, Kerr, J. A., Rossi,

- M. J., and Troe, J.: Summary of Evoluades Kinetic and Photochemin data for atmospheric chemistry. UPAC subcommittee an gas kinetic data evaluation for Atmospheric Chemistry, 2001.
  - Aubinet, M., Grelle, A., Ibrom, A., Rannik, Ü., Moncrieff, J., Foken, T., Kowalski, A.S., Martin, P.H., Berbigier, P., Bernhofer, C., Clement, R., Elbers, J., Granier, A., Grunwald, T., Morgen-
- stern, K., Pilegaard, K., Rebmann, C., Snijders, W., Valentini, R., and Vesala, T.: Estimates of the annual net carbon and water exchange of forests: The EUROFLUX methodology, Advances in Ecological Research, 30, 113–175, 2000.
  - Baker, B., Guenther, A., Greenberg, J., and Fall, R.: Canopy level fluxes of 2-methyl-3-buten-2-ol, acetone, and methanol by a portable relaxed eddy accumulation system, Environ. Sci. Tech., 35 (9): 1701–1708, 2001.
  - Bortoluzzi, E., Epron, D., Siegenthaler, A., Gilbert, D., and Buttler, A.: Carbon balance of a European mountain bog at contrasting stages of regeneration, New Phytologist, 172, 708–718, 2006.

Boy, M., Kulmala, M., Ruuskanen, T.M., Pihlatie, M. Reissell, A., Aalto, P.P., Keronen, P., Dal

Maso, M., Hellen, H., Hakola, H., Janson, R., Hanke, M., and Arnold, F.: Sulphuric acid closure and contribution to nucleation mode particle growth, Atmos. Chem. Phys., 5, 863– 878, 2005,

http://www.atmos-chem-phys.net/5/863/2005/.

Chameides, W. L., Fehsenfeld, F., Rogers, M., Cardelino, C., Martinez, J., Parrish, D., Lonne-

<sup>30</sup> man, W., Lawson, D. R., Rasmussen, R. A., Zimmerman, P., Greenberg, J., Middleton, P. and Wang, T.: Ozone precursor relationships in the ambient atmosphere, J. Geophys. Res., 97, 6037–6055, 1992.

7, 2357–2388, 2007

#### Hydrocarbon fluxes above a Scots pine forest canopy

J. Rinne et al.

| Title Page               |              |  |  |  |
|--------------------------|--------------|--|--|--|
| Abstract                 | Introduction |  |  |  |
| Conclusions              | References   |  |  |  |
| Tables                   | Figures      |  |  |  |
| 14                       | ÞI           |  |  |  |
|                          |              |  |  |  |
| •                        | •            |  |  |  |
| Back                     | Close        |  |  |  |
| Full Screen / Esc        |              |  |  |  |
|                          |              |  |  |  |
| Printer-friendly Version |              |  |  |  |
| Interactive Discussion   |              |  |  |  |
|                          |              |  |  |  |

EGU

- Dabberdt, W. F., Lenschow, D. H., Horst, T. W., Zimmerman, P. R., Oncley, S. P., and Delany, A. C.: Atmosphere-surface exchange measurements, Science, 260, 1472–1481, 1993.
- Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A., Hewitt, N., Lamb, B., Liu, S., Trainer, M., Westberg, H., and Zimmerman, P.: Emissions of volatile organic compouds from vegetation and the implications for atmospheric chemistry, Global Biogeochem. Cy., 6, 389– 430, 1992.
- FFRI: Metsätilastollinen vuosikirja 2005 (Finnish Statistical Yearbook of Forestry 2005), Finnish Forest Research Institute, 424 pp. ISBN 951-40-1985-7, 2005.
- Grabmer, W., Graus, M., Lindinger, C., Wisthaler, A., Rappenglück, B., Steinbrecher, R., and
- Hansel, A.: Disjunct eddy covariance measurements of monoterpene fluxes from a Norway spruce forest using PTR-MS, Int. J. Mass Spectrom., 239, 111–115, 2004.
  - Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability: Model evaluation and sensitivity analysis, J. Geophys. Res., 98, 12609–12617, 1993.
- <sup>15</sup> Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay W. A., Pierce T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873–8892, 1995.

Guenther, A.: The contribution of reactive carbon emissions from vegetation to the carbon

balance of terrestrial ecosystems, Chemosphere, 49, 837–844, 2002.
 Hakola, H., Tarvainen, V., Bäck, J., Ranta, H., Bonn, B., Rinne, J., and Kulmala, M.: Seasonal variation of mono- and sesquiterpene emission rates of Scots pine, Biogeosci., 3, 93–101, 2006.

Hari, P. and Kulmala, M.: Station for measuring ecosystem-atmosphere relations (SMEAR II). Boreal Environ. Res., 10, 315–322, 2005.

Hellén, H., Hakola, H., Reissell, A., and Ruuskanen, T. M.: Carbonyl compounds in coniferous forest air in Hyytiälä, Southern Finland, Atmos. Chem. Phys., 4, 1771–1780, 2004, http://www.atmos-chem-phys.net/4/1771/2004/.

Hellén, H., Hakola, H., Pystynen, K.-H., Rinne J., and Haapanala, S.: C<sub>2</sub>-C<sub>10</sub> hydrocarbon emissions from a boreal wetland and forest floor, Biogeosciences, 3, 167–174, 2006,

http://www.biogeosciences.net/3/167/2006/.

5

25

30

Ilvesniemi, H., and Liu, C.: Biomass distribution in a young Scots pine stand, Boreal Environ. Res., 6, 3–8, 2001.

# 7, 2357–2388, 2007 Hydrocarbon fluxes above a Scots pine forest canopy

J. Rinne et al.



ACPD

- Janson, R. W.: Monoterpene emission from Scots pine and Norwegian spruce, J. Geophys. Res., 98, 2839–2850, 1993.
- Janson, R., de Serves, C., and Romero, R.: Emission of isoprene and carbonyl compounds from a boreal forest and wetland in Sweden, Agric. For. Meteorol., 98, 671-681, 1999.
- 5 Janson, R. and de Serves, C.: Acetone and monoterpene emissions from the boreal forest in northern Europe, Atmos. Environ., 35, 4629-4637, 2001.
  - Karl, T. G., Spirig, C., Rinne, J., Stroud, C., Prevost, P., Greenberg, J., Fall R., and Guenther, A.: Virtual disjunct eddy covariance measurements of organic trace compound fluxes from a subalpine forest using proton transfer reaction mass spectrometry, Atmos. Chem. Phys., 2, 279-291, 2002,
- 10

25

#### http://www.atmos-chem-phys.net/2/279/2002/.

- Karl, T., Guenther, A., Spirig, C., Hansel, A., and Fall, R.: Seasonal variation of biogenic VOC emissions above a mixed hardwood forest in northern Michigan, Geophys. Res. Lett., 30, doi:10.1029/2003GL018432.2003.
- 15 Karl, T., Potosnak, M., Guenther, A., Clark, D., Walker, J., Herrick, D., and Geron, C.: Exchange processes of volatile organic compounds above a tropical rain forest: Implications for modeling tropospheric chemistry above dense vegetation, J. Geophys. Res., 109, doi:10.1029/2004JD004738, 2004.

Karl, T., Harley, P., Guenther, A., Rasmussen, R., Baker, B., Jardine, K., and Nemitz, E.: The

- bi-directional exchange of oxygenated VOCs between a loblolly pine (Pinus taeda) plantation 20 and the atmosphere, Atmos. Chem. Phys., 5, 3015–3031, 2005, http://www.atmos-chem-phys.net/5/3015/2005/.
  - Komenda, M. and Koppmann, R.: Monoterpene emissions from Scots pine (Pinus sylvestris): Field studies of emission rate variabilities, J. Geophys. Res., 107, doi:10.1029/2001JD000691, 2002.
  - Kulmala, M., Hämeri, K., Aalto, P. P., Mäkelä, J. M., Pirjola, L., Nilsson, E. D., Buzorius, G., Rannik, Ü., Dal Maso, M., Seidl, W., Hoffman, T., Janson, R., Hansson, H.C., Viisanen, Y., Laaksonen, A., and O'Dowd, C. D.: Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR), Tellus, 53B, 324-343, 2001.
- 30 Kulmala, M., Suni, T., Lehtinen, K.E.J., Dal Maso, M., Boy, M., Reissell, A., Rannik, Ü., Aalto, P., Keronen, P., Hakola, H., Bäck, J.B., Hoffmann, T., Vesala, T., and Hari P.: A new feedback mechanism linking forests, aerosols, and climate, Atmos. Chem. Phys., 4, 557-562, 2004, http://www.atmos-chem-phys.net/4/557/2004/.

#### ACPD

7,2357-2388,2007

#### Hydrocarbon fluxes above a Scots pine forest canopy

J. Rinne et al.

| Title Page               |              |  |  |  |
|--------------------------|--------------|--|--|--|
| Abstract                 | Introduction |  |  |  |
| Conclusions              | References   |  |  |  |
| Tables                   | Figures      |  |  |  |
|                          |              |  |  |  |
|                          |              |  |  |  |
| •                        | •            |  |  |  |
| Back                     | Close        |  |  |  |
| Full Screen / Esc        |              |  |  |  |
|                          |              |  |  |  |
| Printer-friendly Version |              |  |  |  |
| Interactive Discussion   |              |  |  |  |
|                          |              |  |  |  |

EGU

- Launiainen, S., Rinne, J., Pumpanen, J., Kulmala, L., Kolari, P., Keronen, P., Siivola, E., Pohja, T., Hari P., and Vesala, T.: Eddy-covariance measurements of CO2 and sensible and latent heat fluxes during a full year in a boreal pine forest trunk-space, Boreal Environment Research, 10, 569–588, 2005.
- <sup>5</sup> Lenschow, D. H., Mann, J., and Kristensen, L.: How long is long enough when measuring fluxes and other turbulence statistics? J. Atmos. Ocean. Tech., 11, 661–673, 1994.
  - Lindfors, V., Laurila, T., Hakola, H., Steinbrecher, R., and Rinne, J.: Modeling speciated terpenoid emissions from the European boreal forest, Atmos. Environ., 34, 4983–4996, 2000. Lindinger, W., Hansel, A., and Jordan, A.: Review: On-line monitoring of volatile organic com-
- pounds at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS), Medical applications, food control and environmental research, Int. J. Mass Spec. Ion Proc., 173, 191–241, 1998.

Markkanen, T., Rannik, U., Keronen, P., Suni, T., and Vesala, T.: Eddy covariance fluxes over a boreal Scots pine forest, Boreal Env. Res. 6: 65–78, 2001.

Markkanen, T., Rannik, Ü., Marcolla, B., Cescatti, A., and Vesala, T.: Footprints and fetches for fluxes over forest canopies with varying structure and density, Boundary-Layer Meteorology 106, 437–459, 2003.

Moncrieff, J. B., Massheder, J. M., deBruin, H., Elbers, J., Friborg, T., Heusinkveld, B., Kabat, P., Scott, S., Soegaard, H., and Verhoef, A.: A system to measure surface fluxes of momentum,

- sensible heat, water vapour and carbon dioxide, Journal of Hydrology, 189, 589–611, 1997.
   Nozière, B. and Esteve, W.: Organic reactions increasing the adsorbtion index of atmospheric sulfuric acid aerosols, Geophys. Res. Lett., 32, doi:10.1029/2004GL021942, 2005.
  - Rinne, J., Hakola H., and Laurila, T.: Vertical fluxes of monoterpenes above a Scots pine stand in the boreal vegetation zone, Phys. Chem. Earth, 24, 711–716, 1999.
- Rinne, J., Hakola, H., Laurila, T., and Rannik, Ü.: Canopy scale monoterpene emissions of Pinus sylvestris dominated forests, Atmos. Environ., 34, 1099–1107, 2000.
  - Rinne, H. J. I., Guenther, A. B., Warneke, C., de Gouw, J. A., and Luxembourg, S. L.: Disjunct eddy covariance technique for trace gas flux measurements, Geophys. Res. Lett., 28, 3139– 3142, 2001.
- Rinne, J., Ruuskanen, T. M., Reissell, A., Taipale, R., Hakola, H., and Kulmala, M.: On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a European boreal forest ecosystem, Boreal Environment Research, 10, 425–436, 2005. Rinne, J., Douffet, T., Prigent Y., and Durand, P.: Field comparison of disjunct and conventional

| ACPD  |                    |  |  |  |
|---|--------------------|--|--|--|
| 7, 2357–2   | 7, 2357–2388, 2007 |  |  |  |
| Hydrocarbon fluxes<br>above a Scots pine<br>forest canopy |                    |  |  |  |
| J. Rinn   | e et al.           |  |  |  |
|   |                    |  |  |  |
| Title   | Page               |  |  |  |
| Abstract  | Introduction       |  |  |  |
| Conclusions   | References         |  |  |  |
| Tables Figures  |                    |  |  |  |
| I4 ÞI   |                    |  |  |  |
| •   | <b>F</b>           |  |  |  |
| Back Close  |                    |  |  |  |
| Full Screen / Esc   |                    |  |  |  |
| Printer-friendly Version                                  |                    |  |  |  |
| Interactive Discussion                                    |                    |  |  |  |

EGU

eddy covariance techniques for trace gas flux measurements, submitted, Environmental Pollution, 2007.

- Ruuskanen, T. M., Kolari, P., Bäck, J., Kulmala, M., Rinne, J., Hakola, H., Taipale, R., Raivonen, M., Altimir, N., and Hari, P.: On-line field measurements of monoterpene emissions from Scots pine by proton transfer reaction mass spectrometry, Boreal Environ. Res., 10, 553–567, 2005.
- Schade, G. W. and Goldstein, A. H.: Fluxes of oxygenated volatile organic compounds from a ponderosa pine plantation, J. Geophys. Res., 106, 3111–3123, 2001.
- Shu, Y. and Atkinson, R: Atmospheric lifetimes and fates of a series of sesquiterpenes, J. Geophys. Res., 100, 7275–7281, 1995.
- Simpson, D., Winiwarter, W., Börjesson, G., Cinderby, S., Ferreiro, A., Guenther, A., Hewitt, N., Janson, R., Khalil, M.A.K., Owen, S., Pierce, T., Puxbaum, H., Shearer, M., Skiba, U., Steinbrecher, R., Tarrasón, L., and Öquist, M.G.: Inventorying emissions from nature in Europe, J. Geophys. Res., 104, 8113–8152, 1999.
- <sup>15</sup> Spanke J., Rannik, Ü. Forkel, R., Nigge, W., and Hoffmann, T.: Emission fluxes and atmospheric degradation of monoterpenes above a boreal forest: field measurements and modeling, Tellus, B53, 406–422, 2001.
  - Spirig, C., Neftel, A., Ammann, C., Dommen, J., Grabmer, W., Thielmann, A., Schaub, A., Beauchamp, J., Wisthaler, A., and Hansel, A.: Eddy covariance flux measurements of bio-
- 20 genic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry, Atmos. Chem. Phys., 5, 465–481, 2005,

http://www.atmos-chem-phys.net/5/465/2005/.

5

10

- Strong, C., Fuentes, J. D., and Baldocchi, D.: Reactive hydrocarbon footprints during canopy senescence, Agric. For. Meteorol., 127, 159–173, 2004.
- Suni, T., Rinne, J., Reissell, A., Altimir, N., Keronen, P., Rannik, Ü. Dal Maso, M., Kulmala, M, and Vesala, T.: Long-term measurements of surface fluxes above a Scots pine forest in Hyytiälä, southern Finland, 1996–2001, Boreal Environment Research, 8, 287–301, 2003. Tarvainen, V., Hakola, H., Hellen, H., Bäck, J., Hari, P., and Kulmala, M.: Temperature and light dependence of the VOC emissions of Scots pine, Atmos. Chem. Phys., 5, 989–998, 2005,
- 30 http://www.atmos-chem-phys.net/5/989/2005/.
  - Tunved, P., Hansson, H.-C., Kerminen, V.-M., Ström, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P. P., Komppula, M., and Kulmala, M.: High natural aerosol loading over Boreal forests, Science 312, 261–263, 2006.

ACPD 7, 2357–2388, 2007 Hydrocarbon fluxes above a Scots pine forest canopy J. Rinne et al.



Warneke, C., Luxembourg, S. L., de Gouw, J. A., Rinne, H. J. I., Guenther, A. B., and Fall, R.: Disjunct eddy covariance measurements of oxygenated volatile organic compound fluxes from an alfalfa field before and after cutting, J. Geophys. Res., 107, D8, 10.1029/2001JD000594, 2002.

#### ACPD

7, 2357–2388, 2007

#### Hydrocarbon fluxes above a Scots pine forest canopy



**Table 1.** PTR-MS measurement cycle used in the flux measurements, together with the compounds contributing to the measured masses and integration, or dwell, times. The total cycle length was 5.9 s.

| Protonated mass (amu) | Contributing compound    | Formula of the contributing compound              | Integration<br>(dwell) time |
|-----------------------|--------------------------|---|-----------------------------|
| 21                    | water isotope            | H <sub>2</sub> <sup>18</sup> O                    | 0.2                         |
| 25                    | (control mass)           | -   | 0.2                         |
| 32                    | oxygen                   | O <sub>2</sub>                                    | 0.2                         |
| 33                    | methanol                 | CH₃OH   | 0.5                         |
| 37                    | water cluster            | $H_2OH_2O$  | 0.2                         |
| 39                    | water cluster            | H <sub>2</sub> OH <sup>18</sup> O                 | 0.2                         |
| 45                    | acetaldehyde             | C <sub>2</sub> H₄Ō                                | 0.5                         |
| 55                    | water cluster            | 3(H <sub>2</sub> O)                               | 0.2                         |
| 57                    | water cluster            | 2(H <sub>2</sub> O)H <sub>2</sub> <sup>18</sup> O | 0.2                         |
| 59                    | acetone                  | $C_3H_6O$   | 0.5                         |
| 81                    | fragment of monoterpenes |   | 0.5                         |
| 99                    | hexenal                  | C <sub>6</sub> H <sub>10</sub> O                  | 0.5                         |
| 101                   | hexanal                  | C <sub>6</sub> H <sub>12</sub> O                  | 0.5                         |
| 137                   | monoterpenes             | C <sub>10</sub> H <sub>16</sub>                   | 0.5                         |

## **ACPD**

7, 2357–2388, 2007

#### Hydrocarbon fluxes above a Scots pine forest canopy

| Title Page               |              |  |  |  |
|--------------------------|--------------|--|--|--|
| Abstract                 | Introduction |  |  |  |
| Conclusions              | References   |  |  |  |
| Tables                   | Figures      |  |  |  |
|                          |              |  |  |  |
| 14                       | ►I           |  |  |  |
| •                        | •            |  |  |  |
| Back                     | Close        |  |  |  |
| Full Screen / Esc        |              |  |  |  |
|                          |              |  |  |  |
| Printer-friendly Version |              |  |  |  |
| Interactive Discussion   |              |  |  |  |

**Table 2.** Reaction coefficients of selected VOCs with hydroxyl radical (OH), ozone ( $O_3$ ) and nitrate radical ( $NO_3$ ), and midday photolysis rates in mid-July, calculated as described by Hellén et al. (2004).

|                        | k(OH),<br>cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> | $k(O_3)$<br>cm <sup>3</sup> molecule <sup>-1</sup><br>s <sup>-1</sup> | $k(NO_3), cm^3$<br>molecule <sup>-1</sup> s <sup>-1</sup> | k(photolysis)<br>s <sup>-1</sup> |
|------------------------|--|---|---|----------------------------------|
| methanol               | 9.44×10 <sup>-13</sup> , (1)                                     | _   | _   | _                                |
| acetone                | 2.19×10 <sup>-13</sup> , (1)                                     | -   | 3.00×10 <sup>-17</sup> , (2)                              | 5.03×10 <sup>-7</sup>            |
| acetaldehyde           | 1.58×10 <sup>-11</sup> , (1)                                     | 5.99×10 <sup>-21</sup> , (3)  | 2.72×10 <sup>-15</sup> , (2)                              | 3.39×10 <sup>-6</sup>            |
| isoprene               | 10.1×10 <sup>-11</sup> , (1)                                     | 1.28×10 <sup>-17</sup> , (1)  | 6.78×10 <sup>-13</sup> (1)                                | _                                |
| <i>α</i> −pinene       | 5.37×10 <sup>-11</sup> , (1)                                     | 8.66×10 <sup>-17</sup> , (1)  | 6.16×10 <sup>-12</sup> , (1)                              | _                                |
| $\Delta^3$ –carene     | 8.8×10 <sup>-11</sup> , (1)                                      | 3.70×10 <sup>-17</sup> , (1)  | 9.1×10 <sup>-12</sup> , (1)                               | _                                |
| $\beta$ -caryophyllene | 2.00×10 <sup>-10</sup> , (4)                                     | 1.16×10 <sup>-14</sup> , (4)  | 1.90×10 <sup>-11</sup> , (4)                              | -                                |

(1) Atkinson 1994, 298 K

- (2) Atkinson et al., 2001
- (3) Atkinson et al., 1981, 296 K
- (4) Shu and Atkinson, 1995

### ACPD

7, 2357-2388, 2007

#### Hydrocarbon fluxes above a Scots pine forest canopy

| Title Page                          |  |  |
|-------------------------------------|--|--|
| Abstract                            | Introduction                                     |  |
| Conclusions                         | References                                       |  |
| Tables                              | Figures  |  |
|                                     | _  |  |
|                                     | ►I   |  |
|                                     |  |  |
|                                     | •  |  |
| Back                                | Close  |  |
| Back<br>Full Scre                   | Close<br>een / Esc                               |  |
| Back<br>Full Scre                   | Close<br>een / Esc                               |  |
| Back<br>Full Scree<br>Printer-frier | Close<br>een / Esc<br>ndly Version               |  |
| Back<br>Full Scree<br>Printer-frier | Close<br>een / Esc<br>ndly Version<br>Discussion |  |

**Table 3.** Atmospheric lifetimes of methanol, acetone, acetaldehyde, isoprene,  $\alpha$ -pinene,  $\Delta^3$ -carene and  $\beta$ -caryophyllene. OH concentration, 0.25 ppt, is estimated by the model described by Boy et al.(2005). NO<sub>3</sub> concentration, 2.5 ppt, is taken from Hakola et al. (2003). The O<sub>3</sub> concentration, 40 ppb, was typical for the measurement period.

|  | OH               | O <sub>3</sub>   | NO <sub>3</sub>  | Photolysis | Day:<br>OH+O <sub>3</sub> +<br>photolysis | Night:<br>NO <sub>3</sub> +O <sub>3</sub> |
|--|------------------|------------------|------------------|------------|---|---|
| methanol<br>acetone                          | 2.0 d<br>8.7 d   | -                | –<br>17 a        | –<br>23 d  | 2.0 d<br>8.7 d                            | –<br>17 a                                 |
| acetaldehyde                                 | 2.9 h<br>27 min  | 5.4 a<br>22 h    | /0d<br>67b       | 3.4 d      | 2.9 h<br>27 min                           | 68 d<br>5 2 h                             |
| $\alpha$ -pinene                             | 51 min           | 3.3 h            | 45 min           | _          | 41 min                                    | 36 min                                    |
| $\Delta^3$ –carene<br>$\beta$ –caryophyllene | 31 min<br>14 min | 7.7 h<br>1.5 min | 30 min<br>14 min | -<br>-     | 29 min<br>1.3 min                         | 28 min<br>1.3 min                         |

### ACPD

7, 2357–2388, 2007

#### Hydrocarbon fluxes above a Scots pine forest canopy

| Title Page               |              |  |  |  |
|--------------------------|--------------|--|--|--|
| Abstract                 | Introduction |  |  |  |
| Conclusions              | References   |  |  |  |
| Tables                   | Figures      |  |  |  |
| 14                       | ÞI           |  |  |  |
|                          |              |  |  |  |
| •                        | •            |  |  |  |
| Back                     | Close        |  |  |  |
| Full Screen / Esc        |              |  |  |  |
|                          |              |  |  |  |
| Printer-friendly Version |              |  |  |  |
| Interactive Discussion   |              |  |  |  |
|                          |              |  |  |  |

## **ACPD**

7, 2357–2388, 2007

#### Hydrocarbon fluxes above a Scots pine forest canopy

J. Rinne et al.

| Title Page               |              |  |  |  |
|--------------------------|--------------|--|--|--|
| Abstract                 | Introduction |  |  |  |
| Conclusions              | References   |  |  |  |
| Tables                   | Figures      |  |  |  |
| 14                       | ►I           |  |  |  |
|                          |              |  |  |  |
| •                        | •            |  |  |  |
| Back                     | Close        |  |  |  |
| Full Screen / Esc        |              |  |  |  |
|                          |              |  |  |  |
| Printer-friendly Version |              |  |  |  |
| Interactive Discussion   |              |  |  |  |
|                          |              |  |  |  |

**Table 4.** Average daily ecosystem scale VOC emissions from the Scots pine forest during the measurement period.

|              | $mg m^{-2} d^{-1}$ | %  | $\mu$ mol m <sup>-2</sup> d <sup>-1</sup> | %  |
|--------------|--------------------|----|---|----|
| methanol     | 3.9                | 20 | 120                                       | 43 |
| acetaldehyde | 1.1                | 5  | 24  | 8  |
| acetone      | 3.0                | 15 | 52  | 18 |
| monoterpenes | 12                 | 60 | 87  | 31 |



**Fig. 1.** Schematic of the measurement system. The black lines indicate Teflon tubing with flow direction indicated by arrows. The inner diameter of the long tubing was 8 mm and the flow in it  $15 L \text{ min}^{-1}$ . The side flow of  $0.1 L \text{ min}^{-1}$  was taken to the PTR-MS via tubing with 1.6 mm inner diameter.

EGU

**Printer-friendly Version** 

Interactive Discussion





EGU

**Printer-friendly Version** 

Interactive Discussion



**Fig. 3.** Effect of chemical degradation on cumulative footprints at the height of 22 m as calculated by SLTC model for compounds with different chemical lifetimes. The source height was 11.2 m.





EGU



**Fig. 5.** The normalized vertical flux profiles of trace gases with different chemical lifetimes derived using the SLTC model, with sources in the canopy (panel A) and sources in the ground (panel B). Black horizontal line represents the source height and grey line measurement height used.











**Fig. 7.** Monoterpene fluxes as a function of temperature. The solid line indicates the fitting to the temperature dependent emission algorithm while dashed line is that with a fixed temperature dependence coefficient  $\beta = 0.09^{\circ}C^{-1}$ .

