Measurements of hydrocarbon fluxes by a gradient method above a northern boreal forest

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Abstract

The boreal vegetation is considered as being a major source of hydrocarbons in the atmosphere. Measurements of vertical fluxes of isoprene and monoterpenes above a northern boreal forest are reported in this paper. Measurements were conducted in northern Finland (67° 58′ N, 24° 14′ E) near the northern timber lines for conifers. The hydrocarbon fluxes were measured by the gradient technique. The total daytime fluxes of following four monoterpenes: α- and β-pinene, carene and camphene, were typically 30–60 ng m⁻² s⁻¹. These compounds represented 60–80% of the total monoterpenes in the ambient air. The estimated uncertainty of isoprene fluxes exceeded observed fluxes several times, the mean daytime flux being 4 ± 20 ng m⁻² s⁻¹. The error sources of the measured hydrocarbon fluxes are discussed. The most important source of uncertainty was the hydrocarbon sampling and analysis due to low concentration gradients. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Biogenic VOCs; Flux measurements; Boreal forests; Biogenic emissions; Uncertainty analysis

1. Introduction

Boreal vegetation is assessed as being a major source of volatile organic compounds (VOCs) in the atmosphere (Guenther et al., 1995) and in some countries its contribution to the total national VOC emissions is very significant (Lindfors et al., 1995; Simpson et al., 1995). For instance, almost the whole of Finland belongs to the boreal vegetation zone and 66% of the land area of 305 000 km² is covered by forests. Simpson et al. (1995) estimated that in Finland biogenic VOC emissions are twice as high as anthropogenic emissions. Over the whole globe there is a total of ca. 15.8 × 10⁶ km² of boreal forest (Archibold, 1995).

The biogenic VOCs can have a strong effect on the atmospheric chemistry, for example on the production of tropospheric ozone (Chameides et al., 1992). They can also be a major source of organic aerosols and their oxidation affects hydroxyl radical concentrations in the troposphere (Fehsenfeld et al., 1992).

Much work has been carried out using the cuvette technique to obtain the emission rates for different plant and VOC species (e.g., Isidorov et al., 1985; Juuti et al., 1990; Guenther et al., 1991; Janson, 1993; Street...
et al., 1996; Hakola et al., 1998). Isoprene emissions are generally considered to be temperature and light dependent, whereas monoterpenes emissions are often taken to be dependent on temperature only (Guenther et al., 1991). Using species-specific emission factors, it is possible to calculate the VOC emissions for a specific site or a larger area using forest information and weather data.

Measurements of the vertical fluxes of VOCs above the forest canopy are needed to verify the emissions calculated using species-specific emission factors and forest inventory data. Published results on these vertical fluxes are still rather sparse although there has been recent progress (e.g., Fuentes et al., 1996; Goldstein et al., 1996; Guenther et al., 1996; Reichmann et al., 1996; Cao et al., 1997; Ciccioli et al., 1997; Schween et al., 1997; Valentini et al., 1997; Guenther and Hills, 1998; Rinne et al., 1999).

In this work we present the ambient air concentrations of isoprene and monoterpenes and their vertical fluxes as measured by a gradient method in the northern boreal zone in Finland 150 km north of the Arctic Circle. As an integral part of the study, the basic micrometeorological assumptions are tested and a systematic approach has been taken to identify and quantify the potential error sources.

2. The experiment

2.1. The site

The flux measurements were conducted during the period of the 9–20 July 1996 near the Pallas-Ounastunturi National Park in northern Finland (Finnish Lapland). The measurement site (67°58′ N, 24°14′ E, 330 m above sea level (asl)), henceforth referred to as Kenttärova, was situated on a low ridge between two hills, 350 and 440 m high (Fig. 1). The area is 150 km north of the Arctic Circle and close to the northern timber lines of Norway spruce (Picea abies) and Scots pine (Pinus sylvestris). The forest around the measurement site was composed mainly of mountain birch (Betula pubescens subsp. czerepanovii), which is a subspecies of downy birch (B. pubescens), Siberian spruce (P. abies subsp. obovata), which is a subspecies of Norway spruce, and Scots pine. The average tree density, leaf dry biomass, etc., are shown in Table 1. The average height of the canopy at the measurement site was estimated to be 13 m.

Near to the measurement site is situated the Pallas-Sodankylä GAW (Global Atmosphere Watch) station, where ambient air VOC concentrations are sampled twice a week on an open mountain top at 560 m asl, about 200–300 m above the surrounding terrain (Laurila et al., 1995). The light hydrocarbons (up to C5) are analyzed from whole air samples collected into evacuated electropolished stainless steel canisters using gas chromatography with flame ionization detector (GC/FID). The heavier hydrocarbons are collected onto Tenax adsorbent and analyzed by gas chromatography with mass spectrometer (GC/MS).

The climate of the area is relatively cool. In the warmest month, July, the mean of daily maximum temperatures at the Muonio weather station nearby the
Table 1
Forest inventory data from the micrometeorological measurement site\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>Stem number Trees per ha</th>
<th>Stem volume m(^3) ha(^{-1})</th>
<th>Dry leaf biomass 10(^3) kg ha(^{-1})</th>
<th>Leaf/needle area 10(^3) m(^2) ha(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td></td>
<td>1460</td>
<td>100</td>
<td>86</td>
</tr>
<tr>
<td>Scots pine (\textit{Pinus sylvestris})</td>
<td>118</td>
<td>8</td>
<td>22</td>
<td>26</td>
</tr>
<tr>
<td>Siberian spruce (\textit{Picea abies} subsp. \textit{obovata})</td>
<td>623</td>
<td>43</td>
<td>24</td>
<td>28</td>
</tr>
<tr>
<td>Mountain birch (\textit{Betula pubescens} subsp. \textit{czerepanovi})</td>
<td>679</td>
<td>47</td>
<td>37</td>
<td>43</td>
</tr>
<tr>
<td>Other (Goat willow, \textit{Salix caprea})</td>
<td>39</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^a\)The leaf areas are two-sided and needle areas based on the shape of needles.

measurement site in 1961–1990 was 18.5°C (Finnish Meteorological Institute, 1991). The average yearly rainfall was 450 mm, of which a large part fell as snow. The average rainfall in July was 72 mm.

### 2.2. Methods

#### 2.2.1. Theory

We applied the gradient method, in which vertical fluxes are inferred from the vertical gradient of the mean concentration

\[
F_c = -K_c \frac{\partial \bar{c}}{\partial z},
\]

where \(\bar{c}\) is the mean concentration of the trace gas, \(F_c\) is its vertical flux, upward flux being positive, and \(K_c\) is the turbulent exchange coefficient.

There are two common ways of obtaining the turbulent exchange coefficient in the surface layer. The most direct way is the modified Bowen-ratio method (e.g., Goldstein et al., 1995) which however requires accurate measurements of gradients of another gas (e.g., H\(_2\)O, CO\(_2\)), and when these gradients are small a large error can be introduced into the exchange coefficients.

The other method of obtaining the turbulent exchange coefficient is to use the universal flux–gradient relationships. In this way it is possible to determine the turbulent exchange coefficients without requiring gradient measurements, if the momentum and sensible heat fluxes are measured directly. The vertical flux of a trace gas \(F_c\) can be written as (e.g., Fuentes et al., 1996),

\[
F_c = \frac{-ku_s(\bar{c}(z_2) - \bar{c}(z_1))}{\ln((z_2 - d)/(z_1 - d)) + \psi_h((z_1 - d)/L) - \psi_h((z_2 - d)/L)},
\]

where \(k\) is the von Kármán constant, \(u_s\) is the friction velocity, \(\bar{c}(z_1)\) and \(\bar{c}(z_2)\) are the hydrocarbon concentrations measured at heights \(z_1\) and \(z_2\), \(d\) is the zero-plane displacement height, \(\psi_h\) is the integral form of Monin–Obukhov stability function for heat, which is assumed to be the same for trace gases, and \(L\) is the Obukhov length. \(\psi_h\) is calculated using integral forms of the Businger–Dyer equations (e.g., Garratt, 1994) and the fluxes of heat (buoyancy) and momentum measured by the eddy covariance technique. An important prerequisite of these approaches is that the vertical fluxes remain constant within the observation layer.

Near very rough surfaces, such as forest canopies, the flux gradient laws tend to break down (Garratt, 1980; Chen and Schwerdtfeger, 1989; Högström et al., 1989; Cellier and Brunet, 1992; Mölder et al., 1998; Simpson et al., 1998). The layer in which these laws are not directly applicable is called the roughness sub-layer (RSL). The flux obtained by Eq. (1) can be corrected by multiplying by an enhancement factor

\[
\gamma = \frac{\Phi_s}{\Phi},
\]

where \(\Phi_s\) is the dimensionless gradient of a scalar according to the Monin–Obukhov similarity theory and \(\Phi\) is that according to the measurements. The observed \(\gamma\)-coefficients vary from unity to 3 depending on the measurement height and type of the forest (Simpson et al., 1998, and references therein).

Garratt (1980) assumed RSL depth to be dependent on the average tree spacing, but this view was based on very limited data. According to Cellier and Brunet (1992), the height of the RSL, \(z_s\), is related to the scale of main canopy inhomogeneities, \(\delta\), and as a first approximation \((z_s - d)/\delta \approx 3 - 4\). They suggested
the correction function for heat and water vapour to have form
\[
\gamma = z_a - \frac{d}{z_a - d}.
\] (4)
This equation is also supported by the study by Mölder et al. (1998). Garratt (1980) suggested earlier an
\[
\gamma = 2 \exp \left( -0.7 \frac{z - d}{z_s} \right). 
\] (5)
Using these equations it is possible to calculate the mean enhancement factor, \( \Gamma \), by integrating the \( \gamma \)-coefficient between the measurement heights \( z_1 \) and \( z_2 \). For \( z_1 < z_s < z_2 \) we have
\[
\Gamma(z_1, z_2) = \frac{1}{z_2 - z_1} \left[ \int_{z_1}^{z_s} \gamma dz + \int_{z_s}^{z_2} dz \right],
\] (6)
which can be applied to Eq. (4) or (5). The mean enhancement factor is used to correct fluxes calculated using Eq. (2).

2.2.2. Hydrocarbon sampling
The measurement system consisted of two masts 18 and 31 m high, situated 2 m apart. The vertical gradients of the hydrocarbon concentrations were estimated using samples taken at these two heights. Light hydrocarbons were sampled in 0.85 l stainless steel canisters via teflon tubing from both heights. The canisters were pressurized to about 200 kPa and the flow was controlled by a needle valve. This simple method was calibrated using a pressure sensor and it was found to keep the flow into the canister reasonably constant. The sampling time for light hydrocarbons was 25 min. Terpenes were sampled into 250 mg of Tenax TA using automated samplers (Perkin Elmer STS 25) and pumps with an automatic flow control system (Ametek Alpha-2) situated at both measurement heights. The sampling time was 30 min.

At the near-by Pallas-Sodankylä GAW station VOCs are sampled twice a week using similar methods. The chemical analysis of the samples was conducted by GC/FID (canisters) and GC/MS (Tenax) as described by Hakola et al. (1998).

2.2.3. Micrometeorological measurements
To determine the turbulent exchange coefficients, the vertical fluxes of momentum and buoyancy were measured by the eddy covariance method using three-dimensional acoustic anemometers-thermometers (ATI SWS-211) at both measurement heights (18 and 31 m). The vertical fluxes of \( H_2O, CO_2 \) and \( O_3 \) were also measured by eddy covariance technique. For \( H_2O \) and \( CO_2 \) a sensor based on the differential absorption of IR-radiation (Li-Cor LI-6262) was used, while the \( O_3 \) fluctuations were determined using a sensor based on chemiluminescence (GFAS OS-G-2) at 31 m. Details of the measurement system and data processing procedures are presented by Aurela et al. (1996, 1998) and Tuovinen et al. (1998). The averaging time for the flux measurements was 30 min.

Other meteorological parameters, such as the temperature and humidity inside the forest (Vaisala HMP35D), the ground temperature (Campbell 107), the ground water status (Watermark gypsum block) and photosynthetically active radiation (Li-Cor LI-190SZ), were also measured.

The displacement height was assumed to be two-third of the canopy height, i.e. 8.7 m (e.g., Garratt, 1994).

3. Results

3.1. Meteorological measurements

3.1.1. Conditions during the campaign
Temperatures during the measurement period were relatively low (Fig. 2) due to the northerly winds, which prevailed during the campaign. The observed cloudiness at Muonio weather station varied from half
cloudy to cloudy and there was some rain on several days. The only days during the campaign with no rain were 16, 19, and 20 July. The available soil moisture was sufficient to prevent plants from suffering water stress.

The PAR and fluxes measured by the eddy covariance method showed a clear diurnal cycle in spite of the long daylight period (Fig. 3), as did the air temperature. The carbon dioxide flux was typically $-0.2 \text{ mg m}^{-2} \text{s}^{-1}$ in the afternoon and slightly positive (i.e. upwards) at night. The typical evaporation rate in the afternoon was 0.14 mm h$^{-1}$. The daily cycle of the ozone flux was not as systematic as that of the H$_2$O flux, the hourly median values in the daytime ranging from $-0.2$ to $-0.4 \mu\text{g m}^{-2} \text{s}^{-1}$. The values of these fluxes were of the same order as those measured by Aurela et al. (1996) above a Scots pine stand in eastern Finland.

3.1.2. Validity of the micrometeorological assumptions

As mentioned earlier, an important prerequisite of the gradient method is that the vertical fluxes remain constant within the observation layer. To validate the constant-flux assumption we compared the friction velocities, heat fluxes and roughness lengths measured at both measurement heights.

The measured sensible heat fluxes were similar at both measurement heights, as were the momentum fluxes. Only a small bias was found (Fig. 4). The mean ratio of friction velocity measured at the upper height to that at the lower, $r_\alpha = u_{31\text{m}}/u_{18\text{m}}$, was 1.05, and the same ratio for the sensible heat flux, $r_H = u_{31\text{m}}/u_{18\text{m}}^{1/3}$, was 1.03.

For closer analysis, the data was divided into three classes on the basis of the prevailed wind direction. In the first sector ($315^\circ$–$45^\circ$), the forest was reasonably...
Table 2
The ratios of momentum and sensible heat fluxes measured at 31 m to those measured at 18 m ($r_u = u_{31m}/u_{18m}$ and $r_H = w_{0T31m}/w_{0T18m}$) and roughness heights ($z_0$) measured at both measurement heightsa.

<table>
<thead>
<tr>
<th>Wind direction</th>
<th>Stability</th>
<th>$\xi&lt;0.02$</th>
<th>$-0.02&lt;\xi&lt;0.02$</th>
<th>$\xi&gt;0.02$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r_u$</td>
<td>$r_H$</td>
<td>$z_0(18m)$</td>
<td>$z_0(31m)$</td>
</tr>
<tr>
<td>315–45°</td>
<td>1.06</td>
<td>1.20</td>
<td>1.11 1.3 m</td>
<td>0.94 1.00</td>
</tr>
<tr>
<td></td>
<td>(51) (39)</td>
<td>(23) (23)</td>
<td>(23) (56) (5)</td>
<td></td>
</tr>
<tr>
<td>45–200°</td>
<td>1.08</td>
<td>1.30</td>
<td>1.10 1.3 m</td>
<td>1.0 m 1.24</td>
</tr>
<tr>
<td></td>
<td>(53) (46)</td>
<td>(12) (12)</td>
<td>(15) (12) (0)</td>
<td></td>
</tr>
<tr>
<td>200–315°</td>
<td>1.10</td>
<td>1.15</td>
<td>1.27 1.7 m</td>
<td>1.9 m 0.85</td>
</tr>
<tr>
<td></td>
<td>(44) (35)</td>
<td>(4) (4)</td>
<td>(4) (19) (8)</td>
<td></td>
</tr>
</tbody>
</table>

a Number of observations are in parenthesis.

homogeneous for a little over 1 km, and even beyond that the ground was still reasonably flat. In the second sector (45–200°), the forest changed after 800 m into an area of open wetlands, while in the third sector (200–315°) the steep slope of Mustakero hill rose at a distance of 1 km. Using the footprint formulae by Schuepp et al. (1990) for neutral conditions, 75% of the flux measured at 31 m originated within 1 km of the masts. For the 18 m height, 75% of the measured flux originated within 300 m of the masts. For unstable conditions these source area radii are even shorter.

From Table 2 we notice that $r_u$ is close to unity in unstable conditions. In near-neutral and stable conditions there are larger deviations, but for northerly wind directions the ratio is still reasonably close to unity. The ratio of friction velocities is usually closer to unity than the ratio of heat fluxes, which may be due to the large scatter of the heat fluxes also seen in Fig. 4.

As the second test, the roughness length was calculated from eddy covariance measurements at both heights. The roughness length was calculated using the equation

$$z_0(z) = (z - d) \exp \left\{ -\frac{u(z)k}{u_a(z)} - \psi_m[z(\xi)] \right\}, \quad (7)$$

where $\xi = (z - d)/L$, and accepting near-neutral observations only ($|\xi| < 0.02$).

The roughness lengths obtained from the upper and lower level measurements were closest to each other in northerly wind directions, in which $z_0 = 1.3$ m (Table 2). The differences between the roughness lengths derived from different measurement heights in the other two wind direction classes may arise from nonhomogeneity of the surface roughness. Changing the value of the zero plane displacement height within the limits given by Jarvis et al. (1976) did not explain the observed differences. The close fit of the roughness lengths measured in northerly wind directions gives also confidence in the choice of the zero-plane displacement height.

To summarize, we conclude that northerly wind directions seem to be the most reliable for gradient measurements, and the VOC fluxes presented further were measured under those conditions.

To estimate the effect of the RSL on the turbulent exchange, the exchange coefficients were calculated not only using the flux–gradient relationships, but also using the measured gradients of temperature with sensible heat fluxes. The measured water vapour gradient...
had systematic errors and could not be used in this comparison. The height of the RSL was approximated by $z_a - d = 4\delta$ (Cellier and Brunet, 1992) and the forest inventory data (Table 1). The dominant trees at the site were Siberian spruces and Scots pines. Their stem number per ha was about 700. This leads to $\delta \approx 4$ m and therefore to $z_a \approx 24.7$ m. Thus the upper measurement level seems to be above the RSL according to Cellier and Brunet (1992).

The $\Gamma$-coefficients calculated using Eqs. (4)–(6) with measurement heights of 18 and 31 m and a RSL height of 24.7 m were 1.21 according to Garrett (1980) and 1.15 according to Cellier and Brunet (1992). The $\gamma$-coefficients obtained by Simpson et al. (1998) ranged between 1.1 and 1.5 for measurement height to canopy height ratios between 1.4 and 2.4.

The turbulent exchange coefficients for heat obtained from the theoretical flux-gradient relationships (Eqs. (1) and (2)) were compared with those obtained using temperature gradients and sensible heat fluxes. The data used for comparison is filtered to meet the following criteria: Wind direction is $315^\circ$–$45^\circ$; $|\xi| > 0.2$; $u_0 > 0.1$ m s$^{-1}$ and measurement time is 8:00–18:00 or 22:00–4:00 hours. The least-square line for the data showed that the $\Gamma$-coefficient for heat was 1.20, which is close to the values obtained earlier. There is, however, a large scatter and $r^2$ is only 0.39. The deviation from the universal flux-gradient relationship was not generally dependent on stability, though there was an increase with stronger instability.

As there are both theoretical and practical limitations in the direct method of obtaining the turbulent exchange coefficient for heat, the coefficients obtained from the flux-gradient relationships are used for hydrocarbon flux calculations. These coefficients are corrected by multiplying them by an enhancement factor of $\Gamma = 1.2$ based on the findings mentioned earlier.

Finally, one should be aware of the fact that chemical reactions of trace gases in the surface layer can also lead to a breakdown of the constant trace gas flux layer. In the present case, however, the timescale for vertical mixing, $\tau_m$, is much shorter than the timescale for chemical degradation. If we take the measurement height $z_m \approx 30$ m and the friction velocity $u_0 \approx 0.1$–1.0 m s$^{-1}$ then the timescale $\tau_m = z_m/u_0 \approx 30$–300 s $\approx 0.5$–5 min. According to Finlayson-Pitts and Pitts (1986), the typical lifetimes for $\alpha$- and $\beta$-pinene and carene range from 3 to 18 h. The chemical reactions seem therefore to be of minor importance.

### 3.2. Hydrocarbon concentrations

The total ambient air monoterpane concentrations measured at the Pallas-Sodankylä GAW station were higher than the isoprene concentrations (Fig. 2). This suggests that the total monoterpane emissions are higher than those of isoprene. At the micrometeorological measurement site, Kenttärova, the monoterpane concentrations were slightly higher than at the GAW station and the composition of the total monoterpane concentration differed from that observed on the mountain top (Fig. 5). At the GAW station most of the monoterpenes were in the form of $\alpha$-pinene. It was also the most common monoterpane at the Kenttärova site, but there other species contributed more to the total monoterpane concentration, limonene being almost as abundant as $\alpha$-pinene. The reason for this behaviour may lie in the differences of reactivities of these monoterpenes. Because the reactivity of $\alpha$-pinene in O$3$ and OH reactions is lower
than that of limonene (Atkinson, 1994), α-pinene is more evenly distributed in the atmospheric boundary layer, whereas limonene profiles are affected more by chemistry.

3.3. Hydrocarbon fluxes and their uncertainty

Before the results of the VOC flux measurements are presented, a systematic approach into the potential error sources of these VOC flux measurements is taken. This is accomplished by identifying the error sources and discussing their relative importance.

3.3.1. Sources of uncertainty

For the gradient method, the sources of uncertainty can be divided into those of the gradient itself and those due to the turbulent exchange coefficient. The latter can be further divided into uncertainties originating from the flux measurements and those arising from the parametrisations. A list of uncertainties relevant for the present data is presented for these categories in Table 3, partly based on the review by Businger (1986) of the errors related to micrometeorological techniques. Unfulfilled micrometeorological assumptions may be considered as the third source of uncertainty. These were addressed in Section 3.1.2 and are also dealt with within the data screening procedures. As it is not possible to assess the possible remaining errors in a systematic way, for the following discussion we assume no further uncertainty due to non-ideal flow conditions.

For this data set, the most important error source affecting the measured fluxes is the chemical sampling and analysis of the hydrocarbons. This is due to the small concentration differences between the measurement levels, as compared to the resolution of the chemical analysis. In order to reduce this uncertainty, we calculated the flux as the sum of four monoterpenes (α- and β-pinene, carene and camphene). These compounds make up 60–80% of the total atmospheric monoterpene concentration above the forest and their gradients also correlate with each other. The latter was not true for limonene, which also had problems in the chemical analysis and was therefore not included in the sum.

The uncertainty of hydrocarbon gradient was estimated by running a series of sample pairs with two samplers at same height. The mean concentration difference of the above-mentioned monoterpene sum between concominant sample pairs was about 50 pptv. This includes both the sampling error and the error due to chemical analysis. Later tests have shown that the variations in the blank-level monoterpene concentrations of the Tenax cartridges contribute significantly to the uncertainty of the monoterpene gradient. Thus improvements in the cleaning procedures would improve

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Table 3

<table>
<thead>
<tr>
<th>Source</th>
<th>Correction/error estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Hydrocarbon gradient</td>
<td>Monoterpene: 50 pptv→70–170%</td>
</tr>
<tr>
<td>Sampling and analysis</td>
<td>Isoprene 10 pptv→200–300%</td>
</tr>
<tr>
<td>2. Turbulent exchange coefficient</td>
<td></td>
</tr>
<tr>
<td>2.1 Eddy covariance measurements of the buoyancy flux (B) and friction velocity (u*)</td>
<td></td>
</tr>
<tr>
<td>2.1.1 Density fluctuations due to the latent heat flux</td>
<td>B: Negligible, Kaimal and Gaynor (1991); u*: not affected</td>
</tr>
<tr>
<td>2.1.2 Frequency response of the sensors</td>
<td>B, u*: Negligible</td>
</tr>
<tr>
<td>2.1.3 Spatial separation of the sensors</td>
<td>B: Not affected; u*: corrected, Moore (1986)</td>
</tr>
<tr>
<td>2.1.4 Line averaging of the sensors</td>
<td>B, u*: corrected, Moore (1986)</td>
</tr>
<tr>
<td>2.1.5 Flow distortion</td>
<td>Transducer shadowing corrected, Kaimal and Gaynor (1991), otherwise unknown</td>
</tr>
<tr>
<td>2.1.6 Random noise of the measurements system</td>
<td>2.1.6+2.1.7=20% (random)</td>
</tr>
<tr>
<td>2.1.7 Sampling error</td>
<td></td>
</tr>
<tr>
<td>2.2 Parametrisations</td>
<td></td>
</tr>
<tr>
<td>2.2.1 Businger-Dyer formulas and von Kármán constant</td>
<td>25%</td>
</tr>
<tr>
<td>2.2.2 Displacement height</td>
<td>25%</td>
</tr>
<tr>
<td>2.2.3 Roughness sublayer</td>
<td>Corrected</td>
</tr>
</tbody>
</table>
the accuracy of the monoterpene gradients. For isoprene, the uncertainty of the analysis was estimated at 10 pppt by analyzing several canisters twice. With the range of gradients observed at Kenttärova, these values lead to uncertainties of 200–300% in the isoprene gradient and 70–170% in the monoterpene gradient.

In the eddy covariance measurements of the momentum and buoyancy (virtual temperature) fluxes for the exchange coefficient, a number of the potential errors characteristic of this technique can be identified, many of which can be routinely corrected for. These are listed as Items 2.1.1–2.1.7 in Table 3. A sonic anemometer, such as the type used here, also provides a measurement of the virtual temperature to a close approximation, even without concomitant measurement of humidity fluctuations (Kaimal and Gaynor, 1991). This makes it possible to obtain in a consistent way the fluxes needed for the exchange coefficient.

There is no temporal delay between the anemometer signals nor any spatial sensor separation within the heat flux measurement, but the momentum flux is affected by the sensor configuration of the SWS-211, in which the vertical and horizontal sonic paths are separated. This together with the line averaging over the paths leads to attenuation of high-frequency fluctuations and consequently to a small systematic flux loss. We have corrected for this based on the procedure by Moore (1986), as detailed by Tuovinen et al. (1998).

The random noise in the measurement system and sampling errors introduce a random uncertainty into the flux measurements. It has been estimated that the natural run-to-run variability for the 30-min averaging period is approximately 10–20% at heights of 5–10 m in ideal daytime conditions, and this can be significantly increased by sensor noise (Wesely and Hart, 1985; Businger, 1986). We assume that the random variability in the momentum and heat flux data is dominated by sampling effects, and that after the corrections listed in Table 3 this is the main source of uncertainty in the eddy covariance measurements employed in this study. To summarize, we adopt a value of 20% for the further uncertainty analysis.

The use of universal flux–gradient relationships introduces an uncertainty that can lead to systematic errors in the turbulent exchange coefficient. There exists a consensus on the functional form of these relationships, but a range of values have been reported for the related empirical constants (e.g., Businger et al., 1971; Dyer, 1974; Wieringa, 1980; Högström, 1988; Oncley et al., 1996). This variability is taken here as an indication of the uncertainty due to parametrisation. In principle, the constants used in the Businger–Dyer formulae, together with the von Kármán constant, should be treated as one parameter set, since in practice they are not determined independently. We assessed that the variability between the parameter sets leads up to 25% differences in the calculated exchange coefficients.

The zero-plane displacement height is here taken as an independent parameter. According to Jarvis et al. (1976) the reported ratio of the displacement height and the mean canopy height ranges from 0.61 to 0.92. For our data, this leads to differences of 25% in the exchange coefficient. Similar roughness lengths obtained from both measurement heights give confidence in the value of 0.67 adopted here.

Using the standard error propagation method we can now sum up the uncertainties arising from the Items 1, 2.1.6, 2.1.7 and 2.2 in the Table 3. The summing is done separately for each data point.

### 3.3.2. Observed hydrocarbon fluxes

During daytime, values of monoterpene fluxes range from negative to 150 ng m$^{-2}$ s$^{-1}$ (Fig. 6). At night the fluxes are close to zero. Nightly fluxes should be treated with care because of light winds and stable conditions latter leading to longer footprint areas. Because of the large uncertainties, these values should be taken as order-of-magnitude estimates. The uncertainty of isoprene flux was much higher than observed fluxes. The small fluxes observed are at least partly due to the low temperatures (6–16°C) during the measurements. The lower uncertainty of terpene fluxes on 13 July is due to the more cloudy weather and lower mixing in the boundary layer which lead to larger gradient relative to emission. During these measurements there was also some light rain.

In order to reduce the large uncertainty in the flux estimates, the mean flux of a longer period could be calculated using several consecutive measurements. In this way the effect of random errors will be statistically reduced, though the systematic uncertainties would remain. On the 13 July run the mean flux was $60\pm30$ ng m$^{-2}$ s$^{-1}$ and from five daytime measurements on 16 July we obtained $30\pm60$ ng m$^{-2}$ s$^{-1}$. The mean of all daytime (10:00–15:00 hours LST)
flux measurements of isoprene was 4\pm 20 \text{ng m}^{-2} \text{s}^{-1}. The observed terpene fluxes are an order of magnitude higher than observed isoprene fluxes. This is in line with the ambient air concentrations observed at the Pallas-Sodankylä GAW station.

To study the influence of the individual monoterpenes on the total flux, the data from 13 July is used due to its relatively low uncertainty. During these measurements $\alpha$-pinene was the dominant monoterpenes emitted, making 49% of the monoterpene flux. The abundance of other species were $\Delta^3$-carene: 30%; $\beta$-pinene: 16%; and camphene: 5%.

The temperature dependence of the monoterpenes emission is generally described by the equation

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

(8)

where $E$ is emission rate, $E_{30}$ is the emission normalized to 30$^\circ$C, $T$ is the leaf temperature ($^\circ$C) and $\beta$ is empirically-determined coefficient (Guenther et al., 1991). The temperature dependency in most of the published measurements is of the same order ($\beta \approx 0.1$–0.2) (e.g., Isidorov et al., 1985; Juuti et al., 1990; Guenther et al., 1991; Janson, 1993; Hakola et al., 1998).

Most of the emission factors published are for the total monoterpenes emission but some of them are for specific terpenes. It might be better to use emission factors for the total monoterpenes emission, as Hakola et al. (1998) have observed large differences between emitted terpene species even within a single plant species ($B. pendula$), while the total monoterpenes emission rate was more conservative.

The temperature dependencies of the terpene fluxes measured at Kenttärova are shown in Fig. 7. The temperature coefficients are higher than most of the published ones. The temperature coefficient for the whole
Fig. 7. Temperature dependencies (Eq. (8)) of measured terpene fluxes. The solid line is fitted to the whole data ($\beta=0.41$ in Eq. (8)) and the dashed lines to separate runs: 13 July (+) ($\beta=1.3$), 16 July (*) ($\beta=0.96$) and 17–18 July (o) ($\beta=1.7$). The dotted line is based on $\beta=0.09$ and $E_{30}=240$ ng s$^{-1}$ m$^{-2}$.

data set is closest to those published. One possible reason for these differences is the use of air temperature instead of leaf temperature. As $\beta$-coefficients for individual runs are systematically higher than those for whole data set, it seems possible that other factors than temperature are needed to explain the emission rates. The mean emission normalized to 30°C using $\beta=0.09^\circ C^{-1}$, which is commonly used in the emission models, is 240 ng s$^{-1}$ m$^{-2}$.

4. Conclusions

A measurement campaign has been conducted in the northern boreal zone in order to estimate biogenic VOC emissions by the micrometeorological gradient method. The VOC concentrations were measured at 18 and 31 m using GC-MS with cartridges filled with Tenax TA and stainless steel canisters. The turbulent exchange coefficient was calculated using surface layer flux–gradient relationships and the fluxes of heat and momentum measured by the eddy covariance method. The micrometeorological assumptions were shown to have been satisfactorily fulfilled and the measurement system worked well.

A typical total flux of four important monoterpenes was 30–60 ng m$^{-2}$ s$^{-1}$ during the daytime and close to zero at night. The low emissions observed were at least partly due to the low temperatures. The most abundant monoterpene in the emission was $\alpha$-pinene, $\Delta^3$-carene being the second. The temperature dependency of the measured fluxes was stronger than usually found using cuvette techniques. The mean daytime isoprene flux was very low, 4±20 ng m$^{-2}$ s$^{-1}$. This is in line with the observed ambient air isoprene concentrations, as they are much lower than the total monoterpene concentrations.

The sources of uncertainty of measured VOC fluxes leading to either random or systematic errors, have been discussed. The most important sources of uncertainty were the hydrocarbon gradients, due to the small concentration gradients. The flux values presented should be taken as order-of-magnitude estimates. To reduce the effect of random uncertainties, longer time series would be useful.

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References


