Turbulent exchange and segregation of \( \text{HO}_x \) radicals and volatile organic compounds above a deciduous forest

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Abstract

The eddy covariance method was applied for the first time to estimate fluxes of OH and HO$_2$ together with fluxes of isoprene, the sum of methyl vinyl ketone (MVK) and methacrolein (MACR) and the sum of monoterpenes above a mixed deciduous forest. Highly sensitive measurements of OH and HO$_2$ were performed by laser induced fluorescence (LIF), and biogenic volatile organic compounds (BVOCs) were measured by Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) at a time resolution of 5 s, each. Wind speed was measured by a sonic anemometer at 10 Hz. The one-day feasibility study was conducted at a total height of 37 m, about 7 m above forest canopy, during the ECHO 2003 intensive field study in July 2003. The daytime measurements yielded statistically significant OH fluxes that indicate downward transport of OH into the direction of the canopy and HO$_2$ fluxes mainly upward out of the canopy. This hints towards a significant chemical sink of OH by reaction with BVOCs and conversion of OH to HO$_2$ at the canopy. In addition, the highly time-resolved trace gas measurements were used to calculate the intensity of segregation of OH and BVOCs, demonstrating that the effective reaction rate of isoprene and OH was slowed down as much as 15% due to inhomogeneous mixing of the reactants. The paper describes the applied methods and provides a detailed analysis of possible systematic errors of the covariance products.

1 Introduction

Biogenic volatile organic compounds (BVOCs) have a significant influence on tropospheric chemistry on local to global scales (e.g. Fuentes et al., 2000; Poisson et al., 2000). BVOCs, including isoprene (C$_5$H$_8$) and monoterpenes (C$_{10}$H$_{16}$), influence the atmospheric oxidation capacity by reaction with hydroxyl radicals (OH), nitrate radicals (NO$_3$) and ozone (O$_3$) (e.g. Atkinson and Arey, 2003; Finlayson-Pitts and Pitts, 1986; Seinfeld and Pandis, 1988) and contribute to the formation of secondary products.
chemical products including ozone, oxygenated volatile organic compounds (OVOCs) and secondary organic aerosols (SOA) (e.g. Sanderson et al., 2003; Hallquist et al., 2009). BVOCs contribute also significantly to the carbon budget of the biosphere (e.g. Kesselmeier and Staudt, 1999). For these reasons, their emission from the terrestrial vegetation into the well mixed troposphere is of general interest.

The rate of BVOC emissions depends on many variables and is mainly controlled by plant physiological status and meteorological conditions like temperature, solar radiation and humidity (e.g. Guenther et al., 1995, 2006; Kesselmeier and Staudt, 1999). Estimates of the net emission of organic compounds from forests take these variables into account, but are additionally complicated by chemical loss and transformation processes resulting from reactions with OH, NO$_3$ and O$_3$ in the mixing-layer type flow regime (ML) near canopy top (denoted by height $h_c$) as well as inside the canopy atmosphere (CA). The chemistry impact within and above a forest canopy has been investigated in various model studies (Gao et al., 1993; Makar et al., 1999; Stroud et al., 2005; Forkel et al., 2006; Guenther et al., 2006). For example, the isoprene flux, $F_{iso}$, at $h_c$ was estimated to be reduced by chemical reactions by about 12% (Gao et al., 1993) and up to about 40% (Makar et al., 1999) compared to the vertically integrated emission from leaf surfaces. Experimental evidence for significant chemical conversion of BVOCs in forest stands has been reported from several field studies (e.g. Bouvier-Brown et al., 2009; Di Carlo et al., 2004; Karl et al., 2004; Spirig et al., 2005; Holzinger, 2005; Schaub, 2007; Valentini et al., 1997; Zelger et al., 1997). For example, not only fluxes of primary emitted BVOCs, but also of oxidized reaction products could be measured (e.g. Karl et al., 2003, 2004). Recently, Spirig et al. (2005) determined fluxes of the sum of reaction products of isoprene, methyl vinyl ketone (MVK) and methacrolein (MACR), together with the flux of isoprene above a mixed deciduous forest (near $h_c$) during the ECHO campaign 2003 (see below). Simultaneously measured ratios of MVK + MACR to isoprene were analyzed by Schaub (2007), who estimated a residence time of about 20 to 30 min for isoprene in the canopy atmosphere. This time is long enough that measurable amounts of chemical products can be formed inside the canopy.
Transport and chemistry in the ML and CA are influenced by nonlocal mixing processes which cause inhomogeneities in scalar fields (e.g. Kaimal and Finnigan, 1994; Katul et al., 1997; Raupach et al., 1996; Wahrhaft, 2000). It should be noted that the effective reaction rate (e.g. of OH with biogenic hydrocarbons) is lower for incompletely mixed reactants than for perfectly mixed constituents. This segregation effect is largest, if the characteristic time scale of turbulent mixing, $\tau_T$, is comparable to the characteristic chemical reaction time scale, $\tau_{ch}$ (e.g. Damköhler, 1957; Astarita, 1967; Komori et al., 1991). Krol et al. (2000) modelled reactions of hydrocarbons with OH in the atmospheric mixing layer and found that the effective reaction rates can be smaller by up to about 30% compared to the well mixed case. Recently, Butler et al. (2008) interpreted their aircraft measurements of OH and isoprene mixing ratios in the atmospheric boundary layer above the Guyana rain forest by an influence of segregation with a reduction of the effective reaction rate by about 50%. The quantification of such segregation effects is not only important for estimating net emissions of BVOCs from vegetation, but also for the quantitative understanding of the photochemistry in forested environments. To our knowledge, so far OH segregation has not been measured close to a BVOC emission source above or in a forest canopy.

OH and HO$_2$ radicals play a central role in the chemical processing of organic compounds in the atmosphere (e.g. Ehhalt, 1999). OH is the major daytime oxidant which is primarily formed by reaction of water vapor with O($^1D$) atoms from ozone photolysis. Other OH sources include photolysis of nitrous acid (HONO) and ozonolysis of alkenes. Hydroperoxy radicals (HO$_2$) are intermediate products resulting from reactions of BVOCs with OH, and have the ability to recycle OH by reaction with nitrogen monoxide (NO). Relatively few measurements of atmospheric HO$_x$ (OH+HO$_2$) exist in forest areas. Measurements of OH and HO$_2$ concentrations were performed above a deciduous forest (Tan et al. 2001) and inside a coniferous forest (Carslaw et al., 2001). While the modelled HO$_2$ concentrations almost agreed with measured data at the deciduous forest site, the modelled OH concentrations were substantially lower than the measured values in both studies, by a factor of about 2–3 at the deciduous forest site.
and a factor of two in the corniferous forest. A segregation effect was not considered. It should be noted that the tendency of chemical models to underpredict observed OH at conditions of high VOC (with a strong contribution of isoprene) agrees with those reported by Butler et al. (2008) and Hofzumahaus et al. (2009) at low NO mixing ratios. Di Carlo et al. (2004) interpreted such findings by a missing (not measured) contribution from the reactions of ozone with unsaturated hydrocarbons with a significant net yield of OH (e.g. Kroll et al., 2001).

In order to close some gaps in knowledge related to the emission of BVOCs and the photochemistry in forests, the intense field campaign ECHO 2003 was performed in a mixed deciduous forest at Forschungszentrum Jülich, Germany, in summer 2003. The objectives of the ECHO project (Emission and CHemical transformation of biogenic volatile Organic compounds) were

1. to improve the understanding of the interactions between emissions, deposition, chemical transformation and transport on the scale of a forest stand and the mesoscale, and

2. to find out the conditions a stand acts as a chemical reactor with and without the influence of segregation.

Measurements of vertical profiles of HO\textsubscript{x} were performed by laser-induced fluorescence (LIF) (Hofzumahaus, 2008) in parallel to measurements of mixing ratios and fluxes of various reactive trace gases (e.g. NO, NO\textsubscript{2}, O\textsubscript{3}, HCHO, HONO), BVOCs (e.g. methanol, acetaldehyde, isoprene, methacrolein, methyl vinyl ketone, monoterpenes), photolysis frequencies and micrometeorological parameters (Amman et al., 2004; Aubrun et al., 2005; Spirig et al., 2005; Kleffmann et al., 2005; Bohn, 2006a, b; Schaub, 2007). The results, for example, showed a decreasing mean OH concentration from canopy top (h\textsubscript{c}=30 m) to the ground (Hofzumahaus, 2008) in parallel to the decreasing mean ozone photolysis frequency J(O\textsuperscript{1}D) inside the canopy (Bohn, 2006a, b). In addition, nitrous acid was found to be a major source of OH in the ML above that forest (Kleffmann et al., 2005).
During the ECHO campaign, it became obvious that the concentrations of isoprene, MVK + MACR, monoterpenes, and HO$_x$ exhibited fast and strong fluctuations on a time scale of seconds, which were possibly caused by turbulent transport, vertical concentration gradients and incomplete mixing of the reactive components in ambient air. In order to quantify these possible effects, a one-day feasibility study was performed directly above the forest canopy, using LIF and proton-transfer-reaction mass spectrometry (PRT-MS) in parallel at close distance to measure HO$_x$ and BVOCs, respectively, at a high time resolution. For this purpose, the operation of LIF was adapted to the time resolution (5 s) of the PTR-MS instrument. In addition, meteorological parameter (radiation, humidity, temperature, 3-dimensional wind, photolysis frequencies) were recorded in parallel. In the present paper, the experimental setup is described (Sect. 3) and the time series of the observed trace gases are analyzed, starting from the local mass balance equation of the reactive components (e.g. Businger, 1986; Lenschow, 1995) (Sect. 2). The covariance method is used to estimate, for the first time, turbulent fluxes for radicals, BVOCs, reaction products (MVK + MACR), and sensible heat, together (Sect. 5). Furthermore, the influence of nonhomogeneous mixing (segregation) on the reaction rate of OH with isoprene and monoterpenes is quantified.

2 Flux measurements

2.1 Basic concept

The rules how to perform the measurements are derived from the local mass balance equation for the $i$th constituent (e.g. de Groot and Mazur, 1969; Businger, 1986; Kramm and Meixner, 2000; Kramm et al., 2008) per unit volume of air. For a macroscopic flow, the balance equation reads

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{v} + \mathbf{J}_i) = Q_i - S_i.$$ (1)
Here, the term $\partial \rho_i / \partial t$ is the local derivative of the partial density $\rho_i$ with respect to time, $\mathbf{v}$ is the vector of the barycentric velocity (here the wind vector), $J_i = \rho_i (\mathbf{v}_i - \mathbf{v})$ is the diffusion flux density (hereafter, a flux density is simply denoted as a flux), $\mathbf{v}_i$ is the individual velocity, and $\nabla$ is the nabla or del operator expressed, for instance, in Cartesian coordinates by $\nabla = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z}$, where $i$, $j$ and $k$ are the unit vectors in east ($x$), north ($y$), and vertical ($z$) direction, respectively. Furthermore, $Q_i$ represents the sources and $S_i$ the sinks of matter in the fluid due to chemical reactions and/or phase transition processes. Moreover, the quantities $\rho_i \mathbf{v}$ and $J_i$ are frequently called the convective and non-convective transport of matter, respectively. The further discussion in Appendix A summarizes the essential procedure to derive a simplified form of Eq. (1) for turbulent flows. Thus, applying the Reynolds’ averaging calculus to Eq. (1) yields

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{v} + \rho_i' \mathbf{v}' + J_i) = Q_i - S_i.$$  \hspace{1cm} (2)

It is denoted as the balance equation for the 1st moment (or 1st order balance equation). Here, $\rho_i' \mathbf{v}'$ is the turbulent flux, also called the eddy flux. It is a non-convective flux, too.

For the stationary conditions of an incompressible flow (see Appendix A) and the further assumption that the fields of the wind velocity and the partial densities of the atmospheric constituents are horizontally homogeneously distributed, we will obtain

$$\frac{\partial}{\partial z} \left( \rho_i \overline{w} + \rho_i' \mathbf{w}' + J_i, z \right) = Q_i - S_i,$$  \hspace{1cm} (3)

and

$$\frac{\partial \overline{w}}{\partial z} = 0,$$  \hspace{1cm} (4)

where $\overline{w}$ is the vertical component of the wind vector. From Eq. (4) we may infer that $\overline{w}$ is constant with height. Since at any rigid surface $\overline{w}$ is equal to zero, we may state...
that $\overline{w}$ is generally equal to zero under the conditions that the fluid is incompressible and horizontally homogeneous. Sun (2007) discussed some of these limitations for canopy flow. Under these premises, the vertical contribution to the flux divergence is compensated by the sources and sinks due to chemical reactions and/or phase transition processes. In a fully turbulent flow, the molecular diffusion flux of a gaseous entity can be neglected because $|\overline{\rho_i'w'}| \gg |J_{i,z}|$. Integrating Eq. (4) over a certain height interval, $[z_f, z_R]$, where $z_f$ is a reference height for the foliage ($z_f = 0$ for bare soil), and $z_R$ is a reference height above the canopy at which the eddy flux measurements are performed (e.g. $z_R = 1.23h_c$, as in the present work), yields

$$\left(\frac{\overline{\rho_i'w'}+\overline{J_{i,z}}}{z=z_f}\right)_{z=z_R} = \frac{\overline{\rho_i'w'}}{z=z_f} - \int_{z_f}^{z_R} \left(\overline{Q_i} - \overline{S_i}\right) dz. \tag{5}$$

This equation describes in which way fluxes related to the emission or uptake of gaseous matter at $z=z_f$ can be related to the measured eddy flux $F_i = \overline{\rho_i'w'}$ at $z=z_R$ of this entity under the influence of sources ($Q_i$) or sinks ($S_i$) in the atmospheric layer $\Delta z = z_R - z_f$.

Note that in the case of horizontally inhomogeneous conditions, all other terms like horizontal or vertical advection in Eq. (2) will contribute to the local mass balance. In addition, near sources of reactive BVOCs, not only turbulent or convective mixing, but also an inhomogeneous distribution of sources at surfaces (which appear in the boundary conditions in Eqs. 2 or 5) can influence the net divergence in the volume of the atmosphere (e.g. Krol et al., 2000).

### 2.2 Turbulent transport and chemical reactions

The condition with a non-zero divergence in Eq. (5) is fulfilled especially, if the chemical reaction time scale $\tau_{ch}$ is comparable to the time scale $\tau_T$ for vertical turbulent transport over the distance $z_R$ from the measuring point to the Earth surface ($z_f = 0$) or...
another point in the canopy \((z_f > 0)\), where emission or deposition happens (e.g. Ebel et al., 2007; Dlugi, 1993; Fitzjarrald and Lenschow, 1983; Komori et al., 1991; Kramm and Dlugi, 1994; Kramm et al., 1995; Stockwell, 1995; Vila-Guereau de Arellano et al., 1993; Zelger et al., 1997). For \(\tau_T \ll \tau_{ch}\) the chemical constituents can be considered to be inert like a tracer and the integral term in Eq. (5) vanishes. However, for \(\tau_T \gg \tau_{ch}\) the species occur as if driven by chemical kinetics or to be in chemical equilibrium. Stockwell (1995) analysed reactions of a gas-phase chemical mechanism and found the reactions of OH (e.g. OH+NO\(_2\), OH+CO, OH+BVOC) and the reaction HO\(_2\)+NO to be diffusion limited under typical turbulent atmospheric conditions, or between limitation by diffusion (\(\tau_T \approx \tau_{ch}\)) and kinetics (\(\tau_T \gg \tau_{ch}\)) for vertical transport under near neutral to unstable conditions. This result agrees with findings from model studies by Krol et al. (2000), Verver et al. (2000) and Ebel et al. (2007). As a consequence, the covariances between the vertical velocity component and OH or HO\(_2\), and also reactive biogenic hydrocarbons like isoprene should be considered in terms of sources and sinks in Eq. (5). Incomplete mixing of two reactants \(\rho_i, \rho_j\) (e.g. OH, isoprene) inside a volume of air results in a reduced net reaction rate \(R_{\rho_i,\rho_j}\):

\[
R_{\rho_i,\rho_j} = k \overline{\rho_i \rho_j} \left[ 1 + \left( \frac{\rho_i' \rho_j'}{\overline{\rho_i} \overline{\rho_j}} \right) \right]
\]

(6)

compared to the homogeneously mixed case with \(k \overline{\rho_i \rho_j}\). According to the averaging procedure explained in Appendix A (see also Sect. 2.3), the overbars describe the time averaged quantities, and \(\rho_i' \rho_j'\) the covariance between \(\rho_i\) and \(\rho_j\) (e.g. Vinuesa and Vila-Guerau de Arellano, 2005). The quotient in brackets \((\rho_i' \rho_j' / \overline{\rho_i} \overline{\rho_j})\), the intensity of segregation \(I_s\), is estimated within the two limits \(I_s = 0\) for ideal (homogeneous) mixing and \(I_s = -1\) for non-mixed conditions (e.g. Komori et al., 1991; Wahrhaft, 2000).

Fluxes of OH and HO\(_2\), of isoprene and its reaction products MVK + MACR are presented in Sect. 5.2. In addition, and for comparison with results of Spirig et al. (2005), the flux of the sum of monoterpenes is given. The intensity of segregation \(I_s\) is...
estimated for the sink reactions of OH with isoprene and the sum of monoterpenes in Sect. 5.3.

2.3 The covariance method

The covariance method determines terms like $w'\rho'_i$ in Eqs. (2) and (5), or $\rho'_i\rho'_j$ in Eq. (6). As discussed in Appendix A, the fluctuations $\varphi'(x)$ of quantity $\varphi(x)$ (wind component or partial density) from a mean $\overline{\varphi}(x)$ at a point with the coordinate $x$ are given by $\varphi'(x)=\varphi(x)-\overline{\varphi}(x)$. The mean value $\overline{\varphi}(x)$ is obtained by averaging $\varphi(x)$ over a sufficiently long time period (e.g. Lippmann, 1952; Stull, 1988). Therefore, the covariance for equidistant values of $w$ and $\rho_i$ (i.e. with constant time step $\Delta t$) is given by Eq. (7)

$$w'\rho'_i = \frac{1}{N} \sum_{k=1}^{N} (w_k-w)(\rho_{i,k}-\rho_i)$$

$N$ is the number of data points with distance $\Delta t$ in the integration interval $\Delta=N\cdot\Delta t$ with the common range $600 \leq \Delta \leq 3000$ s (e.g. Lenschow and Hicks, 1989; Beier and Weber, 1992). The coordinate system is given according to the definition of a flux as a quantity transported normal to the Earth surface (e.g. Stull, 1988; Sun, 2007) by the vertical axis parallel to the geopotential and the other axis with a right handed geographic coordinate system ($x=W-E$ component, $y=S-N$ component). In terms of Sun (2007), these are the local Earth coordinates (LEC).

3 Experimental

3.1 General description

The ECHO 2003 intensive field campaign was performed from 17 June to 6 August. Three towers were installed in a mixed deciduous forest with dominating tree species
beech, birch, oak and ash, and a mean canopy height $h_c=30$ m. The vertically integrated one-sided leaf area index in a radius of 50 m around the main tower varied between 5.5 and 5.8. The main tower and the west tower were aligned parallel to the main wind direction (Schaub, 2007). This, for example, allowed to investigate the influence of the spatial distribution of BVOC-sources (isoprene, monoterpenes) on measured fluxes (e.g. Spirig et al., 2005). The flux measurements reported in the present paper were obtained on 25 July, 09:00 to 15:00 CET on the main tower. The main tower with a height of 41 m, and the upper measuring platform at 36 m, was equipped with 9 sonic anemometers/thermometers (METEK, instrument type: USA-1; time resolution 10 Hz) between 2 m and 41 m, and 8 psychrometers (dry and wet bulb temperatures) at the same heights except 41 m. Radiation quantities and photolysis frequencies were obtained by radiometers directly above the canopy ($h_c=30$ m) (Bohn et al., 2004, 2006a, b). OH and HO$_2$ radical concentrations were measured by LIF (Holland et al., 1995, 2003) on a vertically movable platform, which was positioned above the canopy, with the inlet at 37 m height (Kleffmann et al., 2005). A PTR-MS instrument for measurement of isoprene, monoterpenes, MVK and MACR was installed at the ground, using a sampling line to collect air at the height of the ultrasonic anemometer (Ammann et al., 2004; Spirig et al., 2005). The distance of the inlets of the PTR-MS and LIF instruments from the ultrasonic-anemometer measuring volume were 0.45 m and 0.6 m, respectively. This spatial arrangement requires corrections to the calculated fluxes as is outlined below. For all aspects identical to the procedures as applied by Spirig et al. (2005), we refer to their work. Aspects which we handled in a different way are described in more detail in the following. The mean meteorological conditions above the canopy are given in Figs. 1–3 together with the friction velocity as a measure of turbulence.

### 3.2 Operation of PTR-MS instrument

The principle operation of the PTR-MS follows the procedures as given by Ammann et al. (2004) and Spirig et al. (2005). Air was pulled through an inlet of a tube down
to the ground where the PTR-MS was installed in a field laboratory-container. The ion masses (m) at m 69 (isoprene), m 71 (sum of MACR and MVK) and at m 137 (and m 81) (sum of monoterpenes) together with m 21 (H$_3$O$^+\cdot 18$) were recorded in an alternating cycle. The measuring cycle is, therefore, comparable to the cycle given by Spirig et al. (2005) in their Fig. 2. The single ion masses are recorded with 0.2 Hz other than by Spirig et al. (2005) with about 0.3 Hz. The dwell times are 0.1 s for primary ions and 0.75 s for the other masses, somewhat larger than the 0.5 s by Spirig et al. (2005) in their Fig. 2. This modification enhances the detection limit by about 23%. For calibration during the complete campaign, gas standards for methanol, ethanol, acetone, acetaldehyde, isoprene and $\alpha$-pinene from Apel-Riemer, Environmental Inc., Denver, CO, USA were applied. The detection limits (S/N=2) on 25 July 2003 were 42 pptv (m 69), 38 pptv (m 71), and 70 pptv (m 137). The zero point was determined every hour. Other operational parameter were fixed as given by Spirig et al. (2005) in their Table 1 for the main tower also, with a total residence time of the sample gas from the inlet tube (at 37 m height) to the drift tube of the PTR-MS at ground level of about 1 sec.

### 3.3 Operation of LIF instrument

The LIF instrument of Forschungszentrum Jülich was a newly built instrument based on the well established concept used previously by the same group (Holland et al., 1995, 2003). The new instrument was designed to be smaller and more light-weight than the previous instrument, making the instrument suitable for tower based application (e.g. Kleffmann et al., 2005). The radicals are sampled by expansion of ambient air through an inlet nozzle into a low pressure chamber, where OH is detected by LIF at 308 nm. HO$_2$ radicals are monitored in a separate detection chamber, in which HO$_2$ is first chemically converted to OH by reaction with NO, followed by LIF detection of OH. The OH fluorescence is excited by a pulsed narrow-bandwidth UV laser system (DPSS Photonics DS20-532; dye laser LAS Intradye) at a repetition rate of 8.5 kHz and is detected by gated photon-counting after each laser pulse. The laser can be tuned
on- and off-resonance to distinguish the OH fluorescence signal from non-resonant background signals (Hofzumahaus et al., 1996). Calibration is performed by known amounts of OH radicals which are generated by photolysis of water vapor at 185 nm (Holland et al., 2003).

The LIF instrument signals were obtained in the following way. The on-resonance signals contain contributions from (1) the laser-power dependent OH fluorescence, (2) laser dependent straylight, (3) a negligible dark signal of the fluorescence detector, (4) scattered solar radiation entering the entrance nozzle, and (5) a contribution from an ozone interference equivalent to the signal of $3 \times 10^5$ OH cm$^{-3}$ per 50 ppbv O$_3$. The signal components (1)–(5) for on-resonance are detected in a time window of 500 ns after each laser pulse. The signal contributions (3) and (4) are independent of the laser pulse and are detected with a time delay of 25 $\mu$s in a second time window of 25 $\mu$s. The difference from both time windows (normalized and projected to the 500 ns window) is the laser dependent signal (cts) being corrected for the influence of scattered sunlight. It is then normalized to the voltage signal (V) of a UV sensitive photodiode which monitors the laser power. The normalized signal is integrated over successive laser pulses for a time period of seconds to improve the signal-to-noise ratio.

The off-resonance signals contain contributions from (2)–(4) and are treated in the same way as on-resonance signals, in order to correct for solar background and possible laser-power variations. The difference between the normalized on- and off-resonance signals (Fig. 4) is only caused by fluorescence of the radicals and is transformed to concentrations by calibration (Fig. 5). Normally, the LIF instrument is operated in an alternating on- and off-resonance mode with equal integration times, leading to a typical detection limit (S/N=2) of about $5 \times 10^5$ OH cm$^{-3}$ for 30 s on- and off-resonance each. For the flux measurements on 25 July, however, each on-resonance period lasted for nearly one hour during which the normalized signals (cts/V) were integrated over 3 s with a total time step of 5 s, leading to a signal collection frequency of 0.20 Hz. After each on-resonance period, the background signal and laser wavelength stability were controlled. For this purpose the complete OH line profile and the
off-resonance background were scanned repeatedly (3–4 times) in about 6–7 min, before a new on-resonance period was started. Therefore the resulting time series of OH and HO₂ concentrations (Fig. 5) and of second order moments in the following figures exhibit gaps during the time intervals when the calibration procedures were performed.

Measurements of HOₓ were obtained during the following time blocks: 09:34–10:18, 10:25–11:30, 11:37–12:33, 12:39–13:38, 13:44–14:19 CET. Figure 4 shows the time series of sunlight-corrected and normalized on- and off-resonance signals (cts/Vs) with the photodiode signal in the range of 2–3 V. The OH signals are between about 1–15 cts/Vs with a background mean of 0.63 cts/Vs (standard deviation =1.1 cts/Vs). The HO₂ on-resonance signals reach maximum values of about 550 cts/Vs with a mean background of 31 cts/Vs (standard deviation =2.5 cts/Vs). The resulting detection limits (S/N=2) for the OH and HO₂ data in Fig. 5 are 3×10⁶ cm⁻³ and 8×10⁶ cm⁻³, respectively.

A statistical Z-test (Sachs and Hedderich, 2006) is applied to both data sets to estimate if the variability of the signals (Figs. 4 and 5) is influenced by the precision of measurements. For this purpose the deviations of signals from their mean of consecutive 10 min intervals are considered for a confidence level of α=0.05 (e.g. there is only a chance of rejecting the null hypothesis by 5%). For HO₂ the observed variability for the whole time period from 09:00–15:00 CET appears to be mainly real and not influenced by noise. For OH only about one third of the intervals fulfil this criteria with α=0.05. For α=0.15 in 88% of the 10 min-intervals the variability of the signals appears to be real and not caused by the precision of the measurements. These criteria are more restrictive than the determination of the standard error ∆a (Fig. 5) which shows that ∆a(OH) and ∆a(HO₂) are well below 10% of their specific mean concentrations. Therefore one should be aware that for the further analysis and discussion, the resulting HO₂ fluxes can be considered to be quantitative, while part of the calculated OH fluxes is still influenced by measurement precision.

For the consideration of segregation it is important to note that a time resolution of 0.2 Hz was chosen, which allowed to apply the same procedures of time series analysis
3.4 Operation of sonic anemometer

The METEK USA-1 sensor at 37 m height was installed as near as possible to the inlets of the PTR-MS and LIF instruments (0.45 m away from the PTR-MS and 0.6 m away from the LIF inlet). The raw data also contain the exact time stamp, therefore, even small delays in each individual signal could be corrected (Sect. 3.5). The three wind vector components \((u, v, w)\) and the sonic temperature \((T_s)\) were recorded with 10 Hz and post processed together with the data from PTR-MS and LIF. A 3-D sensor correction based on detailed measurements in a wind tunnel of the Meteorological Institute, University Hamburg, Germany was applied to correct wind vector components raw data for the influence of flow distortion. The influence of this correction for the wind vector components \(u\) and \(v\) is below 1.5%, but up to 18% for the vertical wind component \(w\). Before the application of this correction, the inclination of the axis of each sonic against the geopotential is corrected better than 0.5° by use of inclinometer data, which is a prerequisite to apply LEC for analysis of turbulence signals (Beier and Weber, 1992; Foken et al., 1995; Sun, 2007).

3.5 Application of the covariance method

Every turbulent time series of wind vector components, temperature, humidity and trace substances show time dependent trends of their means over each integration interval \(\Delta\), which have to be eliminated to calculate covariances according to Eqs. (5)–(7). Thus, a low frequency instationarity is separated from a higher-frequency turbulence. In our analysis, the trend correction for 1 min up to 10 min data is performed by a cubic polynom, while for the 30 min data a symmetric linear Savitzki-Golay low pass filter signal (Press et al., 2001) is subtracted from the initial data set. This net signal is added to the arithmetic mean. This procedure minimizes the resulting residuum even better than linear detrending, while the mean value is conserved. A corresponding
test for stationarity with consecutive 2min samples within Δ=10 min and 5 min samples within Δ=30 min as described by Foken et al. (1995) shows that all covariances fulfilled a criterion 0.8<(\overline{w_i' \rho_i'}_{2\text{min}})/(\overline{w_i' \rho_i'}_{10\text{min}})<1.2 for stationarity. This is even stronger than the 30% criterion for Δ=30 min which is often applied (e.g. Spirig et al., 2005; Farmer et al., 2006).

The calculation of turbulent and micrometeorological mean quantities is performed in the following way. After applying the trend correction, the first to fourth moments were calculated for fixed time intervals of 1min, 5 min, 10 min, and 30 min. The resulting covariances (fluxes) are given by Eq. (7). All moments and related quantities like turbulence intensities, wind vector, friction velocity $u_*$ or Monin-Obukhov length $L_*$ were calculated in the LEC (Sect. 2.3) and the so-called natural coordinate system ($y_n$-axis orthogonal to the $x_n$-axis; $y_n$-axis parallel to the Earth surface; $z_n$-axis orthogonal on the $x_n$–$y_n$ plane). The sensible heat flux is obtained by calibration of $T_s$ against the data obtained from ventilated psychrometers and the application of a procedure as described by Schotanus et al. (1983). An ogive analysis (Oncley, 1989; Beier and Weber, 1992) was added as a quality test for the convergence of the covariance function for each time interval to compare also with data obtained by Spirig et al. (2005). Their spectral correction to the time series to introduce contributions from higher frequencies above 0.20 Hz to fluxes $(\overline{w_i' \rho_i'})$ of trace substances is not applied in our analysis. Instead flux sampling errors related to the separation of measuring volumes of sensors, their response time and the length of the sampling interval $\Delta$ were estimated as discussed in the following.

In general, signals from the sonic anemometer and gas analyzers like the LIF or PTR-MS instrument are not in coincidence although they were registered with computer systems synchronized by one clock. The time shift relative to the time steps of the sonic anemometer are caused by the time an air parcel needs to move from the measuring volume of the sonic anemometer to the gas analyzer inlets at 37m height (see Sect. 3.1) and in the case of the PTR-MS, the additional transport time of the air sample through tubing to the PTR-MS instrument at ground level. To correct for these time shifts, the
covariance between $w$ and $\rho_i$ is calculated versus lag time between $w$ and $\rho_i$ according to Eq. (7). The maximum $(w\rho')_{\text{max}}$ of the covariances is taken as the eddy correlation flux in each time interval $\Delta$ and for each channel of the instruments as performed also by Beier and Weber (1992), Oncley (1989), Spirig et al. (2005) and Farmer et al. (2006).

The spatial separation of a chemical sensor inlet from the measuring volume of the sonic anemometer causes a flux reduction at the high frequency part of the turbulence spectrum (Moore, 1986). This is most pronounced for frequencies $f > 0.2$ Hz, the limits given by the conditions to run the PTR-MS and the LIF. Using the spectral transfer function of Moore (1986), a maximum loss of 13% for $w'\rho'$ compared to instruments which sample from the same volume and with 10 Hz is estimated independently of the specific characteristics of the instruments. As discussed by Spirig et al. (2005), for the ECHO site the long sampling tube also contributes to the damping of amplitudes for frequencies larger than about 1.5 Hz.

In 2003, both chemical sensors (PTR-MS, LIF) had characteristic response times $\tau_r$ with respect of a sudden stepwise increase of concentrations at the inlet of $\tau_r = 0.3$ s and $\tau_r \leq 0.01$ s, respectively. Horst (1997) estimated that instrumental time constants cause a reduction of the measured flux $F_i$ compared to the true flux $F_t$ measured by an ideal instrument with $\tau_r = 0.0$ resulting in $F_i/F_t < 1$. Horst (1997) showed that the knowledge of the frequency $f_m$ taken at the maximum of the frequency-multiplied cospectrum and $\tau_r$ are sufficient to estimate $F_t$. Applying this method with $f_m \approx 0.018$ Hz and the maximum response times $\tau_r = 0.3$ s (PTR-MS) and $\tau_r = 0.01$ s (LIF), the fractions $F_i/F_t \approx 0.95$ for the fluxes of BVOCs and $F_i/F_t \approx 1.0$ for the fluxes of HO$_2$ or OH are estimated. These fractions agree with data obtained by Farmer et al. (2006) for their determination of fluxes of reactive nitrogen compounds with thermal-dissociation laser induced fluorescence (TD-LIF).

In general, the sampling interval $\Delta$ of 10 min is not long enough to capture all contributions to the covariance from all frequencies. In addition, both chemical sensors are limited to signals with frequencies below 0.20 Hz. This limitation of the sampling interval $\Delta$ causes an increasing fractional flux sampling error, which can be estimated
by the quotient of the variance $\sigma_F$ and the flux $F_i$. It can be expressed by Eq. (8) as given by Lenschow (1995):

$$\frac{\sigma_F(T)}{|F_i|} = \left(\frac{2\tau_F}{T}\right)^{1/2} \left(\frac{1+r_{wc}^2}{r_{wc}^2}\right)^{1/2}. \quad (8)$$

There, $\tau_F$ is the integral timescale of the flux estimated from the spectra of $F_i$ by Lenschow et al. (1994) or the autocorrelation function by Kaimal and Finnigan (1994), and $r_{wc}$ is the correlation coefficient between $w$ and $\rho_i$ for the adjusted time series with $F_i=(w'\rho_i')_{\text{max}}$. Farmer et al. (2006) calculated fluxes of reactive nitrogen compounds and errors for their TD-LIF instrument by this method and could also specify the minimum detectable fluxes. Finkelstein and Sims (2001) compared the results from Eq. (8) with their own and other formula and showed that in general Eq. (8) is a reliable estimation for unstable and neutral conditions, although – for example – Eq. (8) tends to possibly underestimate the fractional flux sampling error by about 25% for the sensible heat flux. A possible overestimation up to about 30% is reported for the fluxes of $\text{H}_2\text{O}$ and $\text{CO}_2$ (Finkelstein and Sims, 2001). Note that $(\sigma_F/F_i)$ increases with increasing $\tau_F$ and decreases with increasing $r_{wc}$. On the basis of earlier measurements at this site, an estimation of this fractional flux sampling error is given and compared to results obtained during ECHO 2003 in Sect. 5.2. Note that all fluxes in this paper are given without correction for this systematic error.

4 Data analysis

The first to fourth moments (mean, variance, skewness, kurtosis) (Figs. 5 and 6) are calculated for the three wind vector components, the temperature as well as isoprene, MVK + MACR, monoterpenes, OH and $\text{HO}_2$ together with their mixed moments (second to fourth order) according to Beier and Weber (1992), Foken et al. (1995) and Cava et al. (2006). For the present discussion, second moments are of special interest,
i.e. variances and covariances according to Eq. (7) like the local vertical flux densities $w'\rho'_i$ ($w',\rho'_i =$ fluctuation of vertical wind velocity $w$ and mixing ratios $\rho_i$ of trace gas compound $i$), the correlation $T'\rho'_i$ between temperature $T$ and $\rho_i$, and of trace gas compounds $i, j$ in $(\rho'_i \rho'_j)$ according to Eq. (6). $T'\rho'_i$ describes the local correlation between the temperature and partial densities of trace compounds, which may give hints towards the spatial distribution of their sinks and sources. The covariance $\rho'_i \rho'_j$ (or its normalized value $I_s = \frac{\rho'_i \rho'_j}{\overline{\rho_i} \cdot \overline{\rho_j}}$) indicates how well the gaseous compounds are mixed (e.g. Verver et al., 2000; Vinuesa et al., 2005; Ebel et al., 2007). Note that in all calculations of covariances, BVOCs are specified in units of mixing ratios (ppbv) and radicals in units of number densities (cm$^{-3}$).

5 Results

5.1 Mean values and higher moments

The time period between 09:00 to 15:00 CET on 25 July 2003 was characterized by cloudy conditions (Fig. 1) with a moderate horizontal wind velocity variation (Fig. 3) and slightly unstable to neutral stratification above the canopy. The broken clouds caused significant fluctuations of all radiation quantities above canopy, as is shown for the net radiation, $Rn$, and $J(O^1D)$ in Fig. 1. The air temperature $T$ increased from 19°C to 26.5°C, while the specific humidity $q$ increased only slightly from 09:00 to 12:00 CET up to about 9.5 g kg$^{-1}$ and then decreased to about 8 g kg$^{-1}$ (Fig. 2). The variability of solar radiation is reflected in the correlated low-frequency variations of OH on a time scale of 10 min to 30 min (Figs. 4 and 5), which can be explained by the primary, photochemical production of OH (Kleffmann et al., 2005). The measured HO$_2$ behaves differently compared to OH (Fig. 5) and increases stepwise following the temperature record (Fig. 2). Temperature ramp-like structures (Figs. 2 and 6b) occurred after 09:30 CET, when net radiation peaked (Fig. 1) and wind turned to a sector from SW to SE, in parallel to maxima in HO$_2$ (Fig. 5b) and isoprene (Fig. 6c). The arithmetic
mean values of the ratio (MVK + MACR)/isoprene = 0.52 at 09:00–12:00 CET and 0.26 at 12:00–15:00 CET hint towards a changing influence of photochemical processes and advection, but are at the upper end of data obtained at daytime by Schaub (2007) and Spirig et al. (2005). Following the discussion by Schaub (2007), this result suggests that the residence times of BVOCs in CA are larger than 20 min.

Most data points of the OH and HO₂ concentrations are within the ±2σ interval and are above the detection limits given in Sect. 3.3 (Fig. 4). For both radicals, the standard error Δa is below 10% of their arithmetic means and the relation σₓ/⟨x⟩<0.42 holds for each 10 min interval. The latter relation suggests also that Taylor’s hypothesis is valid for these chemical species (Stull, 1988). Skewness (Sk) as well as kurtosis (Kur) point towards near normally distributed data with Sk≈0 and Kur≈3 (Fig. 5a, b). This is not the case for J(O¹D) which shows a significant deviation from the characteristics of a normal distribution. The covariance between J(O¹D) and OH is always positive with only small correlation coefficients, r≤0.5, and even two intervals with r≈0 on a time scale up to 10 min (Fig. 8). This is in contrast to the lower-frequency OH variations occurring on a time scale of 10 min to 30 min, which are well correlated with J(O¹D) (cf. Figs. 1 and 5a). The low correlation of OH and J(O¹D) for the shorter time periods is partly caused by instrumental noise and possibly by fast OH variations as a result of fluctuations of OH precursors and reactants.

Other quantities like vertical wind velocity w (Fig. 6a), temperature T (Fig. 6b) and organic compounds (Fig. 6c–e) mainly show a different statistical behaviour with respect to the higher moments Sk and Kur. Most of the w data are still near normally distributed, but occasionally show values with Kur≥4. Temperature data show Sk>0 until about 13:40 CET, with a number of events with Kur>4. This hints towards a more peaked distribution than a normal distribution in atmospheric turbulence (Hollinger and Richardson, 2005), but with a large number of data points (Sk>0) smaller than the arithmetic mean, especially for T until 13:40. Comparable results with Sk>0 are obtained for BVOCs with more data points smaller than the arithmetic means and even more peaked distributions (Kur>4) during some periods. The third and fourth moments...
Sk > 1 and Kur > 4 are found only in time intervals with lower mixing ratios. Comparing the statistics for \( w \) and trace substances in most 10 min intervals, the small values below the mean occur simultaneously. Therefore, according to Eq. (7), the covariances between \( w \) and \( \rho_i \) (respectively the mixing ratio \( c_i \)) are also expected to be small for most 10 min intervals, which is confirmed in Figs. 7 and 9. Note that homogeneously mixed conditions are characterized by \( Sk \approx 0 \) and \( Kur \approx 3 \) (e.g. Warhaft, 2000). Therefore, one might also expect some deviation of the segregation term in Eq. (6) from \( I_s = 0 \), at least for the system OH + isoprene (see Sect. 5.3).

### 5.2 Covariances and fluxes

The fluxes of isoprene, the sum of monoterpenes, MVK + MACR, OH and HO\(_2\) are given for 10 min averaging time in Fig. 7 together with the sensible heat flux. The precisions of the fluxes are 24–30\% for OH and HO\(_2\), and about 14\% for BVOCs. During the slightly unstable to neutral stratified period of this day, characterized by negative values of \( L^* \), the sensible heat flux is mainly directed upwards. Significant emission fluxes of BVOCs are found only around noon reaching maximum values of 0.2 ppbv ms\(^{-1}\) (0.56 µg m\(^{-2}\) s\(^{-1}\)) for isoprene, 0.04 ppbv ms\(^{-1}\) (0.22 µg m\(^{-2}\) s\(^{-1}\)) for monoterpenes, and 0.024 ppbv ms\(^{-1}\) (0.07 µg m\(^{-2}\) s\(^{-1}\)) for MVK + MACR. These values are about 20\% larger than the corresponding noontime values for isoprene and monoterpenes reported by Spirig et al. (2005) for the same measurement site on 17 July 2003, a day with comparable meteorological conditions. Unlike in the present work, Spirig et al. (2005) applied a spectral loss correction in the high-frequency range. If such a correction would be applied to our data, a systematic increase of the specific fluxes of 20\%–38\% would result at the main tower (Table 1). The error analysis in Sect. 3.5 shows that the loss of higher frequencies in the flux calculation is the largest contribution to the total underestimation of fluxes \( F_i \). Given \( \tau_F \approx 2 \text{s} \), the error calculated by Eq. (8) yields a systematic mean underestimation of fluxes by 23\% for isoprene, 33\% for monoterpenes and 35\% for MVK + MACR (Table 1). For OH and HO\(_2\) the fluxes are underestimated by 37\% and 31\%, respectively for the period 09:00–15:00 CET, which
is mainly caused by the correlation coefficients in the range of $0.2 < r_{wc} < 0.4$.

The fractional flux sampling errors can be compared with those calculated from data given by Spirig et al. (2005). For example, for $\tau_F = 2$ s and $r_{wc} = 0.2$ at mass 33 (ethanol) in their work, a value $(\sigma_F/F) \approx 41.6\%$ is obtained. For $\tau_F = 2.5$ s and $r_{wc} = 0.4$ at mass 69 (isoprene), the fractional flux sampling error is about $(\sigma_F/F) \approx 22\%$. Therefore, even with a configuration of instruments which only detect signals below about 0.25 Hz (Spirig et al., 2005) a reliable estimation of the flux can be performed. This result is also valid for our configuration during ECHO 2003 when we used the sonic anemometer together with the LIF and the PTR-MS (Sects. 2.3, 3.1–3.5) at a limiting frequency of 0.20 Hz. A corresponding analysis was also performed for the sensible heat flux $H$ at $z/h_c \approx 1.23$ by comparing 10 Hz flux data and filtered 0.20 Hz data. At a measuring height of 37 m, the filtered data are only 14% lower than the 10 Hz data, which is comparable to the maximum loss of about 13% expected by Moore’s spectral correction.

Although OH is considered to be a short-lived compound, statistically significant fluxes have been detected above canopy top. The direction of the fluxes is downward and the maximum amount is $1 \times 10^6$ cm$^{-3}$ ms$^{-1}$ at 12:00 CET (Fig. 7). The flux direction is plausible since the canopy is a source of BVOCs including isoprene and monoterpenes, which react easily with OH. The measured fluxes of HO$_2$ are larger than of OH. They were mostly directed upwards, reaching a maximum amount of $1 \times 10^7$ cm$^{-3}$ ms$^{-1}$, but partly also downwards with a maximum amount of $7 \times 10^6$ cm$^{-3}$ ms$^{-1}$. The predominant upward direction points to a significant source of HO$_2$ in the canopy, where HO$_2$ is likely produced by reaction of OH with freshly emitted BVOCs.

Additional information can be obtained from the covariances of the trace substances and temperature (Fig. 9), which show that whenever heat is transported upwards (positive values of the sensible heat flux), the same behaviour is found for BVOCs and in most cases for HO$_2$. However, fluctuations of OH and temperature are always negatively correlated (Fig. 9) and positive (upward) sensible heat fluxes are found in parallel to negative (downward) OH fluxes (Fig. 7). The correlation with the sensible heat flux
can be explained by the fact that the surfaces of leaves near canopy top are heated by solar radiation. This effect stimulates BVOC emissions from the leaves and, simultaneously, causes upward transport of air which is in contact with the canopy.

The specific turbulent flow characteristics near the upper part of a forest occasionally allow for downward transport by gusts against a mean concentration or temperature gradient (e.g. Raupach et al., 1996; Cava et al., 2006; Zelger et al., 1997). This results in negative fluxes over the duration of ten minutes averaging time. A first application of the quadrant analysis for momentum, heat and mass transport as proposed by Katul et al. (1997) shows that the negative fluxes of HO\textsubscript{2} were found during periods when sweeps (downdrafts) dominated the turbulent transport.

Following the measuring concept according to Eq. (5), chemical sinks $S_i$ or sources $Q_i$ in the atmosphere may contribute to the turbulent net flux at measuring height $z_R$. Isoprene is locally emitted from the canopy and has no chemical source in the atmosphere above the canopy. The reaction with OH is the dominant chemical sink during daytime. Therefore the isoprene flux at height $z_f$ (canopy) should be compensated by the sum of its flux measured at height $z_R$ and its chemical sink by reaction with OH. The chemical sink term, calculated from the measured concentrations of OH and isoprene and their reaction rate constant ($1 \times 10^{-10}$ cm$^3$ s$^{-1}$; Atkinson et al., 2006), varies from $1.4 \times 10^{-4}$ ppb s$^{-1}$ up to $7.7 \times 10^{-4}$ ppb s$^{-1}$ (11:00–13:00 CET). This is equivalent to fluxes of $1.4 \times 10^{-4}$ ppb ms$^{-1}$ up to $7.7 \times 10^{-4}$ ppb ms$^{-1}$ over a height interval of one meter at the measuring level. This is much less than the correspondingly measured fluxes of isoprene in the range of 0.02–0.2 ppb ms$^{-1}$ (Fig. 7).

For OH the situation is reversed: the maximum amount of downward flux ($1 \times 10^6$ cm$^{-3}$ ms$^{-1}$) is only about 11% of the chemical sink term for OH + isoprene, if a 1m layer is assumed. Since OH is also significantly consumed by reactions with other trace gases (CO, NO$_2$, monoterpenes, OVOCs etc.), direct transport of OH plays no large role for the local OH budget at height $z_R$. The main chemical sink for HO$_2$ is given by the reaction HO$_2$+NO. With NO mixing ratios in the order of 0.2–0.5 ppb (Schaub, 2007), the chemical loss term is in the range of $(0.4–1.6) \times 10^7$ cm$^{-3}$ ms$^{-1}$
at a layer thickness of 1 m. The HO$_2$ fluxes (Fig. 7) are therefore in the order of the chemical loss term if a 1 m layer is assumed at $z_R$.

During this short measuring period of six hours, the ratio MVK + MACR/isoprene is in the order of about 0.2 to 0.5 for mixing ratios (Fig. 6) and about 0.07 to 0.20 for the corresponding fluxes (Fig. 7). A normalization of fluxes by mean mixing ratios yields effective transfer velocities at the height $z_R$ of the measurements. The resulting values vary in the range of $-0.02$ to $+0.3$ ms$^{-1}$ for isoprene, $-0.05$ to $+0.12$ ms$^{-1}$ for monoterpenes, $-0.02$ to $+0.1$ ms$^{-1}$ for MVK + MACR, $-0.14$ to 0 ms$^{-1}$ for OH, and $-0.02$ to $+0.06$ ms$^{-1}$ for HO$_2$, with a negative sign resulting from downward fluxes (Fig. 7). The negative values of local transfer velocities are larger than experimentally determined deposition velocities of many trace gases (e.g. Lenschow and Hicks, 1989).

### 5.3 Segregation

Inhomogeneously mixed concentration fields can be found near emission sources (e.g. Komori et al., 1991; Krol et al., 2000; Wahrhaft, 2000), or under the influence of nonlocal intermittent transport of fluid elements, for example in the ML above a forest and in the CA (e.g. Raupach et al., 1996; Wahrhaft, 2000), and also if convection (e.g. Cava et al., 2006; Verver et al., 2000) suppresses instantaneous mixing (Ebel et al., 2007; Vinuesa, 2005; Vila-Guerau de Arellano, 2005). Among the BVOCs measured at the ECHO field site, isoprene has the largest OH reactivity, because its reaction rate constant and its mean concentration are both larger than of the sum of monoterpenes, assuming a homogeneous, well mixed condition with $I_s \equiv 0$. The analysis using the 0.2 Hz time series shows that the segregation term $I_s$ for the reaction OH + isoprene reaches values (Fig. 10), which are above the significance level of $I_s = -0.03$ valid for isoprene and monoterpenes. Thus, at measuring height, isoprene and OH react slower with each other up to 15% than for homogeneously mixed conditions. The reaction rate for monoterpenes is less influenced under these conditions and is reduced at most by 5%. If a correction for high frequencies is applied to the times series as proposed by Spirig et al. (2005), this would not significantly change these results.
The maximum reduction by 15% of the reaction rate of isoprene + OH is of similar size as the experimental value of 13% reported by Butler et al. (2008) for the mixed layer over the tropical forest at Guyana. Butler et al. (2008) calculated their value from concentrations of isoprene and OH that were measured with time resolutions of 2 s and 5 s, respectively, on board an aircraft in October 2005. They discuss that the spatial segregation effect was probably larger and not fully resolved by their measurements because of the fast flight speed of the aircraft. When using a global chemistry climate model, they require an effective reduction of the isoprene + OH reaction rate by 50% to explain the observed isoprene concentrations by their global model. For comparison, Krol et al. (2000) estimated that the destruction of surface-emitted hydrocarbons by OH may be slowed down by segregation up to 30% in the convective boundary layer. In the present work, the measured segregation effect is smaller despite the large heterogeneity expected in close proximity of the isoprene emitting canopy.

Further analysis shows that the covariance and the correlation coefficient between isoprene and monoterpenes are positive or zero. The correlation coefficient between OH and HO₂ is always near zero and shows only two exceptions. One negative value ($r = -0.29$) is encountered during the time period when the maximum OH concentration is reached (12:15–12:30 CET) and $r(OH, J(O^1D))$ is small, and one positive value ($r = 0.32$) near 13:30 CET when both radicals have concentration maxima and $J(O^1D)$ and $r(OH, J(O^1D))$ are near maximum values.

6 Summary

The covariance method was applied for the first time to determine eddy fluxes of OH and HO₂, as well as segregation of OH and BVOCs (isoprene, monoterpenes) closely above a mixed deciduous forest. The covariance products were calculated for 10 min intervals from radical measurements performed by LIF, from BVOC measurements recorded by PTR-MS, and vertical wind from a sonic anemometer. All instruments were operated simultaneously at 7 m above the forest canopy, which had a height of...
30 m above ground, during the intensive field campaign ECHO 2003 in Jülich, Germany. Accuracy and precision of the covariances were mainly limited by the spatial separation of the measurements and the sampling frequency (0.2 Hz) of the LIF and PTR-MS instruments. The calculated fluxes of OH and HO₂ have precisions between 24%–30% and are systematically underestimated on average by about 37% and 31%, respectively. Though these errors are not small, the results of this first attempt to estimate covariance products of short-lived radicals are very promising. OH was found to be transported mainly in the direction of chemical sinks, while HO₂ is transported upwards from the canopy to the overlaying atmosphere. The upward directed HO₂ transport is well correlated with the upward sensible heat flux, while the local OH flux is anticorrelated with the sensible heat flux. An analysis of the segregation term points to processes which cause inhomogeneous mixing of isoprene and OH near the canopy top, reducing the effective reaction rate up to 15%. Segregation for OH and the sum of monoterpenes played an almost insignificant role (<5%) during this case study. Significant upward directed fluxes of isoprene and its photochemical oxidation products MVK and MACR were determined. The observations support the hypothesis that inside the canopy atmosphere, a significant amount of BVOCs can be chemically transformed and reaction products like HO₂ and MVK + MACR are emitted into the adjacent atmosphere. The present study suggests that the vertical flux and segregation effect had a notable, but relatively small effect on the local budget of OH at the chosen measurement position. The situation may be different at other locations of the forest, which had an inhomogeneous distribution of different tree species, as well as inside and below canopy where vertical gradients of HOₓ were observed. Further studies using highly time resolved LIF measurements at different positions in a forest stand are required to improve the knowledge of the size and extent of these processes. If applied in further experiments, smaller distances of the measuring volumes of instruments would ensure a significant reduction of the systematic underestimate of covariances. An analysis of the impact of the reported results on the local photochemistry and on modelled HOₓ concentrations is subject of a forthcoming publication.
Appendix A

Mathematical background

The basic concept how to perform measurements in the atmospheric flow above the Earth surface is derived from the local mass balance equation for the $i^{\text{th}}$ constituent (e.g. de Groot and Mazur, 1969; Businger, 1986; Kramm and Meixner, 2000; Kramm et al., 2008) per unit volume for a macroscopic flow. This reads

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{v} + \mathbf{J}_i) = Q_i - S_i.$$  \hspace{1cm} (A1)

Here, the term $\partial \rho_i / \partial t$ is the local derivative of the partial density $\rho_i$ with respect to time, $\mathbf{v}$ is the vector of the barycentric velocity (here the wind vector), $\mathbf{J}_i = \rho_i (\mathbf{v}, \mathbf{v})$ is the diffusion flux density (hereafter, a flux density is simply denoted as a flux), $\mathbf{v}_i$ is the individual velocity, and $\nabla$ is the nabla or del operator expressed, for instance, in Cartesian coordinates by $\nabla = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z}$, where $i$, $j$ and $k$ are the unit vectors in west-east (x), south-north (y), and vertical (z) direction, respectively. Furthermore, $Q_i$ represents the sources and $S_i$ the sinks of matter in the fluid due to chemical reactions and/or phase transition processes. Note, an emission or deposition enters into Eq. (A1) by boundary condition. Moreover, the quantities $\rho_i \mathbf{v}$ and $\mathbf{J}_i$ are frequently called the convective and nonconvective transports of matter, respectively. Summing Eq. (A1) over all substances from $i=0, \ldots, k$ leads to the macroscopic balance equation for the total mass per unit volume customarily called the equation of continuity (e.g. Landau and Lifshitz, 1959),

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0.$$  \hspace{1cm} (A2)

where the density of air is given by

$$\rho = \sum_{i=0}^{k} \rho_i$$  \hspace{1cm} (A3)
and the vector of the barycentric velocity by

\[ \mathbf{v} = \frac{1}{\rho} \sum_{i=0}^{k} \rho_i \mathbf{v}_i. \]  

(A4)

The local mass balance equation for a turbulent flow Eq. (2) can be derived by using Reynolds’ averaging calculus, i.e. decomposition of any instantaneous field quantity \( \varphi(r) \) like \( \varphi_i(r) \), \( \varphi(r) \), and \( \mathbf{v}(r) \) by \( \varphi(r) = \bar{\varphi} + \varphi' \) and subsequent averaging according to (e.g. van Mieghem, 1949, 1973; Herbert, 1975; Kramm and Meixner, 2000; Kramm et al., 2008).

\[ \bar{\varphi} = \bar{\varphi}(r) = \frac{1}{G} \int_{G} \varphi(r, r') dG', \]  

(A5)

where \( \bar{\varphi} \) is the ensemble average of \( \varphi(r) \), and the fluctuation \( \varphi' \) is the difference between the former and the latter. Here, \( r \) is the four-dimensional vector of space and time in the original coordinate system, \( r' \) is that of the averaging domain \( G \) where its origin, \( r'=0 \), is assumed to be \( r \), and \( dG' = d^3 r' dt' \). The averaging domain \( G \) is given by \( G = \int dG' \). Hence, the quantity \( \bar{\varphi} \) represents the mean values of \( \varphi(r) \) for the averaging domain \( G \) at the location \( r \). Since \( \bar{\varphi} = \bar{\varphi} \) (e.g. van Mieghem, 1949, 1973; Herbert, 1975; Kramm et al., 1995), averaging the quantity \( \varphi(r) = \bar{\varphi} + \varphi' \) provides \( \varphi' = 0 \).

In accord with the ergodic theorem, ensemble average as expressed by Eq. (A5) may be replaced in practice by time average (Liepmann, 1952). But a basic requirement for using a time averaging procedure is that turbulence is statistically steady (e.g. Falkovich and Sreenivasan, 2006; Lumley and Panofsky, 1964; Tennekes and Lumley, 1972). Consequently, sophisticated procedures for identifying and eliminating non-stationary effects (trends) are indispensable to prevent that computed eddy fluxes of atmospheric constituents are notably affected by non-stationary effects. For our further considerations we suppose that steady-state conditions prevail, i.e. that any local derivative with
respect to time is considered as negligible. But this requires the application of the detrending method in the data analysis (see Sects. 3.5 and 4) to eliminate non-stationary contributions to flux densities \( F_i \) and other moments.

Applying Reynolds’ averaging calculus to Eq. (A1) yields Eq. (A6) respectively Eq. (2) (e.g. Businger, 1986; Kramm and Meixner, 2000; Kramm et al., 2008)

\[
\frac{\partial \rho_i}{\partial t} + \nabla \cdot \left( \rho_i \overline{v} + \rho'_i \overline{v'} + J_i \right) = Q_i - S_i. \tag{A6}
\]

For the equation of continuity we obtain

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot \left( \rho \overline{v} + \rho' \overline{v'} \right) = 0. \tag{A7}
\]

Within the framework of the Boussinesq approximation the term including turbulent fluctuations of \( \rho, \rho'v' \), is considered as negligible in comparison with the term \( \rho \overline{v} \) so that we have

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \overline{v}) \approx 0. \tag{A8}
\]

If we assume that Eq. (A2) or Eq. (A8) can be approximated by \( \nabla \cdot \mathbf{v} = 0 \) (the condition of an incompressible fluid), we will have \( \nabla \cdot \overline{v} = 0 \) and \( \nabla \cdot \mathbf{v}' = 0 \) (e.g. Landau and Lifshitz, 1959; Monin and Yaglom, 1971; Kramm and Mölders, 2005). As discussed in the text, if we further assume that the fields of the wind velocity and the partial densities of the atmospheric constituents are horizontally homogeneously distributed we will obtain Eqs. (2) and (4). As mentioned, from Eq. (4) we may infer that \( \overline{w} \) is constant with height. Since at any rigid surface \( \overline{w} \) is equal to zero, we may state that \( \overline{w} \) is generally equal to zero under the conditions that the fluid is incompressible and horizontally homogeneous. In a fully turbulent flow (but not at the boundaries) the diffusion flux of a gaseous entity can be neglected because \( |\rho'_i w'| \gg |J_{i,z}| \) and under these premises.
Eq. (3) amounts to Eq. (5) or Eq. (A9)

\[
\left( \rho_i' \bar{w}' + J_{i,z} \right)_{z=z_f} = \left. \left( \rho_i' \bar{w}' \right) \right|_{z=z_R} - \int_{z_f}^{z_R} \left( Q_i - S_i \right) dz.
\]  

(A9)

For this concept, the emission or deposition of trace substances is given by the boundary conditions at heights \( z = z_f \). Only in the case of long-lived gaseous species the second term of the right-hand side of Eq. (A9) can be neglected. Under these premises we obtain the so-called constant flux condition:

\[
\left( \rho_i' \bar{w}' + J_{i,z} \right)_{z=z_f} = \left. \left( \rho_i' \bar{w}' \right) \right|_{z=z_R}.
\]  

(A10)

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Table 1. Mean percentage underestimation of fluxes for different compounds. In addition the minimum and maximum values for the measuring period 09:00–15:00 CET (25 July 2003) are given. The calculation (Eq. 8) is for $\tau_F=2$ s.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mean (%)</th>
<th>Minimum (%)</th>
<th>Maximum (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>−37</td>
<td>−33</td>
<td>−42</td>
</tr>
<tr>
<td>HO2</td>
<td>−31</td>
<td>−26</td>
<td>−34</td>
</tr>
<tr>
<td>Isoprene</td>
<td>−23</td>
<td>−20</td>
<td>−29</td>
</tr>
<tr>
<td>Monoterpenes</td>
<td>−33</td>
<td>−28</td>
<td>−39</td>
</tr>
<tr>
<td>MVK + MACR</td>
<td>−35</td>
<td>−32</td>
<td>−40</td>
</tr>
</tbody>
</table>
Fig. 1. Net radiation $R_n$ (W m$^{-2}$) and $J(O^1D)$ – photolysis frequency (s$^{-1}$) for 25 July 2003, 09:00–15:00 CET above canopy.
Fig. 2. Air temperature $T$ (°C) and specific humidity $q$ (g$_{H_2O}$/kg$_{Air}$) from psychrometer at 37 m height for 25 July 2003, 09:00–15:00 CET.
Fig. 3. Horizontal wind velocity $U_h$ (ms$^{-1}$) and friction velocity (10 min mean) $u^*$ (ms$^{-1}$) at 37 m height for 25 July 2003, 09:00–15:00 CET.
Fig. 4. On (P) and off (U) resonance signals (cts/Vs) for OH (upper panel) and HO\textsubscript{x} (lower panel) measured by LIF on 25 July 2003 at 37 m height above ground.
Fig. 5a. Concentration of OH (cm$^{-3}$) with the ±2σ-limits, the mean value, the standard error $\Delta a$ (right ordinate), the skewness $Sk$ and the kurtosis $Kur$, measured at 37 m height by LIF on 25 July 2003, 09:00–15:00 CET.
Fig. 5b. Concentration of HO₂ (cm⁻³) with the ±2σ-limits, the mean value, the standard error Δa (right ordinate), the skewness Sk and the kurtosis Kur, measured at 37 m height by LIF on 25 July 2003, 09:00–15:00 CET.
Fig. 6a. Vertical velocity $w$ (ms$^{-1}$) with the ±2σ-limits the mean value, the standard error $\Delta a$ (right ordinate), the skewness $Sk$ and the kurtosis $Kur$ at 37 m height from a sonic anemometer for 25 July 2003, 09:00–15:00 CET.
Fig. 6b. Temperature $T$ (K) with the $\pm 2\sigma$-limits the mean value, the standard error $\Delta a$ (right ordinate), the skewness $Sk$ and the kurtosis $Kur$ at 37 m height from a sonic anemometer for 25 July 2003, 09:00–15:00 CET.
Fig. 6c. Mixing ratio of isoprene (ppbv) with the ±2σ-limits, the mean value, the standard error $\Delta a$ (right ordinate), the skewness $Sk$ and the kurtosis $Kur$, measured at 37 m height by PTR-MS on 25 July 2003, 09:00–15:00 CET.
Fig. 6d. Mixing ratio of sum of monoterpenes (ppbv) with the ±2σ-limits, the mean value, the standard error Δa (right ordinate), the skewness Sk and the kurtosis Kur, measured at 37 m height by PTR-MS on 25 July 2003, 09:00–15:00 CET.
Fig. 6e. Mixing ratio of methyl vinyl ketone + methacrolein (MVK+MACR; in ppbv) with the ±2σ-limits, the mean value, the standard error Δa (right ordinate), the skewness Sk and the kurtosis Kur, measured at 37 m height by PTR-MS on 25 July 2003, 09:00–15:00 CET.
Fig. 7. Covariances (fluxes) of sensible heat, isoprene, sum of monoterpenes, MVK + MACR, OH and HO$_2$ at 37 m height for 25 July 2003, 09:00–15:00 CET.
Fig. 8. Covariances \( \text{OH}^i \cdot J(O^1D)^i \) and correlation coefficient at 37 m height for 25 July 2003, 09:00–15:00 CET.
Fig. 9. Covariances $\langle T'_s c'_i \rangle$ with $c'_i =$ isoprene, sum of monoterpenes, MVK + MACR, OH and HO$_2$ at 37 m height for 25 July 2003, 09:00–15:00 CET.
Fig. 10. Term $(1+I_a)$ according to Eq. 6 for OH and isoprene, and OH and the sum of monoterpenes.