First measurements of H$_2$O$_2$ and organic peroxides surface fluxes by the relaxed eddy-accumulation technique

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Abstract

The relaxed eddy-accumulation (REA) technique was specially adapted to a high-performance liquid chromatographer (enzymatic method) and scrubbing coils to measure concentrations and fluxes of hydrogen peroxide (H$_2$O$_2$) and organic peroxides with a carbon chain $\leq C_4$, of which only methylhydroperoxide (MHP) and hydroxymethylhydroperoxide (HMHP) were detected. Flux measurements were carried out above the canopy of a Norway spruce forest in Germany (775 m a.s.l.) in NE Bavaria, Germany, during the BEWA2000 research cluster in summer 2001. This period was characterised by H$_2$O$_2$ maximum mixing ratios of 1 ppb and mixing ratios of organic peroxides below 200 ppt. Daily mean H$_2$O$_2$ deposition fluxes of $-0.8 \pm 0.3 \text{ nmol m}^{-2} \text{s}^{-1}$, MHP of $-0.03 \pm 0.03 \text{ nmol m}^{-2} \text{s}^{-1}$ and HMHP of $-0.7 \pm 0.5 \text{ nmol m}^{-2} \text{s}^{-1}$ were obtained. Profile measurements were performed as a qualitative comparison of the controlling mechanism of the surface exchanges. The REA as well as the profile measurements show that during daylight the surface exchanges of H$_2$O$_2$ and MHP over coniferous forest are mainly controlled by dry deposition. The high H$_2$O$_2$ dry-deposition velocity suggests a negligible surface uptake resistance for H$_2$O$_2$, whereas the significantly smaller MHP-deposition velocity indicates a significant surface uptake resistance. However, nighttime surface exchanges of these compounds should be further investigated since the in-canopy ozonolysis reaction is expected to affect exchanges. HMHP REA flux measurements show mainly deposition, whereas the ones based on the profile method suggest in-canopy chemical production.

Keywords: Deposition velocity; Organic peroxides; Hydrogen peroxide; Ozonolysis; Flux divergence

1. Introduction

H$_2$O$_2$ and organic peroxides (ROOH) are key components in the photooxidation of volatile organic compounds, acting as a sink for HO$_2$ and
RO₂ radicals and thus influence the HOₓ cycle. Among the peroxides, H₂O₂ is generally the most abundant species. A major sink for H₂O₂ is its uptake into wet aerosols and cloud droplets; it acts as an oxidant, being responsible for the SO₂ conversion into sulphuric acid (H₂SO₄). Near the Earth’s surface, this dry deposition also provides a major sink for H₂O₂ (Walcek, 1987). Its production occurs mainly in the gas phase by recombination of two HO₂ radicals. Laboratory studies indicate another possible source of H₂O₂; the ozonolysis of anthropogenic and biogenic alkenes (e.g., Großmann, 1999; Hasson et al., 2001a, b). Due to its high solubility and reactivity, H₂O₂ is expected to be effectively removed by dry deposition (Walcek, 1987; Gao et al., 1993; Watkins et al., 1995; Staffelbach et al., 1997; Wesely and Hicks, 2000).

An issue relevant to atmosphere–biosphere exchanges of reactive species is the occurrence of a flux divergence due to fast chemical reactions (Vilà-Guerau de Arellano and Duynkerke, 1992). This can occur when the turbulent and chemical time scales (i.e., net chemical transformation rate normalised with concentration) are of comparable magnitude. For typical daytime turbulent time scales in the order of minutes, photochemical transformations, i.e., production of H₂O₂ by HO₂ radical recombination and sinks by photolysis or reaction with OH are not expected to affect H₂O₂ fluxes since the chemical timescale is hours–1 day. However, H₂O₂ production rates from different ozonolysis reactions may lead to chemical time scales comparable to that of the turbulent transport, i.e., minutes. This reaction efficiency depends on the precursor’s concentrations, i.e., ozone and alkenes and the peroxides yields from the ozonolysis reactions. Laboratory measurements focusing on the production of H₂O₂ through the ozonolysis of alkene suggest that this reaction may be of relevance for tropospheric chemistry (Großmann, 1999; Hasson et al., 2001a, b).

In comparison to H₂O₂, the organic peroxides hydroxymethylhydroperoxide (HMHP) and methylhydroperoxide (MHP) are less abundant in the boundary layer, indicating significant differences between their sources and sinks, including dry deposition. H₂O₂, MHP and HMHP differ largely in their solubility, with possible consequences for their dry deposition fluxes since these are also determined by water solubility (Taylor et al., 1983). The Henry’s Law coefficients of H₂O₂, MHP and HMHP are 7.45 × 10⁴, 227 (Seinfeld and Pandis, 1998) and 1.67 × 10⁶ mol L⁻¹ atm⁻¹ (O’Sullivan et al., 1996), respectively. In the case of HMP, bi-directional exchanges could occur due to fast in-canopy chemical production through the ozonolysis of biogenic alkene and the subsequent ventilation out of the canopy or efficient removal by dry deposition due to its high solubility, comparable to that of HNO₃. On the other hand, MHP yields of alkene ozonolysis reactions are generally very low and production of MHP via CH₃O₂ + HO₂ and destruction by photolysis and OH oxidation are not expected to affect MHP fluxes, since the chemical timescale is ~0.5 day.

Generally, the profile technique is used as a starting point to measure trace-gas fluxes when the application of the eddy correlation technique (EC) (the most direct and reliable technique) is not possible due to the availability of fast response trace-gas sensors (Panofsky and Dutton, 1984). This is the main reason that very few flux measurements of peroxides exchanges have been carried out. The flux-profile technique was used to measure the deposition velocity of total peroxides (VₚROOH) above a wheat field (Heikes et al., 1986) and above a pine forest, showing in general a dry deposition flux of H₂O₂ and ROOH (Hall et al., 1999). This technique has also been used to measure bi-directional summertime H₂O₂ fluxes over the snow pack at Summit, Greenland (Hutterli et al., 2003). As an accurate alternative, the relaxed eddy accumulation (REA) technique can be applied when the fast sensors of the EC technique are replaced by fast response sampling valves combined with a slow analysis technique (Businger and Oncley, 1990). The REA instrumentation was especially adapted and deployed to measure H₂O₂ and organic peroxides surface-exchange fluxes. To our knowledge, these are the first REA measurements of these species ever made. According to the REA technique the flux (Fₜ) for a given trace gas is a function of the standard deviation of the vertical wind velocity (σᵥ), the difference of the mean mixing ratios between ascending air (cₑup) and descending air (cₑdw), and b, an empirical dimensionless parameter (Businger–Oncley parameter) of about 0.4:

\[ Fₜ = σᵥ b (cₑup - cₑdw). \]

The vertical wind velocity determines whether updraft or downdraft mixing ratios are sampled. It has already been demonstrated that the REA technique provides substantial theoretical and practical advantages over the profile technique.
(Ammann, 1999). However, since data-quality assurance by direct comparison with another peroxide REA system was not possible, we also conducted profile measurements to validate the results of the REA measurements in terms of the direction of fluxes.

The Max-Planck-Institute contribution to BEWA2000 (Regional Biogenic Emissions of reactive volatile organic compounds in Forested Areas: Process studies, Modelling and Model Validation) was the measurement and study of H₂O₂ and speciated organic peroxides surface exchange fluxes with the REA technique. The flux measurements also served to identify the potential contribution of ozonolysis reactions as an additional non-photochemical source of H₂O₂ inducing upward (or reducing downward) fluxes, indicating the potential for the occurrence of a flux divergence. Section 3 presents a detailed description of the REA system, its coupling to our detection system and our analysis procedure for H₂O₂, MHP and HMHP. In Section 4 we present the observed mixing ratios and fluxes, followed by a discussion in Section 5, including an evaluation of the measured deposition velocity (V_dX) by comparison with those calculated by the surface resistance analogy.

2. Experimental set-up

2.1. Site description

The measurements took place at the experimental site of the Bayreuther Institut für Terres-trische Ökosystemforschung (BITÖK) from the University of Bayreuth in the Fichtelgebirge, in NE Bavaria, Germany. Both the surrounding orography and the uniform structure of the canopy in the fetch of the 32 m high walk-up tower permit the use of micrometeorological methods to measure surface trace-gas exchanges (Klemm et al., 2006). The forest consisted of ~90% Norway spruce and the canopy had a mean height of 19 m. The ultrasonic anemometer was mounted at 32 m. Profile measurements took place at 32 and 14 m. The sampling coils were located at a height of 4 m.

2.2. Meteorology

Peroxides measurements took place between 12 July and 3 August 2001. Two periods could be distinguished: a wet (12.07.01–21.07.01) and a dry period (22.07.01–03.08.01). The wet period was characterised by southerlies, high air humidity with several rain events, temperatures between 7 and 20 °C and a mean ozone mixing ratio of ~30 ppb. The dry period was characterised by prevailing northerlies, a lower air humidity compared to the wet period, no rain events, temperatures between 15 and 27 °C and a mean O₃ mixing ratio of ~50 ppb (Klemm et al., 2006).

2.3. Measurement of H₂O₂, MHP and HMHP mixing ratios

Two modified thermostatted helix-shaped coil collectors were used for the sampling (Neeb et al., 1997). The coil has 2 mm ID and a total effective length of ca. 100 cm, and was thermostatted at 5 ± 0.3 °C. 18 M KOH water acidified with H₃PO₄ (pH 3.5) was used as scrubbing solution at flow rates (F_a) between 0.15–0.5 ml min⁻¹. The air stream (F_g) drawn through the coils was 3.2 L min⁻¹ (STP). Sampling time was 20 min and samples were analysed immediately after sampling by HPLC (Jasco), using post-column derivatisation with horseradish peroxidase and fluorescence detection (Valverde-Canossa, 2004).

To obtain a statistically robust sample of larger eddies, samples were taken every 20 min, which is the minimum time recommended by Kaimal et al. (1989). In addition, the latter minimizes any bias due to the reaction of peroxides with SO₂ and the hydroxyalkylhydroperoxide (HAHPs) decomposition (decomposition rate up to 11% h⁻¹ for HAHP with a carbon chain longer than C₆). H₂O₂ formation under typical collection conditions (i.e. F_g = 2.9 L min⁻¹ (STP), F_a = 0.35 ml min⁻¹ and T = 5 °C) is ~5–10 pmol mol⁻¹ per 100 nmol mol⁻¹ O₃ in the sample air (Sauer, 1997). Multipoint calibration of the HPLC for the peroxide analysis was performed twice a day using H₂O₂ standard solutions (5 × 10⁻⁸–1.6 × 10⁻⁵ M). Additionally for every sample a 3 µM H₂O₂ standard was added. For the sampling conditions a quantification limit of 5 ppt for H₂O₂ and organic peroxides was obtained.

2.4. REA system

The REA system is schematically depicted in Fig. 1 and consisted of three main components: an ultrasonic anemometer and fast-response sampling valves with a control system, sampling coils and the
HPLC. The controller unit operates the mass flow controllers, pressure sensors and valves. The air was drawn through a PFA (perfluoroalkoxy polymer) sampling inlet with a membrane pump (Vacuubrand GMBH + Co); the flow is regulated to ~3.5 L min\(^{-1}\) with two mass flow controllers (5 L min\(^{-1}\), MKS). An ultrasonic anemometer (Research H.S., Gill) was used for the measurements of the vertical wind speed and the virtual temperature with accuracy of 1 cm s\(^{-1}\) and 0.01 K, respectively. Wind speed error is <1% and virtual temperature error is <0.5%. Depending on the vertical wind direction the air was directed to the up or the down channel by two fast-response three-way solenoid valves (NResearch Inc.). The three ports in the valves were connected to zero air, upward motion (\(w>0\)) and downward motion (\(w<0\)) of air. The valves were connected to a controller unit, permitting their operation in

Fig. 1. Schema of the REA system.
different modes: All Off (sampling zero air through the tubings), All On (sampling with the two tubings simultaneously), Cycle (intermittent sampling at a known frequency) and the Automatic (REA technique) (Valverde-Canossa, 2004). A real-time Linux program controls the up-and-down switching of the valves using the signal of the vertical wind measured by the ultrasonic anemometer as described previously. The criterion of valve switching was based on 5 min running mean values of $\sigma_w$ updated on a 10 Hz basis. Valves were activated according to the current threshold condition $|w_0| = 0.6\sigma_w$. In the case of $-w_0 \leq w \leq w_0$, neither “up” nor “down” samples are taken, but a third high-grade steel valve (dead-band valve) was activated (see also Graus et al., 2006).

The REA experiments required two sampling coils with a similar efficiency, a suitable tubing material and zero air to maintain the equilibrium in the sampling coil. The collection efficiencies for the $\text{H}_2\text{O}_2$, HMHP and MHP were determined experimentally by measuring the mixing ratios from two collectors connected in series (Sauer, 1997). These compounds were produced in the isobutene ozonolysis reaction at 30% RH. Under optimal conditions, i.e. $T = 5 \pm 0.3 \, ^\circC$, $F_a = 0.3–0.4\, \text{ml}\,\text{min}^{-1}$ and $F_g = 2.9–3.2\, \text{L}\,\text{min}^{-1}$ (STP), collection efficiencies of 98%, 100% and 75% were measured for $\text{H}_2\text{O}_2$, HMHP and MHP, respectively. In the field it was not always possible to maintain the scrubbing solution flow rates in the optimal range; these were sometimes lower or higher mainly due to changes in relative humidity. This, in addition to pressure changes due to the long tubing, affected mainly the MHP collection efficiency. Nevertheless, the collection efficiency was calculated for every sample from the on-site conditions and it was generally between 60% and 75%.

The high solubility and reactivity of $\text{H}_2\text{O}_2$ makes peroxide mixing ratio and consequently flux measurements especially challenging due to a possible large error related to tube wall losses. The magnitude of the losses introduced by a PFA tubing was determined in the laboratory. The calculated average loss for $\text{H}_2\text{O}_2$ mixing ratios lower than 1.6 ppb was found to be 3.5% (Valverde-Canossa, 2004). In the field, build up of foreign matter in the tubings, inlets and valves could have also lead to systematic errors besides quantified losses on tubing walls. Additionally, filters in the sampling inlets were not used since laboratory measurements showed that the use of filters with small pore sizes of $\sim 2\, \mu m$ combined with humidity will retain the peroxides and later on release them producing erroneous mixing ratios (Valverde-Canossa, 2004). To impede the entrance of material, such as bugs and pollen, a FEP mesh, diameter $\sim 270\, \mu m$, aperture $\sim 60\%$ (Thomapor) was located on the inlet. Measurements of particle distribution before and after the sampling coil show that the particles with $\leq 1\, \mu m$ pass through the coil with negligible losses (Bonn, 2002). Among various materials MnO$_2$ (IV) was selected as the most appropriate to produce zero air (Valverde-Canossa, 2004), removing 99% of the $\text{H}_2\text{O}_2$, 99.5% HMHP and 100% of other peroxides. In addition, MnO$_2$ catalytically destroys the peroxides needing not to be changed periodically and together with the presence of cotton wadding it also removes ozone. Daily check of systematic errors was performed by taking samples in the All On and All Off modes before the actual measurements started when the difference in the mixing ratio measured in the two tubings was $\leq 2\%$.

2.5. Data rejection criteria and error calculation

Measurements of trace-gas fluxes are influenced by many different factors. During the first two weeks intermittent precipitation events did not allow any REA measurements and from the rest of the period 45% of the measured data were rejected due to non-stationary conditions. Data measured at wind directions between 135° and 225° and at wind speed below 2 m s$^{-1}$ were rejected due to the geometry of the tower and weak turbulence, respectively. In addition, changes in the global radiation and sensible heat flux over 30 min intervals were also used as rejection criteria (Grunhage et al., 2000).

The error in the 20-min fluxes was estimated by error propagation (Skoog et al., 1997). The error of the mixing ratio difference introduces the largest error in the flux measurements. Consequently, high priority was given to maintain a low detection limit by adding standards with each sample to determine online any possible instrumental error. For example, the samples of 14 July were rejected due to a high analytical error on the order of 10%. A proper functioning of the analytical system is critical since the difference between the upward and downward mixing ratios was normally less than 20% for $\text{H}_2\text{O}_2$ and less than 9% for organic peroxides. The analytical error was normally less than 2%. 
3. Results

3.1. Measurement of peroxide mixing ratios

H₂O₂ and organic peroxides with a carbon chain ≤C₄, were measured, of which only MHP and HMHP were present at detectable levels. An overview of the observed peroxide mixing ratios is shown in Fig. 2. The time in the figures is given in Central European Time (CET), which is Universal Time plus 1 h. The mixing ratios during the wet period were generally lower than 200 ppt for H₂O₂ and lower than 40 ppt for MHP. In addition, several isolated short periods occurred where HMHP mixing ratios of about 15 pptv were observed.

During the dry period the mean H₂O₂ mixing ratio was about 600 ppt. It reached a maximum of 960 ppt on 21 July and the lowest mixing ratios were observed on the 1 and 2 August (<110 ppt). The low mixing ratios on 1 August could be a consequence of a low relative humidity, low ozone concentrations and cloud cover, whereas on the 2 August condensation of water in the tubings might have resulted in the scavenging of the peroxides, so pointing at a possible measurement bias. The MHP mixing ratios show a similar behaviour as H₂O₂, and were lower than 150 ppt most of the period, except for the 27 July, where they reached 300 ppt and 2 August, with values lower than 50 ppt. HMHP was rarely observed and few data are available. The mixing ratios were usually lower than 30 ppt and the highest values were observed on 25 July were the mixing ratios reached 300 ppt.

3.2. Surface exchange fluxes measured with the REA method

Although measurements were taken with the REA as well as with the Profile method only the fluxes measured with the REA method are shown. Measurements of fluxes of organic peroxides are specially challenging since the observed mixing ratios of MHP are normally about a factor of 5 smaller compared to those of H₂O₂, whereas HMHP was rarely detected.

3.3. H₂O₂ surface exchanges

The 20-min H₂O₂ fluxes showed negative, downward fluxes as well as positive, upward fluxes; therefore the exchange velocity (EV) (Müller et al., 1993) (calculated by dividing the flux by the mixing

Fig. 2. Peroxide mixing ratios from 12.07.01 to 03.08.01. Two periods can be distinguished: wet period: 12.07.01–21.07.01 and dry period: 22.07.01–03.08.01. Mixing ratios at 32 and 14 m correspond to measurements carried out with the profile technique. For the REA technique mean mixing ratios at 32 m of upwards and downwards mixing ratios are plotted.
ratio), was used to describe the bi-directional exchanges. By averaging three 20-min H$_2$O$_2$ samples, 1-h averages were calculated to obtain a statistically representative mean flux and are shown in Fig. 3. The fluxes, $F_c$, are between $-0.4$ and $-1.1$ nmol m$^{-2}$ s$^{-1}$ (see Fig. 3b). Due to small mixing ratio differences, the relative error of the fluxes is between 25% and 40%. The mean H$_2$O$_2$ deposition flux is $-0.8 \pm 0.3$ nmol m$^{-2}$ s$^{-1}$ (averaged between 0730 CET and 1830 CET). The mean daily mixing ratios observed at 32 m were between 0.2 and 0.6 ppb (see Fig. 3c). No obvious dependency of the mean daily fluxes on the mixing ratio was observed except on 1 August, where the small mixing ratios resemble relative small fluxes. One-h exchange velocities were also calculated from the 1-h average fluxes and mixing ratios. After the averaging, just one emission event remained with an exchange velocity value of $\sim 7$ cm s$^{-1}$ and it was observed on 25 July as shown in Fig. 3a. The latter can occur due to micrometeorological events like a turnover of the canopy air (Hall et al., 1999), non-fulfilment of the stationary conditions (Schween et al., 1997) or due to chemical interferences (Vila`-Guerau de Arellano et al., 1995). The average $V_{dH_2O_2}$, calculated from only those events when downward transport occurred, is $5 \pm 2$ cm s$^{-1}$. Higher values were usually found around 1400 CET whereas the lowest occurred during the morning hours.

3.4. MHP and HMHP surface exchanges

Since the MHP mixing ratio differences were very small, it was decided to calculate daily averages, weighted with the number of data per day, which were about 15. These averages are plotted in Fig. 4b, where the error-bars represent the standard deviation. The observed mixing ratios were

![Fig. 3. Hourly and daily average (a) H$_2$O$_2$ exchange velocities (b) H$_2$O$_2$ fluxes and (c) H$_2$O$_2$ mixing ratios measured from the 25 July to 2 August. The error is the standard deviation calculated from the 20-min values.](image-url)
generally lower than 100 ppt. The mean flux of MHP is \(-0.03 \pm 0.03\) nmol m\(^{-2}\) s\(^{-1}\) (average from 77 MHP-flux data) reflecting that MHP seems to be removed at the surface (see Fig. 4a). A \(V_{\text{dMHP}}\) \(= 0.4 \pm 1.0\) cm s\(^{-1}\) was estimated from the days with mixing ratios above 50 ppt in order to reduce the error. Consequently, the observations from 25 July and 1 August were excluded. REA measurements obtained for HMHP on 25 July indicated that mainly deposition took place with a mean diurnal flux of \(-0.7 \pm 0.5\) nmol m\(^{-2}\) s\(^{-1}\). However, we could not infer an HMHP dry deposition velocity due to scarce amount of data with concentrations above 200 pptv (\(\approx 6\) points) where concentrations \(<200\) pptv give unrealistic results.

4. Discussion

There are few measurements of peroxide surface exchange fluxes above forests. According to our knowledge, the only available measurements are those carried out by Hall et al. (1999) above deciduous and pine forests using profile technique. They obtained an average daytime \(V_{\text{dH2O2}}\) of \(\approx 5.0\) cm s\(^{-1}\) and \(V_{\text{dROOH}}\) of \(\approx 1.6\) cm s\(^{-1}\) for ROOH and concluded from previous measurements and modelling that MHP likely contributes a substantial portion to the observed organic peroxide flux above coniferous forest. To our knowledge this is the first study of speciated organic peroxides fluxes.

In this work, average \(V_{\text{dH2O2}}\) is \(5\) cm s\(^{-1}\), which agrees well with values found by Hall et al. (1999). A large \(V_{\text{dHNO}}\), has been observed over coniferous forests, (Müller et al., 1993; Sievering et al., 2001) with values as large as \(7.6\) cm s\(^{-1}\), suggesting that dry deposition is controlled by turbulent transport. The large \(V_{\text{dH2O2}}\) obtained in this study suggest that turbulence is also controlling \(V_{\text{dH2O2}}\) and that there is a negligible surface uptake resistance for H\(_2\)O\(_2\), consistent with findings by Hall et al. (1999).

On 25 July HMHP fluxes measured with REA show mainly deposition and that HMHP is effectively removed by the forest. During this day a typical high mixing ratios of HMHP \(>100\) pptv, were measured. The large observed mixing ratios suggest that there must have been quite efficient chemical production, i.e. through ozonolysis of biogenic and anthropogenic alkenes. The ozonolysis of the biogenic alkenes would result in an efficient in-canopy HMHP production. The latter would actually result in a significant decrease in the deposition flux or even the occurrence of emissions. The reason for this enhanced HMHP mixing ratios, i.e chemical production need to be further investigated including the role of enhanced NO\(_x\) mixing ratios (<13 ppb), an increase in aerosol mass but also an increase in cloudiness, effecting photolysis reactions, observed on 25 July. For example, the aerosol mass increased from 23–25 to 25–27 July of around 70\% at 24 m and 36\% at 12 m (Plewka et al. [296x405].
At 24 m the amount of OC (organic carbon) and EC (elemental carbon) increased by a factor of two, whereas at 12 m only OC increased and EC remained unchanged. The increase on EC load is strongly related to combustion processes due to anthropogenic activities. This points to a potential role of additional sources of alkenes in the planetary boundary layer (PBL), e.g., through advection from anthropogenic source regions as well as efficient vertical upward transport of biogenic alkenes and subsequent chemical transformation. Unfortunately, during this day no alkene measurements were available.

The average measured daytime $V_{dMHP}$ is 40.4 ± 1.0 cm s$^{-1}$. This low $V_{dMHP}$ suggests a significant surface uptake comparable to that for ozone over coniferous forest (Finkelstein et al., 2000), despite a significantly larger MHP solubility compared to ozone. Such a larger dry deposition velocity for the more-soluble MHP would be more obvious during the presence of surface water. However, during the REA measurement period no dew or rain was present, which indicates that other explanations for this comparable MHP and ozone dry-deposition velocities, e.g., stomatal versus non-stomatal uptake, must be further explored.

Hall et al. (1999) measured a larger $V_{dROOH}$ than the ones we observed for MHP. This is actually expected since, even though they concluded that MHP rather than HMHP is responsible for a substantial portion of the observed organic peroxide, the influence of undetectable concentrations of some very soluble hydroperoxides i.e. HMHP and hydroxylethylhydroperoxide (HEHP) could have systematically enhanced the $V_{dROOH}$.

During this campaign, MHP was detected continuously while HMHP just in isolated events. One possible explanation is the difference in solubility between MHP and HMHP (HMHP is 7000 times more soluble than MHP), resulting in expected significant different dry-deposition fluxes. In addition, their different sources (MHP is mainly produced by $\text{HO}_2 + \text{CH}_3\text{O}_2$ reaction, while HMHP is mainly produced by ozonolysis, via reaction of stabilised Criegee intermediate $\text{CH}_2\text{OO}$ with $\text{H}_2\text{O}$) result in a significantly different location, i.e. within the canopy or higher up in the PBL, and timescales of their chemical production. Analysis with a Single-Column chemistry and climate Model (SCM) (Ganzeveld et al., 2006) has been used to simulate the peroxides concentrations within the PBL. The largest concentration gradient is observed for HMHP and the smallest for MHP. Vertical profiles of peroxides show also quite contrasting distributions of the sources and sinks with the largest source of $\text{H}_2\text{O}_2$ and MHP being calculated with the SCM higher up in the PBL in the morning whereas the main source of HMHP and HAHP is at nighttime inside the canopy. This can unfortunately not be confirmed by measurements, which were limited to the surface layer and the canopy. Due to the contrasting vertical profiles of peroxides sources and sinks distributions and large differences in solubility, it is strongly recommended to speciate ROOH deposition fluxes instead of measuring the bulk organic peroxide exchanges.

The concentration-gradient measurements suggest, consistent with REA-flux measurements, the presence of an efficient sink for $\text{H}_2\text{O}_2$ and MHP in the canopy, which can only be explained by the removal by dry deposition, and not by some chemical destruction mechanism deposition. In the case of HMHP, it was not possible to determine which process was controlling the exchanges since some profile measurements indicate that deposition as well as emission processes took place (Valverde-Canossa, 2004).

The high daytime $V_{dH_2O_2}$ of 5 ± 2 cm s$^{-1}$, which resembles the turbulent velocity, imply that there is negligible surface-uptake resistance (Baldocchi, 1988; Hall et al., 1999). For highly soluble and reactive gases, such as $\text{HNO}_3$, the estimated surface resistance, $R_s$, is often assumed to be near zero (e.g. Walcek, 1987). In this case $V_d$ is controlled by aerodynamic ($R_a$) and quasi-laminar boundary layer ($R_b$) resistances, which can be relatively well characterised (Baer and Nester, 1992; Wesely and Hicks, 2000). $R_s$ is parameterised as a function of wind speed, surface roughness and atmospheric stability (for more information on the meteorology see also Klemm et al., 2006) whereas $R_b$ is a function of turbulent intensity, expressed by the friction velocity $u*$, and diffusivity of gas being deposited. Comparison of the measured $V_{dH_2O_2}$ and those calculated according to $V_d = 1/(R_a + R_b)$ (e.g. Wesely, 1989), presented in Fig. 5, shows good agreement, indicating that $\text{H}_2\text{O}_2$ exchanges over the on-site coniferous forest is controlled by turbulent exchanges and molecular diffusion. Consequently, it is anticipated to find a good correlation between the measured $V_{dH_2O_2}$ and turbulent parameters, i.e. wind speed and friction velocity, shown in Figs. 6a and b, respectively. The friction velocity was computed from the ultrasonic observations at 32 m.
with values ranging between 0.03 and 0.86 m s\(^{-1}\) between 12.07.01 and 03.08.01. Atmospheric stability was not directly computed from the turbulence data also since this parameter does not play a key role in the exchanges over the hilly terrain with relatively high wind speeds and surface roughness. In addition, strong stratification does typically not develop during the summer period (Klemm et al., 2006) and situations with considerable stabilisation were not analysed in this study.

The correlation between the measured friction velocity and \(V_{dH_2O_2}\) is actually relative small (\(r\sim0.60\)) indicating that there is a large variability (\(r^2\sim0.4\)). However, there is good agreement between the measurement period average observed and calculated \(H_2O_2\) deposition velocities of 5 ± 2 cm s\(^{-1}\) and 6 ± 1 cm s\(^{-1}\), respectively, indicating that there is indeed a negligible \(H_2O_2\) surface uptake resistance. The large variability is expected to be mainly due to the error in the measured \(H_2O_2\) exchanges.
but the role of other factors, e.g., ozonolysis, cannot be excluded. Although the 1-h average exchange fluxes showed mainly a downward (deposition) flux, with velocities comparable to the turbulent velocity, several 20-min average upward H$_2$O$_2$ fluxes, or emission events, were observed. However, more observations, preferably of peroxide fluxes at multiple heights are required to study to what extent such upward fluxes reflect the role of in-canopy chemical production or that these events reflect more the role of intermittent turbulent exchanges. Since measurements took place during daytime (for logistical reasons) we can unfortunately not infer from our observations the potential role of ozonolysis on peroxide exchanges for those conditions that exchanges is more likely to be affected by ozonolysis, e.g., early morning, evening and night time with significantly longer mixing timescales.

Comparison of observed and simulated H$_2$O$_2$ fluxes using the SCM (Ganzeveld et al., 2006) indicates that the model underestimates H$_2$O$_2$ fluxes due to the fact that H$_2$O$_2$ dry deposition in the SCM uses non-stomatal uptake resistances, estimated according to Wesely’s (1989) approach, that are significantly larger compared to SCM’s stomatal resistance. Consequently, the model simulated $V_{dH_2O_2}$ for dry conditions are controlled by stomatal uptake in contrast to the observed $V_{dH_2O_2}$ which are controlled by turbulence and molecular diffusion. Simulations using a near-zero surface-uptake resistance show a much better agreement between observed and simulated H$_2$O$_2$ dry deposition fluxes.

Ozone–alkene reaction is an important chemical source of peroxides, independent of NO$_x$ and photochemistry (Großmann, 1999; Valverde-Canossa et al., 2001). The principal VOC emitted by Norway spruce are myrcene, camphene $\Delta^3$-carene with $\alpha$-pinene, $\beta$-pinene and limonene as dominating compounds (Steinbrecher and Ziegler, 1997, Grabmer et al. 2006). Ozonolysis of exocyclic alkenes, i.e. myrcene and limonene is relatively fast and produces high yields of H$_2$O$_2$ (18.5% and 9.3%, respectively) as well as of HMHP; 20.5% and 12%, respectively. Model analysis (Ganzeveld et al., 2006) indicates that daylight H$_2$O$_2$ production rate from terpene ozonolysis is on the order of 100 pptv h$^{-1}$ and estimated first-order timescales of chemistry and turbulence (~1 h) suggest that in the early evening and morning, in the lower part of the canopy, with suppressed nocturnal turbulent mixing, ozonolysis of terpenes becomes as fast as turbulent transport, pointing at the possible occurrence of a flux divergence. However, this could only be confirmed by conducting direct flux measurements at different heights, something not very feasible with the current logistical challenges to measure peroxide fluxes.

5. Conclusions

A relaxed eddy-accumulation (REA) method was especially adapted and used for the first time to measure H$_2$O$_2$, MHP and HMHP surface exchanges over a coniferous forest. REA as well as profile measurements show that daytime surface exchanges of H$_2$O$_2$ and MHP over coniferous forest are mainly controlled by dry deposition. H$_2$O$_2$ removal at the surface actually appears to be very efficient, such that turbulent transport and molecular diffusion control its exchanges. On the other hand, $V_{dMHP}$ values are significantly smaller compared to turbulent velocity, indicating the role of a significant surface-uptake resistance. HMHP fluxes measured with REA show mainly deposition whereas profile measurements show also in-canopy chemical production, consistent with our hypothesis of the role of alkene ozonolysis. However, drawing more firm conclusions is limited due to scarcity of HMHP flux and mixing-ratio measurements.

Due to the different solubility, and consequently the expected efficiency of removal by dry deposition, and different chemical production mechanisms of organic peroxides it is strongly recommended to measure speciated MHP and HMHP exchanges instead of measuring the bulk ROOH exchanges.

Ozonolysis reaction does not seem to affect daytime peroxide fluxes, which are controlled by turbulent transport and dry deposition. However, early morning and evening and nocturnal observations of peroxides exchanges should be pursued since the timescale of the ozonolysis of alkenes and turbulent timescale is comparable to the timescale for suppressed turbulent mixing.

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