

## J6.4 FIRST MEASUREMENTS OF H<sub>2</sub>O<sub>2</sub> AND ORGANIC PEROXIDES SURFACE FLUXES BY THE RELAXED EDDY ACCUMULATION TECHNIQUE

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### 1. SUMMARY

The first measurements of H<sub>2</sub>O<sub>2</sub> surface fluxes applying the Relaxed Eddy Accumulation Technique (REA) were successfully carried out above the canopy of a spruce forest in Germany. The REA technique was specially adapted for the measurements of H<sub>2</sub>O<sub>2</sub> and organic peroxides. The results presented here focus on the H<sub>2</sub>O<sub>2</sub> measurements. Measured concentrations and fluxes show a clear diurnal cycle. The fluxes were mainly downward with deposition velocities of about  $4 \pm 1 \text{ cm s}^{-1}$ . However, upward fluxes (emission) were also observed. These measurements were made in order to determine the importance of the ozonolysis reaction for the H<sub>2</sub>O<sub>2</sub> surface exchanges.

### 2. INTRODUCTION

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is an important chemical constituent of the troposphere. Its production occurs mainly in the gas phase by recombination of two HO<sub>2</sub> radicals. The primary sink for H<sub>2</sub>O<sub>2</sub> is the uptake into existing aerosols acting as an oxidant, which is mainly responsible for the conversion of SO<sub>2</sub> into sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). Near the surface dry deposition also represents a major sink for H<sub>2</sub>O<sub>2</sub> due to its high solubility and reactivity. Recent reports indicate another possible source of H<sub>2</sub>O<sub>2</sub>: the ozonolysis of both anthropogenic and biogenic alkenes.

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A study of the ozonolysis of isoprene and other monoterpenes has shown that H<sub>2</sub>O<sub>2</sub> and other organic peroxides are produced by the reaction of the Criegee intermediate with water vapour in the absence of light (Sauer et al., 1999; Großmann, 1999).

Measured H<sub>2</sub>O<sub>2</sub> yields from a series of anthropogenic and biogenic hydrocarbons have already been used to predict the relevance of the ozonolysis reactions for tropospheric chemistry (Großmann, 1999).

Very few field measurements of H<sub>2</sub>O<sub>2</sub> exchange have been carried out so far. However, they are necessary for an appropriate quantification and modelling of H<sub>2</sub>O<sub>2</sub> exchange at the Earth's surface. The Flux-Gradient technique was used to measure the deposition velocity of peroxides above a wheat field and above a pine forest, showing in general a dry deposition flux of H<sub>2</sub>O<sub>2</sub>, reflected by a dry deposition velocity of about  $5 \text{ cm s}^{-1}$  (Hall and Claiborn, 1997). This gradient technique is usually used as a starting point to measure fluxes of trace gases, where the Eddy Correlation technique, the most direct and reliable technique, is not possible since it requires fast sensors. Nevertheless, the alternative Relaxed Eddy Accumulation technique (REA) can be applied (Businger and Oncley, 1990) since the fast response trace gas sensors are replaced by fast response sampling valves combined with slow analysis techniques. The flux estimate  $F_c$  for trace gas is a function of the standard deviation of the vertical wind velocity  $\sigma_w$ , the difference of the mean concentrations between ascending air ( $c_{up}$ ) and descending air ( $c_{dw}$ ), and an empirical coefficient  $b$ :

$$F_c = \sigma_w b (c_{up} - c_{dw}) \quad (1)$$

The vertical wind velocity determines whether updraft or downdraft concentrations are sampled. The REA technique is rather new and few measurements are available, but it has already shown substantial theoretical and

practical advantages compared to the profile technique. This abstract shows the first results of  $\text{H}_2\text{O}_2$  flux measurement applying the REA method.

### 3. OBJECTIVES

Field measurements of  $\text{H}_2\text{O}_2$  fluxes will be also interpreted to identify the potential contribution of ozonolysis reactions as an additional non-photochemical source of  $\text{H}_2\text{O}_2$ . Micrometeorological REA measurements will be used to study the  $\text{H}_2\text{O}_2$  surface exchange processes. As has been stated previously, it is expected that  $\text{H}_2\text{O}_2$  is effectively removed by dry deposition at the surface, but the ozonolysis can result in a significant source of  $\text{H}_2\text{O}_2$  resulting in a chemical flux divergence.

### 4. ACTIVITIES

#### 4.1 Site Description

The measurements took place at the experimental area of the Institut für Terrestrische Ökosystemforschung (BITÖK) from the University of Bayreuth in Fichtelgebirge, Germany. The location of the 32 m high tower was selected based on the surrounding orography and the uniform structure of the canopy, which allows the use of micrometeorological methods (EC, REA) to measure surface trace gas exchanges.

#### 4.2 Concentration measurement

The  $\text{H}_2\text{O}_2$  was collected with a time resolution of 20 min using two modified thermostatted helix-shaped coil collectors (Neeb et al., 1997). The coil has 2 mm I.D. and a total effective length of ca. 100 cm, and was thermostatted at  $5 \pm 0.3$  °C. A schematic representation of the coil collector is published (Sauer et al., 1999). 18 MΩs water acidified with  $\text{H}_3\text{PO}_4$  (pH 3.5) was used as scrubbing solution at flow rates between 0.15-0.5  $\text{ml min}^{-1}$ . The air stream drawn through the coils was 3.2  $\text{L min}^{-1}$  (STP). The samples were analysed immediately after sampling by HPLC, using post-column derivatisation with horseradish peroxidase and fluorescence detection.

### 4.3 REA system

Data acquisition was performed by a real-time Linux program. It also controls the up and down switching of the valves using the signal of the vertical wind measured by an ultrasonic anemometer. The air was drawn through a PFA sampling inlet of 1.5 m long 2.4 mm internal diameter. The residence time was 0.06 s. Depending on the vertical wind direction the air was directed to the up or the down channel by two fast-response three way selenoid valves. A dead band of  $0.05 \text{ cm s}^{-1}$  in the vertical velocity was used for switching the valves. The sampling tubes of PFA were 28 m long and had an internal diameter of 3.96 mm. The residence time was 2.9 s in the tube and a pressure drop of approximately 94 mbar was introduced. In order to maintain the equilibrium in the coil collector, zero air was added when no sample was taken either in the up or down lines (see Figure 1).

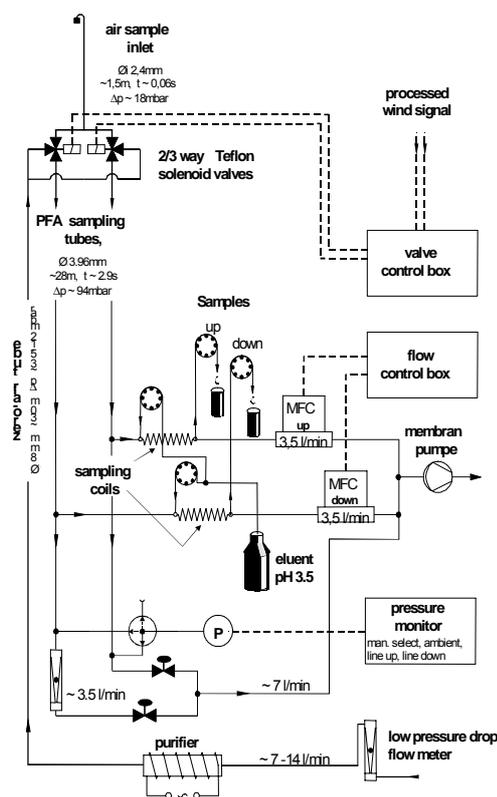


Figure 1. Schema of the REA system

## 5. Results

### 5.1 H<sub>2</sub>O<sub>2</sub>

Here, the preliminary results of one day are shown to demonstrate the performance of the Relaxed Eddy Accumulation method for determining the H<sub>2</sub>O<sub>2</sub> flux. The measurements were carried out during daytime. The Upward, Downward and mean H<sub>2</sub>O<sub>2</sub> concentrations are plotted in Figure 2. It can be clearly seen that the concentration differences are large enough to be detected, which is actually favourable for applying the REA technique.

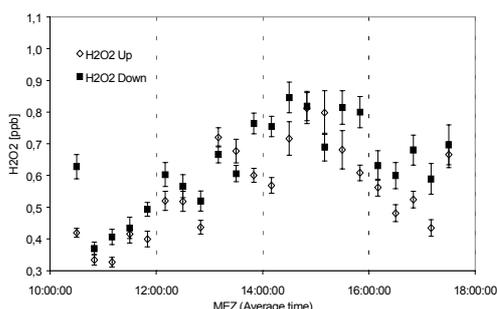


Figure 2. Diurnal course of measured Upward and Downward concentrations for H<sub>2</sub>O<sub>2</sub> on 27 July 2001 and calculated mean concentration for H<sub>2</sub>O<sub>2</sub>. The error bars represent the analytical error.

The calculated fluxes of H<sub>2</sub>O<sub>2</sub> plotted in Figure 3 show mainly Downward fluxes with a diurnal cycle similar to the ones observed for the concentrations. The Downward fluxes suggest that there is dry deposition of H<sub>2</sub>O<sub>2</sub>, whereas the few observed Upward fluxes indicate a possible emission due to chemical production in the canopy. However, for an appropriate interpretation and verification of the flux results, it is necessary to correlate them with information about the meteorological conditions (i.e. radiation, wind direction).

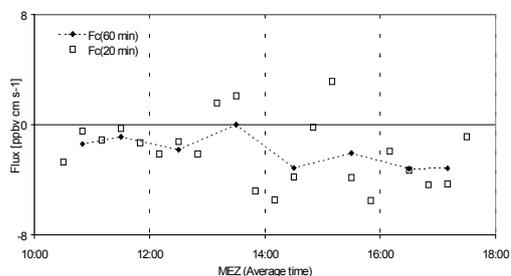


Figure 3. H<sub>2</sub>O<sub>2</sub> fluxes obtained by REA method on the 27 July 2001.

To compare our data with other observations, the deposition velocity ( $V_d$ ) was calculated for each sampling period, every 20 min. In Figure 4, the individual deposition velocities are plotted together with the mean values of every three samples (60 min). For this particular day the deposition velocity had a typical value of  $4 \pm 1 \text{ cm s}^{-1}$ .

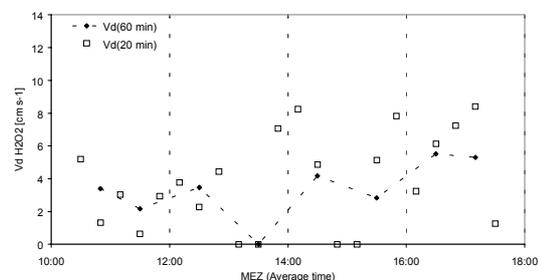


Figure 4. H<sub>2</sub>O<sub>2</sub> deposition velocity on the 27 July 2001.

### 5.2 Organic Peroxides

Methylhydroperoxide (MHP) and hydroxymethylhydroperoxide (HMHP) were also measured. HMHP was rarely seen during the whole field campaign and for the chosen case study the compiled data is insufficient for the fluxes determinations. MHP upward and downward concentrations are plotted in Figure 5. The REA concentration differences ( $C_{up}-C_{dw}$ ) can be observed but are in most of the cases smaller than its estimated analytical error ( $\pm C_{up}-C_{dw}$ ). Therefore it was not possible to measure the fluxes of MHP by means of this technique.

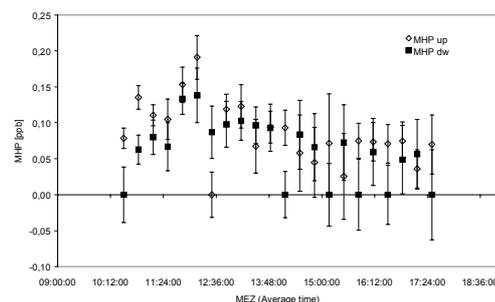


Figure 5. Diurnal course of measured Upward and Downward concentrations for MHP on 27 July 2001. The error bars represent the analytical error.

## 6. Conclusions

The  $\text{HNO}_3$  dry deposition velocity over coniferous forest is about  $7.6 \text{ cm s}^{-1}$  (Sievering et al., 2001), whereas Finkelstein et al. (2000) measured an ozone deposition velocity of about  $0.4 \text{ cm s}^{-1}$ , probably due to differences in the solubility and reactivity. The mean  $V_d$  measured in this work is  $4 \pm 1 \text{ cm s}^{-1}$ . Since this  $V_d$  is between the ones obtained for  $\text{O}_3$  and  $\text{HNO}_3$ , it will be of interest to determine if this species is controlled by the surface resistance as  $\text{O}_3$  and  $\text{SO}_2$ , or by turbulence as  $\text{HNO}_3$ . The solubility of  $\text{H}_2\text{O}_2$  is comparable to  $\text{HNO}_3$  and is also very reactive. This may explain that basically deposition fluxes were observed, suggesting that the dry deposition process mainly controls the  $\text{H}_2\text{O}_2$  Earth's surface exchange. Nevertheless, based on the few observed upward fluxes, it cannot be ruled out that there is a possible chemical source of peroxides due to ozonolysis of hydrocarbons emitted by the canopy. However, these emission events can also occur due to meteorological events like a turn-over of the canopy air or a well-mixed condition. Our goal now is to address these questions using all the available meteorological and chemical information and also by means of modelling.

The concentrations of organic peroxides in the studied area were too low in the case of MHP and HMHP was rarely detected. Therefore, it was not possible to calculate the fluxes. Nevertheless, this method should be tested for areas with higher concentrations.

The measured information will not only help to identify the role of the ozonolysis for  $\text{H}_2\text{O}_2$  surface exchanges but it can also provide additional valuable information to decide to what extent hydrogen peroxide can be used as an indicator species to identify the photochemical state of polluted atmospheres (Sillman, 1995).

## 7. Acknowledgements

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