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H_2O_2 and organic peroxide measurements in an orographic cloud: The FEBUKO experiment

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Abstract

The H_2O_2 and organic peroxides are known to be important oxidants in cloud-water, influencing the oxidising capacity of the atmosphere. Measurements of H_2O_2 in cloud-water have shown a wide range of concentrations depending on the season and measuring site. Moreover, organic peroxide measurements are scarce in spite of their importance. Measurements of peroxides were carried out in the Thuringian Forest, Germany, during the FEBUKO research cluster in the Fall 2001. The measuring stations were located at three sites: upwind (gas phase), summit (cloud-water and gas phase) and downwind (gas phase). Analysis was achieved by high performance liquid chromatography (enzymatic method). From the different peroxides only H_2O_2 was detected in the gas phase at the upwind site with mixing ratios <130 ppt. In the cloud-water, besides hydrogen peroxide (H_2O_2), hydroxymethylhydroperoxide (HMHP), 1-hydroxyethylhydroperoxide (1-HEHP) and methylhydroperoxide (MHP) were also detected with concentrations normalised with the liquid water content up to 1.30, 0.075, 0.065 and 0.015 nmol m^{-3}, respectively. Organic peroxides (HMHP + 1-HEHP + MHP) constitute up to 80% of the total peroxides during nighttime while during daytime they accounted for about 14%. Consequently, organic peroxides might play an important role in nighttime cloud chemistry.

Keywords: Organic peroxides; Hydrogen peroxide; Ozonolysis; Sulphate production

1. Introduction

H_2O_2 and organic peroxides (ROOH) are key components in the photooxidation of volatile organic compounds. They act as a sink for HO_2 and RO_2 radicals and thus influence the HO_x cycle. Another major role of H_2O_2 and the organic peroxides in the atmosphere is the efficient oxidation of sulphur dioxide (SO_2) to sulphuric acid (H_2SO_4) in cloud droplets and in wet aerosol surfaces (Penkett et al., 1979). In the gas phase, during daytime, the main source of H_2O_2 is the recombination of HO_2 radicals and the major source of ROOH is the $HO_2 + RO_2$ reaction. The only known mechanism to the formation of peroxides in the absence of light is the ozonolysis reaction of alkenes (Großmann, 1999; Valverde-Canossa, 2004), which involves the reaction of the Criegee Intermediate with water vapour. This reaction is the main source of 1-hydroxyalkylhydroperoxides (1-HAHP) such as hydroxymethylhydroperoxide (HMHP) and 1-hydroxyethylhydroperoxide (1-HEHP) and a source of OH radicals (Atkinson and Aschmann, 1993; Paulson et al., 1999).

In the aqueous phase, most of the pathways proposed for the formation of peroxides in cloud-water involve sunlight (Finlayson-Pitts and Pitts, 2000). As for the gas phase, the main source of H_2O_2 is the HO_2 radicals, via

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$HO_2 + O_2^-$ reaction. CH_3OOH is formed by an analogous reaction, $CH_3O_2 + O_2^-$. Cloud chemistry involves gas and aqueous phase chemistry; the link between both phases is described in detail by Lelieveld and Crutzen (1991).

Several investigators have measured H_2O_2 in cloud-water from mountain sites (Watanabe et al., 2001). Samples taken throughout the year show significantly seasonal variation i.e., with higher concentrations in summer than in winter (Olszyna et al., 1988). Additionally, measurements carried out in the eastern United States at several non-urban sites show differences between H_2O_2 concentrations measured in rain samples (0.1–100 μM), precipitating clouds (0.1–100 μM) and non-precipitating clouds (median values $<10\mu M$) (Kelly et al., 1985). A summary of observed concentrations of H_2O_2 and other compounds in cloud-water can be found in Gunz and Hoffmann (1990), Pruppacher and Klett (1997) and Lee et al. (2000). Measurements of speciated organic peroxides are scarce and to our knowledge, besides this study, only Sauer et al. (1996) carried out such measurements. They found the contribution of HMHP + 1-HEHP to the total peroxides to be between 0% and 81%, pointing out that these compounds play also a major role as oxidants in cloud-water and should be included into modelling studies of the aqueous phase oxidation of S(IV).

The general objective of Field Investigations of Budgets and Conversions of Particle Phase organics in Tropospheric Cloud Processes (FEBUKO) is to investigate the fate of organic substances in front of, inside and behind an orographic cloud under conditions of connected flow (= "flow reactor"). The results will serve as a database for a comparison of current knowledge on the budget of organics in multiphase environments in central Germany and in tropospheric multiphase models (Müller et al., 2005). The specific objective of this work is the study of the fate of H_2O_2 and ROOH in an air mass during its passage through an orographic cloud. In this paper the in-cloud production and/or destruction of the peroxides will be assessed from the influence of physical (i.e., temperature, pH, liquid water content (LWC), cloud base height) and chemical parameters (i.e., sulphate, sulphur dioxide, carbonyl compounds) on the peroxides concentrations. Additionally, the peroxides concentrations measured at the upwind and calculated at the downwind sites are compared in order to give further insight into the understanding of the influence of cloud processing on these compounds.

2. Experimental

2.1. Site description

FEBUKO took place at the DWD (German Weather Service)/UBA (Umweltbundesamt) mountain station 'Schmücke', located in the Thuringian Forest near Zella-Mehlis, Germany. The measuring stations were selected prior to the field campaign by means of modelling and tracer experiments showing that identical air masses flow over Goldlauter, Schmücke and Gehlberg at a wind direction range of 210°–240° (Heinold et al., 2005). Goldlauter is located upwind of the Schmücke (summit) at 605 m a.s.l, 10° 45′ 20″ E and 50° 38′ 25″ N and Gehlberg is located downwind of the summit at 732 m a.s.l at 10° 47′ 32″ E and 50° 40′ 21″ N. The cloud measurements took place at the Schmücke (summit located at 937 m a.s.l at 10° 48′ 15″ E and 50° 39′ 19″ N) at a tower height of 20 m.

2.2. Meteorology and cloud events description

The air masses characterised at the DWD/UBA station Schmücke are comprised of aged air masses, which have been anthropogenically influenced first and then exposed to biogenic emissions on their way southeast from the Rhein-Main area to the Thuringian forest. The DWD/UBA research station at the Schmücke Mountain is found to be within an orographic cloud for 170 days in a year and should therefore be well suited for a cloud experiment. Furthermore, the months of October and November have the highest probability of cloud formation, which is about 80% (Müller et al., 2005). The field campaign took place from 1st October to 8th November 2001 (6 weeks). Our measurements took place between 25th October to 8th November. During this period two main cloud events took place, i.e. on the 26 October and the 26/27 October hereafter referred as EIV and EI. From these cloud events only the EI satisfied the criteria described in detail by Tilgner et al. (2005) and Heinold et al. (2005), which included suitable synoptical conditions, completeness of the data and adequate flow characteristics. The latter allows the comparison between the three stations. EI took place on the 26/27 October in a timeframe between 2200, 26.10.01 UTC and 1300, 27.10.01 UTC and lasted 15 h. This event was characterised by low stratiform clouds in a moist boundary layer, air mass from the Mid-Atlantic and stable flow conditions particularly after the front passage at 0600, 27.10.01 UTC (Heinold et al., 2005). EIV did not satisfy the above criteria due to the large Froude number, which indicated stagnant flow (Heinold et al., 2005). Nevertheless, these measurements are also of relevance due to the scarcity of organic peroxide measurements in cloud-water. EIV took place on the 26th October between 08:30–16:30 UTC and had a total duration of 8 h. This event was characterised by air masses from the Mid-Atlantic, constant southwesterly flow and was not influenced by frontal processes. In addition, a *stratus nebulosus* bank was formed, which is characterised by a marked stability in the planetary boundary layer and decoupling from the free atmosphere (Heinold et al., 2005).

2.3. Gas phase and cloud-water sampling

The air samples in Goldlauter were collected by the Leibniz-Institut für Troposphärenforschung (IfT-1). The equipment was set up in a container and the samples were collected using PFA tubing at a height of 2.5 m, where the air was directed through the sampling coil. Since the H_2O_2 and the ROOH are stable in cold aqueous acid, they are stripped from the gas phase by drawing the air sample and scrubbing solution through a thermostated helix-shaped coil (Lazrus et al., 1986). The scrubbing solution is 18 M Ω water acidified with H_3PO_4 (pH 3.5), which also has metal-complex forming properties, inhibiting the decomposition of the peroxide. The coil itself is approx. 25 cm long and the tube has an effective length of about 100 cm, 24-turn and 2 mm internal diameter (Sauer et al., 1999). The collection was performed using an airflow of 3.2 $L\,min^{-1}$ (STP), a stripping-solution flow (Fa) of 0.17 $L\,min^{-1}$ and a coil temperature of 2 °C (Sauer, 1997; Valverde-Canossa, 2004). The sampling interval was between 5 and 15 min. The samples collected upwind and transported by the IFT-1 to the Schmücke (~20 min) at an ambient temperature ~7 °C, where they were analysed (see analytical system). During this 20 min the samples decompose ~10% (the sample was given twice). The air samples in Gehlberg (downwind site) were collected and analysed by Zentrum für Umweltforschung/ Universität Frankfurt/(ZUF) with the flow injection chemiluminescence technique (Jaeschke et al., 2005), which is based on reaction of H_2O_2 with bis-trichlorophenyloxalate.

Cloud-water was collected with the Single-Stage slit jet Impactor (SSI) and the Two-Stage Cloud-water Impactor (TSCI). The collectors were always conditioned 1 h before starting the measurements. The SSI has a cut-off drop diameter of 5 μm and the air enters the device through two parallel slit jets at 120 $m^3\,h^{-1}$. The TSCI operation is based on the principle of inertial impaction on plane surfaces, a standard technique for the collection of dry aerosol particles (Schell, 1998). The air is sampled isokinetically and enters the device through three vertical slit impaction stages at 180 $m^3\,h^{-1}$, one to collect the larger droplets (cut-off diameter 12 μm), followed by two identical stages in parallel (cut-off diameter 5 μm). The sampling interval was of 30 min or 1 h, depending if the amount of sample necessary for the different analyses was collected within this time interval. The team of the Brandenburgische Technische Universität Cottbus (BTU) collected these samples.

2.4. Analytical system

The gas and aqueous phase samples were analysed immediately after sampling by high performance liquid chromatography, (HPLC) (Jasco) using post-column derivatisation with horseradish peroxidase (HRP) and fluorescence detection (Valverde-Canossa, 2004). The HRP catalyses the reduction of H_2O_2 (Guibault et al., 1968) in the presence of p-hydroxyphenyl ethanoic acid (POPHA), a hydrogen donor molecule. H_2O_2 and alkylhydroperoxides react directly with the enzyme. Nevertheless, other peroxides, i.e. 1-HAHP and peroxy acids are temperature- and pH dependent and do not react directly with peroxidase. Therefore, to favour their decomposition into compounds that can later react with the enzyme, the post-column derivatisation reaction takes place at 40 °C and at a pH between 8.5 and 9.5. For every hydroperoxide consumed, one dimer is formed. The fluorescence of this dimer is directly proportional to the peroxide concentration and is detected in a fluorescence detector. Multipoint calibration for the peroxide analysis was performed twice a day using H_2O_2 standard solutions (5×10^{-8}–1.6×10^{-5} M). Additionally, before every sample a 3 μM H_2O_2 standard solution was injected. For the sampling conditions a quantification limit of 5 ppt for H_2O_2 and organic peroxides was obtained. As no standards are available on the market with the exception of H_2O_2 and peracetic acid and since the HPLC responds to organic hydroperoxides and H_2O_2 with equal sensitivity, the calibration of the system were performed with H_2O_2 (Kurth, 1992; Staffelbach and Kok, 1993). The organic hydroperoxides were identified by comparing the relative retention times of the organic peroxides (elution time of the organic hydroperoxide/elution time of the H_2O_2) obtained experimentally (Valverde-Canossa, 2004).

A comparison of the H_2O_2 concentrations measured in cloud-water samples with the fluorescence and chemiluminescence methods was performed during the field campaign. Despite the different cloud samplers and sample intervals, the measured H_2O_2 concentration are in general in good agreement (Jaeschke, 2005, personal communication).

3. Results

3.1. Measurements in goldlauter (upwind site)

The measurements in Goldlauter took place from 30 October to 4 November 2001 when no clouds were present and were not performed simultaneously with the cloud events. No other peroxides besides H_2O_2 were detected in the gas phase. The mixing ratios of H_2O_2 were below 130 ppt with an average mixing ratio of 49 ppt and maximum mixing ratios around 1400 UTC.

Table 1 contains a summary of the mixing ratios observed.

3.2. Measurements at the schmücke (summit)

The measurements at the Schmücke took place from 26 to 29 October 2001. Cloud-water samples were taken with the SSI and the TSCI. Most of the samples were taken with the SSI for which the LWC (Liquid Water Content, mg of water per m^3 air) was also measured. The peroxide concentrations measured in μM were normalised with the LWC to $nmol\,m^{-3}$ as recommended by Möller et al. (1996). Both the normalised and the μM concentrations of H_2O_2, HMHP, 1-HEHP and MHP are shown in Fig. 1. The time denotes the average time of the interval measured. Results of the measurements carried out with the TSCI are not shown here (for details see Valverde-Canossa, 2004) but in general the peroxide concentrations from the second stage of the TSCI show a similar trend to those collected with the SSI but are consistently higher in most of the samples. The latter is attributed to the different values of LWC, which is not available for the TSCI at the present time and it is not yet possible to verify this. Only three samples of cloud-water from the first stage of the TSCI are available since it was not always possible to collect enough sample volume for the peroxide measurements. Due to the few samples collected from the first stage of the TSCI, a comparison with the second stage of the TSCI is limited and it was not possible to establish a clear tendency of the concentrations of H_2O_2, HMHP and 1-HEHP measured in the two stages.

The H_2O_2 was detected during the daytime (06:00–18:00 UTC) as well as during the nighttime (18:00–06:00 UTC). A clear day profile can be observed on the 26th of October, with daytime concentrations between 0.04 and 13.6 μM (0.02–1.30 $nmol\,m^{-3}$) and night-time concentrations (26th/27th of October) between 0.04 and 2.76 μM (0.02–0.65 $nmol\,m^{-3}$). Normalised concentrations do not show always the same trend as the μM concentrations, showing that other factors besides the LWC may control the H_2O_2 concentrations.

Daytime concentrations of HMHP oscillate between 0.009 and 0.114 μM (0.003–0.0078 $nmol\,m^{-3}$) and nighttime concentrations between 0.048 and 0.319 μM (0.022–0.075 $nmol\,m^{-3}$). Normalised concentrations of HMHP show the same trend as the μM concentrations; therefore the main factor controlling the HMHP concentrations is the LWC. Daytime 1-HEHP concentrations are between 0.015 and 0.177 μM (0.006–0.012 $nmol\,m^{-3}$) and concentrations between 0.028 and 0.277 μM (0.013 and 0.065 $nmol\,m^{-3}$). The 1-HEHP concentrations are in the same order as the ones found for HMHP but higher concentrations were observed during the day-hours.

The MHP was detected just in a few samples, predominantly during nighttime. Daytime concentrations were lower than 0.037 μM (0.0025 $nmol\,m^{-3}$) and night-time concentrations lower than 0.046 μM (0.015 $nmol\,m^{-3}$).

The H_2O_2 and the organic peroxides have similar daily patterns differing in the maxima occurrence. In the case of H_2O_2 the maxima occur during the daylight, whereas organic peroxides maxima occur during nighttime. Organic peroxides (HMHP + 1-HEHP + MHP) constitute up to 80% of the total peroxides during nighttime, while during daytime they accounted for about 14%. Organic peroxides might play an important role in nighttime chemistry.

3.3. Measurements in gehlberg (downwind site)

The H_2O_2 measurements in the gas phase at this station were carried out by the ZUF. The H_2O_2 concentrations measured were below the detection limit (300 ppt) during the entire field campaign (Jaeschke, 2005, personal communication).

4. Discussion

Gas phase peroxide mixing ratios in FEBUKO were <130 ppt. The mixing ratios are comparable with the ones measured at the Kleiner Feldberg, Germany, which not only took place in the fall but were also influenced by anthropogenic emissions: H_2O_2 mixing ratios during the Kleiner Feldberg Cloud Experiment were <70 ppt (Fuzzi et al., 1994) and during the FELDEX field campaign <45 ppt (Sauer et al., 1996). In the latter field campaigns no organic peroxides were observed in the

Table 1
Measurements of peroxides in the gas phase

Date	Number of samples	Time interval (UTC)	H_2O_2 (ppt)	Organic Peroxides (ppt)
30.10.01	2	11:45–12:15	n.d.	n.d.
02.11.01	3	10:30–15:10	n.d.-34	n.d.
03.11.01	3	10:30–14:00	6-126	n.d.
04.11.01	3	09:00–15:00	n.d.-30	n.d.

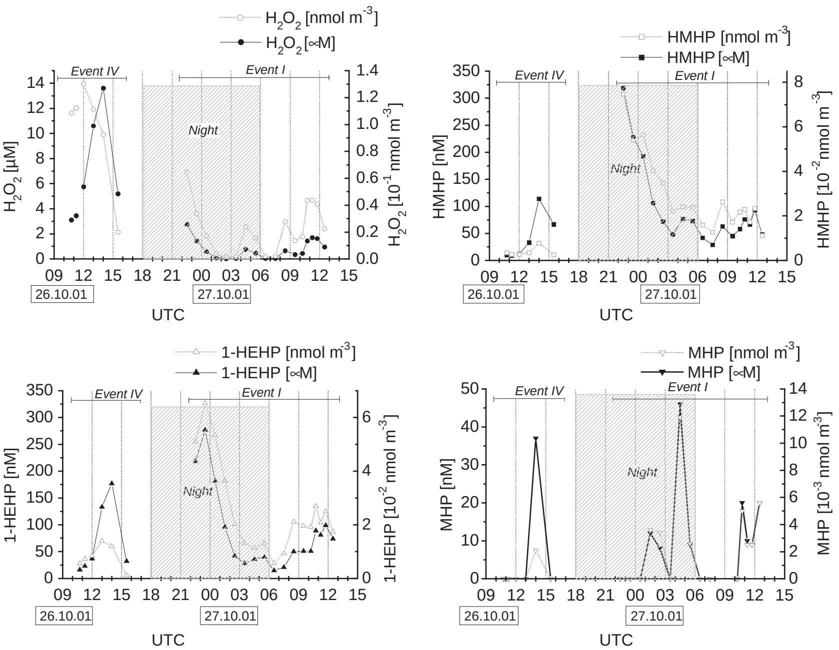

Fig. 1. Time profiles of the H_2O_2, HMHP, 1-HEHP and MHP measurements in cloud-water sampled with the SSI. Left axis: concentration and right axis: normalised concentration.

gas phase. A summary of measurements of gas phase H_2O_2 and ROOH measurements in the troposphere can be found in Lee et al. (2000).

In *cloud-water*, organic peroxides have only been measured by Sauer et al. (1996). They observed concentrations of HMHP $<1\,\mu M$ and of 1-HEHP $<0.01\,\mu M$. During FEBUKO, concentrations of HMHP were $<0.32\,\mu M$, 1-HEHP $<0.28\,\mu M$ and MHP $<0.046\,\mu M$. HMHP, MHP, 1-HEHP and EHP have also been measured in rain water at concentrations $<0.8\,\mu M$ during the same season (Hellpointner and Gäb, 1989; Hewitt and Kok, 1991; Sauer et al., 1996).

Measurements in the fall show concentrations of $H_2O_2 < 3.2\,\mu M$ in the FELDEX field campaign (Sauer et al., 1996), $<1\,\mu M$ in the Kleiner Feldberg Cloud experiment (Fuzzi et al., 1994) and $<130\,\mu M$ (Olszyna et al., 1988) at Whitetop Mountain. The latter concentrations are quite different to the ones observed in FEBUKO during the same season, where we observed concentrations $<15\,\mu M$. These variations give an indication of the complexity of cloud-chemistry.

4.1. *Influence of physical and chemical parameters of clouds on the peroxide concentration*

A description of the temporal evolution of the cloud events can be found in Fig. 2. This figure shows the time profiles of the cloud-base height above Goldlauter Station, the LWC measured at the Schmücke Station at 352 m above Goldlauter, and the time profiles of the H_2O_2 concentrations measured in cloud-water. During EIV the cloud progressively thins during the early morning until the afternoon 16:30 UTC. The concentrations of H_2O_2 in cloud-water increase at a rate of $3.6\,\mu M\,h^{-1}$ peaking at 14:00 UTC and later decreasing until the cloud breaks. Therefore, it is possible to recognize a very marked H_2O_2 diurnal cycle, which could be a result not only of the inversion separating the boundary layer from the free troposphere and/or transport of pollutants, but also of an enhanced production or decomposition of the peroxides in the water phase. During this event the measurements took place in the cloud as well as at the cloud base height, and higher concentrations were observed near the base of the cloud, where the LWC is lower. During EI, in the 26.10.01 at 22:00 UTC, the cloud thickens progressively during the night until the early morning hours ~08:00 UTC after which it starts thinning, finally breaking at 13:00 UTC. In addition, from 03:30 to 05:00 UTC a decrease in the peroxides concentrations is accompanied by an increase in the wind speed from 7 to $10\,m\,s^{-1}$, an increase in O_3 of 8 ppb and a decrease of NO_x of 3.3 ppb in less than two hours (see also Brüggemann et al., 2005). This could be the product of vertical mixing and air entrainment resulting in a decrease in the LWC from 475 to $320\,mg\,m^{-3}$ at this time.

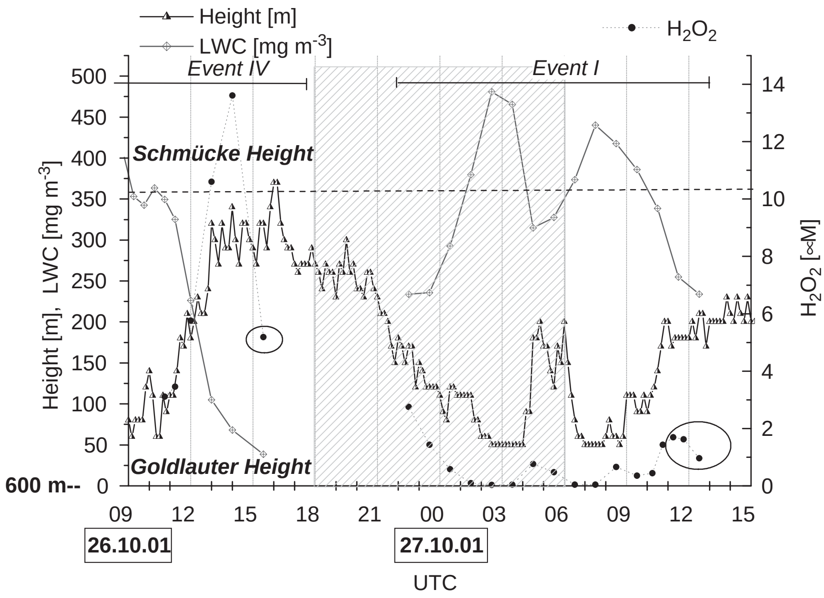

Fig. 2. Time profiles for EI and EIV. Right axis: H_2O_2 time profiles, left axis: LWC measured at Schmücke and cloud base height (H) measured at Goldlauter (see also Wieprecht et al., 2005).

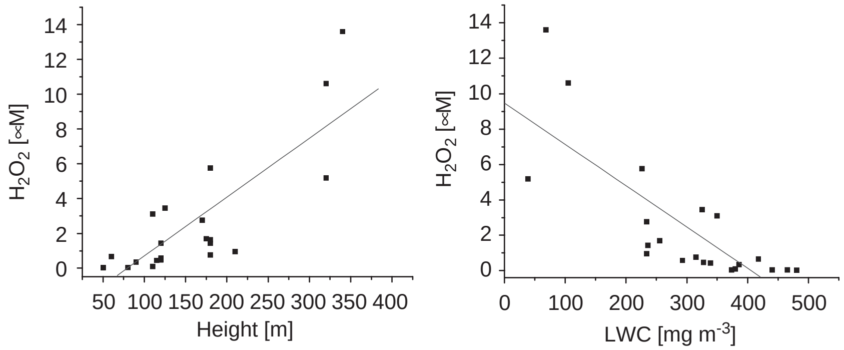

Fig. 3. Correlations between H_2O_2 concentration and LWC and cloud-base height.

In general, the H_2O_2 concentrations measured are correlated with the LWC ($r^2 = 60\%$, negative correlation) and cloud-base height ($r^2 = 67\%$, positive correlation) as can be observed in Fig. 3. Nevertheless, if the last points when the cloud breaks on the 26th and on the 27th are excluded (these points are circled in Fig. 2), the correlations of H_2O_2 with the LWC ($r^2 = 69\%$) as well as with the cloud-base height ($r^2 = 77\%$) are stronger. This stronger correlation is expected, since from Fig. 2 it can be qualitatively observed that these points have a different behaviour. This observation together with the residual correlation (31% in the case of the LWC and 23% in the case of cloud base height) means that other factors besides the variability in LWC and cloud-base height are linked with the variance of the concentrations of H_2O_2, for instance, a very efficient release of trace gases towards the end of the event.

Temperature and pH are plotted in Fig. 4 together with the peroxide concentrations. The low temperatures (<7 °C) increase the solubility of the trace gases and the stability of the peroxides is directly related to the pH. From the organic peroxides observed, HMHP and 1-HEHP will decompose into H_2O_2 and the corresponding aldehyde at pH > 5 and pH > 3, respectively (O'Sullivan et al., 1996). The pHs measured are between 3.7 and 4.4. Therefore, H_2O_2, HMHP and MHP are stable and will not tend to decompose, but the 1-HEHP will start decomposing after contact with the cloud and its decomposition will contribute to H_2O_2 and acetaldehyde formation. Additionally, the S(IV) oxidation pathways

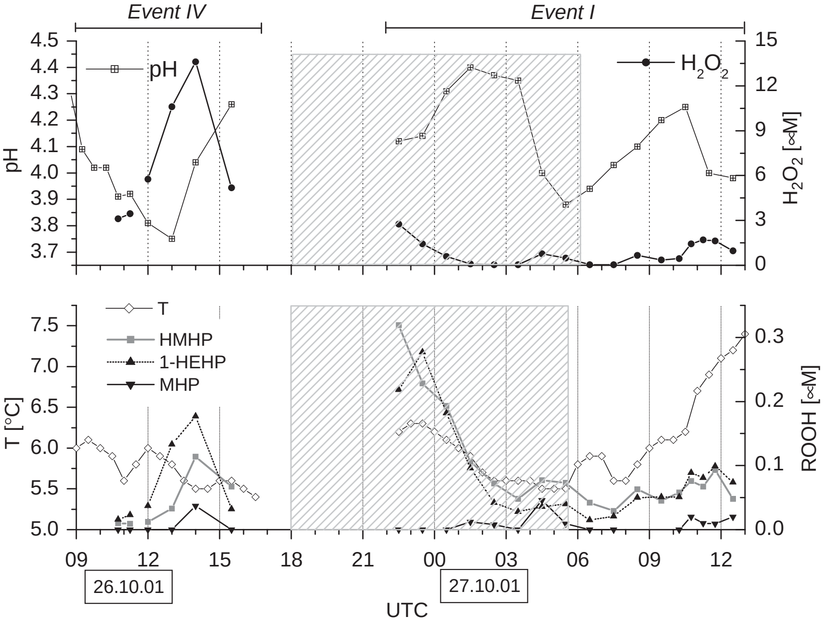

Fig. 4. Temperature and pH time profiles and their comparison with peroxide time profiles (details of the *T* and pH measurements can be found in Wieprecht et al. (2005).

are dependent on the pH and temperature, preferring the oxidation by dissolved H_2O_2 at pH < 5 (Finlayson-Pitts and Pitts, 2000). The faster decrease of the concentrations of 1-HEHP in comparison with HMHP towards the end of EIV could be explained as an effect of the solubility; where the 1-HEHP due to its lower solubility is released faster into the gas phase.

In Fig. 5, H_2O_2 and organic peroxides are plotted together with a series of carbonyl compounds, which were grouped according to their concentration and included: formaldehyde (HCHO), acetaldehyde (CH_3CHO), unsaturated carbonyl compounds: methylvinylketone (MVK) and methylethylketone (MEK), hydroxycarbonyls: glycolaldehyde and hydroxyacetone and dicarbonyls: glyoxal, methylglyoxal and biacetyl (van Pixteren et al., 2005).

During the two events, for the following carbonyl compounds glyoxal, biacetyl, HCHO, CH_3CHO, methylglyoxal, MVK and MEK the maxima clearly occurred during daylight as for H_2O_2. However, in the case of hydroxyacetone and glycolaldehyde during EI nighttime and daytime maxima are comparable in magnitude. The dominant source of aldehydes in rain or in cloud-water is thought to be transfer from the gas phase, where they are either photochemically produced or directly emitted. Some of these compounds are primary (HCHO, MVK) or secondary products (hydroxyacetone, methylglyoxal and glycolaldehyde) of the photooxidation of isoprene, which is one of the major hydrocarbons of biogenic origin. Methylglyoxal and glyoxal are degradation products of aromatic organic compounds and are readily photooxidised during the daytime (Großmann et al., 2003). The chemistry of the carbonyl compounds is strongly related to that of the peroxides. The formaldehyde is immediately hydrated after dissolution in water forming methylene glycol, which later participates in a series of reactions leading to the production of H_2O_2 (Lelieveld and Crutzen, 1991). In addition the carbonyl compounds and the peroxides have a common source, the ozonolysis of alkenes reaction. This reaction is known to be the main source of peroxides, especially of hydroxyalkylhydroperoxides in the absence of HO_2 radicals, but is not expected to take place in the aqueous phase due to the low solubility of the precursors.

The common pattern observed for organic peroxides and carbonyl compounds can be attributed to chemical reactions occurring near to the measuring station, where these compounds are later taken up by the cloud or due to transport of aged air masses. The fact that the reaction of MVK with OH is the solely source of hydroxyacetone and that this reaction will occur only during daylight indicates that the pattern observed can be attributed mainly to transport of aged air masses, which was also implied from the observations of SO_2, O_3, HCl, HNO_3 and CO by Brüggemann et al. (2005). Nevertheless, HMHP and 1-HEHP show relative higher concentrations than those measured for the carbonyl compounds during nighttime. Therefore, other factors may also be controlling the nighttime organic peroxide

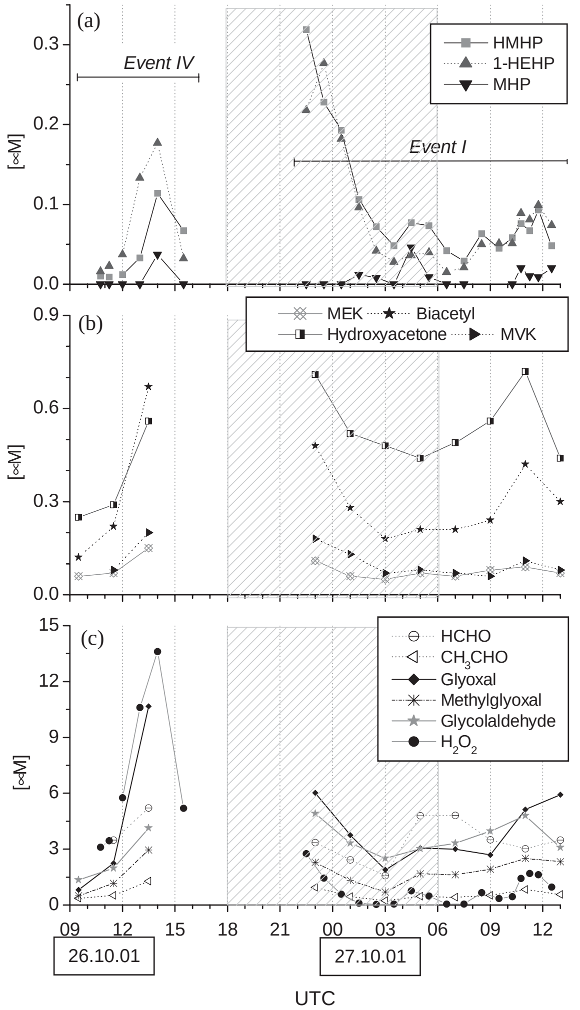

Fig. 5. Several carbonyl compounds found in cloud-water at the Schmücke (the carbonyl compounds were measured by Brüggemann et al. (2005).

concentrations such as the ozonolysis reaction in the interstitial phase.

Fig. 6 shows SO_2 mixing ratios measured at the three stations (measurements at the summit and downwind were performed by Brüggemann et al. (2005)) and sulphate (SO_4^{2-}) and H_2O_2 measured at the Schmücke. During the night of the 26/27th of October 2001 (EI), the cloud was formed together with an injection of high mixing ratios of SO_2 ~2 ppb. SO_2 mixing ratios measured at Gehlberg are lower than those measured upwind and at the summit stations. Therefore it seems that SO_2 was effectively scavenged during its passage through the cloud. In this event the concentrations of H_2O_2 were very low, including in the morning hours when an increase in H_2O_2 concentrations is expected. Scavenging of SO_2 may be one of the reasons for this process since at the pH measured (<4.4), SO_2 will be preferentially scavenged by H_2O_2. In EI at the Schmücke, H_2O_2 aqueous-phase concentrations were <3 μM, which correspond to calculated gas phase mixing ratios of <5 ppt, while SO_2 has gas phase mixing ratios <1 ppb and calculated aqueous-phase concentrations $<5 \times 10^{-3}$ μM. The gas phase H_2O_2 as well as the aqueous phase SO_2 concentration were calculated from the Henry's Law constant. The high mixing ratios in the gas phase of SO_2 compared to the one of H_2O_2 shows that the reaction was oxidant limited. Nevertheless, during this event it is not possible to observe an anti-correlation between SO_2 and H_2O_2, probably because of changing air masses. During EIV an apparent anti-correlation between H_2O_2 and SO_4^{2-} can be observed. Nevertheless, this cannot be attributed to in-cloud oxidation of SO_2 since the sulphate-time profile in the aqueous phase is similar to the one for the anions and cations measured (Wieprecht et al., 2005), where dilution seems to be the controlling factor. Therefore, from the product of $SO_2 + H_2O_2$ reaction, SO_4^{2-}, cannot be quantified since it is not possible to distinguish which is its origin: the latter reaction or from dissolved SO_4^{2-} from aerosols. In addition, due to the large formaldehyde concentrations, the HSO_3^- and SO_3^{2-} reaction in cloud-water with dissolved formaldehyde producing hydroxymethanesulfonic acid (HMSA) also could be of importance (Gunz and Hoffmann, 1990).

4.2. Comparison between the three stations

This comparison is limited since even though simultaneous measurements in the three stations were performed, the concentrations measured by the ZUF downwind were always below the detection limit (300 ppt). In addition, gas phase upwind concentration measurements did not take place simultaneously. Therefore, NO_x, O_3 and SO_2 mixing ratios are used as indicators of pollution and similar concentrations of these compounds were set as a requisite to enable a comparison between these stations. During the gas-phase measurements upwind, on 30th October high NO_x (6–14 ppb) and SO_2 (0.6–1.2 ppb) mixing ratios and low O_3 mixing ratios ~25 ppb were measured. The 2nd November was characterised by average mixing ratios of O_3 of 25 ppb, $SO_2 < 0.6$ ppb and very high NO_x mixing ratios during the morning hours peaking 25 ppb at 0722 UTC with mean values of 10 ppb between the time scales measured. The 3rd November was characterised by SO_2 mixing ratios <1 ppb, O_3~30 ppb and average NO_x mixing ratios of about 9 ppb during the measured interval. The 26/27 October at the summit station mean O_3 and NO_x mixing ratios were 21 and 7 ppb, respectively, together with SO_2 mixing ratios between 0.5 ppb and 2.0 ppb (Brüggemann et al., 2005). Therefore, the

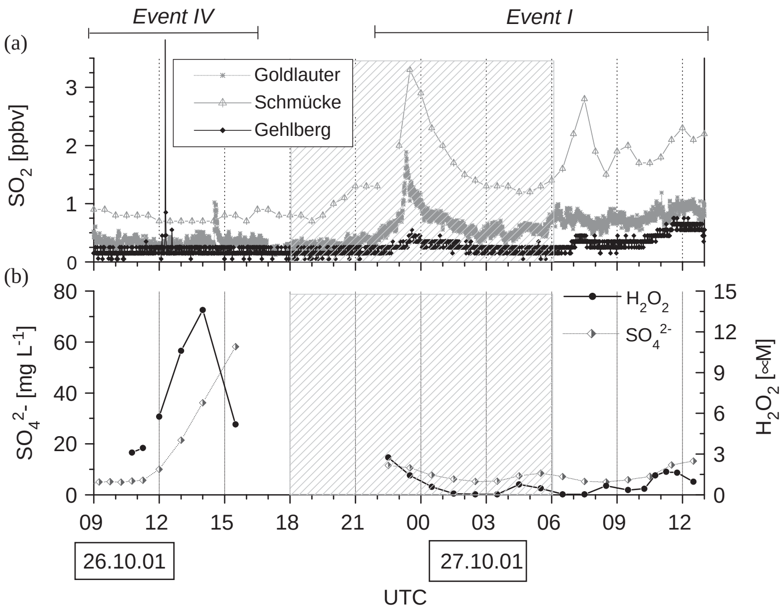

Fig. 6. Sulphur dioxide oxidation in clouds at Schmücke (details of the measurements of SO_2 and SO_4^{-2} can be found in Wieprecht et al. (2005) and Brüggemann et al. (2005).

peroxide mixing ratios were measured under similar conditions of NO_x, O_3 and SO_2 mixing ratios and are used to enable a comparison between these stations. Additionally, for comparison purposes the mixing ratios of the peroxides in the gas phase at the summit station were estimated from the cloud-water measurements, by assuming that aqueous–gas phase equilibrium is reached. The Henry's Law constants (H) for H_2O_2, HMHP, 1-HEHP and MHP at 25 °C have been determined by several different authors (Lind and Kok, 1986), but there is still some uncertainty. Even though the measurements took place at an average temperature of 279 K, we took for our analysis the experimentally determined Henry constants from O'Sullivan et al. (1996), since all the peroxides of interest were measured by these authors under the same conditions, i.e., pH = 3 and $T = 278\,°C$. The calculated mixing ratios (Fig. 7) in the gas phase are very low: $H_2O_2 < 30$ ppt, HMHP < 0.020 ppt, 1-HEHP < 3.5 ppt and MHP < 40 ppt. Therefore, gas-phase measurements at the Schmücke can provide information about H_2O_2 and MHP if available but not for 1-HEHP and/or HMHP since they are under the detection limit of the analytical instrument (DL = 5 ppt). H_2O_2 and the HMHP have very high Henry's Law constants, and thus remain mainly in the aqueous phase. However, this will not be the case for 1-HEHP and MHP since the former occurs in both phases and the latter one mainly in the gas phase. According to the gas–aqueous phase fractions, the fraction of A that exists in the aqueous phase X_{aq}^{A} is given by

$$X_{aq}^{A} = f_A/(1 + f_A)$$

where f_A is the distribution factor for a species A, defined as the ratio of its aqueous-phase mass concentration c_{aq}^{A} ($g\,L_{air}^{-1}$) to its gas- phase mass concentration c_{g}^{A} ($g\,L_{air}^{-1}$). Assuming Henry's Law equilibrium:

$$f_A = 10^{-6} HRTLWC = HRTw_L,$$

where H is the Henry's Law constant ($M\,atm^{-1}$), R is the ideal gas constant ($0.08205\,atm\,L\,mol^{-1}\,K^{-1}$), T is the temperature (K) and LWC is the liquid water content ($g\,m^{-3}$). The conversion factor 10^{-6} results of the units since w_L (vol water/vol air) = 10^{-6} LWC (Seinfeld and Pandis, 1998).

The fraction in the aqueous phase will then depend not only on the Henry's constant but also on the LWC. During the field campaign, for LWC between 0.1 and $0.48\,g\,m^{-3}$ the average fraction of peroxides in the aqueous phase are: $X_{aq}^{H_2O_2}$ is 96%, $X_{aq}^{HMHP} = 100\%$, $X_{aq}^{MHP} = 8\%$ and $X_{aq}^{1-HEHP} \approx 82\%$, assuming the H chosen to be correct. The latter means that H_2O_2 and HMHP are completely dissolved in the cloud. 1-HEHP is moderately soluble and is in both phases in significant fractions, 80% of the aqueous phase and 20% in the gas phase. MHP is rather insoluble since only 8% is in the aqueous phase; the remaining 92% is in the gas phase. Furthermore, even though the mixing ratios of MHP in the summit are high enough to be measured upwind,

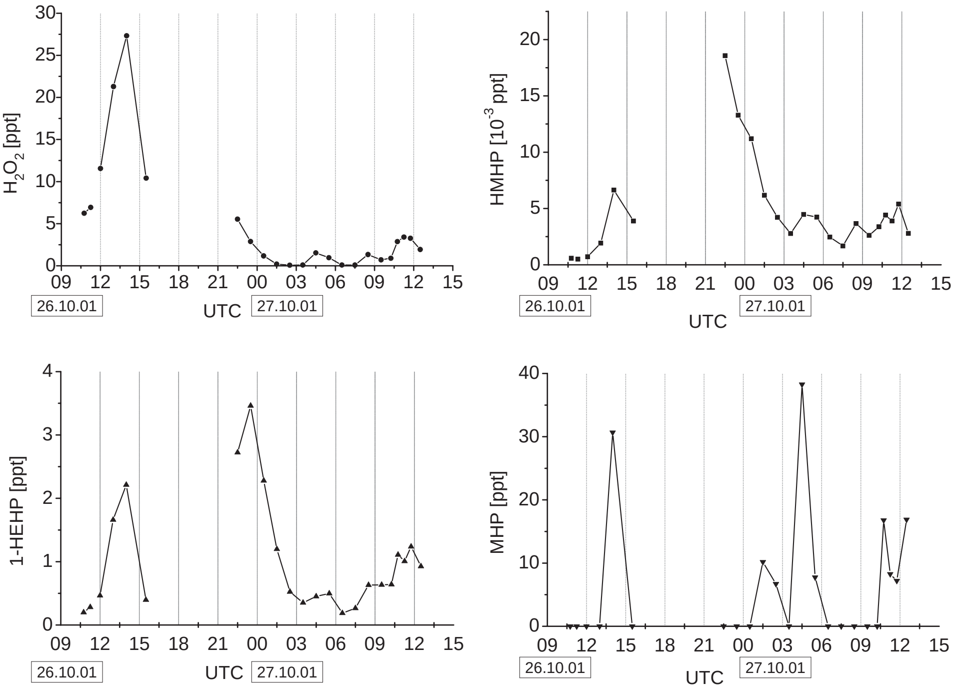

Fig. 7. Calculated gas phase mixing ratios of H_2O_2 and ROOHs from the measured concentrations in cloud-water at the Schmücke.

only H_2O_2 was observed. The MHP concentrations can be influenced by a single event, probably linked to anthropogenic influence but due to the low solubility of its precursors it is unlikely to be caused by in-cloud production.

If all the H_2O_2 in the water phase evaporates after cloud dissipation, calculated H_2O_2 mixing ratios during EI are <125 ppt, which is in agreement with the downwind measurements, where H_2O_2 concentrations were always below the detection limit of the instrument (300 ppt) (Jaeschke, 2005, personal communication) and also agrees with our measurements upwind mixing ratios of $H_2O_2 < 130$ ppt. Moreover, it agrees with the measurements carried out in 2002, where Jaeschke (2005, personal communication) observed similar concentrations of H_2O_2 upwind and downwind. Measurements of organic peroxides in the upwind station are below the detection limit (<5 ppt) and were not carried out at the downwind site. Nevertheless, our calculations show that if the peroxides measured in cloud-water are entirely evaporated HMHP and 1-HEHP will not be detected, since the HMHP, 1-HEHP and MHP expected maximum mixing ratios are in the order of 2, 20 and 42 ppt, respectively. Therefore, more sensitive equipment downwind will give information about the fate of H_2O_2 and MHP but not necessarily of the fate of HMHP and 1-HEHP at this site and at this time of year.

5. Conclusions

In cloud water H_2O_2 and the following organic peroxides: HMHP, 1-HEHP and MHP were observed. These measurements are in agreement with the findings of Sauer et al. (1996) and show that these compounds are common constituents of cloud-water. The low temperatures and pH values measured favours the detection especially of H_2O_2, HMHP and 1-HEHP. In addition, it was found that these organic peroxides (HMHP + 1-HEHP + MHP) constitute up to 80% of the total peroxides during nighttime , while during daytime they accounted for about to 14%. Therefore, organic peroxides might play an important role in the nighttime chemistry. It is believed that the ozonolysis reaction is the main source of H_2O_2 during nighttime and of HAHP throughout the day. Therefore their detection during nighttime indicates that this reaction took place. Due to the low solubility of the precursors, the appearance of these peroxides cannot primarily be attributed to in-cloud ozonolysis reaction. In addition, whether the ozonolysis occurred in the gas phase previous to cloud contact or in the cloud-interstitial phase cannot be established.

The carbonyl compounds presented similar patterns to those of the peroxides. Hydroxyacetone was one of these, its presence indicates that this pattern can also be attributed to transport of air masses.

The role of H_2O_2 in the SO_2 oxidation to SO_4^{2-} was also studied, but the amount of sulphate produced by this reaction cannot be quantified since it is not possible to distinguish its origin: the latter reaction or from dissolved SO_4^{2-} from aerosols.

Besides the in-cloud chemistry, H_2O_2 concentrations were also found to be strongly linked to the cloud physics. It was observed that the H_2O_2 concentration strongly decreased upon cloud dissipation, which can be attributed to evaporation of this compound, and higher H_2O_2 concentrations were observed in the basis of the cloud, which normally coincided with low liquid water content.

It is not possible to establish the fate of the H_2O_2 and organic peroxides after passage through the cloud due to the lack of data in the downwind site, where more sensitive equipment is needed or a site or time of the year where higher concentrations of these compounds are expected. In addition, future experiments should be planned by selecting different measuring stations in the cloud, another measuring station at the side of the cloud should be useful to determine if entrainment took place and a higher sampling resolution should be applied mainly towards the beginning and end of the cloud event for a better understanding of the uptake of gases by the cloud and the effect of cloud dissipation on the concentration of trace components.

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