Hydrogen Peroxide, Organic Peroxides and Higher Carbonyl Compounds Determined during the BERLIOZ Campaign

G. K. MOORTGAT[1], D. GROSSMANN[1*], A. BODDENBERG[2**],
G. DALLMANN[2], A. P. LIGON[2], W. V. TURNER[2], S. GÄB[2], F. SLEMR[3‡],
W. WIEPRECHT[4], K. ACKER[4], M. KIBLER[5], S. SCHLOMSKI[5] and
K. BÄCHMANN[5]

[1]*Max Planck Institut für Chemie (MPI), Division of Atmospheric Chemistry, PO Box 3060,
D-55020 Mainz, Germany, e-mail: moo@mpch-mainz. mpg.de*
[2]*Bergische Universität-Gesamthochschule Wuppertal (BUGH) FB 9, Analytische Chemie,
Gaussstr. 20, D-42119 Wuppertal, Germany*
[3]*Fraunhofer Institut für Atmosphärische Umweltforschung (IFU), Kreuzeckbahnstr. 19,
D-82467 Garmisch-Partenkirchen, Germany*
[4]*Brandenburgische Technische Universität Cottbus (BTU), Chair for Atmospheric Chemistry and
Air Quality, Ernst-Hellmann-Weg, Haus 215, Germany, e-mail: wie@btu-lc.fta-berlin.de*
[5]*Technische Universität Darmstadt (TUD), Institut für Chemie, Petersenstr. 8, D-64287 Darmstadt,
Germany, e-mail: baechman@hrzpub.tu-darmstadt.de*

Abstract. Gas-phase H_2O_2, organic peroxides and carbonyl compounds were determined at various sites from Mid-July to early August 1998 during the BERLIOZ campaign in Germany. The sites were located northwest of Berlin and were chosen to determine pollutants downwind of the city emissions during a summer smog episode. Hydrogen peroxide (H_2O_2), methyl hydroperoxide (MHP, CH_3OOH) and occasionally hydroxymethyl hydroperoxide (HMHP, $HOCH_2OOH$) were quantified in air samples by commercial fluorimetric methods and classical HPLC with post-column derivatisation by horseradish peroxidase/p-hydroxyphenyl acetic acid and fluorimetric detection. Carbonyl compounds were determined in ambient air by a novel method based on O-pentafluorobenzyl hydroxylamine as derivatisation agent. Mixing ratio profiles of the hydroperoxides and the carbonyl compounds are reported for the intensive phase of the campaign, 20–21 July, 1998. Peroxides showed pronounced diurnal variations with peak mixing ratios in the early afternoon. At times, a second maximum was observed in the late afternoon. The major part of the H_2O_2 was formed through recombination reactions of HO_2 radicals, but there is some evidence that H_2O_2 is also formed from ozonolysis of anthropogenic and/or biogenic alkenes. Diurnal variations of mixing ratios of various carbonyl compounds are reported: alkanals (C_2 to C_{10}, isobutanal), unsaturated carbonyl compounds (methacrolein, methylvinylketone, acrolein), hydroxycarbonyl (glycolaldehyde, hydroxyacetone) and dicarbonyl compounds (glyoxal, methylglyoxal, biacetyl), aromatic compounds (benzaldehyde, *o*- and *m*-tolylaldehyde) and pinonaldehyde.

Key words: H_2O_2, organic peroxides, carbonyl compounds, city plume, photosmog.

★ Present address: Sachtleben Chemie GmbH, P.O. Box 170454, D-47184 Duisburg, Germany, e-mail: dgrossma@sachtleben.de

★★ Present address: Schwarz Pharma AG, Alfred-Nobel-Str. 10, D-40789 Monheim, Germany

‡ Present address: MPI für Chemie, Division of Atmospheric Chemistry, PO Box 3060, D-55020 Mainz, Germany, e-mail: slemr@mpch-mainz.mpg.de

1. Introduction

One of the main presuppositions of the BERLIOZ summer campaign was a persistent and homogeneous southeasterly wind, such as usually prevails during photosmog episodes within the Berlin region. The design of the BERLIOZ experiment was strongly dependent upon this meteorological presumption. Unfortunately, the meteorological conditions during the experiment were unfavourable, and only a few short episodes complied with the optimal conditions. One such episode occurred on 20 and 21 July 1998, when a high-pressure zone settled over Berlin, bringing winds from the southeast and warm air over the Berlin area (Becker, 2001).

The aim of the BERLIOZ campaign was to study the formation of oxidation products, especially of ozone and other photooxidants, within a city plume during typical hot summer days. A number of ground-based stations were set up at selected sites downwind of the city. Pabstthum, about 50 km northwest of Berlin, was chosen as a major rural ground station. All important trace gases (NO_x, NO_y, O_3, biogenic/anthropogenic VOC's, etc.) and meteorological parameters (temperature, wind direction, wind speed and relative humidity) were monitored by various groups at this station (Becker, 2001; Corsmeier *et al.*, 2002; Volz-Thomas *et al.*, 2001, 2002). Measurements of hydrogen peroxide, organic peroxides, carbonyl compounds, and organic acids at Pabstthum over a period of the whole BERLIOZ campaign are discussed by Grossmann *et al.* (2001).

In addition to measurements at Pabstthum, several other ground sites (Blossin, Eichstädt, Lotharhof and Menz) with a limited number of parameters were operated along the southeast to northwest axis of the experiment given by the expected southeastern wind. This paper reports and discusses the measurements of H_2O_2, methyl hydroperoxide (MHP, CH_3OOH) and occasionally hydroxymethyl hydroperoxide (HMHP, $HOCH_2OOH$) and a number of carbonyl compounds during the BERLIOZ intensive campaign on 20 and 21 July.

2. Experimental

The measurement sites at Eichstädt, Pabstthum, Lotharhof, and Menz are located in the northwest of Berlin along the line of expected southeastly wind. Eichstädt was about 20 km, Pabstthum 50 km, and Lotharhof and Menz about 70 km from Berlin. The sites were selected to investigate the chemical processes in the plume of Berlin at different stages of its photochemical development. In addition to the investigation of the plume of Berlin, the incoming air masses were characterised by measurements upwind of the city at Blossin. The location and the instrumentation of the stations are given by Becker (2001), Corsmeier *et al.* (2001) and Winkler *et al.* (2002).

2.1. H$_2$O$_2$ AND ORGANIC PEROXIDES

On 20 and 21 July 1998, peroxides were measured at field stations Eichstädt, Pabstthum, Lotharhof, and Menz. At Eichstädt and Lotharhof, H$_2$O$_2$ and the sum of organic hydroperoxides were determined with commercially available hydroperoxide analysers, while at Pabstthum and Menz optimised HPLC methods resolving individual peroxide compounds were used. All the results presented here are based upon the reaction of the hydroperoxides with p-hydroxyphenyl acetic acid, catalysed by horseradish peroxidase. The sampling by the hydroperoxide analysers at Eichstädt, Lotharhof and the HPLC method in Pabstthum was carried out by means of sampling coils. In Menz, cryosampling at –78 °C was used. The instruments were calibrated using peroxide solutions of known concentrations. Unlike the HPLC procedures, which identify and quantify the individual hydroperoxides after chromatographic separation, the commercial hydroperoxide analysers can only distinguish between H$_2$O$_2$ and the sum of organic hydroperoxides.

At Pabstthum, the instruments operated by MPI-Mainz were located in a container mounted on a 6 m high platform. Ambient air was drawn in through a $\frac{1}{4}$-inch Teflon tube extending 1.5 m above the roof of the container, so that samples were taken about 10 m above the ground. All peroxides were collected with modified thermostatted (at 15 ± 0.3 °C) coil collectors (Hartkamp and Bachhausen, 1987; Neeb *et al.*, 1997; Sauer *et al.*, 1999). Sampling was performed in a quasi-continuous mode. After passing through the coil collector, 2 ml of the stripping solution (acidified 18 MOhm water, H$_3$PO$_4$ at pH 3.5) were injected into a sample vial of an autosampler, from which 500 μl were processed by the HPLC. Peroxide mixing ratios were determined by reversed-phase HPLC with post-column derivatisation involving p-hydroxyphenyl acetic acid and horseradish peroxidase (Hellpointner and Gäb, 1989; Kurth *et al.*, 1991; Gäb *et al.*, 1995; Lee *et al.*, 1995; Sauer *et al.*, 1996, 1997; Sauer, 1997; Grossmann, 1999). Fluorescence detection of the biphenyl derivative formed in the derivatisation reaction was done at wavelengths of $\lambda_{ex} = 287$ nm and $\lambda_{em} = 412$ nm with a programmable Hewlett Packard 1046b fluorescence detector. The collection efficiencies of the coil for the peroxides were determined to be >98% (H$_2$O$_2$), 100% HMHP, 41–73% (MHP) (Sauer, 1997). Blanks were taken during each of the intensive periods by passing pure N$_2$ through the coil under the same conditions applied in the analyses of ambient air. H$_2$O$_2$ was found only occasionally in the blanks, and then only in small amounts. Multipoint calibration of the HPLC for peroxide analysis was performed once a day with H$_2$O$_2$ standard solutions with mixing ratios in the range of 10^{-6}–10^{-7} mol l^{-1}. Fresh H$_2$O$_2$ standards were prepared by serial dilution of a 30% stock solution, which was titrated against I$_2$/Na$_2$S$_2$O$_3$ weekly. The detection limit, defined as three times the standard deviation of the analytical blanks, was 0.008 μmol l^{-1} with a 100-μl sampling loop. Under typical sampling conditions this corresponded to a detection limit of about 15 pptv for H$_2$O$_2$ and the organic peroxides in the gas phase.

An HPLC method was also used by BUGH-Wuppertal in Menz. Hydroperox-
ides from air were cryogenically enriched at –80 °C. The technique for quantifica-
tion of H_2O_2 and organic hydroperoxides by means of HPLC is described in detail
by Hellpointner and Gäb (1989). The detection by the enzyme-catalysed reaction
of hydroperoxides is almost identical to the method of Lazrus *et al.* (1985), as
described above for Pabstthum (Weller *et al.*, 2000). Eluent and reagent solutions
were prepared from de-ionised and doubly distilled water and degassed once a
day with high-purity helium (99.999%). The detection limit was 20 pptv for H_2O_2,
40 pptv for MHP and hydroxymethyl hydroperoxide (HMHP) and between 60 pptv
and 90 pptv for other organic hydroperoxides. Aqueous standards, prepared daily
from pure MHP and a solution of 30% H_2O_2 (Merck), were used for calibration.

The instruments operated by BTU-Cottbus in Eichstädt and by IFU-Garmisch-
Partenkirchen at Lotharhof used a dual channel continuous enzyme fluorimet-
ric method with commercial hydroperoxide analyzers based on the fluorimet-
ric method of Larzus *et al.* (1985, 1986) and manufactured by Aero-Laser in
Garmisch-Partenkirchen (Model AL1002 Aero-Laser). An air stream of 2000 cm^3
min^{-1} was drawn through the sampling line and stripped with a buffer solution
(pH 5.8, flow 0.42 cm^3 min^{-1}) in a 50.2-cm-long glass coil (ID 2 mm). Af-
ter separation of the air behind this stripping coil, the liquid stream was split
into two channels. In the first, the fluorimetric reagent (*p*-hydroxyphenyl acetic
acid (HPAA)) and horseradish peroxidase (HRP) were added to determine the
total amount of peroxides. The enzyme-catalyzed reaction of HPAA with hy-
droperoxides or peroxides forms a dimer whose fluorescence signal at 415 nm
($\lambda_{ex} = 320$ nm) depends upon the peroxide concentration. In the second channel
the enzyme catalase was added before HPAA and HRP. Catalase selectively de-
stroys H_2O_2, the difference between the two channels being the amount of H_2O_2.
The destruction efficiency of the catalase is normally 85–95%. Investigations with
pure methyl hydroperoxide (MHP) standards show a 5–7% concurrent loss of MHP
at catalase efficiencies of 90–95% (Weller *et al.*, 2000). The destruction of H_2O_2
by catalase failed at Lotharhof and, therefore, only the total hydroperoxide con-
centration can be reported for this station. The estimation of the total hyroperoxide
concentration neglects the error caused by partial collection of MHP (about 60%)
and assumes the same sensitivity for organic peroxides as for H_2O_2.

In order to assure the quality of the various analytical techniques, intercalibra-
tion studies were performed before the campaign. One exercise took place at the
BUGH in Wuppertal on 25–28 August 1997, where the cited instruments of the
various groups were checked for linear response and performance against diluted
standard solutions and gaseous mixtures of H_2O_2 (about 1 ppb), HMHP and HMP
(each 200 ppt) (Boddenberg, 1997, 1998). Additional instruments and techniques
involving UV detection (non-enzymatic) were used during this intercalibration
study. On the average, all instruments performed similarly and measured H_2O_2
concentrations within 10 to 15% of the preset gaseous mixing ratios. Deviations
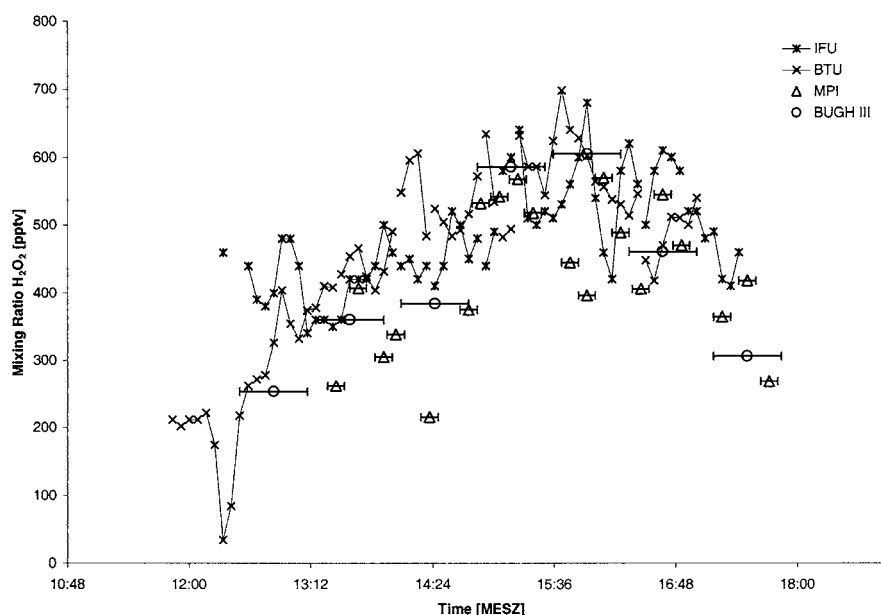for HMHP and HMP were somewhat larger (30%). Finally, the same ambient

Figure 1. Instrument intercalibration measurement of H_2O_2 performed on 27 August 1997 by IFU, BTU, MPI and BuGH as preparation for the BERLIOZ Campaign.

air (university campus) was supplied to all instruments in order to measure the H_2O_2 mixing ratio. The results are presented in Figure 1 for 27 August 1997, when mixing ratios up to 700 ppt were measured. All instruments produced similar H_2O_2 profiles, except that the MPI results were occasionally lower. In general, the reproducibility of the HPLC for H_2O_2 was found to be better than $\pm 10\%$. The scatter of the data along the daily profile was calculated by means of a 3rd degree polynomial, and resulted in an $R^2 = 0.87$. For the organic hydroperoxides the total error of the sampling and analytical method, losses in the sampling manifold and errors in the calibration was estimated to be ± 20–30%.

2.2. CARBONYL COMPOUNDS

Carbonyl compounds were measured using various cartridge methods, cryosampling coupled to a gas chromatograph, Hantzsch analysers and differential optical absorption spectrometers (DOAS) (Grossmann *et al.*, 2001). Of this broad range of analytical techniques, this article focusses only on the determination of aldehydes and ketones in Pabstthum and Menz by a new cartridge method with subsequent gas chromatographic analysis (Schlomski *et al.*, 1997; Kibler *et al.*, 1999). The technique was successfully tested by synthetic test gas mixtures and by ambient air with standard addition (Slemr, 1999). These determinations were carried out by the TU-Darmstadt, predominantly at Pabstthum, but occasionally at Menz. In Pabstthum, where the instruments used for the collection and analysis of carbonyl

compounds were in a container mounted on a platform, air was drawn through a $\frac{1}{4}$-inch Teflon tube from 1.5 m above the roof of the container, so that samples were taken about 10 m above the ground. No filters were placed in the inlet system. In Menz air samples were drawn from a 7 m high sampling line.

Although the most commonly used method for analysing aldehydes and ketones in air is based on trapping carbonyl compounds by reaction with DNPH (2,4-dinitrophenyl hydrazine) and HPLC analysis (Schlomski, 2000; Vairavamurthy *et al.*, 1992), in this work solid sorbent cartridges were used, which were coated with O-pentafluorobenzyl hydroxylamine (PFBHA) as derivatisation reagent, according to the reaction shown below:
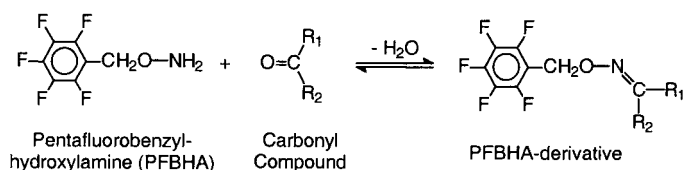
The resulting oximes consist of *syn-* and *anti-* isomers. These exhibit good gas chromatographic properties and can be detected by a mass spectrometer (base peak at m/z 181) or, at higher sensitivity, by an electron capture detector.

Sep-Pak tC$_{18}$ cartridges (Waters, Millipore Corp.) were used for sampling. Each cartridge was cleaned with 5 ml hexene, dried and conditioned with 5 ml methanol. The cartridges were coated with 5 ml PFBHA solution (25 mg PFBHA in 50 ml water $\cong 0.05\%$) drawn through the cartridges with a syringe. After removing the excess liquid and the cartridges were dryied by a flow of nitrogen gas (25 ml/min, 12 h). The cartridges were stored under nitrogen in a freezer and were stable for at least six weeks. Samples were taken by drawing air through the coated cartridges. The sampling train consisted of a pump and a flow controller. The cartridges were exposed for one hour at a flow rate of 500 ml/min with the exception that the sampling intervals were extended at night to 3 hours at a flow rate of 333 ml/min. The cartridges were resealed after loading and stored in a freezer. Stability tests showed neither degradation nor increase in blank levels over a period of one month.

For analysis, the cartridges were eluted in the reverse sampling direction with 1 ml of hexene. One tenth of the organic extract was injected with a programmed-temperature vapouriser (PTV) into the gas chromatograph (HP 6890, Agilent, Bad Homburg, Germany). The PTV was operated in the solvent-vent mode. After the separation on a non-polar column (HP-5, 60 m $\times$ 0.32 mm ID $\times$ 0.25 μm d$_f$) with hydrogen as carrier gas (5.5 ml/min), the PFBHA derivatives were detected with an electron capture detector (350 °C, 60 ml/min N$_2$). For identification purposes, a GC-MS system (HP 5890/5970) was used. The PFBHA cartridges were calibrated with liquid carbonyl compound standards of various concentrations. After the coated sampling tubes had been spiked with the aqueous solutions (100 μl, 1–100 μM RCHO), they were left for 15 minutes at room temperature for complete

reaction. The cartridges were then dried (N_2, 1 hour, 200 ml/min), eluted and analysed. The results of the described calibration procedure were confirmed by analyses of a certified gas-phase standard. In addition, the cartridge method and the FTIR spectroscopic technique correlated well in an intercomparision experiment.

The collection efficiencies of the PFBHA cartridges were tested with parallel sampling at different flow rates and resulted in an enrichment of >95% for all analytes $\geqslant C_3$. Formaldehyde could not be determined because of the high volatility of its PFBHA derivative. Measurements in road tunnels and smog chambers have shown that the influence of NO and NO_2 on PFBHA sorbent tubes is negligible. This is in contrast to the DNPH cartridges (Nishikawa and Sakai, 1995; Lange and Eckhoff, 1996), which show unfavourable effects (degradation products, loss of hydrazones) at higher concentrations of NO_2. The influence of ozone depends on the sorbent material. In the case of reversed-phase material, ozone led to destruction of the carbon chain and the formation of a set of aldehydes. Consequently, a KI cartridge was used as ozone scrubber. The scrubbing efficiency of the KI cartridges was tested with synthetic ozone/air mixtures, together with the adsorptive properties of the material.

In general, over 50 carbonyl compounds can be identified with standard compounds in combination with a liquid derivatisation (Schlomski, 2000). Between 20 and 30 aldehydes and ketones were found in air samples taken during the BERLIOZ experiment. Typical detection limits for most of the analytes vary between 10 and 50 ppt at a signal-to-noise ratio of two. The analytes acetone and methylethyl ketone were not considered because of their high and varying blank values, which prevented a reliable quantification.

3. Results and Discussion

3.1. PEROXIDES

Atmospheric H_2O_2 mixing ratios measured during the whole campaign at Pabstthum ranged from <15 pptv (detection limit) to 1.5 ppbv. With regard to the observed H_2O_2 mixing ratios and the photochemical activity of the atmosphere, two distinct periods could be distinguished during the campaign. High photochemical activity produced H_2O_2 mixing ratios larger than 0.6 ppbv (see below); those levels were observed only during the period 21 to 24 July. For most of the rest of the campaign, cloudy weather led to low photochemical activity, which was reflected in diurnal H_2O_2 mixing ratios below 0.6 ppb.

In this section only the results obtained during the intensive phase of the BERLIOZ campaign from 20 to 21 July 1998 will be discussed. During this period a high pressure zone was established, with winds from the southeast bringing warm air and clear sky over the Berlin metropolis, which led to a pronounced increase in radiation and temperature relative to the previous days. The air temperature reached a maximum over 30 °C in the area. During that day the high relative humidity (about 90% the night before) decreased to near 25% at noon. One should note

that the wind direction was southeast in the morning of 20 July and turned to southwest later in the day, indicating that the downwind sites Eichstädt, Pabstthum and Menz were only temporaly influenced by the Berlin plume. For 20 July the transport of the polluted and transformed ground-level air mass from Berlin to the various stations was studied in detail by Becker *et al.* (2002). According to this study only 32% of the air mass was imported in Eichstädt on this day and only 5% in Pabstthum and Menz. Due to its westernmost position, Pabstthum observed the Berlin plume for the shortest period of time and probably only its border (Winkler *et al.*, 2002). This resulted in a complex transport, mixing and deposition situation afflicting the interpretation of the observations (Becker *et al.*, 2002). It is interesting to mention that elevated NO_x levels (up to 15 ppb) were observed during the early morning hours of 20 and 21 April, which originated from accumulation of local surface emission nearby the station below the nocturnal inversion layer. The high NO_x levels dissipated around mid-morning due to growing height of the mixing layer (Grossmann *et al.*, 2001).

The diurnal variations of the mixing ratio of the peroxides at the stations Pabstthum (MPI), Menz (BUGH), Lotharhof (IFU) and Eichstädt (BTU) are similar. Figure 2 displays the diurnal variations of H_2O_2, Figure 3 of total hydroperoxides (sum of H_2O_2 and organic peroxides) and Figure 4 of the organic peroxides (MHP and HMHP). On 20 July, the H_2O_2 mixing ratio rose from near zero in the night to a maximum in the late afternoon of 1.2 ppb in Eichstädt, 0.7 ppb in Pabstthum, and 0.6 ppb in Menz. At these stations air is advected from lateral regions where photooxidation of the VOC occurs, forming peroxides by the conventional reaction of HO_2 with HO_2 and/or RO_2 radicals. This diurnal variation is a result of H_2O_2 transport from adjacent regions during the daytime and dry deposition from a shallow night-time boundary layer. A second peak appeared in the evening hours in Pabstthum and, more pronounced, in Menz (see later). A third night-time H_2O_2 peak in Menz was not observed at any other site. On early afternoon of 21 July, H_2O_2 reached maximum values of 2.1, 1.6 and 1.5 ppb at the stations Eichstädt, Pabstthum and Menz, respectively, the highest during the BERLIOZ campaign. In view of the measurement uncertainty of about 30%, the noon H_2O_2 mixing ratios are in reasonable agreement suggesting a rather homogeneous large scale H_2O_2 distribution. The H_2O_2 mixing ratios on 20 July are comparable to those observed at the tower of Frohnau on 22–26 July 1994, during the FluMOB campaign (Stark and Lutz, 1997) and with airborne measurements in the PBL made over the northeastern U.S. in August and September 1988 (Tremmel *et al.*, 1993). The higher mixing ratios on 21 July are still within the range of other PBL measurements (Lee *et al.*, 2000). In the afternoon of 21 July, the weather conditions were similar between Eichstädt and Lotharhof but quite different between Eichstädt and Pabstthum. Sudden local thunderstorms with rain influenced the stations Pabstthum and Menz, so that measurements had to be interrupted to avoid damage from lightning strokes. At the onset of rain, both stations recorded a sudden drop in H_2O_2 due to its uptake into rain droplets. In Eichstädt and Lotharhof only the wind direction
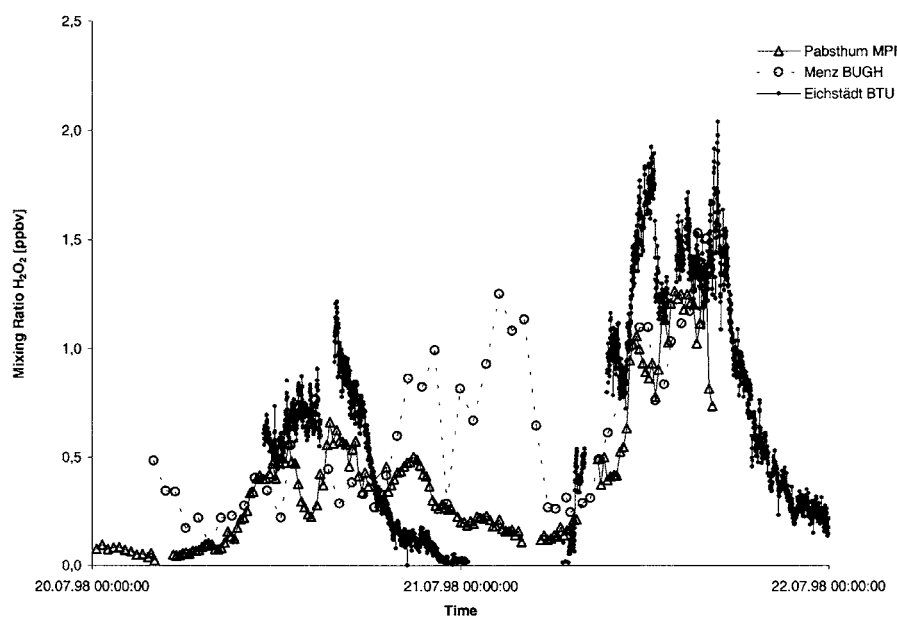
Figure 2. Comparison of the H_2O_2 mixing ratios measured on 20–21 July 1998 at Pabstthum, Menz and Eichstädt during the BERLIOZ campaign.

changed at noon to west (270°) and some high level clouds has been observed. These stations were neither influenced by thunderstorms nor by rain. Therefore a normal summer day diurnal variation of the total peroxide mixing ratio were measured at both stations and H_2O_2 mixing ratio decreased slowly to a night-time minimum as on 20 July (Figure 2, Eichstädt line).

Mixing ratios of total peroxide (H_2O_2 + organic peroxides) show a similar diurnal variations as H_2O_2 on 20 and 21 July with measurements at Lotharhof and Eichstädt being in a very good agreement over most of the time. Total peroxide mixing ratios at Lotharhof are also in good agreement with measurements in Menz during the first peak in the late afternoon. However, total peroxides in Menz and Pabstthum (sum of H_2O_2, MHP, and HMHP) are substantially lower over most of the daylight hours on both days. A sudden drop in total peroxide was observed at Lotharhof about 4 hours later than in Menz and Pabstthum. No rain was observed during this time but meteorological observations suggest transport of air from nearby thunderstorms. On average, H_2O_2/total peroxide ratio was about 2:3 during the daylight hours on 20 and 21 July, which is comparable to measurements at the tower of Frohnau on 22–24 July 1994, and other places (Stark and Lutz, 1997; Tremmel *et al.*, 1994).

The major hydroperoxide present throughout the campaign was H_2O_2, but the organic peroxides MHP and HMHP were occasionally found as well. Diurnal variations of the MHP and HMHP mixing ratios observed in Pabstthum and Menz are shown in Figure 4(a). The diurnal variations were much less pronounced than those
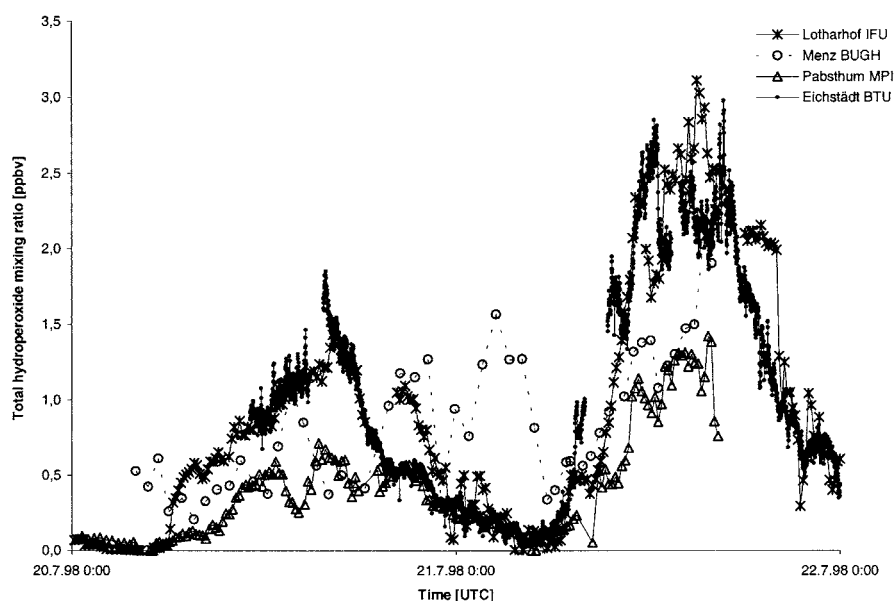
Figure 3. Comparison of the total hydroperoxide (H_2O_2 + organic hydroperoxides) mixing ratios measured on 20–21 July, 1998 at Pabstthum, Menz and Eichstädt (also shown 19 July, 1998) during the BERLIOZ campaign.

of H_2O_2. Figure 4(b) displays the organic hydroperoxides measured in Eichstädt, and the sum of MHP and HMHP mixing ratios measured in Menz and Pabstthum. MHP mixing ratios in Pabstthum were very low, ranging from below the detection limit of 15 pptv to 60–70 ppt during the intensive phase of the campaign, while ca. five times as much (up to 400 ppt) was found in Menz.

The total hydroperoxide concentration during the intensive part of the campaign amounted to as much as 3 ppb in the afternoon of 21 July 1998, at Lotharhof and Eichstädt (Figure 3). At neither of the other two stations (Menz and Pabstthum), however, did the total hydroperoxide concentration attain these very high levels. Any explanation of these results has to take into consideration the fact, that this great increase in the hydroperoxide concentrations was also observed with the HPLC system with a sampling coil, which during the preparatory intercalibration did not differ statistically from the cryosampling, even with real samples. HMHP could be found in only a few samples on 20 and 21 July, with a maximum mixing ratio of 25 pptv in Pabstthum, but again larger values up to 130 ppt in Menz. The reason for these large differences is not clear. Recent laboratory measurements have indicated that HMHP decomposes heterogeneously at glass surfaces to formic acid (Neeb *et al.*, 1997). Thus HMHP in the air may have been converted to formic acid at the glass wall of the manifold during sampling.

It has been noted that on 20 July a second H_2O_2 maximum was observed at Pabstthum and Menz in the evening hours (22 UT) (see Figure 2). At the Menz
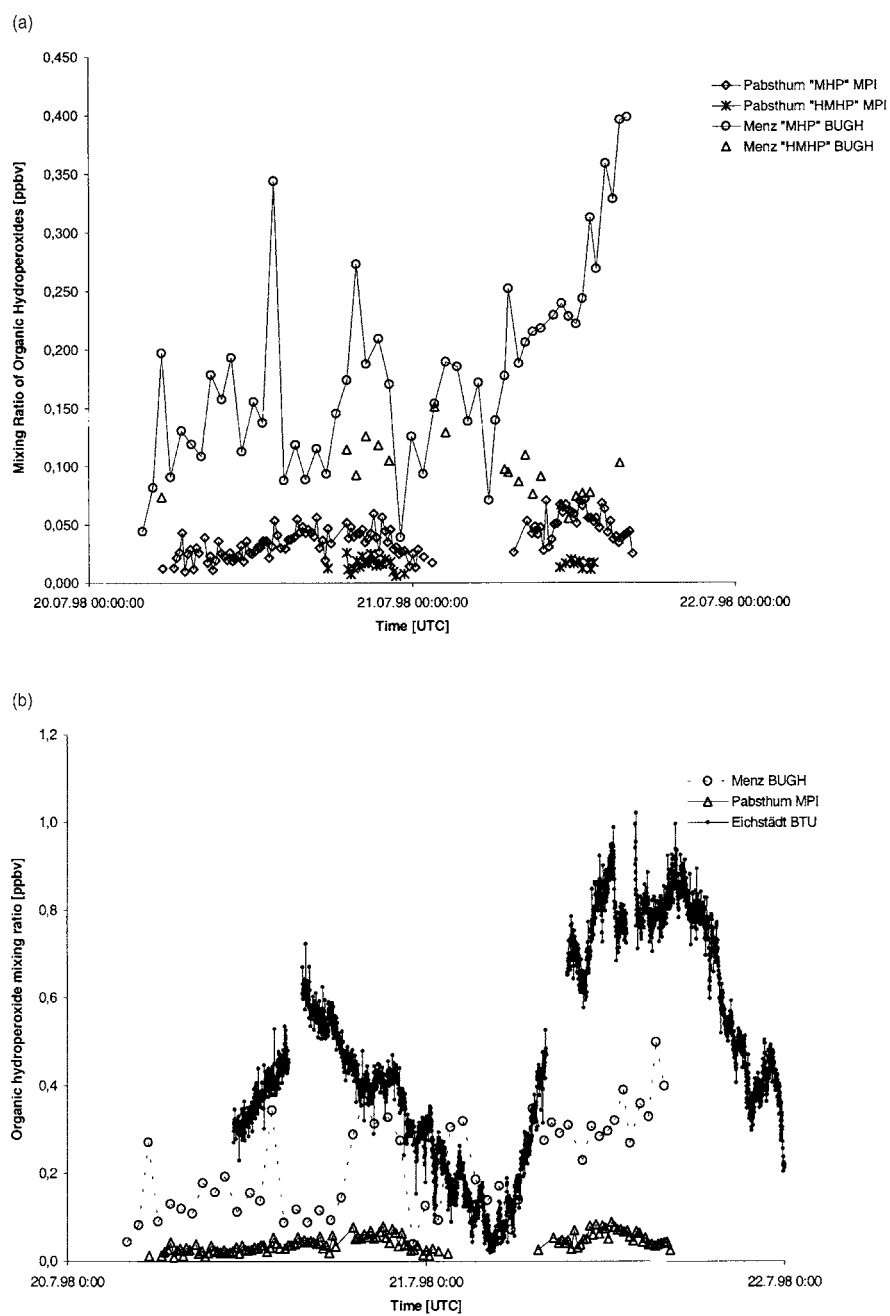
Figure 4. (a) Comparison of organic hydroperoxides (MHP and HMHP) at Pabstthum and Menz during the BERLIOZ campaign on 20 and 21 July 1998. (b) Comparison of total organic hydroperoxides at Eichstädt, Pabstthum and Menz during the BERLIOZ campaign on 20 and 21 July 1998.

station another strong maximum was observed during the night. During the evening period the HO_x concentrations were significant above the detection limit, which can be explained by reactions of VOC with O_3 (Platt *et al.*, 2002). There are some indications that H_2O_2 is produced from another source, namely from the reaction of ozone with alkenes under humid conditions (Grossmann *et al.*, 2001). Indeed, recent laboratory investigations (Grossmann, 1999; Valverde-Canossa *et al.*, 2001) have reported enhanced H_2O_2 and $HOCH_2OOH$ (HMHP) yields in the ozonolysis of a series of anthropogenic and biogenic alkenes in the presence of water vapour. Evidence of this HO_x independent additional source is substantiated by the fact that very high mixing ratios of unsaturated organic species (Konrad *et al.*, 2001) were observed during this period, and model calculation by Geyer *et al.* (2001) have shown that ozonolysis reactions were dominant during the evening hours. In addition, HMHP was observed in Pabstthum only on 20 July, and is a unique product from the ozonolysis of exocyclic biogenic alkenes.

3.2. CARBONYL COMPOUNDS

This sensitive method for the analysis of carbonyl compounds allowed the determination of a series of straight (C_2 to C_{10}) and branched (isobutyraldehyde, 3-methylbutyraldehyde) alkanals, saturated (acetone, 2- and 3-pentanone, 2- and 3-hexanone) and unsaturated carbonyls (methacrolein, methylvinylketone, acrolein, crotonaldehyde), hydroxy carbonyls (glycolaldehyde, hydroxyacetone) and dicarbonyls (glyoxal, methylglyoxal, biacetyl), aromatic compounds (benzaldehyde, *o*- and *m*-tolylaldehyde) and aldehydes derived from the biogenic VOCs (pinonaldehyde, nopinone, methyl-5-heptene-2-one, *trans*-2-hexenal, among many others (Schlomski, 2000)). In the following section, diurnal profiles of a series of selected carbonyls will be presented and discussed.

3.2.1. *Diurnal Profiles of Carbonyl Compounds*

The diurnal profiles of C_2 to C_{10} straight aldehydes from Pabstthum for the intensive period on 20 and 21 July are displayed in Figure 5. These aldehydes exhibit local concentration maxima during daytime and minima at night. The maxima mixing ratios decrease from C_2 to C_5, i.e., acetaldehyde (max ca. 0.6 ppb) to pentanal (max about 0.1 ppb). The main formation pathway for the lower carbonyl compounds ($<C_5$) result from the NO_x-mediated photooxidation of both anthropogenic and biogenic precursors, mainly via reaction with OH radicals and O_3 (Carlier *et al.*, 1986; Atkinson, 1997). These precursor hydrocarbons (not shown) exhibit highest concentrations during the morning hours and a minimum mixing ratios during the day (Konrad *et al.*, 2001).

In contrast to C_4–C_5 carbonyl compounds, with nearly identical daily profiles, hexanal, nonanal and decanal reach mixing ratios up to 0.25, 0.17 and 0.13 ppb, respectively. The mixing ratios of heptanal and octanal are in the range of 0.07 and 0.04 ppb, respectively. There is strong indication that hexanal is mainly emit-
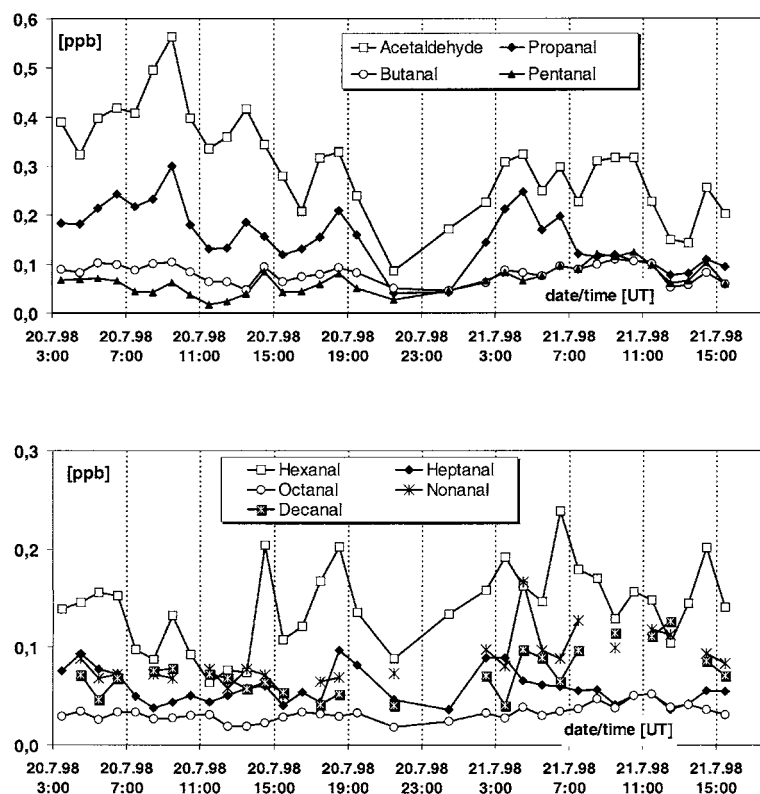
Figure 5. Temporal variations of a series of straight alkanals measured at Pabstthum during BERLIOZ.

ted from grassland (Kirstine *et al.*, 1998). Higher aldehydes including hexanal, nonanal, decanal and have been observed in air and in emissions of various plants species (Owen *et al.*, 1997; Kotzias *et al.*, 1997). *Trans*-2-hexenal was occasionly observed in Pabstthum during mowing activities of nearby pasture; this compound is emitted by plants in response of mechanical injury (Kirstine *et al.*, 1998).

Photolysis and reactions with OH radicals account for the removal of carbonyl compounds. Other physical sinks like wet deposition and transfer into the aerosol phase might also be important for carbonyl compounds, the latter being highly polar and soluble in water (Forstner *et al.*, 1997).

3.2.2. *Photooxidation Products of Isoprene*

The OH-initiated oxidation of isoprene, as the most abundant biogenic hydrocarbon, under NO_x conditions involves the formation of many carbonyl compounds. The major primary products are formaldehyde, methylvinylketone (MVK) and methacrolein (MACR), and secondary products are hydroxyacetone and glycolaldehyde (Grosjean *et al.*, 1993; Carter and Atkinson, 1996). Diurnal profiles for
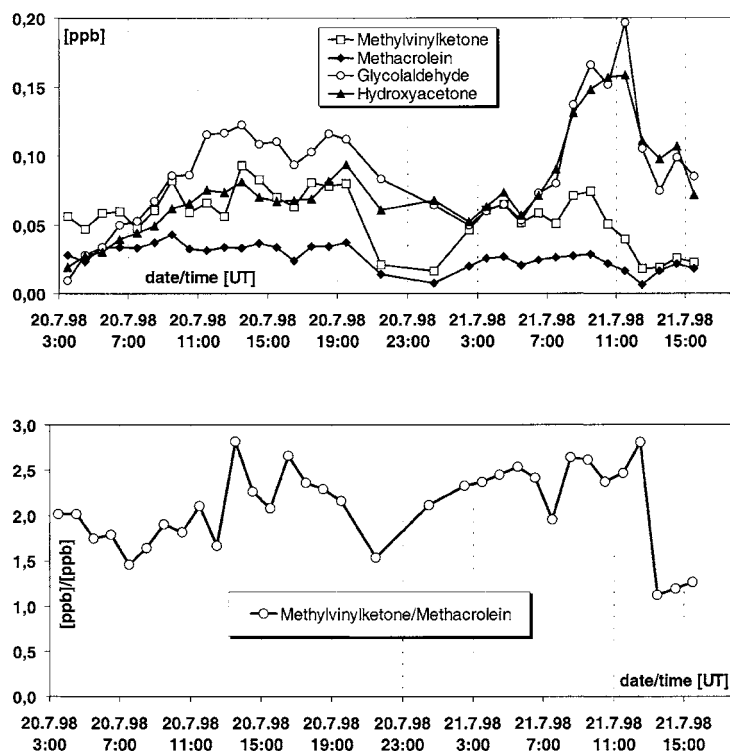
Figure 6. (a) Diurnal variation of carbonyl products generated from the oxidation of isoprene: Methylvinylketone (MVK), methacrolein (MACR), glycolaldehyde and hydroxyacetone. (b) Ratio of MVK/MACR for the same period. The data were obtained in Pabstthum during BERLIOZ.

these carbonyl compounds are shown in Figure 6. MVK and MACR reach maximum mixing ratios of ca. 0.10 and 0.04, respectively, on 20 and 21 July. As can be expected from the degradation mechanism of the OH-initiated reaction, MVK is more abundant than MACR by roughly a value of 2.5 at the daytime maximum. The MVK/MACR ratio is also plotted in Figure 6. The night-time ratio decreased to values in the range 1.5–1.0, and is consistent with the enhanced role of ozone-initiated reactions with isoprene and the unsaturated carbonyl compounds. Similar diurnal variation of MVK/MACR ratio was also observed by Martin *et al.* (1991), Yokouchi (1994), Montzka *et al.* (1995) and Biesenthal *et al.* (1997) in rural sites.

The secondary oxidation products of isoprene, hydroxyacetone and glycolaldehyde are also displayed in Figure 6. These products exhibit distinct concentration maxima (up to 0.16 and 0.20 ppb, respectively) during the day. The good correlation ($R^2 = 0.88$) of their mixing ratios (Schlomski, 2000) is another indication for isoprene as their common source. Glycolaldehyde has been previously measured in the boundary layer by Lee *et al.* (1998) with mixing ratios up to 3 ppb. However,
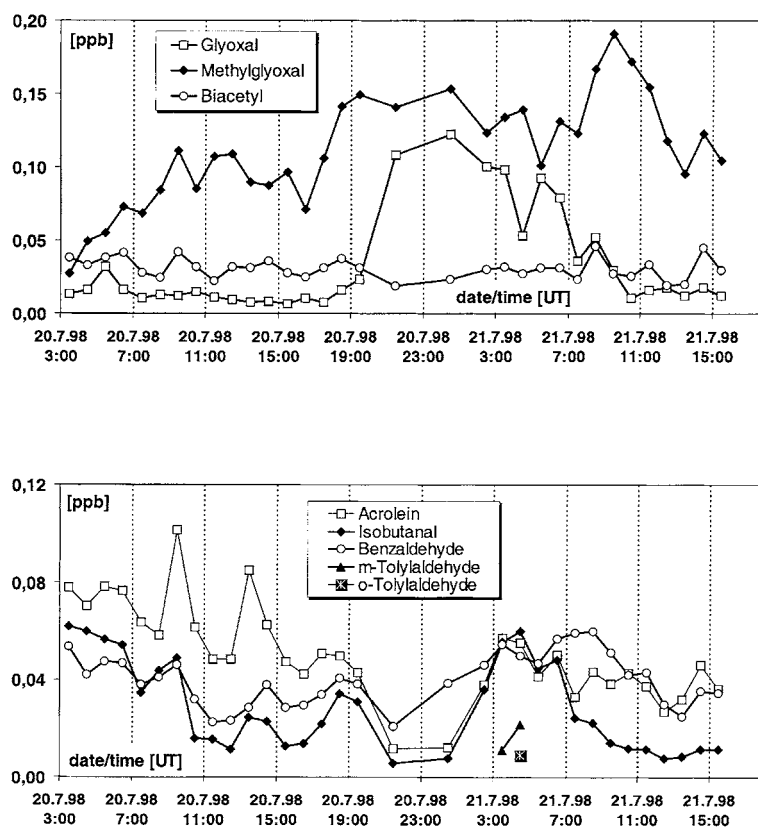
Figure 7. Diurnal variation of a series of dicarbonyl compounds, acrolein, isobutanal and several aromatic aldehydres as measured at Pabstthum during BERLIOZ.

no previous measurements of hydroxyacetone have been reported, showing the excellent performance of the novel analytical method.

3.2.3. *Other Selected Carbonyl Compounds*

In addition to the compounds shown in Figures 5 and 6, a series of other carbonyl compounds have been detected in Pabstthum, and are displayed in Figure 7. The dicarbonyl compounds glyoxal, methylglyoxal and biacetyl show different diurnal behaviour. The mixing ratio of methylglyoxal, also a secondary product of iso-prene, attains 0.1 and 0.2 ppb during daytime on 20 and 21 July, respectively, but does not follow the same diurnal pattern as the primary and other secondary products from the isoprene oxydation, shown in Figure 6. This is caused by variety of its sources, especially ozonolysis of low-molecular-weight branched alkenes and the breakdown of aromatic compounds (Atkinson, 1997). Figure 7 shows also carbonyl compounds derived from the degradation of aromatic compounds, benzaldehyde and *m*-tolylaldehyde (Finlayson-Pitts and Pitts, 1999).
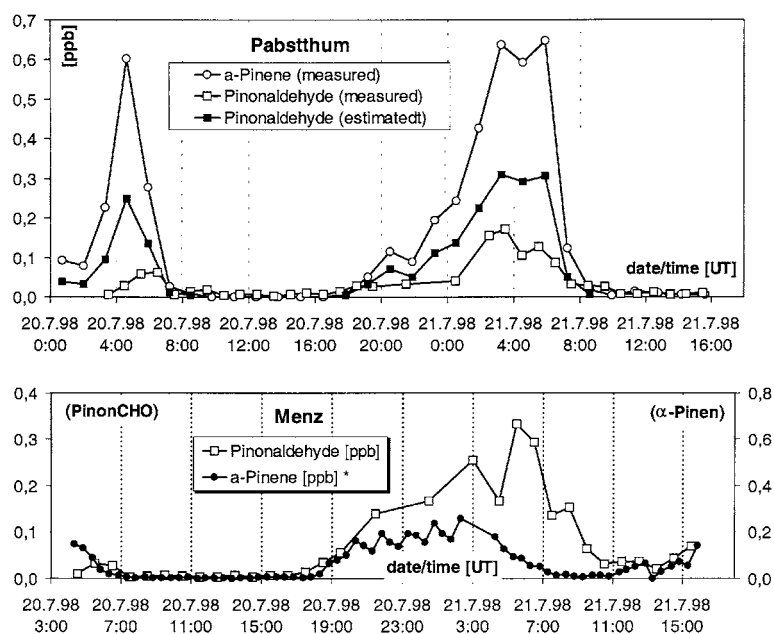
Figure 8. Diurnal variation of α-pinene and pinonaldehyde in Pabstthum and Menz. Hydro-carbon data from FZ-Jülich, ICG-2 (Pabstthum) and BUGH Wuppertal (Menz).

Pinonaldehyde has been found as one of the major products of the tropospheric oxidation of α-pinene with OH and NO_3 radicals and ozone (Grosjean *et al.*, 1992; Wängberg *et al.*, 1997; Jenkin *et al.*, 2000). Because α-pinene is the only precursor for pinonaldehyde in the atmosphere, the latter is an example of a carbonyl compound that is exclusively of secondary biogenic origin. During the BERLIOZ campaign, parallel measurements of α-pinene and pinonaldehyde were achieved for the first time. Both compounds were determined at the stations Pabstthum and Menz and are shown in Figure 8. α-Pinene had very low mixing ratios during the day, but pronounced maxima during the night. The chemical breakdown of α-pinene is initiated by the reactions with NO_3 radicals and ozone and results in the build-up of pinonaldehyde during the night. Both oxidants, NO_3 and ozone, were found in substantial concentrations during this period (Platt *et al.*, 2001; Volz-Thomas *et al.*, 2001a).

On the assumption that the night-time situation can be regarded as a closed reactor, it is possible to estimate the pinonaldehyde concentration from the concentrations of α-pinene, NO_3 and ozone in Pabstthum, averaged over one hour (Platt *et al.*, 2001; Volz-Thomas *et al.*, 2001a). Pseudo-first-order kinetics were assumed with kinetic parameters (in units of cm^3 molecule^{-1} s^{-1}) for α-pinene: $k_{OH} = 5.37 \times 10^{-11}$, $k_{NO_3} = 6.16 \times 10^{-12}$, $k_{O_3} = 8.66 \times 10^{-17}$ (Atkinson, 1997) and for pinonaldehyde: $k_{OH} = 9.1 \times 10^{-11}$, $k_{NO_3} = 5.4 \times 10^{-14}$ and $k_{O_3} = 8.9 \times 10^{-20}$ (Calogirou *et al.*, 1999). A comparison of the estimated and the

measured mixing ratios in Figure 8 shows lower values for the measured concentrations. The difference between the estimate and the measurement may be explained by dry deposition and phase transition (gas-particle) of pinonaldehyde. The specific reaction relationship between α-pinene and pinonaldehyde in combination with known rate constants and reaction yields could possibly be used to estimate radical concentrations without extensive measurement devices.

4. Conclusions

Mixing ratios of H_2O_2, HMP and HMHP at the four stations Eichstädt, Pabstthum, Lotharhof and Menz, leeward from Berlin, reflected the local photochemical production via the recombination of peroxy radicals, especially under typical high-summer conditions, when polluted air is transported from Berlin. There is, however, some evidence that an additional, light-independent source of H_2O_2 exists, namely the reaction of ozone with anthropogenic and/or biogenic alkenes.

The diurnal profiles of a series of linear alkanals (up to C_{10}) were measured. Primary and secondary carbonyl compounds derived from the isoprene oxidation products: methylvinylketone, methacrolein, glycolaldehyde and hydroxyacetone. The latter compound has been determined for the first time in rural air samples. Also pinonaldehyde as the direct photooxidation product of α-pinene was detected during the night. This can be used for source identification and assignment (α-pinene/pinonaldehyde) or to estimate radical concentrations without measuring them.

Acknowledgements

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