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Hydrogen peroxide, organic peroxides, carbonyl compounds, and organic acids measured at Pabstthum during BERLIOZ

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[1] Gas-phase H_2O_2, organic peroxides, carbonyl compounds, and carboxylic acids were measured from mid-July to early August 1998 during the Berlin ozone (BERLIOZ) campaign in Pabstthum, Germany. The rural site, located 50 km northwest from Berlin, was chosen to measure the pollutants downwind during a summer smog episode. The hydroperoxides showed pronounced diurnal variations with peak mixing ratios in the early afternoon. The maximum mixing ratios were 1.4 ppbv (H_2O_2), 0.64 ppbv (methylhydroperoxide), and 0.22 ppbv (hydroxymethyl-hydroperoxide). H_2O_2 was formed through photochemical activity, but originated also from vertical transport from air residing above the local inversion layer in the morning hours. Sometimes a second maximum was observed in the late afternoon-evening: This H_2O_2 might be formed from ozonolysis of biogenic alkenes. Ratios of H_2O_2/HNO_3 were used as indicators for the determination of NO_x-sensitive versus volatile organic compound (VOC)-sensitive regimes for photochemical production of ozone. Diurnal profiles were measured for alkanals (C_2-C_{10}), showing maximum mixing ratios decreased from C_2 (0.6 ppbv) to C_5 (0.1 ppbv) alkanals, which originate primarily from anthropogenic hydrocarbon degradation processes. However, higher C_6, C_9, and C_{10} alkanals show strong fluctuations (0.25, 0.17, and 0.13 ppbv, respectively), showing evidence of biogenic emissions. Both primary unsaturated carbonyl (methyl vinyl ketone, methacrolein) and secondary oxidation products of isoprene (hydroxyacetone and glycolaldehyde, up to 0.16 and 0.20 ppbv, respectively) showed excellent correlation. Diurnal profiles of glyoxal, methylglyoxal, biacetyl, benzaldehyde, and pinonaldehyde were also obtained. Formaldehyde was measured continuously by long-path DOAS and by an instrument based on the "Hantzsch" reaction; however, mixing ratios measured by DOAS (maximum 7.7 ppbv) were systematically larger by a factor of 1.3 on average, but by a factor of 1.7 during high photochemical activity. Homologous series of monocarboxylic acids were determined: Formic and acetic acid varied between 0.6 and 3.0 ppbv. The mixing ratio of the other dropped from 0.1 to 0.2 ppbv for C_3 to typical 0.01 to 0.03 ppbv for C_6, and from 0.01 to 0.002 ppbv for C_7 to C_9 monocarboxylic acids. *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry

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1. Introduction

[2] The aim of the Berlin ozone (BERLIOZ) campaign, conducted in July/August 1998, was to study the formation of photooxidants and oxidation products formed within a city plume during typical hot summer days. During such weather episodes, the expected wind direction is mainly coming from the southeast. Several ground based measurement stations were located at selected sites downwind the city. As discussed by *Volz-Thomas et al.* [2003a], Pabstthum was chosen as a central ground measurement station located about 50 km northwest from Berlin. The area around Pabstthum is extremely sparse populated (5 residences), with two small villages (<500 inhabitants) located about 6 km northeast and southwest, and a small town (Neuruppin, 38000 inhabitants) located 12 km northwest from the measuring site. A wide-spread meadows was chosen for the setup of the instrumentation. Radicals (OH, HO_2, RO_2, NO_3), all major trace gas species (NO, NO_2, NO_y, O_3, biogenic/anthropogenic VOCs, etc.), and meteorological parameters (temperature, wind-direction, wind speed, and relative humidity) were monitored by various groups at this station [*Alicke et al.*, 2003; *Geyer et al.*, 2003; *Glaser et al.*, 2003; *Holland et al.*, 2003; *Konrad et al.*, 2003; *Mihelcic et al.*, 2003; *Volz-Thomas et al.*, 2003a, 2003b]. In order to minimize any effects of the ground, most instruments were housed in containers, which were mounted on a 5-m platform.

[3] This paper describes the measurement of H_2O_2, organic peroxides, carbonyl compounds (aldehydes and ketones) and carboxylic acids measured at the Pabstthum site. The purpose of the measurements of these photooxidation products was to provide new data for an environment with high mixing ratios of anthropogenic and biogenic precursor hydrocarbons, in order to better understand their formation mechanisms within a city plume.

[4] Hydrogen peroxide (H_2O_2), methylhydrogenperoxide (MHP, CH_3OOH) and occasionally hydroxymethylhydroperoxide (MHP, $HOCH_2OOH$) were quantified in air samples. It is supposed that the major part of H_2O_2 and the organic hydroperoxides (ROOH) is formed via bimolecular and termolecular recombination reactions of peroxy radicals (HO_2, RO_2) [*Gunz and Hoffmann*, 1990; *Sakugawa et al.*, 1990; *Lee et al.*, 2000]. On the other hand, recent investigations have indicated that a significant amount of H_2O_2 and $HOCH_2OOH$ might come from the gas phase ozonolysis of alkenes, according to the reaction of stabilized Criegee-biradicals with water, thus without the participation of HO_2 [*Becker et al.*, 1990, 1993; *Simonaitis et al.*, 1991; *Gäb et al.*, 1985; *Neeb et al.*, 1997; *Sauer et al.*, 1999; *Grossmann*, 1999]. In this study we show evidence for this HO_2 independent source of H_2O_2 during the intensive phase of the campaign.

[5] An efficient method of determination of carbonyl compounds was tested during the campaign [*Schlomski*, 2000]. This method allowed the measurement of carbonyl compounds at the low pptv level: alkanals (C_2 to C_{10}), saturated (acetone, 2- and 3- pentanone, 2- and 3-hexanone) and unsaturated carbonyls (methacrolein, methyl vinyl ketone, acrolein, crotonaldehyde), hydroxycarbonyls (glycolaldehyde, hydroxyacetone) and dicarbonyls (glyoxal, methylglyoxal), benzaldehyde and pinonaldehyde, among many others. Formaldehyde was detected by two independent methods, via the Hantzsch technique and by differential optical absorption spectroscopy (DOAS) [*Alicke et al.*, 2003; *Geyer et al.*, 2003]. Also a novel procedure was used for the determination of carboxylic acids, allowing the simultaneous measurement of monocarboxylic acid (up to C_{10}) at the pptv level [*Kibler*, 1999].

2. Experimental Methods

2.1. H_2O_2 and Organic Peroxides

[6] The instruments for the collection and analysis of the peroxides in Pabstthum were located in a container mounted on a 5-meter high platform. Ambient gaseous H_2O_2, organic peroxides and also carbonyl compounds were pumped through a 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. No filters were placed in the inlet system. All peroxidic substances were collected using modified thermostatted (15 ± 0.3°C) coil collectors [*Hartkamp and Bachhausen*, 1987; *Neeb et al.*, 1997; *Sauer et al.*, 1999, 2001]. Technical details of the applied coil collector is described by *Sauer et al.* [1999, 2001] and *Grossmann* [1999]. Airflow rates were in the range of 2.5–4.5 sl min^{-1}, whereas the stripping solution, acidified 18 MOhm water (H_3PO_4, pH 3.5), was pumped with a peristaltic pump (Fa. Iamatek). Sampling was performed in a quasi-continuous mode. After passing through the coil collector, 2 mL of the stripping solution were injected into a sample vial of an autosampler, from which 500 μl was processed by HPLC. Analysis was performed immediately after collection and automatic sampling method allowed the measurement of peroxides every 22.5 min, which was the sampling interval during the intensive periods, also during the night.

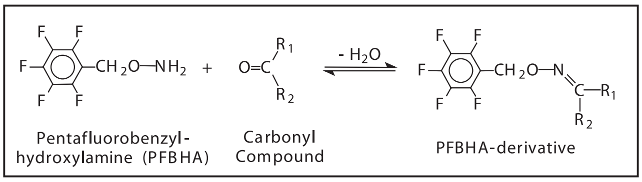
[7] Peroxide mixing ratios were determined by reversed-phase HPLC with postcolumn derivatization of *p*-hydroxyphenyl acetic acid through horseradish peroxidase. The method has been described in detail elsewhere [*Gäb et al.*, 1985; *Hellpointner and Gäb*, 1989; *Kurth et al.*, 1991; *Lee et al.*, 1995; *Sauer*, 1997; *Sauer et al.*, 1996, 1997, 1999, 2001; *Grossmann*, 1999]. Fluorescence detection of the biphenyl derivative formed in the derivatization reaction was done at wavelengths of λ_{Ex} = 287 nm and λ_{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% for H_2O_2, 100% for HMHP, and ~70% for MHP [*Sauer*, 1997]. Blanks were taken during each of the intensive measurement periods by passing pure N_2 through the coil under the same conditions applied in the measurements of ambient air. Occasionally, only small amounts of H_2O_2 were found in the blanks. Multipoint calibration of the HPLC for the peroxide analysis was performed once a day using H_2O_2 standard solutions with mixing ratios in the range of 10^{-6}–10^{-7} mol l^{-1}. Since it has been found that the method has the same response for HMHP, MHP, and EHP (ethylhydroperoxide) as for H_2O_2, the HPLC was calibrated with H_2O_2 only [*Kurth et al.*, 1991; *Staffelbach and Kok*, 1993; *Kok et al.*, 1995]. Organic hydroperoxides were identified by calculating the retention times relative to H_2O_2 and comparing the values with those of reference substances. Reference

substances were obtained as previously described [*Kok et al.*, 1995; *Lee et al.*, 1995; *O'Sullivan et al.*, 1996; *Sauer et al.*, 1997; *Sauer*, 1997]. The detection limit (d.l.), defined as three times the standard deviation of the analytical blanks, was 0.008 μmol l^{-1} using a 100 μl sampling loop. With regard to typical sampling conditions this corresponded to a detection limit of about 15 pptv for H_2O_2 and the organic peroxides in the gas phase. The formation of H_2O_2 from sampled O_3 was found to be <20 pptv per 100 ppbv of O_3. No correction of the H_2O_2 data with regard to this artifact was made. The loss of H_2O_2 and organic peroxides during sampling due to the oxidative reaction with SO_2 was estimated to be <10%.

[8] Peroxide measurements were not only performed during the BERLIOZ campaign in Pabstthum, but also at other ground stations Eichstädt, Lotharhof, and Menz [*Moortgat et al.*, 2002]. Prior to the BERLIOZ field campaign all the procedures were subjected to intercalibration. Details of the peroxide measurements performed at the various stations are described by *Grossmann* [1999] and *Moortgat et al.* [2002]. On the average, all instruments showed similar performance and measured H_2O_2 concentrations within the 10 to 15% of the preset gaseous mixing ratios. Deviation for HMHP and HMP were somewhat larger (30%).

2.2. Carbonyl Compounds

[9] Although the most commonly used method for measuring aldehydes and ketones in air is based on trapping carbonyl compounds according to the reaction with DNPH (2,4-dinitrophenylhydrazine) and HPLC analysis [*Vairavamurthy et al.*, 1992], another novel analytical technique was used at Pabsthum [*Schlomski et al.*, 1997]. Here solid adsorbent cartridges were used, which were coated with O-pentafluorobenzylhydroxylamine (PFBHA) as derivatization reagent, according to the reaction shown below:



The resulting oximes form *syn*- and *anti*-isomers. They exhibit excellent gas chromatographic properties and can be detected using a mass spectrometer (base peak at m/z 181) or, at higher sensitivity, with an electron capture detector.

[10] Sep-Pak tC_{18} cartridges (Waters, Millipore Corp.) were used for sampling. The cartridges were coated with 5 mL PFBHA solution (25 mg PFBHA in 50 mL water ≅0,05%) pulled through the cartridges with a syringe and stored under nitrogen in a freezer. Sampling was performed by drawing ambient air, via a PFA tubing, through the coated cartridges. Air was pumped through the cartridges for 1 hour at a flow rate of 500 ml/min. At night, the sampling intervals were extended to 3 hours at a flow rate of 333 ml/min. After sampling, the cartridges were resealed and stored in a freezer. Stability tests showed no degradation, nor increase in blank impurity levels over a period of 1 month.

[11] The collection efficiency of the PFBHA cartridges was tested by parallel sampling at different flow rates and resulted in an enrichment >95% for all analytes $\geq C_3$. Formaldehyde could not be measured due to the high volatility of its PFBHA derivative, but was determined by other techniques (see later). The PFBHA cartridges were calibrated with liquid carbonyl compound standards of various concentrations. Additionally, a laboratory comparison experiment was performed which showed a good correlation between the cartridge method and the FTIR spectroscopic technique [*Schlomski*, 2000].

[12] For analysis, the cartridges were eluted in the reversed sampling direction with 1 mL of hexene. One tenth of the organic extract was injected with a programmed temperature vaporizer (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 nonpolar column (HP-5, 60 m × 0.32 mm ID × 0.25 μm d_f) with hydrogen as carrier gas (5.5 ml/min) the PFBHA derivatives were determined with an electron capture detector (350°C, 60 ml/min N_2). For identification, a GC-MS system (HP 5890/5970) was used.

[13] Between 20 and 30 aldehydes and ketones were found in air samples taken during the BERLIOZ experiment [*Schlomski*, 2000]. A typical chromatogram of an air sample together with a cartridge blank is shown in Figure 1. Typical detection limits for most of the analytes varies between 10 and 50 pptv at a signal-to-noise ratio of two. The analytes acetone and methyl ethyl ketone were not considered due to the high and varying blank values which prevents a reliable quantification.

2.3. Formaldehyde

[14] The mixing ratio of formaldehyde was measured continuously at Pabstthum throughout the BERLIOZ campaign by two different techniques: (1) by **D**ifferential **O**ptical **A**bsorption **S**pectroscopy (DOAS) along a light path of 2 × 2.5 km length at an average height of 2.65 m, and (2), in-situ at the site in a height of 10 m by an instrument based on the "Hantzsch" reaction.

[15] The long path (LP) DOAS system used for the HCHO measurements consists of a single long light path, which is folded once between sending and receiving telescope. A telescope collimates light of a Xe-arc lamp and sends it onto a quartz cube-corner retroreflector array, which reflects the beam back into a receiving telescope. The light is then fed through a quartz-fiber mode mixer [*Stutz and Platt*, 1997] into a spectrograph-detector system. The instrument measures trace gas concentrations averaged over the length of the light path. A detailed description of the instrument used is given by *Platt* [1994], *Stutz* [1996], and *Geyer et al.* [1999]. Typically, a HCHO measurement was made every 30–90 min. During the BERLIOZ campaign, a mean detection limit of 0.7 ppbv (2σ) for formaldehyde was determined (the detection limit as twice the 1σ error [*Stutz and Platt*, 1997]). The error was determined for each spectrum from residual structures, which can not be explained by the reference spectra. The uncertainty of the formaldehyde cross section is ±5% [*Meller and Moortgat*, 2000], and the systematic error of the DOAS spectrometer was determined by *Stutz* [1996] as <±3%. The total systematic error of the HCHO concentration measured by DOAS is therefore <±6%.

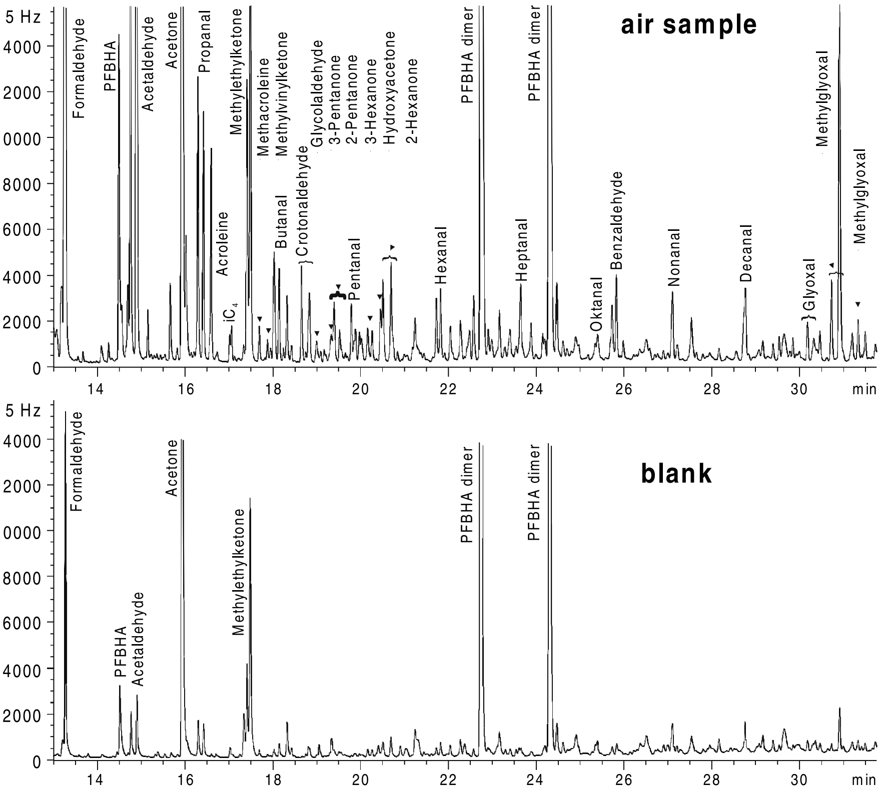


Figure 1. Chromatogram of a derivatized PFBHA air sample and a blank cartridge: Analytical system HP6890, with PTV injector 100μ; column HP-5, 60 m × 0.32 mm × 0.25 μm d$_f$; H_2 carrier gas, 70 cm s^{-1}, ECD Detector with 55 mL min^{-1}.

[16] A commercial instrument (AL4001, AeroLaser GmbH, Garmisch-Partenkirchen) was used to continuously determine the HCHO mixing ratio with a time resolution of 1 minute. The inlet of the Hantzsch system was located at the measurement site at a height of 10 m. The detection of formaldehyde is based on the so-called "Hantzsch" reaction [*Nash*, 1953; *Slemr*, 1999]. Formaldehyde in the gas-phase is trapped in aqueous solution in a stripping coil by pumping the ambient air via a stripping solution. The reaction of HCHO with a solution containing acetylacetone and ammonium generates a yellow color due to the production of diacetyldihydrolutinide, which is detected by its fluorescence at 412 nm. The system was calibrated once per day with liquid standards. Determination of the instrumental background was performed every 6 hours by switching a hopcalite scrubber into the sample flow. The variance (1σ) of the sensitivity and of the instrumental background was ±3% and ±100 pptv, respectively.

2.4. Organic Acids

[17] During the preparation of the BERLIOZ field experiment, a new procedure for the determination of carboxylic acids in the atmospheric gas phase was developed with a time resolution of less than 1 hour, and the system was successfully used in the field measurements [*Kibler et al.*, 1999]. As sampling technique a scrubber system for atmospheric carboxylic acids was optimized, using a flow rate of 8 L/min for a typical sampling time of 50 min. The scrubbing solution consisted of a 1 mmol/L NaOH with 50 μmol/L KI. A filter with 10 nm cut-off size was inserted to separate the particles. Capric acid (C_{10} MCA; monocarboxylic acid) was added as internal standard to the sample solution, which was adjusted to pH 2.

[18] The determination of carboxylic acids is based on the sequential reaction of dicyclohexylcarbodiimide (DDC) and 4-aminofluoresceine, followed by analysis by capillary electrophoresis and laser-induced fluorescence [*Kibler*, 1999]. The carboxylic acids in the aqueous solution react with an added solution of DCC in diethyl ether, forming in the organic phase unpolar *n*-acyl derivatives. This procedure results in enrichment by a factor 10 during sample preparation. A schematic diagram of the reaction is shown in Figure 2. After the reaction with 4-aminofluoresceine, the derivatives are extracted with a 10 mM NaOH-solution. This solution is analyzed by capillary zone electrophoresis combined with laser-induced fluorescence detection. The limits of detection of the analytical system are in the low nM-range. The required high matrix compatibility against carbonate, chloride or other ions is given. This method can be used for the simultaneous analysis of mono- and dicarboxylic acids.

[19] The entire analytical system was checked for its application in field experiments. An efficiency of almost 100% was found for all analyzed carboxylic acids. The relative standard deviation of the analytical system (incl. sampling) is 20% for acetic acid and 10% for pelargonic acid (C_9-MCA). For acetic acid, the analytical procedure was compared to a second method including a duplicate analysis of 74 scrubber samples with the newly developed

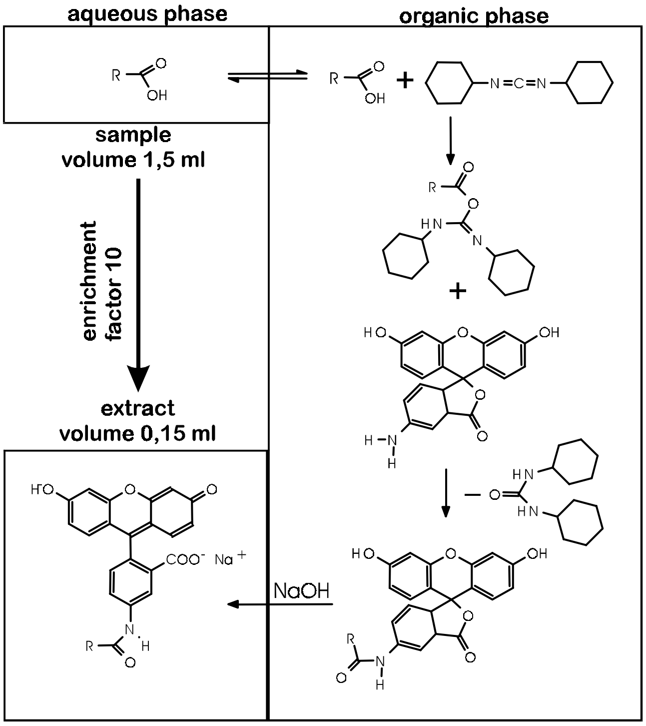


Figure 2. Derivatization of carboxylic acids with dicyclohexyl-carbodiimid (DCC) and 4-aminofluoresceine by phase transfer reaction.

CE-LIF detection and a home-built CE-system with indirect UV-detection. A good agreement of the two methods was found during this comparison study.

3. Results and Discussion

3.1. H_2O_2 and Organic Peroxides

3.1.1. General Pattern

[20] Samples were taken almost continuously between 14 July and 8 August 1998. Temporal profiles of the H_2O_2 and MHP mixing ratios for the time of the campaign are shown in Figures 3a and 3b. H_2O_2 was the major hydroperoxide at Pabstthum with mixing ratios between <15 pptv (detection limit) and 1.4 ppbv. The organic peroxides MHP and HMHP were found occasionally besides H_2O_2, whereas the other organic peroxides, such as bis-(hydroxymethyl)-peroxide (BHMP, $HOCH_2OOCH_2OH$) or performic acid (PFA, HC(O)OOH), were always below the detection limit (15 pptv). As tests showed, heterogeneous decomposition of the different peroxides in the coil was not of importance under the experimental conditions applied.

[21] For most of the campaign, southwesterly winds prevailed with relatively low concentrations of primary anthropogenic pollutants, because of the absence of major emission sources in this sector, except from the motorway A24 (10 km distance). On these days daily O_3 levels remained below 50 ppbv and H_2O_2 mixing ratios did not exceed 0.6 ppbv. During the period between 21 and 24 July, when the highest ozone levels (up to 100 ppbv) and the highest O_3 production rates were observed [*Volz-Thomas et al.*, 2003b; *Mihelcic et al.*, 2003] H_2O_2 levels were also enhanced. The maximum H_2O_2 mixing ratio measured at Pabstthum occurred on 21 July during the intensive period of the campaign (see later).

[22] The general diurnal cycle of H_2O_2 observed at Pabstthum is similar to that observed in earlier studies [e.g., *Sakugawa et al.*, 1990; *Das and Aneja*, 1994; *Watkins et al.*, 1995a, 1995b; *Jackson and Hewitt*, 1996; *Balasubramanian and Husain*, 1997; *Gnauk et al.*, 1997; *Staffelbach et al.*, 1997; *Sauer et al.*, 2001] with low values at night and a maximum in the afternoon (1200–1600 UT). Occasionally, a second peak occurred in the late afternoon-evening at 1800–2200 (UT). MHP was not detected on all days; the mixing ratios were very low and ranged from <15 pptv (d.l.) to maximum 50 pptv observed during the intensive phase of the campaign. The diurnal variations were much less pronounced than for H_2O_2. HMHP could be found in a few samples only, on 20 and 21 July, with a maximum mixing ratio of about 25 pptv.

3.1.2. Intensive Phase

[23] During the intensive phase from 20 to 21 July 1998, a high-pressure zone (cloud free) was established with winds from the southerly directions, bringing warm air over the Berlin area. The maximum temperature registered at Pabstthum was 34°C on 21 July. The relative humidity decreased from about 90% at night to 25% at noon. The H_2O_2 mixing ratio rose from about 0.1 ppbv at 0400 UT to 1.4 ppbv at 1500 UT, the highest value registered at the Pabstthum during BERLIOZ. In the afternoon of 21 July, a frontal system with lightning activity passed the BERLIOZ area, so that the measurements had to be interrupted to prevent damage of the instruments. When the rainfall started, a sudden drop of the H_2O_2 was registered, due to its uptake into rain droplets.

[24] In Figure 4 the measured wind velocities and wind directions are displayed for the 4 consecutive days from 20 to 23 July. On the average, the wind reached maximum speed around midday (4 to 6 m s^{-1}), to decrease in the late afternoon and evening. Also shown in Figure 4 are the mixing ratios of NO, NO_2, and O_3 and the photochemical activity (J_{NO2}) during the 4 days. Information on other days is presented by *Volz-Thomas et al.* [2003b].

[25] In the morning (0800–1000 UT) of 20 July NO_x-rich air (ca. 7 to 15 ppbv) was advected from the city plume of Berlin. The high NO_x mixing ratios observed during the night and in the early morning hours were caused by the accumulation of surface emissions below the nocturnal inversion layer [*Volz-Thomas et al.*, 2003b]. Above 100 m low concentrations of NO_x and hydrocarbons were measured [*Glaser et al.*, 2003]. At 1000 UT a sudden drop of NO_x was observed, leading to low NO_x-levels (few ppbv). A similar pattern was observed on 21 July, when high NO_x values of up to 30 ppbv occurred in the early morning, followed by a rapid drop due to the growing height of the mixing layer and changes in advection before the front which passed Pabstthum at 1100 UT. Behind the front, the wind turned clockwise via west to north and on 22 July back to west and later southwest. During the morning of 23 July the wind came from southeast (Berlin) and turned to the southwest over the day. The NO_2 peak seen on 23 July shows a clear signature of air from polluted areas. The slightly structured NO trace during daytime on 22 and 23 July is possibly due to advection of air from the motorway A24.

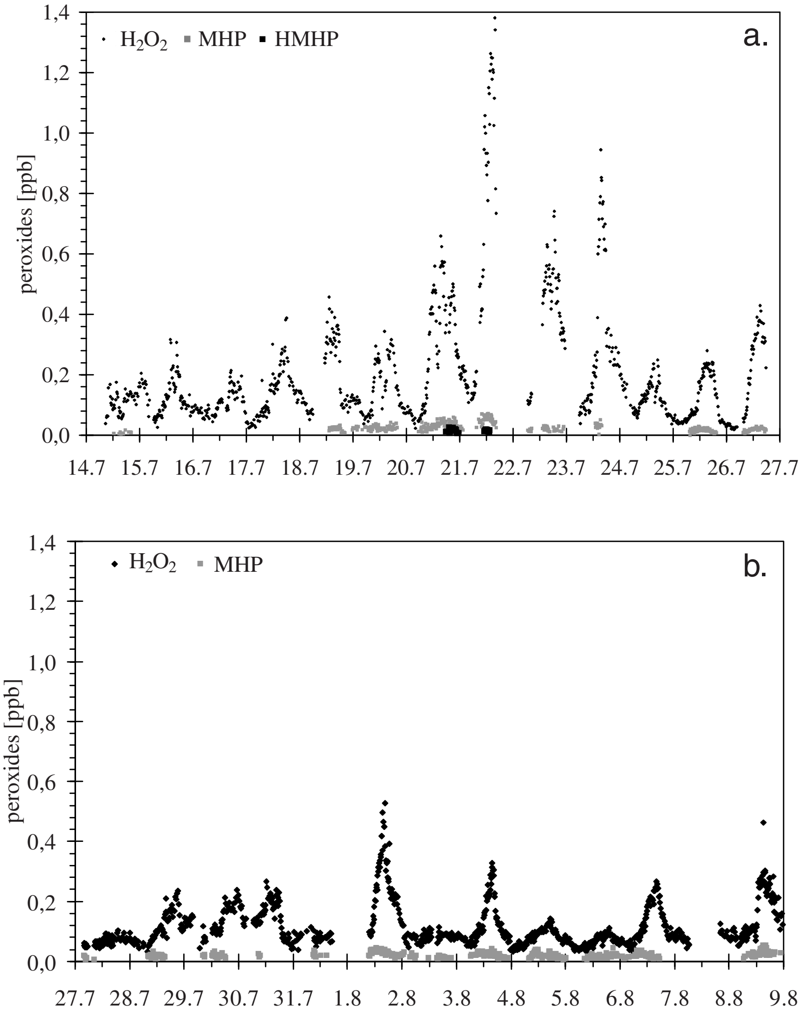


Figure 3. (a) Mixing ratios (ppbv) of H_2O_2, MHP and HMHP in Pabstthum from 14 to 26 July 1998. (b) Mixing ratios (ppbv) of H_2O_2, MHP and HMHP in Pabstthum from 27 July to 8 August 1998.

[26] Because of its high solubility, H_2O_2 is efficiently removed by deposition to the Earth's surface, which becomes most obvious at night under a shallow inversion and at low wind speeds, as it was often observed at Pabstthum [cf. *Glaser et al.*, 2003; *Volz-Thomas et al.*, 2003b]. In the morning upon break-up of the inversion, H_2O_2 concentrations at the surface increase by both, downward mixing of air from the residual layer aloft and by photochemical production from the HO_2 self-reaction

$$HO_2 + HO_2(+M) \rightarrow H_2O_2(+M).$$

[27] Chemical production is inhibited at high NO_x concentrations where HO_2 is converted into OH by the reaction

$$HO_2 + NO \rightarrow OH + NO_2$$

followed by the loss of HO*x* via reaction of OH with NO_2. The apparent anticorrelation of H_2O_2 with NO_x (see Figure 4) is thus expected from a pure chemical point of view. HO_2 radicals were measured at Pabstthum by chemical conversion to OH, which was subsequently detected by laser-induced fluorescence [*Holland et al.*, 2003]. It is thus possible to obtain some insight into the relative magnitude of chemical production.

[28] The concentration of HO_2 measured on 20 July are also displayed in Figure 5. At the high NO_x concentrations before 1000 UT, the concentrations of HO_2 are virtually zero and H_2O_2 remains at very low values with a slight decrease, most likely due to losses by deposition. The sharp increase of H_2O_2 at about 0930 UT on 20 July coincides with the drop in the NO_x mixing ratio and can be explained by vertical mixing and changes in advection. Between 1000 and 1200 UT, H_2O_2 continues to increase at a rate of roughly 0.14 ppbv h^{-1}. During this time, the chemical H_2O_2 production rate is 0.08 ppbv h^{-1}, as determined from the measured HO_2 concentration of about 3×10^8 molecule cm^{-3} [*Holland et al.*, 2003; *Mihelcic et al.*, 2003] and a rate coefficient of 7×10^{-12} cm^3 $molecule^{-1}$ s^{-1} [*Stockwell*, 1995] for conditions of 50% humidity. When assuming the HO_2 concentration at Pabstthum to be representative for the region upwind of the location, one could conclude that about half of the observed increase is due to in-situ formation, the rest still being due to the net effect of vertical exchange and dry deposition. The relatively strong variation of H_2O_2 after 1200 UT has no correspondence in the HO_2

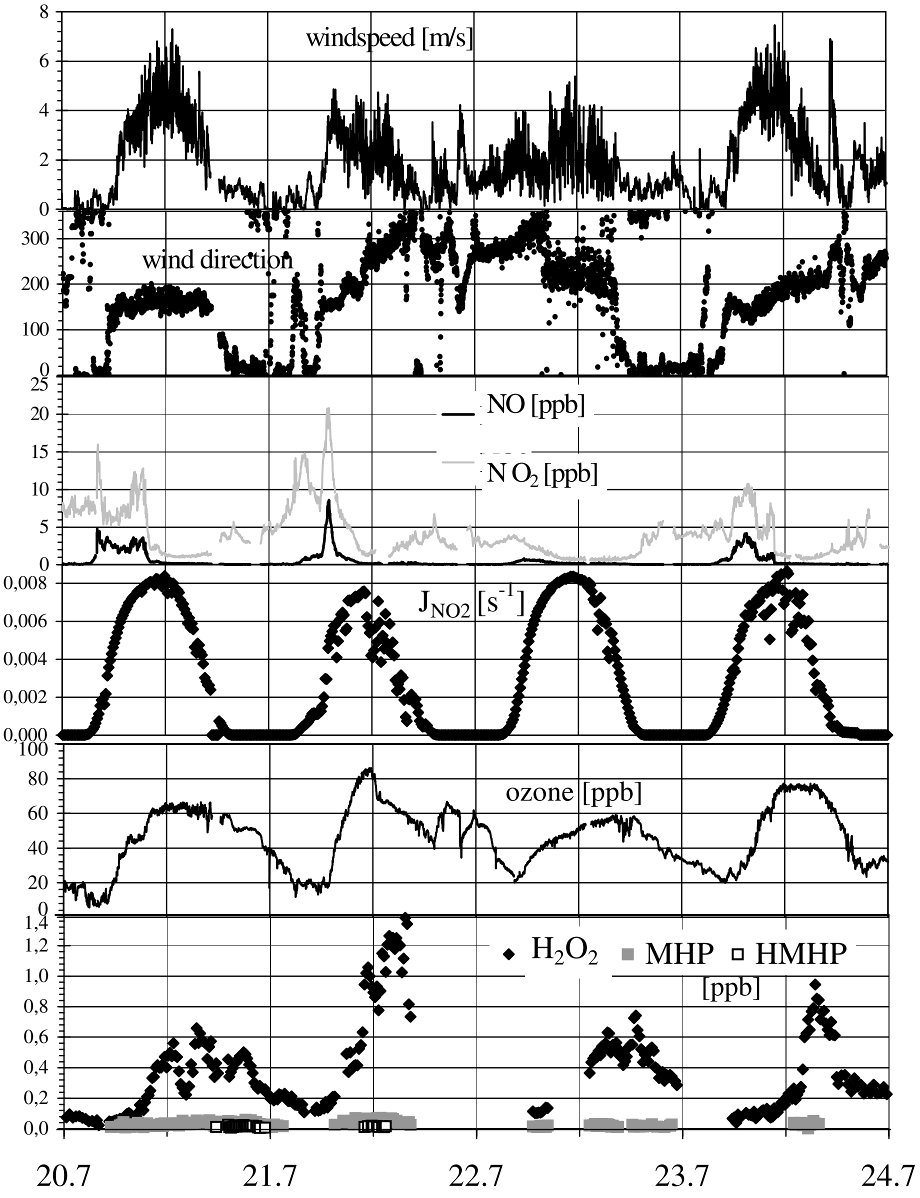


Figure 4. Wind speed (m s^{-1}), wind direction, J_{NO2} (s^{-1}), and mixing ratios of NO, NO_2, O_3, H_2O_2, MHP, and HMHP (ppbv) measured at Pabsthum during the BERLIOZ Campaign during the period 20 to 25 July 1998.

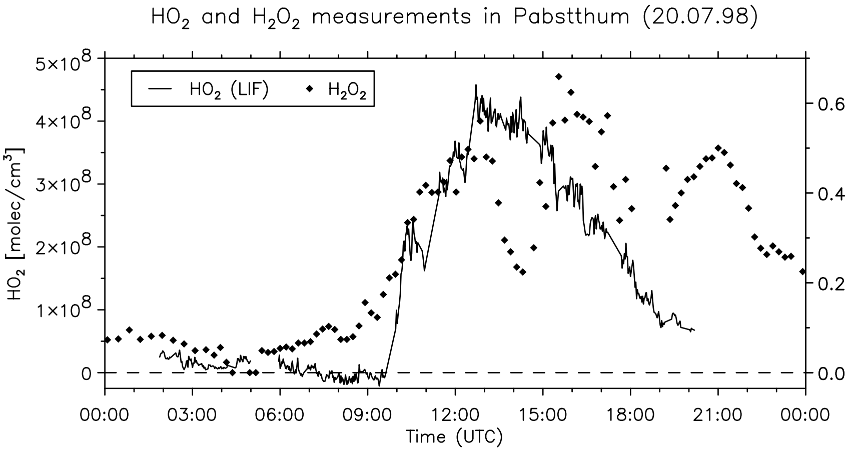


Figure 5. Concentration profiles of HO_2 and H_2O_2 measured at Pabstthum on 20 July 1998.

concentration and thus gives a clear indication for transport processes dominating the observed changes in the local H_2O_2 mixing ratios at the surface.

3.1.2.1. H_2O_2 Formation From Ozonolysis Reactions

[29] There are some indications that peroxides are produced in the reaction of ozone with alkenes [*Gäb et al.*, 1985; *Becker et al.*, 1990, 1993]. 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 vapor. Ozone adds to the double bond of the alkene molecule forming a primary ozonide (POZ), which decomposes to form excited so-called "Criegee intermediates" and carbonyl compounds:

$$RR'C = CH_2 + O_3 \rightarrow POZ \rightarrow [RR'COO]^* + CH_2O$$
$$\rightarrow [CH_2OO]^* + RR'CO$$

The excited Criegee intermediate can decompose to OH, HO_2, and other radical species [*Neeb and Moortgat*, 1999; *Mihelcic et al.*, 1999], or be thermalized by collisions to form stabilized Criegee intermediates:

$$[RR'COO]^* \rightarrow OH,\ \text{peroxy radicals, etc}$$

$$[CH_2OO]^* \rightarrow OH, HO_2, CO, CO_2$$

$$[RR'COO]^* + M \rightarrow RR'COO$$

$$[CH_2OO]^* + M \rightarrow CH_2OO$$

The OH yields of up to 100% were found depending on the structure of the alkene [*Calvert et al.*, 2000]. The direct formation of OH, HO_2 and peroxy radicals via ozonolysis reactions might be important for nighttime or low-solar intensity conditions [*Paulson and Orlando*, 1996; *Ariya et al.*, 2000; *Bey et al.*, 1997].

[30] It was, however, recently shown by *Grossmann* [1999] and *Valverde-Canossa et al.* [2001] that the stabilized Criegee intermediates, RR′COO, formed by the reaction of ozone with alkenes, react under atmospheric conditions with water vapor, thus forming RR′C(OH)OOH. This hydroxyalkyl hydroperoxide (HAHP) decomposes primarily to H_2O_2 and the carbonyl compound RCOR′, when R and R′ are alkyl groups:

$$RR'COO + H_2O \rightarrow RR'C(OH)OOH$$

$$RR'C(OH)OOH \rightarrow RCOR' + H_2O_2$$

In the case of terminal alkenes, the simplest CH_2OO is the precursor of $HOCH_2OOH$ (HMHP) [*Neeb et al.*, 1998]:

$$CH_2OO + H_2O \rightarrow HOCH_2OOH$$

[31] Evidence of H_2O_2 formation after sunset (1913 UT) is seen in Figure 5 from the measured H_2O_2 mixing ratios measured during the evening hours on 20 July 1998. The chemical regime of this night was determined by very high mixing ratios of organic species [*Konrad et al.*, 2003]. Model calculations by *Geyer et al.* [2003] showed that ozonolysis was the dominant source of OH and HO_2 radicals during the evening hours. The mixing ratio of HO_2 during this time period was 4 ± 1 pptv, about 20% of the maximum value observed at mid day [*Mihelcic et al.*, 2003]. Since nearly identical H_2O_2 levels (0.5 ppbv) were observed at 1200 and 2200 UT, the H_2O_2 production cannot uniquely been explained by the recombination of HO_2 radicals and advection of surrounding air, suggesting that the production via the ozonolysis process under atmospheric conditions (50% relative humidity) is an important nighttime source of H_2O_2. Further evidence for this source is substantiated by the fact that $HOCH_2OOH$ (HMHP) was only observed during these periods on 20 and 21 July (see Figures 3a and 3b). $HOCH_2OOH$ is an unique product from the ozonolysis of exocyclic biogenic alkenes [*Grossmann*, 1999; *Valverde-Canossa et al.*, 2001].

[32] Diurnal variations of the MHP and HMHP mixing ratios observed in Pabstthum are shown in Figure 3. MHP mixing ratios in Pabstthum were very low, ranging from <15 pptv (d.l.) to 60–70 pptv during the intensive phase of the campaign, while higher values were found in other stations [*Moortgat et al.*, 2002]. The daytime MHP levels were similar (or lower) to those reported from other field studies [*Das and Aneja*, 1994; *Fels and Junkermann*, 1994; *Watkins et al.*, 1995a; *Staffelbach et al.*, 1997].

[33] The HMHP mixing ratios at Pabstthum (about 25 pptv) were but were much lower than those reported by *Hewitt and Kok* [1991], *Lee et al.* [1993], and *Staffelbach et al.* [1997]. These data sets are difficult to compare directly, because of differences in location, emission patterns, and chemical regime. For instance, *Lee et al.* [1993] reported HMHP values up to 5 ppbv in southern-eastern United States during photochemical episodes with high ozone and isoprene concentrations. *Staffelbach et al.* [1997] reported day maxima of 0.25 ppbv during a photochemical episode in southern Switzerland. However, considering the high values seen by *Lee et al.* [1993], it has to be taken into account that artifact formation of HMHP is possible during sampling, especially when using cryogenic methods [*Moortgat et al.*, 2002; *Staffelbach et al.*, 1995].

3.1.3. Analysis According to Sillman-Indicator H_2O_2/HNO_3

[34] The photochemical production of ozone depends in a complex fashion on the concentrations of nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds (VOC). At good approximation, the photochemistry can be separated into an NO_x-sensitive and a VOC-sensitive regime. *Sillman* [1995] proposed a concept of using different trace gases and trace gas ratios in order to determine if the ozone concentration measured at a given location was produced under NO_x- or VOC-sensitive conditions. From a series of model simulations, the H_2O_2/HNO_3 ratio was found to be most suitable indicator, with the NO_x-sensitive regime being represented by enhanced values of H_2O_2/HNO_3 and vice versa.

[35] *Hammer et al.* [2002] discuss an investigation of the indicator concept using the nonhydrostatic model system KAMM/DRAIS [*Vogel et al.*, 1995] for different areas,

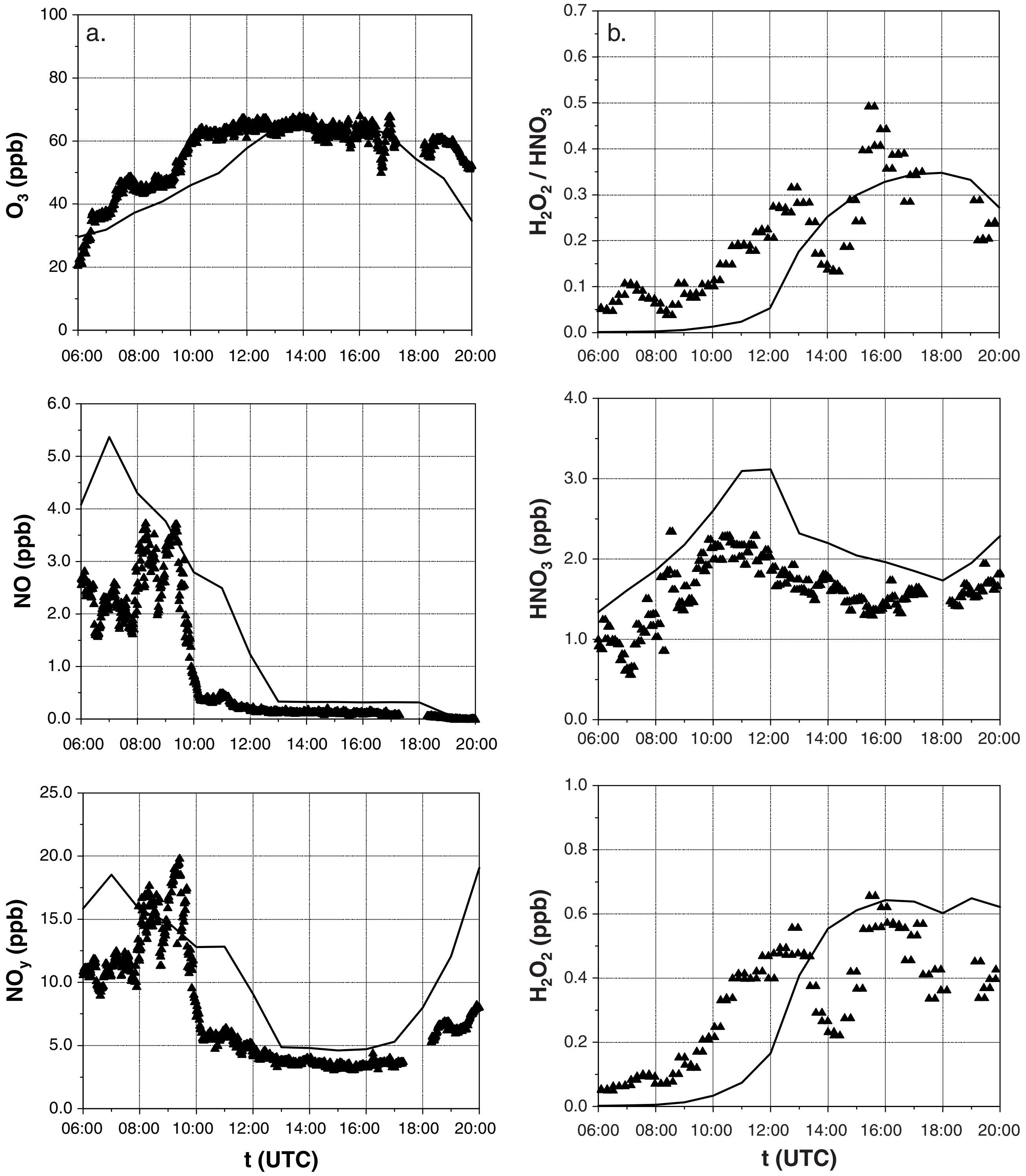


Figure 6. (a) Observed (points) and simulated (full lines) time series of O_3, NO, and NO_y, during 20 July 1998 at Pabstthum. (b) Observed (points) and simulated (full lines) time series of H_2O_2, HNO_3, and H_2O_2/HNO_3 during 20 July 1998 at Pabstthum. The grey line gives the transition value of H_2O_2/HNO_3 found by *Hammer et al.* [2002].

meteorological, and emission conditions. The grid size in this application was 2 × 2 km^2 with 25 layers in the vertical direction varying from 16 m close to the surface to 450 m at the top of the domain (6 km above sea level). Chemistry was treated with the RADM2 mechanism [*Stockwell et al.*, 1990]. KAMM/DRAIS was extensively validated against observations in the past [*Vogel et al.*, 1995; *Nester et al.*, 1995; *Fiedler et al.*, 2000; *Corsmeier et al.*, 2002]. The calculations yielded a fairly robust transition value for H_2O_2/HNO_3 of 0.2, almost independent of the ambient and the emission conditions.

[36] The simulations were also carried out for the first intensive measuring phase of the BERLIOZ campaign. A detailed description of the input data and the set-up of the model are described by *Hammer et al.* [2002] and *Hammer* [2001]. The model results for O_3, NO, NO_y, H_2O_2, HNO_3, and H_2O_2/HNO_3 are compared in Figure 6 with the measurements made at Pabstthum on 20 July. Between 0600 and 1000 UT the concentrations of H_2O_2 were below 0.2 ppbv. After 1000 UT H_2O_2 increased and reached its maximum ($\sim$0.65 ppbv) at 1530 UT. The measured concentrations of HNO_3 showed a maximum (2.7 ppbv) between 1000 and 1200 UT. Later, the concentration of HNO_3 decreased slightly. With some exceptions the diurnal cycles of H_2O_2 and HNO_3 are reproduced by the model. Especially for H_2O_2 larger differences are obvious. The underestimation of H_2O_2 by the model before 1300 UT has two reasons. First the concentration of H_2O_2 is initialized with very small values. Second the development of the boundary layer and the transition from the city plume to clean air at Pabstthum occurs earlier and more rapidly than in the model. The observed decrease of H_2O_2 between 1300 UT and 1600 UT is not reproduced by the model. The simulated HNO_3 values are higher than the observed ones, partly because the simulated concentrations corresponded to a height of 16 m above ground, whereas the measurements were made at 10 m. Another reason is that the KAMM/DRAIS simulations did not include aerosols. Although the method for the measurement of HNO_3 at Papstthum [*Volz-Thomas et al.*, 2003b] should include a significant fraction of aerosol nitrate (e.g., NH_4NO_3), the modeled HNO_3 concentrations are expected to be somewhat higher than the observed ones. Simulated and observed diurnal cycles of HO_2 (not shown) are in agreement for the occurrence of the peak concentration at 1300 UT. The absolute concentrations are overestimated by about 20% (4.50×10^8 cm^{-3} observed versus 5.60×10^8 cm^{-3} calculated). This result is similar to chemical box model calculations by *Mihelcic et al.* [2003] and *Konrad et al.* [2003].

[37] The upper panel in Figure 6b shows the diurnal cycle of the indicator H_2O_2/HNO_3. The thick gray line represents the transition between VOC and NO_x sensitivity. The measurements indicate that the observed ozone concentration at Pabstthum was produced under VOC-sensitive conditions until 1000 UT and under NO_x-sensitive conditions after 1500 UT. Usually, the indicator method is applied to well mixed conditions only. However, *Hammer* [2001] found that the method also gives reasonable results during the rest of the day. The measured level and temporal evolution of H_2O_2/HNO_3 are reproduced by the model, predicting VOC sensitivity in the morning, NO_x sensitivity in the afternoon and the transition regime around noon. Reasons for the temporal shifts are the above discussed initialization for H_2O_2 and the slight delays in boundary layer development and advection.

3.2. Carbonyl Compounds

[38] The PFBHA 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 (2- and 3-pentanone, 2- and 3-hexanone) and unsaturated carbonyls (methacrolein, methyl vinyl ketone, acrolein, crotonaldehyde), hydroxycarbonyls (glycolaldehyde, hydroxyacetone) and dicarbonyls (glyoxal, methylglyoxal, biacetyl), benzaldehyde, toluylaldehydes and aldehydes derived from the biogenic VOCs (pinonaldehyde, nopinone, methyl-5-heptene-2-one, *trans*-2-hexenal, among many others). In the following section, diurnal profiles of a series of selected carbonyls measured during the intensive phase period during 20–21 July 1998 will be presented and discussed. Formaldehyde was measured by the DOAS and Hantzsch techniques and will be discussed separately.

3.2.1. Comparison of Diurnal Profiles of Carbonyl Compounds and Hydrocarbons

[39] The diurnal profiles of linear *n*-alkanals from C_2 to C_{10}, and the branched isobutanal are shown in Figures 7a and 7b for 20 and 21 July 1998. These aldehydes exhibit local concentration maxima during daytime, and minima during nighttime. The mixing ratios decrease from C_2 to C_5, i.e., acetaldehyde (max ca. 0.6 ppbv) to isobutyraldehyde (max 0.07 ppbv). The diurnal profiles of the linear C_4 and C_5 alkanals are similar with local mixing ratios near 0.1 ppbv. On the other hand, *n*-hexanal, *n*-nonanal, and *n*-decanal show strong fluctuations with mixing ratios reaching up to 0.25, 0.17, and 0.13 ppbv, respectively. The mixing ratios of *n*-heptanal and *n*-octanal are typically 0.07 and 0.04 ppbv.

[40] 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 precursors hydrocarbons (not shown) exhibit highest concentrations during the morning hours and a minimum mixing ratios during the day [*Konrad et al.*, 2003]. Due to its low reactivity and its sole origin from anthropogenic emissions, acetylene can be used as a marker for the meteorological situation and the contribution of anthropogenic emissions to the overall concentration of carbonyl compounds [*Possanzini et al.*, 1996; *Christensen et al.*, 2000]. The acetylene profile is shown in Figure 7c, and normalized concentration profiles are displayed for acetaldehyde, *n*-propanal and *n*-hexanal. Figure 7c shows more pronounced maxima during the day compared to the not-normalized profiles (see Figures 7a and 7b). This confirms the importance of photochemical reactions and/or primary biogenic emissions as sources for carbonyl compounds in the atmosphere. Photolysis and reactions with OH radicals account for the removal of carbonyl compounds. Other physical sinks are wet and dry deposition as well as phase transfer into the aerosol phase [*Munger et al.*, 1995; *Singh et al.*, 1994; *Forstner et al.*, 1997; *Denis et al.*, 1997].

[41] It is possible to compare the measured homologous *n*-alkanals with the *n*-alkanes, as presented in Figure 8 for the period of the intensive phase from 20 July, 0300 UT to 21 July, 1500 UT. The mean mixing ratios of the alkanes decrease from ethane (1.1 ppbv) to *n*-octane (0.014 ppbv), but increase slightly again for *n*-nonane and *n*-decane (0.022 ppbv). The mean mixing ratio of the *n*-alkanals decrease from acetaldehyde (0.30 ppbv) to *n*-pentanal

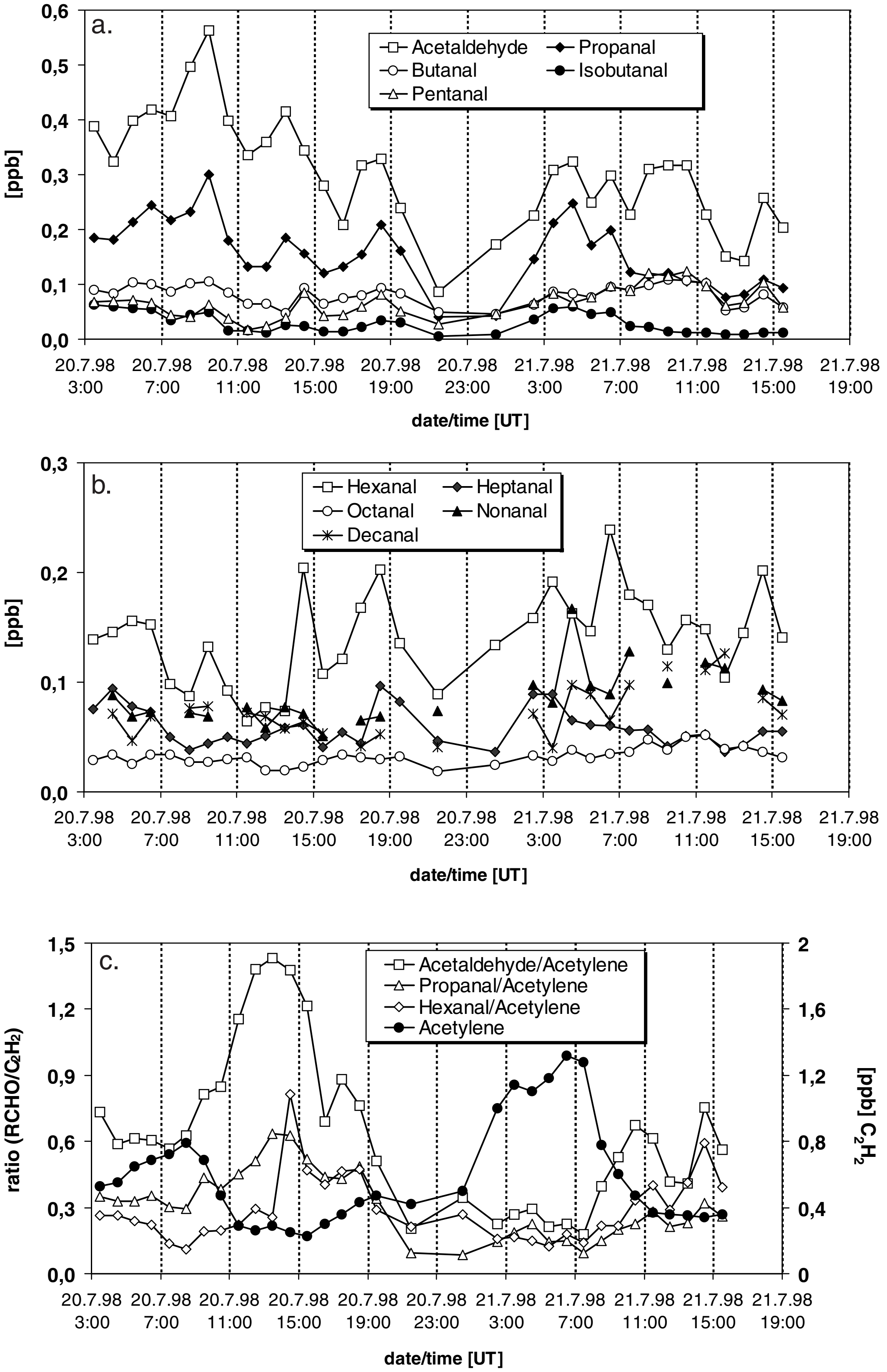


Figure 7. Temporal variations of aldehydes measured on 20–21 July 1998 at Pabstthum. Upper (a) C_2–C_5 Aldehydes; Lower (b) C_6–C_{10} linear alkanals; (c) Diurnal profiles of acetaldehyde, propanal, and hexanal normalized to acetylene.

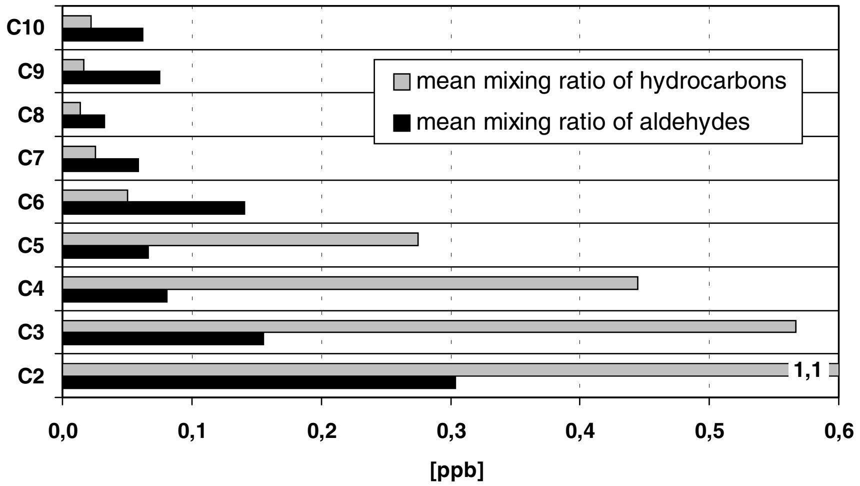


Figure 8. Comparison between the total measured mixing ratio of C_2 to C_{10} carbonyl compounds and hydrocarbons during the 20 July 1998, 0300 UT and 21 July 1998, 1500 UT at Pabstthum.

(0.067), but from *n*-hexanal on, the mixing ratio of the *n*-alkanals more than twice exceed those of the alkanes. If one assumes that the *n*-alkanals are generated from the OH-initiated oxidation of alkanes, it is evident that this is the mainly the case for species $\leq C_5$ [*Lange and Eckhoff*, 1996]. One must therefore assume that part of the *n*-alkanals $>C_5$ are biogenically emitted. There is strong indication that *n*-hexanal is mainly emitted from grassland [*Kirstine et al.*, 1998]. Higher aldehydes including *n*-hexanal, *n*-nonanal, *n*-decanal and have been observed in air and in emissions of various plants species [*Kotzias et al.*, 1997; *Owen et al.*, 1997]. Similar concentration distributions of longer chain aldehydes can be found elsewhere [*McClenny et al.*, 1998; *Ciccioli et al.*, 1993], together with the interesting detail that aldehydes higher than *n*-decanal show a much lower mixing ratio. The reason for this atmospheric phenomenon is still unknown. *Trans*-2-hexenal was occasionally observed in Pabstthum during mowing activities of nearby pasture; this compound is emitted by plants in response of mechanical injury [*Kirstine et al.*, 1998].

3.2.2. Photooxidation Products of Isoprene

[42] The OH-initiated oxidation of isoprene, as the most abundant biogenic hydrocarbon, under NO_x conditions involves the formation of many carbonyl compounds. The main primary products are formaldehyde, methyl vinyl ketone (MVK) and methacrolein (MACR), and secondary products are hydroxyacetone, glycolaldehyde [*Grosjean et al.*, 1993; *Carter and Atkinson*, 1996]. Diurnal profiles of isoprene and these carbonyl compounds are shown in Figure 9. MVK and MACR reach maximum mixing ratios of ca. 0.10 and 0.04, respectively, on 21 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. This ratio $[MVK]/[MACR] \approx 2.5$ was obtained during on both days during midday hours [*Moortgat et al.*, 2001]. The nighttime 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 in rural sites. [*Martin et al.*, 1991; *Yokouchi*, 1994; *Montzka et al.*, 1993, 1995; *Biesenthal and Shepson*, 1997].

[43] It is interesting to note in Figure 9 that the isoprene levels during daytime are much larger (factor 7) on 21 July than on 20 July. The levels of the primary oxidation products MVK and MACR are nearly identical on both days and even decrease on the 21, a few hours after the strong increase in isoprene. The photochemical lifetimes of isoprene, MVK and MACR with respect to OH are about 0.7, 4, and 2.2 hours, respectively, using an OH concentration of 4×10^6 molecule cm^{-3} [*Holland et al.*, 2003] and neglecting the minor pathway by reaction with ozone. In an air mass experiencing constant isoprene emissions during transport, MVK and MACR will reach photostationary state after a few hours. Under such conditions, the ratios between isoprene and its products is given by the inverse lifetimes and the product yields. While the absolute yields are not well known [*Montzka et al.*, 1993], chamber experiments by *Tuazon and Atkinson* [1990] suggest a relative product yield of around 3/2 for MVK/MACR. In such a situation, one would expect the mixing ratios of all three species to be of similar magnitude, with MVK exhibiting about 2 times higher concentrations than MACR. This situation is indeed observed during the early afternoon of 20 July (see Figure 9), suggesting that the air mass advected to Pabstthum on that day had indeed experienced relatively constant, albeit small, emissions for a longer period.

[44] The strong increase in isoprene observed between 0700 and 1500 UT on 21 July without a corresponding increase in the mixing ratios of MVK and MACR, on the other hand, can only be explained through very recent emissions of isoprene due to close-by sources. Indeed, as can be seen on Figure 4, the wind started to change direction in the morning hours from southeast to southwest and west. A few hundred meters west of the station was a mixed forest [*Volz-Thomas et al.*, 2003b], which is the likely source of the enhanced isoprene mixing ratios observed on that day.

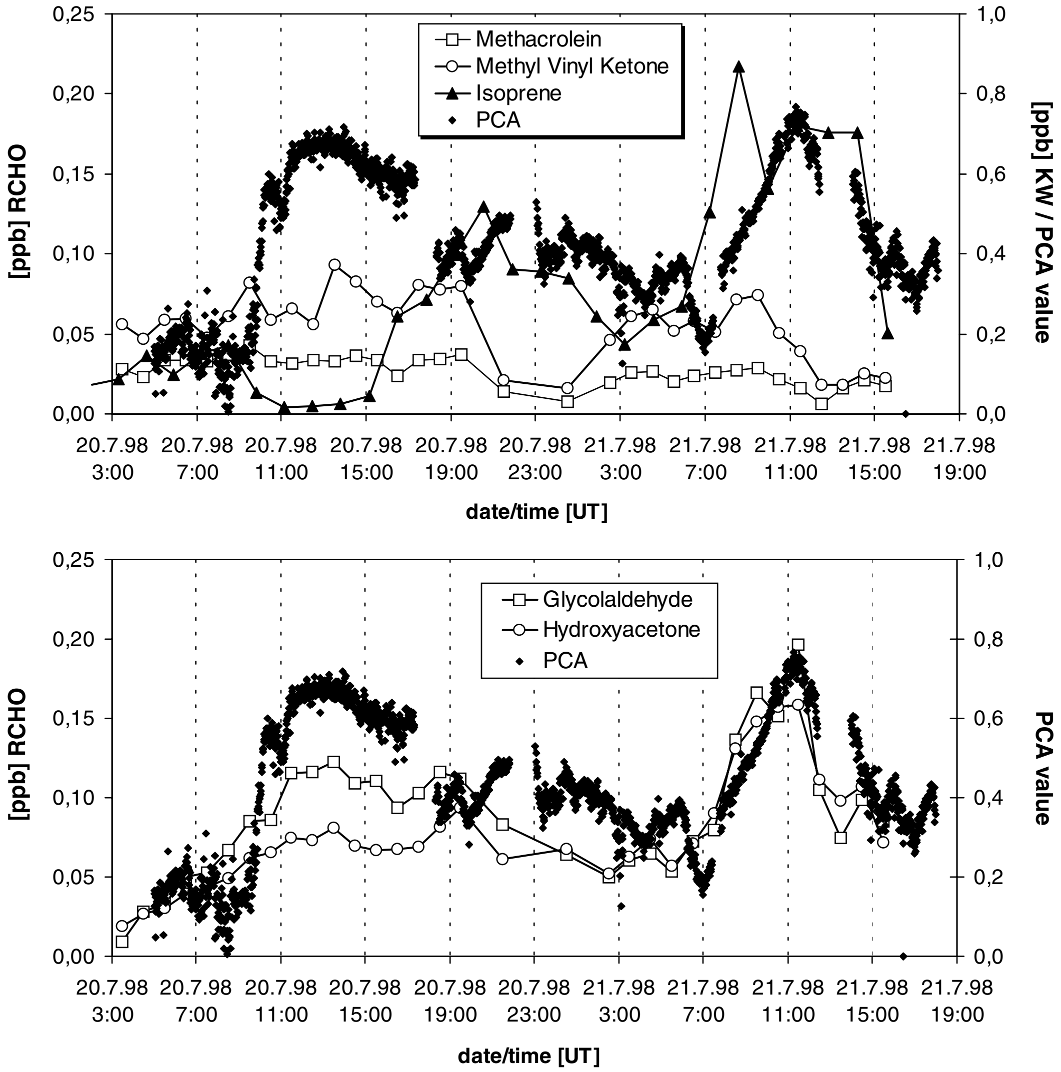


Figure 9. Diurnal variation of isoprene, its main primary photooxidation products methacrolein and methyl vinyl ketone, and the secondary products glycolaldehyde and hydroxyacetone during 20–21 July 1998 in Pabstthum. The fully dotted profiles reflects the calculated photochemical age.

[45] The secondary oxidation products of isoprene, hydroxyacetone and glycolaldehyde are also displayed in Figure 9. These products exhibit distinct concentration maxima (up to 0.16 and 0.20 ppbv, respectively) during the day, being larger than its direct precursors MVK and MACR on 21 July 1998. Glycolaldehyde and hydroxyacetone have been previously measured in the boundary layer by *Lee et al.* [1996] and *Spaulding et al.* [1999] with mixing ratios up to 3 ppbv respectively 0.5 ppbv. However, no previous diurnal profile of hydroxyacetone together with glycolaldehyde have been reported to our knowledge. Both the primary (MVK and MACR) and secondary (glycolaldehyde and hydroxyacetone) products show excellent correlation (0.85 and 0.88, respectively).

[46] Another possibility to assert the origin of these carbonyl compounds is to consider the photochemical age (PCA) of an air mass. Generally, the aging of air is characterized by the increase of conversion of NO_x into NO_y compounds, whereby $NO_x = NO + NO_2$ and $NO_y = NO_x + HNO_3$, PAN, N_2O_5, nitrates, etc. In young air $[NO_x]$ is nearly identical to $[NO_y]$, and the ratio $[NO_x]/[NO_y]$ can be taken as an indicator for the age of an air parcel. Thus photochemical age is defined as

$$\mathrm{PCA} = 1 - [\mathrm{NO}_x]/\left[\mathrm{NO}_y\right].$$

If a compound correlates with the PCA-value, then this would give evidence for predominant photochemical origin. The correlation diminishes by increasing primary emissions, or if this specific compound has a short atmospheric lifetime [*Christensen et al.*, 2000].

[47] The mixing ratio profiles for the secondary products of isoprene (glycolaldehyde and hydroxy-acetone) correlate well with the PCA-values calculated from the available NO_x and NO_y values, as shown in Figure 9. The excellent correlation confirms that both carbonyl compounds are formed by photooxidation processes. For the primary products MVK and MACR, the agreement is not so good, which

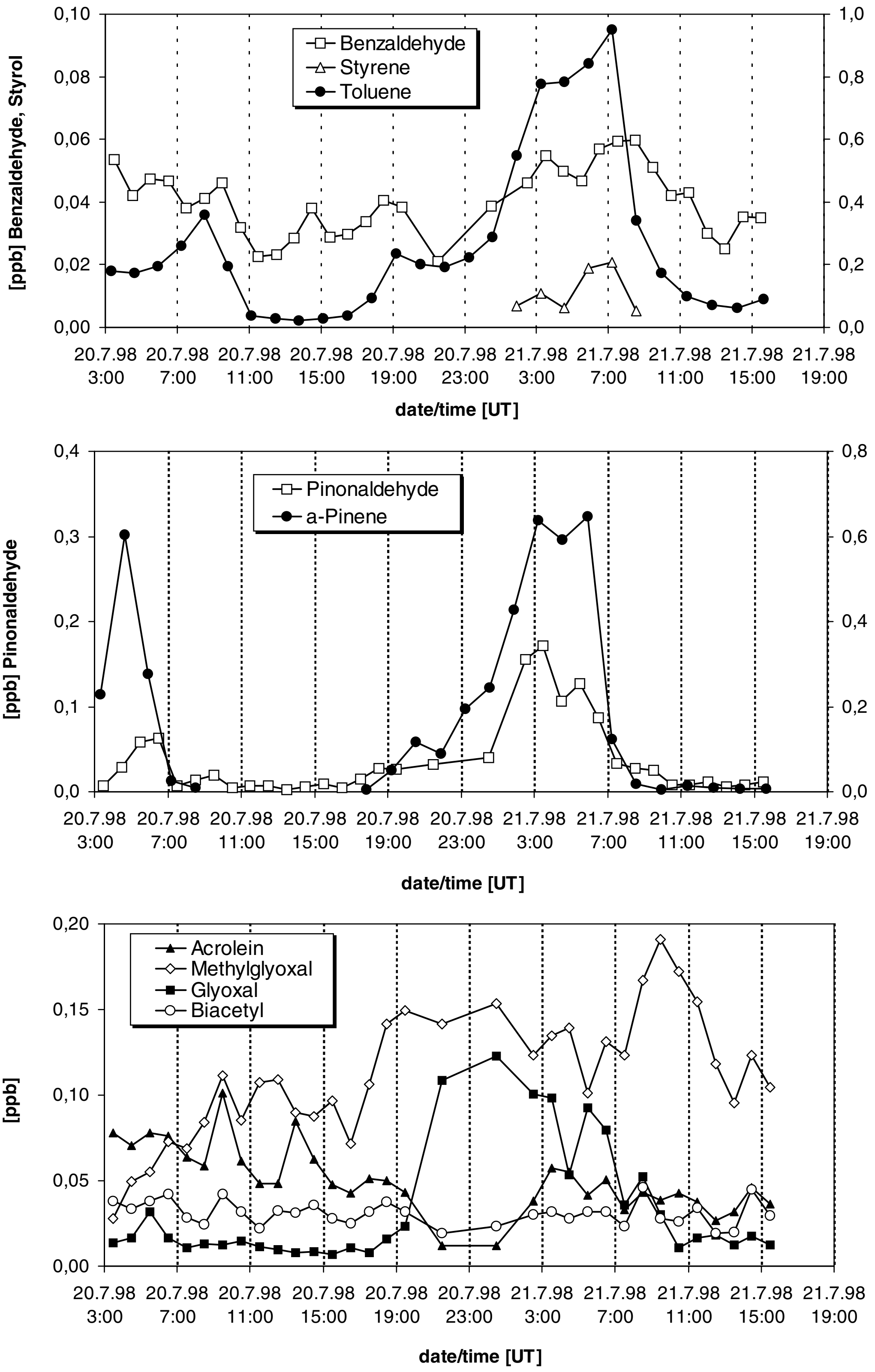


Figure 10. Diurnal variation of various carbonyl compounds on 20–21 July 1998 at Pabstthum. Upper: benzaldehyde and precursors toluene and styrene; Middle: pinonaldehyde and precursor α-penene; Lower: acrolein, glyoxal, methylglyoxal and biacetyl.

might be explained by the short lifetime of the both compounds (τ_{MVK} = 2.5 hours, τ_{MACR} = 1.3 hours for [OH] = 6 × 10^6 molecule cm^{-3}).

3.2.3. Various Other Carbonyl Compounds

[48] Profiles of several other carbonyl compounds are shown in Figure 10 (upper plot). The mixing ratio of benzaldehyde is presented together with possible photooxidation precursors toluene and styrene [*Atkinson*, 1994]. Toluene peaks at 0830 UT in the morning on 20 July, and in the morning hours of 21 July, and may be considered as indicator for polluted air transported from the Berlin area. Enhanced mixing ratios of NO_x were also observed during the same time period (see Figure 4). Nevertheless the profiles of benzaldehyde do not seem to follow closely the toluene precursor. The reason might be the dilution of air parcels which lowers the primary emitted part of benzaldehyde to an negligible concentration and that benzaldehyde is removed faster by OH radicals than toluene (about factor 2 [*Atkinson*, 1994]). The diurnal profile of benzaldehyde is also modified through biogenic emissions [*Kesselmeier et al.*, 2000].

[49] Interesting is the pinonaldehyde profile and the precursor α-pinene, shown in Figure 10 (center plot). 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 known precursor for pinonaldehyde in the atmosphere, the latter is an example of a carbonyl compound that is exclusively of secondary biogenic origin. Parallel measurements of α-pinene and pinonaldehyde were achieved for the first time. α-Pinene displays very low mixing ratios during the day, but pronounced maxima during the night. The chemical breakdown of α-pinene at night proceeds by the reactions with NO_3 radicals and ozone, which results in the build-up of pinonaldehyde during the night. Both oxidants, NO_3 and ozone, were found in substantial concentrations during this period [*Volz-Thomas et al.*, 2003b; *Geyer et al.*, 2003; *Platt et al.*, 2002].

[50] Profiles of acrolein and the bicarbonyl compounds glyoxal, methylglyoxal and biacetyl are shown in the bottom plot of Figure 10. Glyoxal and methylglyoxal arise from the degradation of aromatic compounds. Methylglyoxal is also produced in the photooxidation of MVK and MACR, which are main products of the isoprene degradation. Both compounds are readily photolyzed during daytime [*Moortgat et al.*, 2001]. This would explain the pronounced maximum seen at night. There have been only sparse measurements of glyoxal and methylglyoxal in the atmosphere with mixing ratios between 0.1 and 2 ppbv in urban air [*Grosjean et al.*, 1990, 1996]. The cited results should be regarded as preliminary because there were recorded with an analytical method that is sensitive to ozone interference (DNPH coated reversed phase cartridges operated without ozone scrubber).

3.2.4. Radical Production Rates

[51] From measurements of the photolysis frequencies for a series of carbonyl compounds relative to that of NO_2 made in the European Photoreactor [*Moortgat*, 2000, 2001], the photolysis frequencies of the higher carbonyl compounds around noon on 20 July can be estimated to 1.0 × 10^{-5} s^{-1} for the C_3–C_{10} alkanals and glycolaldehyde, and 1.0 × 10^{-4} s^{-1} for the dicarbonyls. The radical yields from the photolysis channel $RCHO \rightarrow R + CHO$ vary from 70% for C_3–C_4 alkanals to 20% for pentanal and hexanal, and about 10% for C_7–C_9 alkanals [*Tadic and Moortgat*, 2001; *Tadic et al.*, 2001a, 2001b]. HO_2 radical yields for the photolysis of dicarbonyls and glycolaldehyde are near 100% [*Moortgat*, 2000]. With the concentrations in Figure 7 (about 1.0 ppbv for the C_3–C_{10} alkanals, 0.15 ppbv for the bicarbonyls glyoxal, methylglyoxal, and biacetyl, and 0.15 ppbv for glycolaldehyde), the HO_2 production rates are calculated to 0.010 ppbv h^{-1} for C_3 + C_4 alkanals, 0.002 ppbv h^{-1} for C_5 + C_6 alkanals, 0.001 ppbv h^{-1} for C_7 + C_8 + C_9 + C_{10} alkanals, 0.054 ppbv h^{-1} for the bicarbonyls and 0.036 ppbv h^{-1} for glycolaldehyde. This can be compared to the HO_2 production rate from HCHO photolysis of (0.6–1.1) ppbv h^{-1}, calculated for a concentration of (4–8) ppbv, and the photolysis frequency (radical channel only) of 3.7 × 10^{-5} s^{-1} [*Holland et al.*, 2003]. For acetaldehyde the photolytic HO_2 production rate is estimated to 0.009 ppbv h^{-1}. In total, photolysis of the observed carbonyl compounds $>C_1$ provides an HO_2 production rate of 0.1 ppbv h^{-1}, which is about 10–20% of the radical production by HCHO photolysis.

[52] *Mihelcic et al.* [2003] show the radical budgets as derived from the measurements for 21 and 21 July. The contribution of HCHO photolysis to HO_2 production is around 10% during both days based on the Hantzsch data. Therefore, the discrepancy of less than a factor of 2 between DOAS and Hantzsch for the HCHO concentration (see next paragraph) contributes less than 10% to the uncertainty in the HO_2 production rate.

3.2.5. Formaldehyde

[53] Figure 11 shows the time series of HCHO as measured by both systems from 13 July to 6 August 1998. It is apparent that the HCHO levels measured by DOAS are significantly higher than that of the Hantzsch system. From 13–20 July and 25 July to 6 August the formaldehyde concentrations were low showing a typical daily pattern

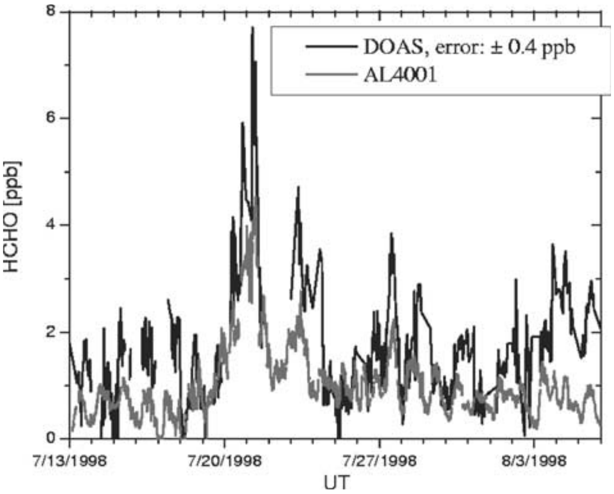


Figure 11. Time series of HCHO at Pabstthum as measured by long-path DOAS and a Hantzsch system (AL4001) from 13 July to 6 August 1998.

Table 1. Results of the Regression Analysis of the HCHO Intercomparison Between DOAS and a Hantzsch System for the BERLIOZ Campaign at Pabstthum

	X ↔ Y	Measurement	Intercept	Slope	R^2
All data	DOAS ↔ Hantzsch	327	0.56 ± 0.04	1.23 ± 0.03	0.66
	Hantzsch ↔ DOAS	327	−0.46 ± 0.04	0.81 ± 0.02	0.66
Daytime only	DOAS ↔ Hantzsch	203	0.42 ± 0.05	1.33 ± 0.04	0.62
	Hantzsch ↔ DOAS	203	−0.31 ± 0.05	0.75 ± 0.02	0.62

with minimum values during night and higher levels during daytime. The DOAS values varied between 0 and 3.8 ppbv, the Hantzsch system measured between 0 and 2.2 ppbv. With the beginning of the photosmog episode on 20 July formaldehyde levels increased to a maximum of 7.7 ppbv (DOAS) and 4.5 ppbv (Hantzsch system).

[54] The correlation between the two data sets is summarized in Table 1, and plotted in Figure 12. Due to the different measurement intervals, the Hantzsch data are integrated over the longer measurement interval of the DOAS system. Values below the detection limit of the DOAS system are excluded. To investigate the influence of the nighttime inversion on the measurements (the DOAS values were measured at an average height of 2.65 m) the comparison is also carried out for daytime values only. The error of the regression is dominated by the uncertainty of the DOAS data, which is on average about 3 times larger than the scatter of the Hantzsch monitor (typically 110 pptv, in accordance with the variance in the instrumental background). While an average slope of 1.23 (all data, DOAS versus Hantzsch), respectively 1.33 (daytime only, DOAS versus Hantzsch) is achieved, the difference of the two measurements is almost a factor during two during days with high photochemical activity, e.g., for the 21.7 at 9:43 the DOAS showed (7.1 ± 0.4) ppbv and the Hantzsch monitor (4.5 ± 0.2) ppbv of formaldehyde. This discrepancy is highly significant since the statistical the error of the DOAS system is less than ±6% at the high concentration levels.

[55] Differences of similar magnitude were observed between the DOAS instruments and Hantzsch monitors deployed at the BERLIOZ sites Eichstädt (between Pabstthum and Berlin) and Blossin (south east of Berlin, cf. Figure 1 of *Volz-Thomas et al.* [2003a]). It was not possible to identify the reasons for the discrepancy.

[56] A potential weakness is that gaseous standards were not available for calibration of the Hantzsch monitors so that losses of HCHO in the inlet lines or incomplete sampling cannot be excluded beyond doubt [*Gilpin et al.*, 1997]. However, the collection efficiency of the scrubber in the commercial Hantzsch monitor used in BERLIOZ (AL4001) was extensively tested and found to be 98% [*Krinke*, 1999], leaving little room for changes due to environmental conditions. Furthermore, the stripping coil in the Al4001 monitor is operated at constant temperature and the monitor was operated in a temperature-controlled environment. Likewise, inlet losses not a likely reason since the largest discrepancies were observed during the warmest days with very low relative humidity.

[57] Recently, simultaneous measurements of formaldehyde between DOAS, Hantzsch, DNPH cartridges, and FT-IR spectroscopy were performed in the "European Photo-Reactor" (Euphore) at Valencia, Spain (Wirtz, personal communication). Good agreement within the experimental uncertainties was observed between all techniques at HCHO mixing ratios above 10 ppbv, thus confirming the absorption cross sections used for the DOAS evaluation. However, at levels of a few ppbv HCHO, an uncertainty of about a factor of two was found between the DOAS and the Hantzsch values with the higher values from DOAS.

[58] An overview of previous HCHO intercomparisons among different atmospheric measurement techniques is

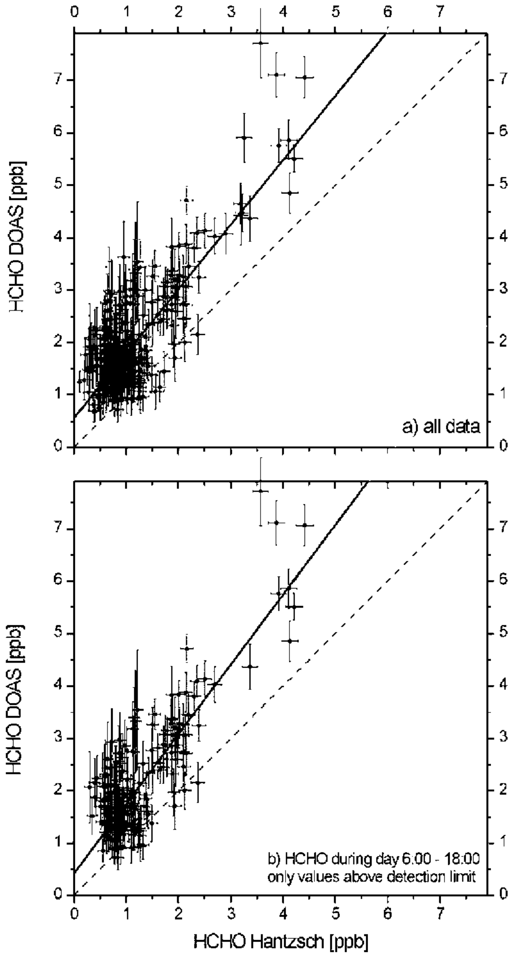


Figure 12. Intercomparison of the LP-DOAS HCHO measurements with the in situ Hantzsch monitor. The upper plot shows the correlation for the whole data set and the lower shows the daytime values. The error bars of the DOAS values refer to the total 1σ-uncertainty.

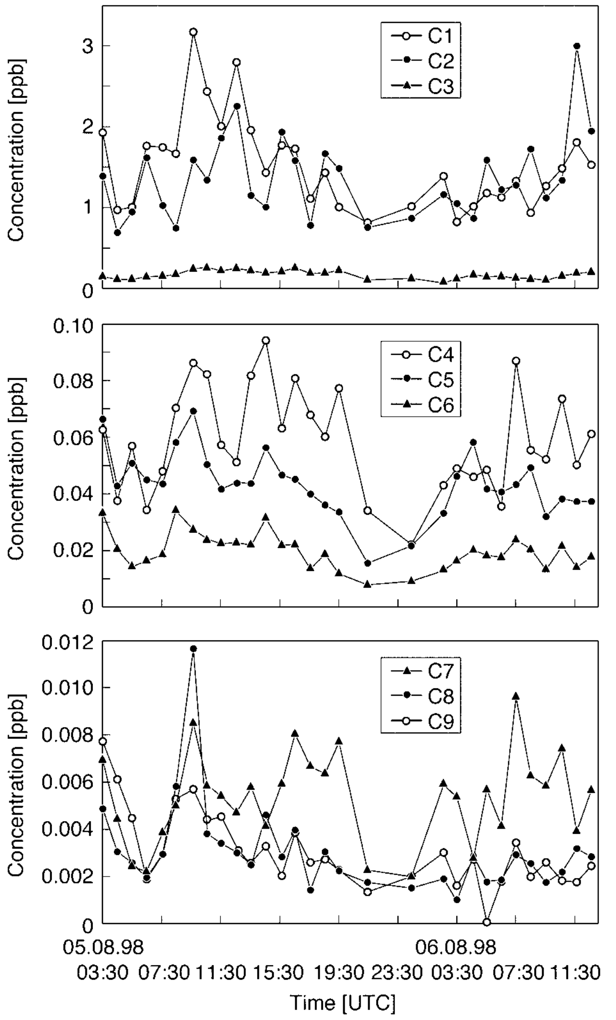


Figure 13. Diurnal profile of C_1 to C_9 monocarboxylic acids. Pabstthum 5–6 August 1999.

given by *Cardenas et al.* [2000]. Simultaneous measurements by DOAS, tunable diode laser spectroscopy (TDLS) and a Hantzsch system at the marine sites Mace Head, Ireland, and Weyborne, England [*Cardenas et al.*, 2000] showed relatively good agreement at formaldehyde levels above 4 ppbv. There, the DOAS values were generally below that of the Hantzsch system (e.g., the slope was 0.6 between the DOAS (of IUP) and the Hantzsch monitor at Weyborne). During the 1999 SOS campaign at Nashville, a LP-DOAS system was compared to a tunable laser diode spectroscopy (TDLS) system. The intercorrelation [*Alicke et al.*, 2003] had a slope of 1.07 ± 0.01 with an intercept of 0.47 ± 0.03 with the DOAS system providing lower values than the TDLS. This is in contrast to the comparisons during BERLIOZ were the DOAS always showed the higher concentrations.

[59] During the Schauinsland Ozone Precursor Experiment, the Hantzsch monitor used at Pabstthum was compared to measurements made with DNPH cartridges and a TDLS [*Pätz et al.*, 2000]. The Hantzsch monitor yielded about 10–20% higher values than the HPLC analysis of the DNPH samples, whereas the TDLS gave lower concentrations during episodes of photochemical activity. Another comparison between the same TDLS and Hantzsch monitor was made during the EVA experiment at Augsburg. There, very good agreement was found during days with high wind speeds and low photochemical activity, whereas the Hantzsch monitor yielded higher values than the TDLAS during episodes when ozone was found to increase [*Klemp et al.*, 2002].

[60] In view of these widely differing results it is not possible to elucidate the origin of the difference between the DOAS and Hantzsch measurements. It remains the possibility that the discrepancy is due to the different sampling positions of the systems, although the comparison of the NO_2 measurements made with the same DOAS instrument and the in-situ NO_2 monitor were in good agreement (slope (DOAS/CLD): 1.06 ± 0.02, intercept: 0.16 ± 0.06 ppbv, R^2 = 0.85). We thus suggest to apply both formaldehyde data sets in chemical modeling studies and to investigate the sensitivity of the radical budgets to the uncertainty in the HCHO mixing ratio. It is planned to conduct another instrument comparison in ambient air in spring 2002 (Brockmann, personal communication) in order to further investigate this important analytical problem.

3.3. Organic Acids

[61] For the first time, diurnal profiles of the homologous series monocarboxylic acids (C_1–C_9) were recorded with a time resolution of 1 hour at Pabstthum, as shown in Figure 13 for 5–6 August 1998. Due to contamination of the inlet line by insects that were sucked in the inlet line on 20–21 July, data for HCOOH were not reliable for this period. Therefore measurements performed during the other intensive operational period on 5–6 August 1998 are shown. The measured profiles show that the long-chain carboxylic acids ($>C_6$) differ considerably from the short-chain acids ($<C_3$). On that day, concentrations of formic and acetic acid varied between 0.6 and 3.0 ppbv. The concentration level of the monocarboxylic acids dropped from 0.1 to 0.2 ppbv for C_3 to typical 0.01 to 0.03 ppbv for C_6, and from 0.01 to 0.002 ppbv for C_7 to C_9 monocarboxylic acids. C_1 to C_7 monocarboxylic acids show distinct built-up during the day. A pronounced maximum was observed for butyric (C_4) and heptanoic (C_7) acid until the late evening hours. The profiles of the long-chain acids ($>C_6$) do not display a diurnal pattern. However, a concentration minimum was observed for all acids at night.

4. Conclusion

[62] In this paper we have investigated the levels of H_2O_2, organic peroxides and carbonyl compounds during two intensive days of the BERLIOZ Campaign in Pabsttum, located in a regional site 50 km from the city center of Berlin. H_2O_2 was the dominant peroxide present in the air. MHP was the major organic peroxide observed, and occasionally HMHP was found. H_2O_2 showed maximum mixing ratios between 1200 and 1400 UT. Evidence was found that in the morning hours, 0900–1200 UT H_2O_2 was locally transported from layers above the small inversion layer. On 20 July the *observed* production rate of H_2O_2 was roughly 0.14 ppbv h^{-1}, but the local H_2O_2 photochemical production rate was calculated from the measured HO_2 concentration as only 0.08 ppbv h^{-1}, so that vertical mixing is as important as

chemical production. There is some evidence that H_2O_2 is also formed from ozonolysis of biogenic alkenes during the evening hours of 20 July 1998. Ratios of H_2O_2/HNO_3 were used as indicators for the determination of NO_x- versus VOC-sensitive regimes for photochemical production of ozone.

[63] Diurnal profiles were measured for alkanals (C_2–C_{10}): Maximum mixing ratio decrease from C_2 (0.6 ppbv) to C_5 (0.1 ppbv) alkanals and originate primary from anthropogenic hydrocarbon degradation processes. However, higher C_6, C_9 and C_{10} alkanals show strong fluctuations (0.25. 0.17, and 0.13 ppbv, respectively), showing evidence of biogenic emissions. Both primary unsaturated carbonyl compounds (MVK and MACR) and secondary oxidation products of isoprene (hydroxyacetone and glycolaldehyde, up to 0.16 and 0.20 ppbv, respectively) show excellent correlation. The bicarbonyl compounds (glyoxal, methylglyoxal, biacetyl), show different diurnal profiles of benzaldehyde and pinonaldehyde, among many others. Formaldehyde was measured continuously by long path DOAS and by an instrument based on the "Hantzsch" reaction; however, DOAS measured mixing ratios (max 7.7 ppbv) were systematic larger during daytime by about a factor 1.7 during the intensive measuring period. The origin of the difference between both measurements is not clear. Finally homologous series of monocarboxylic acids were determined: Maximum concentrations of formic and acetic acid varied between 0.6 and 3.0 ppbv. The concentration level of the monocarboxylic acids dropped from 0.1 to 0.2 ppbv for C_3 to typical 0.01 to 0.03 ppbv for C_6, and from 0.01 to 0.002 ppbv for C_7 to C_9 monocarboxylic acids.

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