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# Inorganic trace gases and peroxy radicals during BERLIOZ at Pabstthum: An investigation of the photostationary state of $NO_x$ and $O_3$

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[1] Meteorological and chemical measurements, including peroxy radicals, made during the Berlin Ozone Experiment (BERLIOZ) in summer 1998 at Pabstthum, a rural site about 50 km NW of the city, are described. The analytical techniques and data quality are discussed, including the comparison of different methods deployed side by side at Pabstthum. The highest concentrations of $NO_x$ (>20 ppb) and other precursors were observed on days when relatively young air was advected to Pabstthum from the greater Berlin area. $NO_x$ often increased during the night due to emissions from the surrounding soils under stagnant conditions with a shallow boundary layer as is evident in the strong negative correlation between nocturnal NO mixing ratios and product of ozone and wind speed. The ozone production rate ($PO_3$) calculated from the photostationary state (PSS) of $NO_x$ and $O_3$ increased with NO and reached values of up to 90 ppb $h^{-1}$. $PO_3$ calculated from NO and the measured peroxy radical concentrations was much lower, around or below 10 ppb $h^{-1}$. The lower production rates obtained from the peroxy radical measurements are consistent with the ozone budget in the city plume of Berlin. The new JPL recommendation for the rate coefficient of the reaction of NO with $O_3$ slightly improves the disagreement between PSS and measured peroxy radicals. However, another enhancement of 10–20% in the rate coefficient would be required in order to match the results within the uncertainty of the measurements in the high $NO_x$ regime. Even then, PSS remains to overpredict $PO_3$ by a factor of 2 at low $NO_x$ concentrations. Hence, a yet unidentified process must exist in the atmosphere that converts NO to $NO_2$ without leading to a net production of ozone. The PSS results from other studies are similar as at Pabstthum, suggesting that the overestimation of peroxy radicals and $PO_3$ by the PSS approach is not a particular feature of the conditions at the site. *INDEX TERMS:* 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; *KEYWORDS:* Peroxy radicals, RO2, photostationary state, PSS, field campaign, air quality

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## 1. Introduction

[2] The role of areas with large emission sources for the budget of ozone and other photooxidants in a region has received a lot of interest. An important question is the effectiveness of ozone formation in air masses with high concentrations of precursors, i.e., $NO_x$, CO, and hydrocarbons. Directly related is the question about the dependence of the concentrations of hydroxyl and peroxy radicals on the concentrations of the precursors. It was addressed in several modeling studies [e.g., *Logan et al.*, 1981; *Liu et al.*, 1987; *Lin et al.*, 1988; *Trainer et al.*, 1987; *McKeen et al.*, 1997; *Ehhalt*, 1999], however, little quantitative experimental information exists to date. Most field experiments, e.g., SOS [*Cantrell*, 1993a, 1993b; *Frost et al.*, 1998], OCTA [*Volz-Thomas et al.*, 1997; *Mihelcic et al.*, 2002], SOAPEX [*Carpenter et al.*, 1997; *Monks et al.*, 1998; *Penkett et al.*, 1997], FREETEX [*Zanis et al.*, 2000], POPCORN [*Holland et al.*, 1998; *Brandenburger et al.*, 1998], and ALBATROS

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[*Brauers et al.*, 2001] MPI Israel campaign [*Weißenmayer*, 1994], provided important information on radical concentrations and precursors in clean and rural air. However, little information exists for $NO_x$ mixing ratios above 3 ppb, with exception of the LAFRE experiment in Los Angeles [*George et al.*, 1999] and the SLOPE campaign at Schauinsland [*Volz-Thomas et al.*, 2000]. The few existing data sets qualitatively confirm the expected maximum of [OH] around 1–3 ppb of $NO_x$ [*Ehhalt and Rohrer*, 2000; *Volz-Thomas and Kolahgar*, 2000].

[3] For the measurement of peroxy radicals ($HO_2$ and its organic homologues $RO_2$), there is one direct spectroscopic technique available, i.e., Matrix Isolation followed by ESR spectroscopy (MIESR) [*Mihelcic et al.*, 1985, 1990, 2002]. The chemical amplifier (CA) [*Cantrell et al.*, 1984] provides information on the sum of OH, $HO_2$ and the organic peroxy radicals (henceforth denoted $RO_x$). The laser induced fluorescence (LIF) [*Hard et al.*, 1995; *Holland et al.*, 2002] is employed for the measurement of $HO_2$ after conversion to OH. Finally, an indirect approach for the determination of ozone formation rates and peroxy radicals has been used by a number of investigators [e.g., *Kelly et al.*, 1980; *Parrish et al.*, 1986; *Volz et al.*, 1988; *Ridley et al.*, 1992; *Cantrell*, 1993a, 1993b; *Davis et al.*, 1993; *Kleinman et al.*, 1994, 1995; *Carpenter et al.*, 1998; *Frost et al.*, 1998; *Baumann et al.*, 2000]. It is based on the deviation of the atmospheric $NO_2/NO$ ratio from the so-called Leighton ratio [*Leighton*, 1961].

[4] In this paper, we describe measurements of total peroxy radicals (by chemical amplification), nitrogen oxides, ozone, CO, and PAN that were made at Pabstthum and discuss the observed variance in terms of the prevailing meteorological conditions. The data quality is investigated on the basis of results from the integrated quality assurance activities in TFS and of parallel measurements made with different techniques at Pabstthum. The ozone production rate and radical concentrations as derived from photostationary state (PSS) are compared with results from peroxy radical measurements made by CA and MIESR. Significant differences between the two approaches are discussed in view of potentially fundamental problems with the PSS approach.

## 2. Experimental

[5] Figure 1 shows the arrangement of the different measurements at Pabstthum. A detailed description of the observational site is given by *Volz-Thomas et al.* [2002]. The area around Pabstthum (5 residences), is extremely sparsely populated. The nearest villages Wall and Radensleben (<500 inhabitants) are located about 5 and 7 km to the SE and NW, respectively. The closest city is Neuruppin (38,000 inhabitants), 12 km in the NW. Berlin (3.4 million inhabitants) is situated in SE direction (140°) at a distance of about 50 km (center; 35 km to the suburbs). Local emissions from traffic, industry, and residences in the vicinity are negligible, except for the motorway A24, about 10 km west of Pabstthum. A mixed forest dominated by Scots pine (*Pinus sylvestris*) extends from the station in westerly and northerly direction. About 50 m in westerly direction of the station is a line of Holm oaks (*Quercus ilex*) along the trail to the site. The grass land is used for cattle farming, except for an area of about 100 m in southeasterly direction, which was kept clear during the campaign.

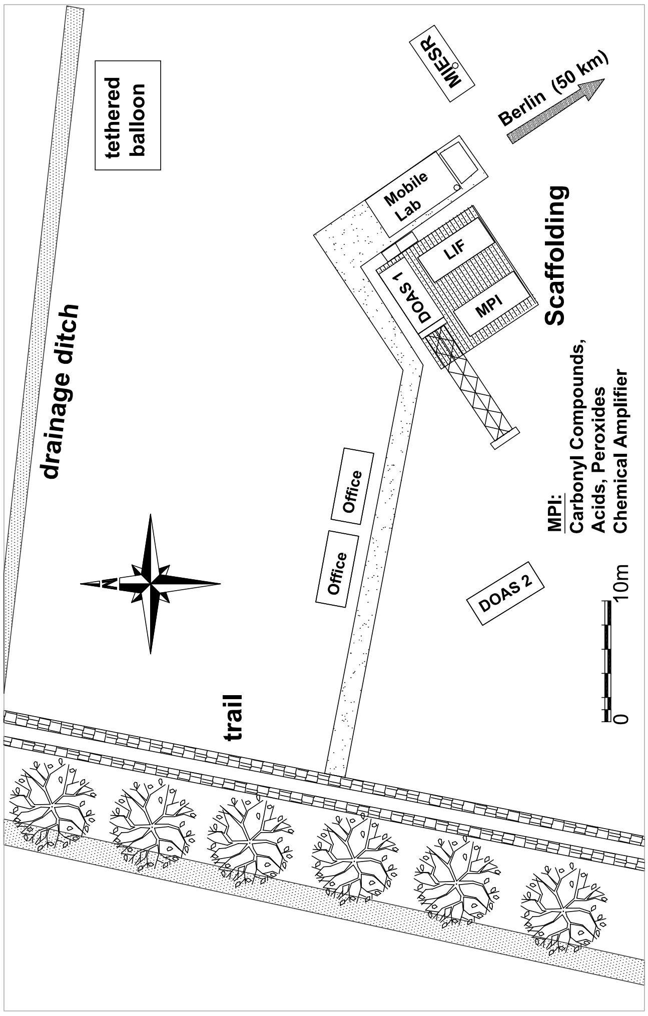

**Figure 1.** Experimental arrangements at the field site Pabstthum during the BERLIOZ campaign. The measurements of meteorological parameters, $JNO_2$, CO, $NO_x$, $NO_y$, PAN, and $O_3$ were made in the Mobile Lab. The CA was located in the MPI container on the scaffolding.

### 2.1. Trace Gas Measurements

[6] The instrumentation is summarized in Table 1 together with information on instrumental uncertainty and time resolution. The instruments for odd nitrogen compounds, ozone, CO, PAN, HCHO, and speciated hydrocarbons were housed inside an air conditioned mobile laboratory. The inlets were mounted about 10 m above ground on a pneumatic mast, which also carried the meteorological sensors and the photometers for the measurement of $J_{NO2}$. The instrumentation used for the measurement of inorganic trace gases was identical to that deployed before at Schauinsland, as described by *Pätz et al.* [2000].

[7] Briefly, ozone was measured with two identical UV monitors (TE-49). Carbon monoxide was measured with a slightly modified infrared filter correlation instrument (TE-48). The sample air was dried and zero readings were

**Table 1.** Analytical Techniques Employed at Pabstthum

| Parameter | Instrument | Relative error[a] (±1σ) | Absolute error (±1σ) | Accuracy[b] (±1σ) | Time resolution |
|---|---|---|---|---|---|
| nitrogen monoxide (NO) | CLD770AL ppt (EcoPhysics) | 1% | 15 ppt | 5% | 1 min |
| NO + $NO_2$ ($NO_x$) | CLD770AL ppt (EcoPhysics) photolytic converter (PLC 760) | 2% | 25 ppt | 5%[c] | 1 min |
| odd nitrogen ($NO_y$) | CLD770AL ppt (EcoPhysics) with gold converter | 5% | 20 ppt | 10% | 1 min |
| water insoluble $NO_y$ ($NO_{yu}$) | CLD770AL ppt (EcoPhysics) stripper and gold converter | 5% | 25 ppt | 10% | 1 min |
| ozone ($O_3$) | TE 49 (Thermo Env. Instr.) | 1% | 1 ppb | 5% | 1 min |
| carbon monoxide (CO) | TE 48 (Thermo Env. Instr.) | 2% | 20 ppb | 10% | 1 min |
| peroxyacetylnitrate (PAN) | GC-ECD (Metcon) | 2% | 30 ppt | 5% | 10 min |
| $HO_2$ + $RO_2$ | Chemical Amplifier (MPI) | 10% | 1–8 ppt[d] | 20% | 1.2 min |
| $NO_2$ photolysis freq. $JNO_2$ | Filter radiometer (Metcon) | 3% | $10^{-4}$ $s^{-1}$ | 5%[c] | 1 min |
| condensation nuclei | TSI model 3022 | | | | 1 min |
| Temperature | PT100 (Thies) | | 0.1 K | 0.2 K | 1 min |
| wet bulb temperature | PT100 (Thies) | | 0.1 K | 0.2 K | 1 min |
| wind direction | wind vane (Thies) | | | 3° | 1 min |
| wind speed | 3 cup anemometer (Thies) | | | 0.5 m $s^{-1}$ | 1 min |
| hydrocarbons ($C_2-C_{10}$) | custom-built instrument | *Konrad et al.* [2002] | | | 90 min |
| hydrocarbons ($C_5-C_{10}$) | HC1010 (Airmotec) | *Konrad et al.* [2002] | | | 20 min |
| formaldehyde (HCHO) | Hantzsch Monitor (Aerolaser) | *Grossmann et al.* [2002] | | | 1 min |

[a] At mixing ratios >10× absolute error.
[b] From QA experiments [*Kanter et al.*, 2002].
[c] From comparison at Pabstthum.
[d] Depending on humidity.

determined every hour by passing the sample air over a hopcalite bed. $JNO_2$ was derived indirectly from measurements of the spherically integrated actinic flux in the appropriate wavelength interval with upward and downward facing hemispherically integrating filter radiometers (Metcon, Königstein). The radiometers were calibrated against a chemical actinometer as described by *Volz-Thomas et al.* [1996]. Since the downward facing radiometer was biased high by reflections of the instrument containers at the site, we used the readings from the upward facing radiometer multiplied by a factor of 1.05 in order to account for the actinic flux from the lower hemisphere on the basis of earlier measurements and model calculations for ground level [*Volz-Thomas et al.*, 1996].

[8] NO, $NO_x$, and $NO_y$ were measured with three modified ECO Physics CLD 700 Alppt instruments. A photolytic converter was used for conversion of $NO_2$ and a gold converter for $NO_y$. The gold converter (T = 300°C, 0.1% $H_2$ as reducing reagent) was mounted on the mast at the inlet. A fourth NO detector was operated with an aqueous stripper and a gold converter in front of the CLD to measure the sum of water insoluble $NO_y$ compounds. PAN was measured by an automatic capillary gas chromatograph with an electron capture detector (Metcon).

[9] The calibration and data reduction procedures are also described by *Pätz et al.* [2000]. We like to note that a photochemical model is used for retrieving the $NO_x$ and $NO_2$ concentrations from the signal of the CLD with the photolytic converter and the measurements of NO, and $O_3$. The use of this model is particularly important at high $NO_x$ concentrations, where the conversion efficiency of the photolytic converter becomes a non linear function of $NO_x$, in addition to the dependence on $O_3$. The four CLDs were corrected for the measured influence of temperature and ambient water vapor on the sensitivity (1.3% $K^{-1}$ and −0.27% per mbar $H_2O$). The NO data were also corrected for small losses in the inlet line (0.04% per ppb $O_3$) as determined from calibrations.

### 2.2. Peroxy Radical Measurements

[10] The sum of peroxy radicals and oxyradicals ($RO_x$) was measured by a CA, which was located inside the MPI container on the platform shown in Figure 1. The inlet of the CA was 7 m above ground. The details of the CA and its calibration are described by *Hastie et al.* [1991] and *Arnold* [1997]. Briefly, the measurement is based on the conversion of peroxy radicals into $NO_2$ in a chain reaction. For this purpose, the sample air is mixed with 4 ppm of NO and 10% of CO. The $HO_x$ radicals (OH and $HO_2$) are recycled about 100 times in reactions (R1) and (R2), producing one $NO_2$ molecule per cycle. Chain termination occurs mainly by wall recombination and by reaction of HO with NO and $HO_2$ with $NO_2$ (reactions (R3) and (R4)) The $NO_2$ concentration behind the reaction chamber is determined by chemiluminescence with luminol (Scintrex, LMA-3).

$$\text{(R1)} \qquad HO_2 + NO \Rightarrow OH + NO_2$$

$$\text{(R2)} \qquad HO + CO + O_2 \Rightarrow HO_2 + CO_2$$

$$\text{(R3)} \qquad HO + NO + M \Rightarrow HONO + M$$

$$\text{(R4)} \qquad HO_2 + NO_2 + M \Rightarrow HNO_4 + M$$

$$\text{(R5)} \qquad RO_2 + NO \Rightarrow NO_2 + RO$$

$$k_5 = 8 \times 10^{-12}\ cm^3\ s^{-1}$$

$$\text{(R6)} \qquad RO + O_2 \Rightarrow HO_2 + \text{carbonyl compounds}$$

[11] Organic peroxy radicals are detected by the CA since the alkoxy radicals formed in the reaction with NO (reaction (R5)) are in the following converted into $HO_2$ (reaction

(R6)). The CA thus measures the sum of oxyradicals and peroxy radicals ($RO_x$: OH, $HO_2$, $CH_3O$, $CH_3O_2$, etc.). Because of the low concentrations of OH and the organic alkoxy radicals, the measurement is usually interpreted as the sum of $HO_2$ and $RO_2$. The chain reaction is also supported by active chlorine [*Arnold*, 1997; *Perner et al.*, 1999], although this should be of minor importance for the data presented here.

[12] The chain length of the CA, i.e., the $NO_2$ yield per $HO_x$ radical, and the conversion factors for the different organic radicals must be determined through calibrations, in addition to the sensitivity of the $NO_2$ detector. The calibration for $HO_2$ was based on $H_2O$ photolysis at 185 nm [*Schultz et al.*, 1995]. The accuracy of the MPI $HO_2$ calibration source was investigated as part of the European project PRICE II [*Heitlinger et al.*, 1998]. The agreement with other sources of similar design and with absolute measurements made by MIESR was <20%, in accordance with the estimated accuracy of the calibration source.

[13] The chain length appears to be strongly influenced by the ambient water vapor concentration [*Mihele and Hastie*, 1998]. This was taken into account for the measurements presented here by using the functional dependence of the $HO_2$ calibration curve on $H_2O$ determined prior to Berlin Ozone Experiment (BERLIOZ) in the laboratory (between 12% and 90% relative humidity at RT).

[14] Under conditions of low humidity (<20%) and due to the small variability of the background signal ($O_3 + NO_2$), during BERLIOZ, the 1$\sigma$ statistical error of the CA was $3 \times 10^7$ $cm^{-3}$ for an individual measurement (72 s measurement cycle), corresponding to a detection limit of 2 ppt. Because of the decreasing chain length, detection limit and precision deteriorated with increasing humidity (about 8 ppt at 90% humidity, i.e., at night and early morning).

### 2.3. Data Quality

[15] Data quality was investigated immediately before the BERLIOZ campaign at the small airfield Schönhagen. The results are described by *Kanter et al.* [2002]. We participated in these activities with the following results:

1. $O_3$: <5% disagreement with the reference instrument (calibrated against the NIST traceable primary standard of the Eidgenössische Materialprüfungs- und Forschungsanstalt, EMPA, Dübendorf, CH).
2. NO: <1% disagreement with the reference standard (NIST traceable via EMPA).
3. CO: 3–8% disagreement with the reference (2 canister samples collected at Pabstthum and measured against certified standards traceable to NOAA CMDL, Boulder).

[16] For $NO_2$, $NO_y$, and PAN, the instruments described in this paper served as the reference. The dynamic PAN calibration systems (quantitative chemical conversion of a NO standard gas to PAN by peroxy acetyl radicals produced by acetone photolysis in a flow system) [*Pätz et al.*, 2000, 2002] used by the different investigators agreed within 10% [*Kanter et al.*, 2002].

[17] The data quality of the $NO_2$ measurements is investigated in Figure 2 which shows the comparison of the $NO_2$ measurements by CLD/PLC with simultaneous measurements made by DOAS (Differential Optical Absorption Spectroscopy) [*Alicke et al.*, 2002] and MIESR [*Mihelcic et al.*, 2002] at Pabstthum. Although the comparison was not organized in a strictly blind fashion, we should like to note that the different instruments were calibrated independently and the data sets in Figure 2 were not harmonized in any way. The CLD/PLC data which have the highest time resolution (1 min) and data coverage of all three systems are plotted on the abscissa after averaging over the sampling intervals of MIESR and DOAS, respectively. Altogether, 1024 data pairs exist for the comparison with DOAS and 18 half-hourly averages for the comparison with MIESR. The results from linear regression fits to the data are also depicted in Figure 2. On average, the deviation between the three techniques is less than 5% with slightly higher values determined by the spectroscopic methods. Similar agreement is obtained with the balloon borne Luminol instrument of IGV (LMA-4) [cf. *Glaser et al.*, 2002], although the number of data pairs is somewhat limited since the tethered balloon was operated during the intensive observational periods only.

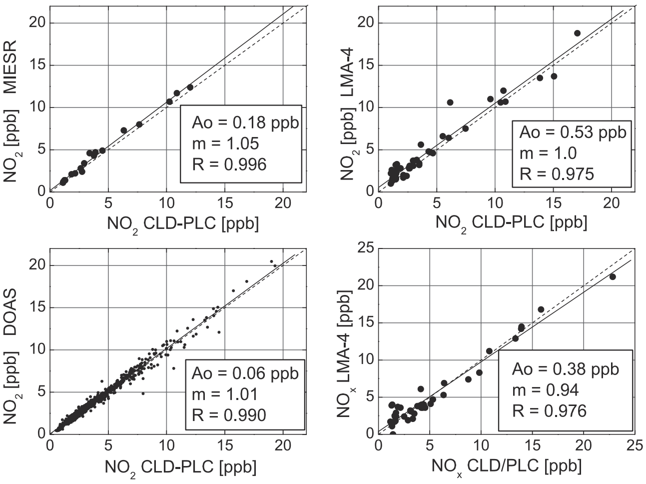

**Figure 2.** Comparison of $NO_2$ and $NO_x$ measurements made at Pabstthum. CLD/PLC is plotted on the abscissa, since it has the best time resolution and data coverage. Upper left: MIESR [*Mihelcic et al.*, 2002]; lower left: DOAS [*Alicke et al.*, 2002]; upper right: LMA-4 [*Glaser et al.*, 2002]; lower right: $NO_x$ by LMA-4. Solid lines: linear regression; dotted lines 1:1.

[18] The correlation between the different $NO_2$ measurements at Pabstthum is much better than those observed in earlier comparisons [*Harder et al.*, 1995, 2001; *Zenker et al.*, 1998] which suffered from inhomogeneous conditions with very low concentrations interrupted by short spikes due to local traffic. The excellent agreement of four independent methods gives a high level of confidence to the accuracy of the $NO_2$ measurements performed at Pabstthum and the tight correlation demonstrates the homogeneity of the $NO_x$ concentrations at the site due to its remote location.

[19] Peroxy radicals were also measured at Pabstthum by Matrix Isolation ESR spectroscopy (MIESR) [*Mihelcic et al.*, 2002]. Accuracy and detection limit of the method (1$\sigma$) are 5% and 1 ppt, respectively. The correlation between CA and MIESR in Figure 3 has a slope of 0.87 and an offset of 3 ppt. The latter is hardly significant, given the combined detection limits of the two techniques, in particular as some

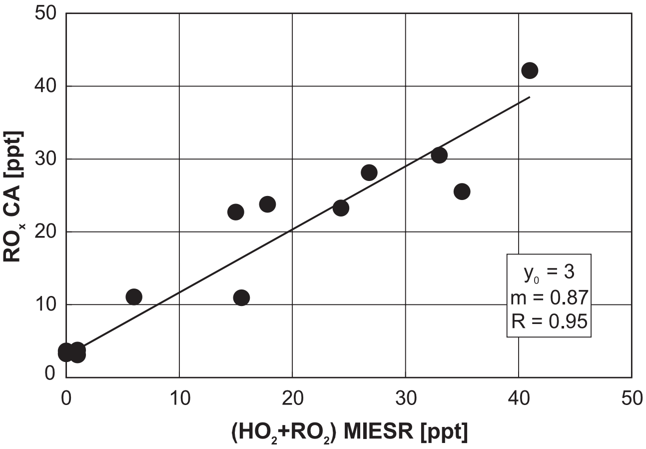

**Figure 3.** Comparison of the peroxy radical measurements by CA and MIESR at Pabstthum. The CA data are averaged over the sampling intervals of the MIESR.

of the low RO$_x$ concentrations coincided with relatively high humidity.

[20] The JNO$_2$ sensors and the chemical actinometer used for its calibration were compared in 1997 with a different chemical actinometer and with an independently calibrated spectroradiometer [*Kraus et al.*, 1998]. The disagreement of the different instruments involved in this study was less than 7%. At Pabstthum, another independently calibrated JNO$_2$ filter radiometer and a spectral radiometer were operated in addition to our instrument [cf. *Holland et al.*, 2002] The instruments agreed on average within ±2.5% for solar zenith angles <70°, the data from the spectral radiometer showing the lowest values. We corrected the signals from our radiometer by dividing with the average bias to the spectral radiometer (1.048 ± 0.001).

## 3. Results

[21] The time series of trace gases and meteorological parameters obtained during the BERLIOZ campaign at Pabstthum is shown in Figure 4. On most days, southwesterly winds prevailed (see Figure 5) with relatively low concentrations of the primary anthropogenic pollutants because of the absence of major emission sources in this sector, except for the motorway A24. At night, winds usually calmed down and fog was often observed in the early morning. The temperature remained below 25°C except for the period 20–23 July and on the last day of the campaign. During these periods, the only cloud-free days occurred. The peroxy radicals exhibited a pronounced diurnal cycle with maximum concentrations in the early afternoon.

[22] The dependence of the primary and secondary pollutants on the prevailing wind direction is summarized in Figure 6, which gives the median and interquartile range for the entire campaign in 15° wind sectors. Note that the easterly sectors (from 60° to 120°) have a very low frequency of occurrence (cf. Figure 5). The concentrations of NO$_x$, NO$_y$, and CO are significantly enhanced in the SE sector where Berlin, Potsdam, and Oranienburg are located. The enhanced NO$_x$/NO$_y$ ratio in this sector demonstrates the influence of relatively fresh emissions. The maximum in

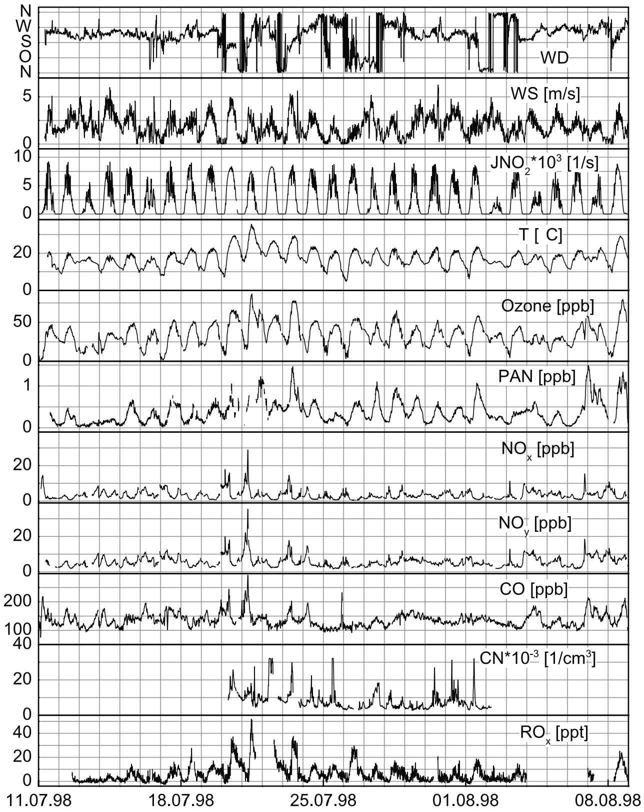

**Figure 4.** Time series of trace gas mixing ratios and meteorological parameters measured during the BERLIOZ campaign at Pabstthum.

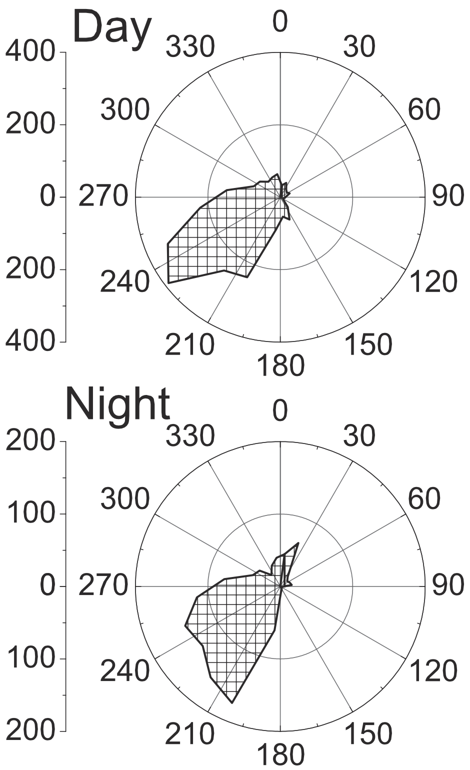

**Figure 5.** Wind roses for day and night at Pabstthum during BERLIOZ.

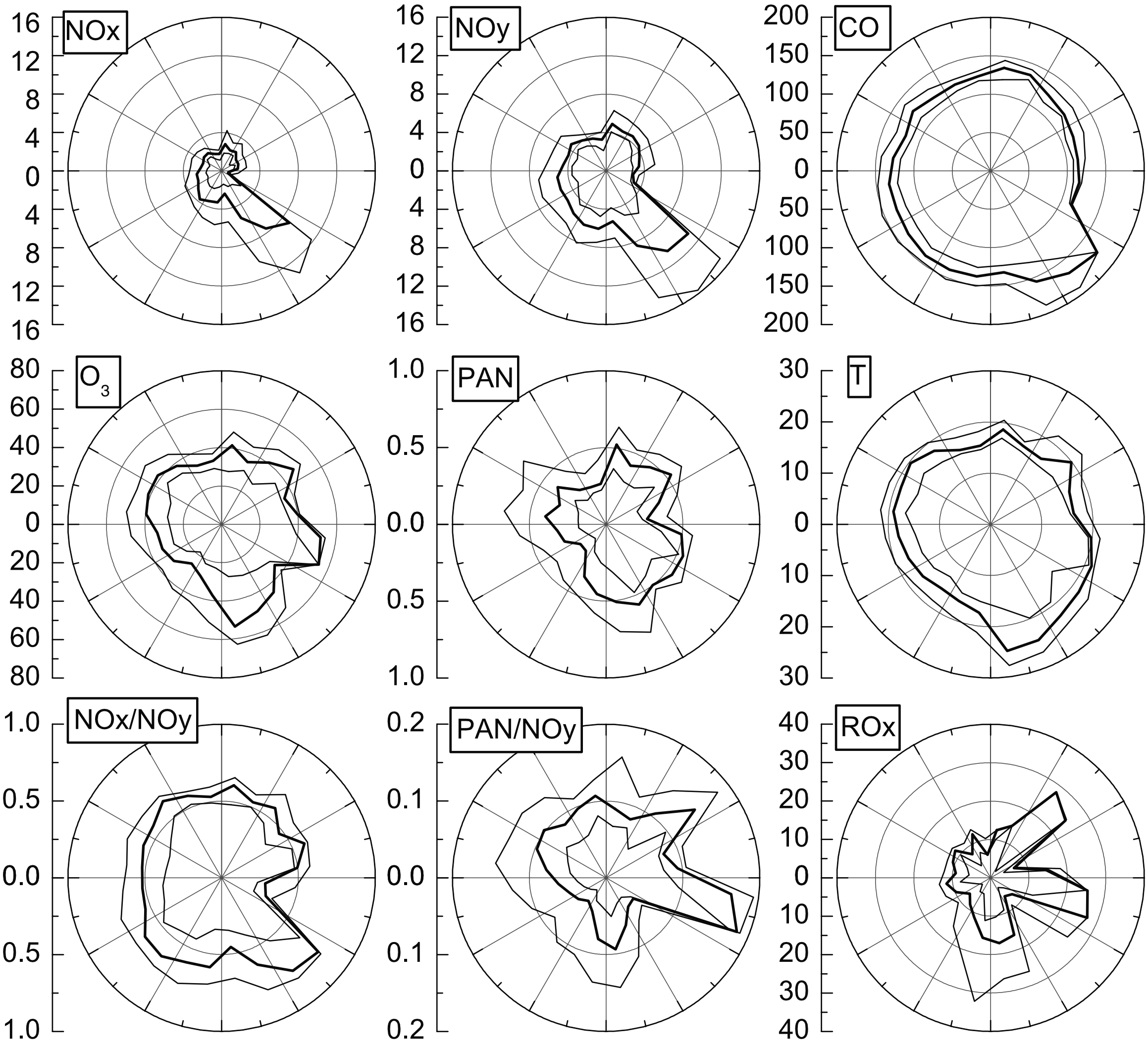

**Figure 6.** Trace gas roses during BERLIOZ at Pabstthum. Shown are median and interquartile range for 15° sectors. Measurements made at wind speeds below 0.6 m $s^{-1}$ are omitted. Note that some sectors are statistically not representative (cf. Figure 5). The $RO_x$ concentrations are selected for $JNO_2 > 0.006$ $s^{-1}$.

the median ozone mixing ratios is slightly shifted to the south. The $RO_x$ mixing ratios (selected for $JNO_2 > 0.006$ $s^{-1}$) exhibit the highest values in the SE sector. The maxima in the E and NE sectors are statistically not significant.

[23] Figure 7 shows the average diurnal variation of the trace gases at Pabstthum during BERLIOZ. The pattern is typical for a surface site in flat terrain. Ozone decreases during the night due to dry deposition and titration by NO emissions under calm winds into a shallow surface layer of <100 m, as is exhibited by the vertical profiles [*Glaser et al.*, 2002] obtained during the intensive observational periods (IOPs). The nitrogen oxides show the inverse behavior with increasing concentrations until early morning, most likely due to emissions from the surrounding soils and vegetation [e.g., *Williams et al.*, 1992; *Wildt et al.*, 1997]. The shallow inversion and low wind speeds enable even minor sources to produce significant concentrations. The average diurnal behavior of the $NO_x$ concentration at Pabstthum during BERLIOZ is almost identical with that observed in August 1994 during the POPCORN campaign [*Plass-Dülmer et al.*, 1998, and ancillary publications] at a rural site located in NE Germany between Schwerin and Rostock, about 130 km NW of Pabstthum. *Rohrer et al.* [1998] concluded that emissions from the surrounding soils were responsible for the enhanced nocturnal $NO_x$ concentrations during POPCORN.

[24] The local origin of the nocturnal $NO_x$ increase at Pabstthum is supported by enhanced $NO_x/NO_y$ ratios and the presence of significant NO mixing ratios at night. The latter are important for the budget of $NO_3$ radicals [*Geyer*, 2001] since NO reacts extremely fast with $NO_3$ (reaction (R12) below) so that even small concentrations effectively limit its lifetime. Figure 8 shows the dependence of the nocturnal NO concentrations (for solar zenith angles of >100°) on wind speed, wind direction, and ozone. Significantly enhanced NO mixing ratios, with individual spikes of up to 300 ppt, occur at low wind speeds and/or low ozone mixing ratios, whereas the lowest NO mixing ratios are observed when high wind speeds coincide with high ozone concentrations (see fourth panel). The median values for nighttime NO (thick line in Figure 8) extrapolate to an instrumental artifact ("fake NO") of 8 ± 2 ppt, similar to

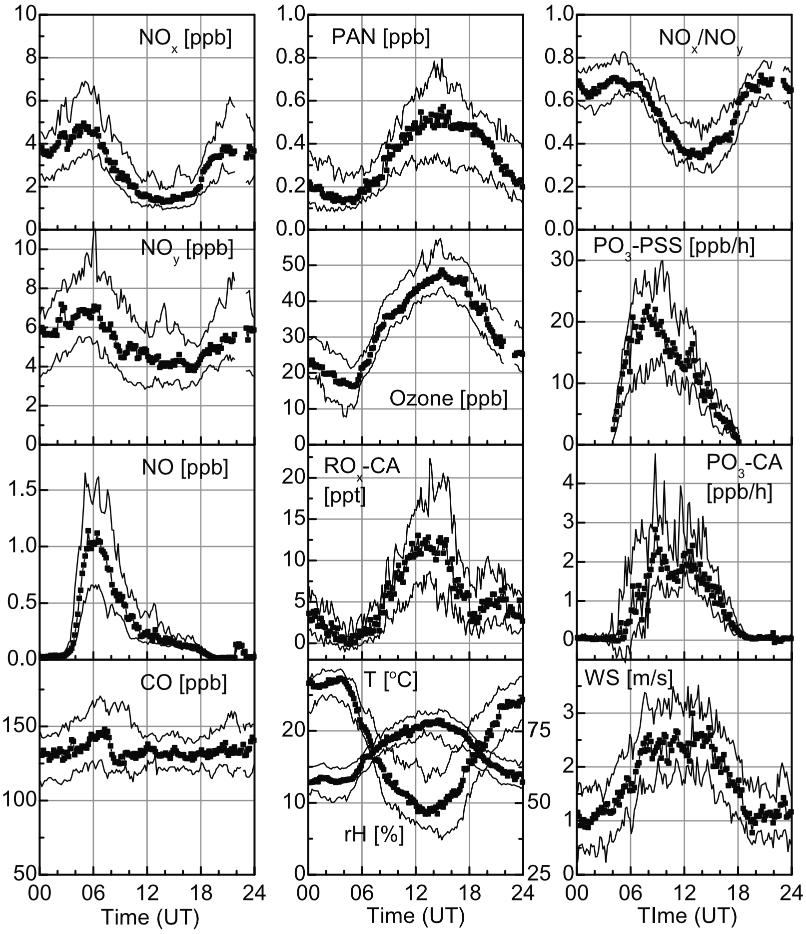

**Figure 7.** Average diurnal variation of $NO_x$, $NO_y$, CO, $O_3$, PAN, $RO_x$, $PO_3$ (from PSS and $RO_x$), and meteorological parameters during BERLIOZ at Pabstthum (median and interquartiles).

what was observed in earlier campaigns with the same instrument [e.g., *Mihelcic et al.*, 1993].

[25] The dependence of NO on $O_3$ and wind speed can be rationalized by a simple model with an emission flux (E) into a moving box with the scale height $\zeta$ and chemical destruction by $O_3$ (reaction (R7) below).

$$d[NO]/dt = E/\zeta - [NO]*[O_3]*k_7 \quad (1)$$

[26] Under the assumption of a constant and homogeneous emission flux upwind of Pabstthum the steady state NO concentration in the box is

$$NO = E/(\zeta[O_3]k_7)$$

[27] When further assuming $\zeta$ to depend on wind speed, an inverse dependence of NO on the product of $O_3$ concentration and wind speed as suggested by the envelop of the data and by the curves for the median and percentiles in the upper panel of Figure 8 is indeed expected.

[28] Local traffic emissions in the area around Pabstthum were insignificant at night except for sporadic activities of the PHOEBE participants themselves. The cars were normally left about 200 m SW of the site, although transport to the site itself was not completely prohibited, in particular outside of the IOPs. The absence of traffic emissions is supported by the rather constant CO mixing ratios at night (Figure 7). The small increase by 15 ppb occurs around 7 UT, about 2–3 hours after the $NO_x$ peak. In summary, the strong dependence of the nocturnal NO mixing ratio on $O_3$ and wind speed thus suggests the presence of emissions from the surrounding soils and pasture, similar to the conclusions of *Rohrer et al.* [1998] for POPCORN.

[29] The highest NO mixing ratios are confined to two nights when wind speed was $<0.5$ m $s^{-1}$ and hence wind direction is not well defined. Therefore, a possible contamination of the NO measurement by the LIF and/or the CA instrument (see Figure 1), where several ppm of NO are mixed into the sample gas for the conversion of $HO_2$ to OH, cannot be ruled out completely although the exhaust of both instruments was placed about 50 m in the NW of the inlets at the drainage ditch.

### 3.1. PSS and Ozone Formation

[30] According to our present understanding and neglecting the minor reaction pathway of the higher $RO_2$ radicals in forming organic nitrates, the local photochemical ozone production rate $PO_3$ is at good approximation given by the rate at which peroxy radicals ($HO_2$ and $RO_2$) convert NO to $NO_2$ (reactions (R1) and (R5)). Provided that the different peroxy radicals react with NO at similar rates [*Eberhard and Howard*, 1997], $PO_3$ can be estimated from

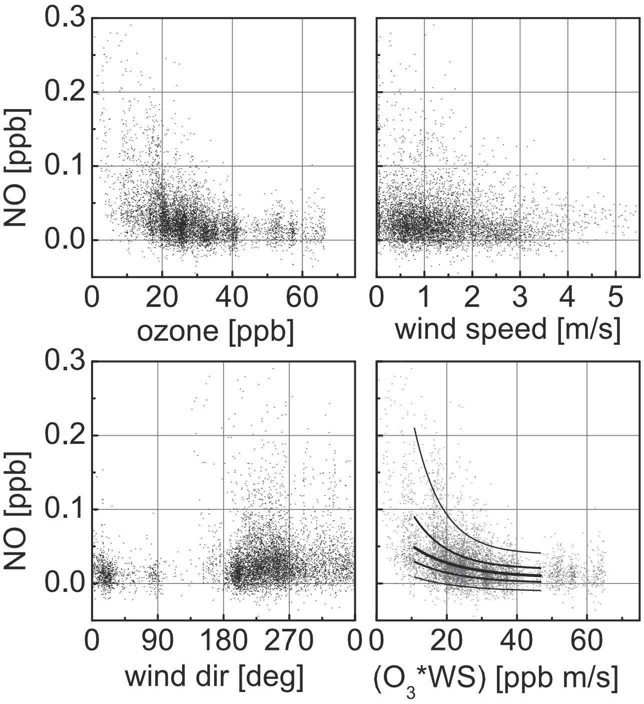

**Figure 8.** Dependence of the nocturnal NO mixing ratio on ozone, wind speed, wind direction, and product of $O_3$ and wind speed (dots: 1 min averages; lines in lower right panel: 5, 25, 50, 75, and 95 percentiles).

simultaneous measurements of NO and the peroxy radicals (equation (2)).

(R7) $NO + O_3 \Rightarrow NO_2 + O_2$

$$k_7 = 1.8 \times 10^{-12} \exp(-1370/T) cm^3\ s^{-1}$$

(R1) $HO_2 + NO \Rightarrow OH + NO_2 \qquad k_1 = 9.6 \times 10^{-12} cm^3\ s^{-1}$

(R5) $RO_2 + NO \Rightarrow NO_2 + RO \qquad k_5 = 8 \times 10^{-12} cm^3\ s^{-1}$

(R8) $NO_2 + hv + O_2 \Rightarrow NO + O_3$

$$JNO_2 = (0 - 9) \times 10^{-3}\ s^{-}\ \text{(measured in situ)}$$

$$P(O_3) = [NO] \cdot \left( \bar{k}_5 \sum_i [R_iO_2] + k_1 \cdot [HO_2] \right) \qquad (2)$$

[31] In several studies an indirect approach (equation (3)) was used to determine $PO_3$ based on the PSS of $NO_x$ and $O_3$, which is assumed to be determined by reactions (R1)–(R4) [e.g., *Kelly et al.*, 1980; *Parrish et al.*, 1986; *Volz et al.*, 1988; *Ridley et al.*, 1992; *Hauglustaine et al.*, 1996; *Volz-Thomas et al.*, 1997; *Frost et al.*, 1998; *Baumann et al.*, 2000; *Pätz et al.*, 2000].

$$P(O_3) = J_{NO_2} \cdot [NO_2] - [O_3] \cdot [NO] \cdot k_7 \qquad (3)$$

[32] By assuming an average rate coefficient $\bar{k}_{1,5}$ for the reaction of $RO_2$ and $HO_2$ radicals with NO, the PSS approach can also be used to estimate the peroxy radical concentrations by equating (2) and (3).

$$\sum_i [R_iO_2] + [HO_2] = \frac{J_{NO_2} \cdot [NO_2] - [O_3] \cdot [NO] \cdot k_7}{[NO] \cdot \bar{k}_{1,5}} \qquad (4)$$

[33] A value of $\bar{k}_{1,5} = 8.8 \times 10^{-12}$ $cm^3\ mol^{-1}\ s^{-1}$ was estimated from the individual rate coefficients for $HO_2$ [*Bohn and Zetzsch*, 1997] and $RO_2$ [*Eberhard and Howard*, 1997] and the measured $RO_2/HO_2$ ratio. The latter was usually around one during daytime [cf. *Mihelcic et al.*, 2002]. The small negative temperature dependence (300/T) was neglected as its influence was less then 3%.

[34] The ozone production rates as calculated from PSS (equation (3)) and from the radical concentrations provided by the CA (equation (2)) are shown in Figure 9. $PO_3$ from PSS reached daily maxima of approximately 30 ppb $h^{-1}$, except on 20, 21, and 23 July when air was advected from the greater Berlin area. Then the maximum production rates are 80–120 ppb $h^{-1}$. The ozone production calculated from $RO_x$ and NO show a similar pattern with the highest values on 20, 21, and 23 July. The absolute values, however, are on average by a factor of 3–5 lower. On the days with the highest production rates, the ozone concentration also exhibited significantly larger daily maxima than the 50 ppb observed during the rest of the campaign (cf. Figure 4).

[35] The average diurnal variation of $PO_3$ is included in Figure 7. The median values of $PO_3$ from PSS exhibit maximum values around 20 ppb $h^{-1}$ in the morning around 8 UT (about 10 o'clock local time). The values for $PO_3$ calculated from the radical concentrations and NO are much lower and exhibit a broad maximum in the median values of approximately 2 ppb $h^{-1}$ almost symmetrically distributed about local noon (9–13 UT). They also show a secondary maximum at night due to $NO_3$ chemistry [cf. *Geyer*, 2001].

[36] Figure 10 shows the diurnal variation of $PO_3$ and the peroxy radical concentrations from the PSS approach and the radical measurements by CA and MIESR on 20 and 21 July, the first IOP of BERLIOZ. For comparison, meteorological parameters, $JNO_2$ and the mixing ratios of $NO_x$, $O_3$ and PAN are also shown. The PSS data are selected for $JNO_2 > 0.006$ $s^{-1}$. $PO_3$ from PSS varies between 10 and 90 ppb $h^{-1}$. The

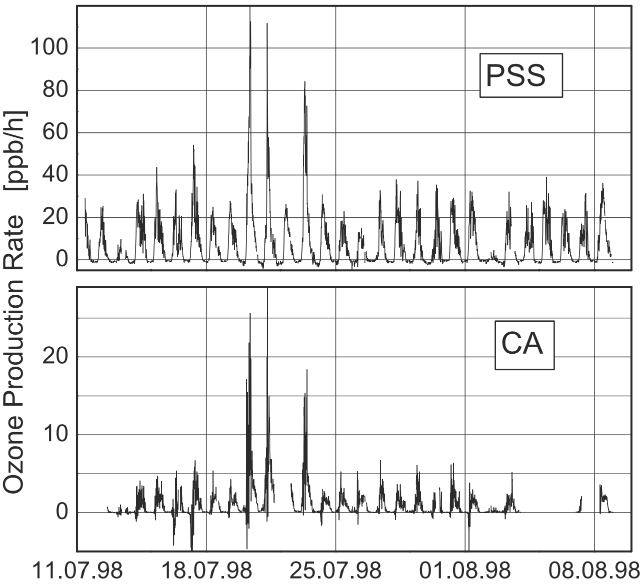

**Figure 9.** Time series of the ozone production rate $PO_3$ calculated from PSS (upper panel) and peroxy radicals (lower panel).

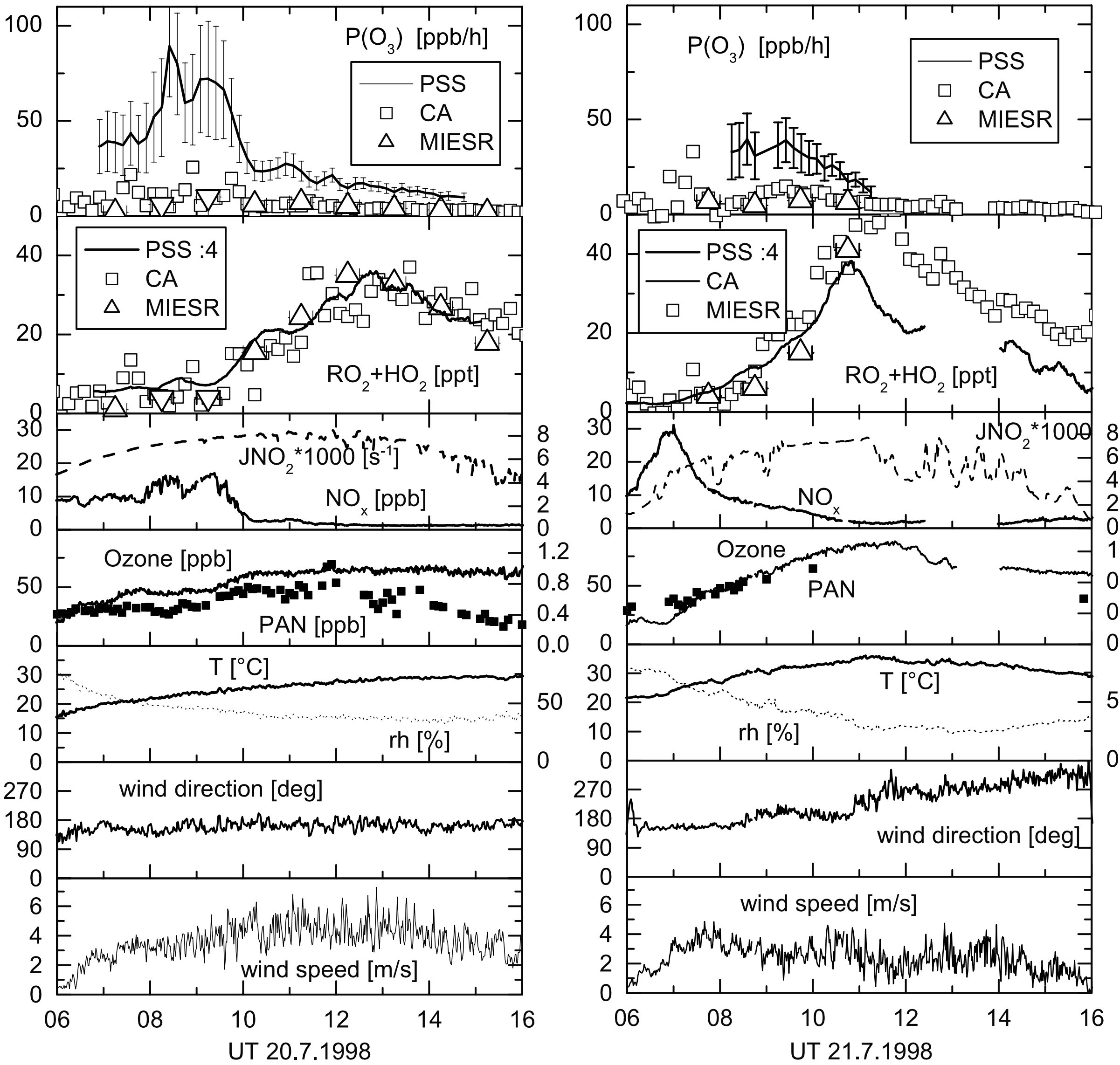

**Figure 10.** Trace gas concentrations during the first IOP (20–21 July). Upper panels: ozone production rate and peroxy radical mixing ratios as derived from PSS (solid line) with those determined from the measurements by CA (rectangles) and MIESR (triangles) [*Mihelcic et al.*, 2002]. For the samples at 0815 and 0915 (downward triangles), when $RO_2$ + $HO_2$ was below the detection limit of the MIESR (2 ppt, 2σ), an upper limit was calculated for $PO_3$. The error bars for PSS-P($O_3$) are propagated from the systematic errors. The lower panels show the mixing ratios of selected trace gases and meteorological parameters for comparison. Note that $JNO_2$ (broken line), PAN (squares), and relative humidity (broken line) are plotted against the right ordinate.

highest production rates are observed simultaneously with the highest $NO_x$ mixing ratio, similar to earlier observations at Schauinsland [*Volz-Thomas et al.*, 1997]. The production rates calculated from NO and the peroxy radicals measured by CA are substantially lower, between 2 and 30 ppb $h^{-1}$. The maximum occurs after the decrease in $NO_x$. The production rates derived from the MIESR measurements do not exceed values of 10 ppb $h^{-1}$. Between 8 and 9 UT, when the highest values of $PO_3$ are calculated from PSS, the mixing ratios of $RO_2$ and $HO_2$ are below the detection limit of the MIESR (open triangles in Figure 10). The corresponding upper limit for $PO_3$ of 6 ppb $h^{-1}$ (assuming [$RO_2$ + $HO_2$] < 2 ppt, i.e., 2σ) is in good agreement with the simultaneous CA measurements and more than a factor of 10 below the value derived from PSS in this time period. The largest deviations between PSS and MIESR occur in photochemically young air masses (i.e., at high $NO_x/NO_y$ ratios). At $NO_x$ < 5 ppb and $NO_x/NO_y$ < 0.5, the deviation of $PO_3$ from PSS and MIESR decreases to values around four.

[37] The error bars denote the 1σ uncertainties of $PO_3$ from PSS which are calculated from error propagation, e.g., $\sigma^2(PO_3) = \Sigma(\partial PO_3/\partial x_i)^2 * \sigma^2(x_i)$, where $\sigma(x_i)$ are the uncertainties of the individual terms in equation (3) which are propagated from the absolute and relative errors listed in Table 1. For values well above the detection limit of the instruments (see column "absolute error" in Table 1) and

by averaging over long enough time periods, the uncertainty is predominated by the systematic errors. As listed in the last column of Table 1, these are 5% (1σ) for each of the ambient measurements entering equation (3). As PSS-derived $PO_3$ is the difference of two terms, its relative uncertainty depends on the actual atmospheric situation. When including the uncertainty in the rate coefficient $k_7$ (8% at 298 K) [*Atkinson et al.*, 1997] the total uncertainty in $PO_3$ from PSS is 40–50% (5–60 ppb $h^{-1}$). The error of the MIESR-derived $PO_3$ is dominated by the error of $\bar{k}_{1,5}$(20%) and is always <2 ppb $h^{-1}$. The discrepancy between PSS and the radical measurements is significant at the 1σ level for all data and at the 2σ level at $NO_x$ concentrations <5 ppb.

## 4. Discussion

[38] Figure 11 shows the ozone production rate at Pabstthum in comparison to data collected at Schauinsland, Black Forest, 1200 m asl and Izana, Tenerife, 2370 m asl, which were obtained using almost identical instrumentation [*Volz-Thomas et al.*, 1997]. Also shown is $PO_3$ calculated from radical measurements made by MIESR [cf. *Mihelcic et al.*, 2002] and CA. At the high altitude site Izana, where $NO_x$ rarely exceeded 1 ppb, there is good agreement between all three measurements [*Schultz*, 1995], whereas at Schauinsland a similarly large discrepancy between PSS-derived $PO_3$ and the radical measurements is observed as during BERLIOZ. The CA measurements at Schauinsland [*Heitlinger et al.*, 1998, not shown] were even lower than the MIESR data because the necessary correction for the humidity dependence of the CA [*Mihele and Hastie*, 1998] was not yet established. A posteriori correction of the Schauinsland data leads to relatively large uncertainties, whereas the humidity correction for the CA at Izana is small. The PSS data exhibit a similar increase of $PO_3$ with the NO mixing ratio at all three sites, whereas $PO_3$ derived from the radical measurements tends to level off at higher NO concentrations, as is discussed in more detail by *Mihelcic et al.* [2002].

[39] Figure 12 compares the peroxy radical concentrations obtained in BERLIOZ with PSS estimates from other studies. Although most of the data sets are obtained at relatively low $NO_x$ mixing ratios (mostly below 1 ppb), there is sufficient overlap with the BERLIOZ data to demonstrate the similarity between the PSS results obtained elsewhere and those determined in this study. It is thus suggested that the overprediction of $PO_3$ and $RO_2$ by the PSS approach is not a special feature of the BERLIOZ data set but pertains at least to the continental boundary layer.

[40] In several of the older data sets data quality issues were discussed as potential causes for the large values of PSS-derived $PO_3$ or $RO_2$, particularly concerning the accuracy of the $NO_2$ measurements [e.g., *Davis et al.*, 1993]. We also note that in many of the published data sets, $JNO_2$ was inferred from model calculations with adjustments for cloudiness made by flat plate radiometers. As noted above, the contributions from imprecision can always be sufficiently reduced by selecting data well above the instrumental detection limits and for relatively homogeneous atmospheric conditions as well as by averaging over long enough time periods. The contributions from accuracy, however, remain.

[41] At Pabstthum, the accuracy of the $NO_2$ measurements is confirmed by the comparison of four independent methods. In fact, when taking the spectroscopic $NO_2$ measurements as the true values and correcting the CLD/PLC measurements accordingly, the deviation between $PO_3$ from equations (2) and (3) would become slightly larger. For NO, a direct independent method was not available at Pabstthum. However, problems with the NO measurement are difficult to conceive because the $NO_2$ measurement by CLD/PLC is based on the measurement of NO which should thus have a similar or better accuracy than $NO_2$. The NO calibration agreed with the certified standard within 1%. Finally, $NO_x$ measured by the balloon borne LMA4 instrument employing conversion of NO to $NO_2$ on $Cr_2O_6$ (fourth panel of Figure 2) agreed with the CLD/PLC data as well as the $NO_2$ measurements. A direct comparison of the NO concentrations was not possible as the LMA4 on the tethered balloon measured $NO_x$ and $NO_2$ sequentially and thus at different heights. The ozone monitor agreed with the primary ozone standard within <5% and the two independently calibrated $JNO_2$ instruments agreed within <3%. The uncertainty in $k_7$ (8%) [*Atkinson et al.*, 1997] represents the largest single contribution to $\Delta PO_3$ from PSS at Pabstthum.

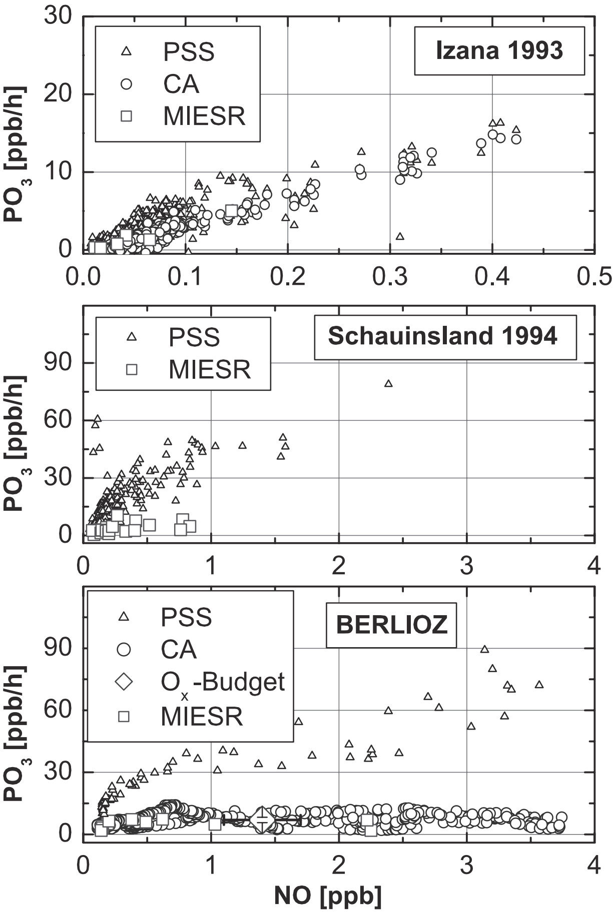

**Figure 11.** Comparison of $PO_3$ from PSS (triangles) and from radical measurements by MIESR (squares) and CA (circles) on 20 July 1998 at Pabstthum (lower panel) with data obtained at Izana, Tenerife, 2400 m asl (upper panel) [*Schultz et al.*, 1996] and Schauinsland, Black Forest, 120 m asl (middle panel) [*Volz-Thomas et al.*, 1997].

[42] The absolute value and the temperature dependence of $k_7$ was revised in the latest recommendation by the

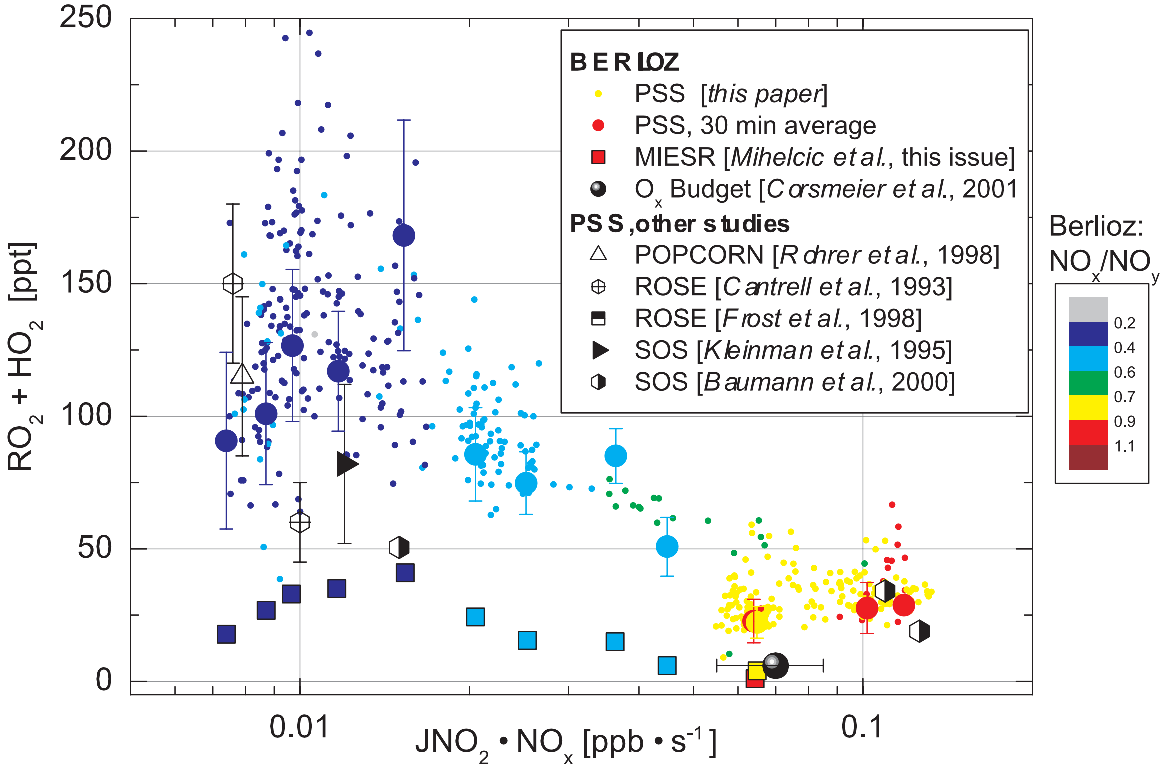

**Figure 12.** PSS derived peroxy radical concentrations and data from direct measurements by CA and MIESR in BERLIOZ versus $JNO_2 \times [NO_x]$. The color of the symbols refers to the $NO_x/NO_y$ ratio. Data are selected for $JNO_2 < 0.006\ s^{-1}$. Also shown are the results of PSS-derived $RO_2$ from several other campaigns and from the ozone budget on the basis of aircraft measurements made during BERLIOZ [*Corsmeier et al.*, 2002; *Konrad*, 2000].

NASA panel ($k_7 = 3 \times 10^{-12} \exp(-1500/T)\ cm^{-3}\ s^{-1}$) [*Sander et al.*, 2000], leading to 7% larger values at 298 K. The influence of this change is investigated in Figure 13, which shows the dependence of $PO_3$ on the prevailing NO mixing ratio. In order to highlight the principal problems of the PSS approach, we also investigate in Figure 14 the PSS data in terms of the Leighton ratio ($\Phi_L$) (equation (5)). According to the theory of PSS, $\Phi_L$ is expected to equal unity in the absence of peroxy radicals.

$$\Phi_L = \frac{J_{NO_2} \cdot [NO_2]}{[NO] \cdot [O_3] \cdot k_7} \qquad (5)$$

[43] Figures 13 and 14 show all PSS data obtained during BERLIOZ at Pabstthum for $JNO_2 > 0.006\ s^{-1}$. The error bars are propagated from the errors in the ambient measurements. The rate coefficient $k_7$ is treated as a parameter: the upper panels are calculated with $k_7$ of *Atkinson et al.* [1997] and the new recommendation. In the lower two panels, the new value for $k_7$ is further increased by 10% and 20%.

[44] For comparison, $\Phi_L$ was also calculated from the radical concentrations by substituting [NO] * $[O_3]$ * $k_7$ in equation (5) from equation (3), i.e.,

$$\Phi_L^* = \frac{J_{NO_2} \cdot [NO_2]}{J_{NO_2} \cdot [NO_2] - [NO] \cdot \bar{k}_{1,5} \cdot ([HO_2] + \Sigma[RO_2])} \qquad (6)$$

[45] According to our current understanding of the radical chemistry, the concentrations of peroxy radicals should vanish for high $NO_x$ concentrations, as the sink for $HO_2$ and $RO_2$ (reactions (R1) and (R5)) increases with NO and because OH, the precursor of $RO_2$, is removed by reaction with $NO_2$. (Because of the selection for high values of $JNO_2$, the general behavior of the data in Figures 13 and 14

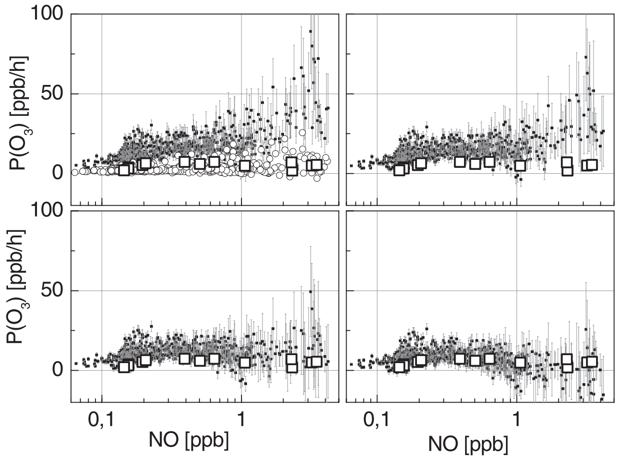

**Figure 13.** Dependence of $PO_3$ on the NO mixing ratio for the different values of $k_7$. Upper left: previously recommended value: $1.8 \times 10^{-12} \exp(-1370/T)$ [*Demore et al.*, 1997]; upper right: new JPL recommendation [*Sander et al.*, 2000]: $3 \times 10^{-12} \exp(-1500/T)$; lower left: new value multiplied by 1.1; lower right: new value multiplied by 1.2. Open circles: $PO_3$ calculated from CA data (equation (6)); open squares: $PO_3$ from MIESR data.

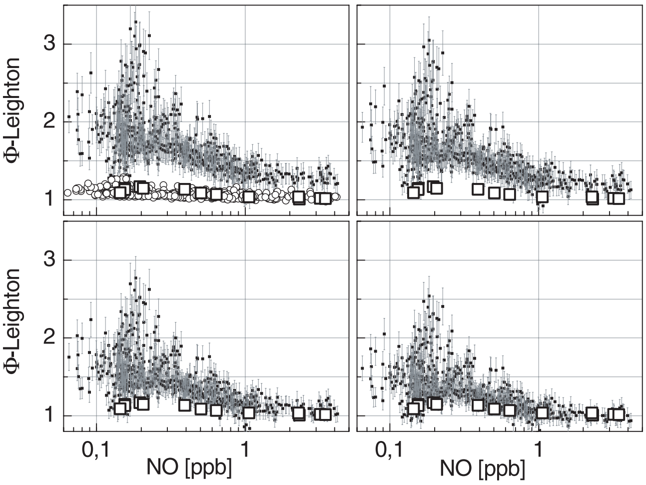

**Figure 14.** Dependence of the Leighton ratio $\Phi_L$ (equation (5)) on the NO mixing ratio for different values of $k_7$ as in Figure 13.

remains similar when NO is exchanged by $NO_2$ or $NO_x$). The Leighton ratio thus is expected to approach unity at the highest NO concentrations. The value of $PO_3$ is more difficult to predict without a detailed model calculation, as the expected decrease in the radical concentrations is, at least to some extent, compensated by the increasing NO concentration. The net effect depends in a nonlinear fashion on the coupling of the radical cycles and on the degree of recycling of radicals during VOC degradation, as well as the presence of radical sources other than ozone photolysis, e.g., ozonolysis of olefinic hydrocarbons or photolysis of HONO.

[46] Qualitatively, $\Phi_L$ from PSS exhibits the expected NO dependence by decreasing from values around 2 at low NO to a value of 1.3 ± 0.2 at NO > 1 ppb. The values of $\Phi_L$ calculated from the radical measurements is always much smaller. The MIESR data reach a maximum of 1.2 at 0.2 ppb NO and approach unity for NO > 1 ppb, in accordance with theory. The CA data, albeit more scattered, are consistent with the MIESR data. The comparison of Figures 13 and 14 highlights a fundamental problem of the PSS approach: At low NO mixing ratios, relatively small values of $PO_3$ are derived from relatively large deviations in $\Phi_L$ (around 2), whereas the high values of $PO_3$ at the high NO mixing ratios are in fact derived from the lowest values of $\Phi_L$, leading to a substantial uncertainty in $PO_3$ at the high NO levels. The precise determination of $PO_3$ from the radicals' measurements, on the other hand, would require detection limits far below 1 ppt at high $NO_x$.

[47] The new recommendation for $k_7$ brings the PSS results into slightly better agreement with the radical data. However, an increase of 20% (i.e., twice the quoted uncertainty at 298 K) above the new value for $k_7$ (or a corresponding change in one or more of the other parameters in equation (5)) is required in order to bring the Leighton ratio to unity at the high NO concentrations. While this would be just conceivable within the estimated uncertainties, it would require all changes to go into the direction of reducing $\Phi_L$. Moreover, a significant overestimation of $\Phi_L$ and $PO_3$ remains at low NO mixing ratios. It seems therefore unlikely that the large overestimation of $PO_3$ by PSS is a consequence of measurement errors. In fact, we measured $k_7$ in the laboratory [*Konrad*, 1997] and found a value of $1.8 \times 10^{-12} \exp(-1384/T)$ $cm^3$ $s^{-1}$ in agreement with the recommendation by *Atkinson et al.* [1997]. We should also like to emphasize that the calculation of $PO_3$ from PSS is more likely a lower limit, since the $NO_2$ concentrations by CLD/PLC are slightly lower than those measured by MIESR, the $NO_x$ and thus the NO concentrations by CLD are slightly higher than the LMA4 data (Figure 2), and the $JNO_2$ data were adjusted to the lower values of the three radiometers deployed. Finally, the inclusion of local NO emissions in equations (3) and (5) (see discussion by *Rohrer et al.* [1998]) would also produce higher values of $\Phi_L$ and $PO_3$.

[48] *Frost et al.* [1998] discuss the possibility of a larger average rate coefficient $k_5$ for explaining the discrepancy between PSS and $RO_x$ measurements. In order to explain the discrepancy between PSS-derived radicals and the two independent measurements observed at Pabstthum (second panels in Figure 10), the average value of $k_{1,5}$ would have to be increased by approximately a factor of four. With the $HO_2/RO_2$ ratio of 1:1 as measured by MIESR [*Mihelcic et al.*, 2002] this would imply that either the recommended values for $k_1$ and $k_5$ are low by a factor of four, or that the average value of $k_5$ for the radical mix at Pabstthum would have to be increased by a factor of 7 above the current recommendation.

[49] Requesting such an extreme revision of our kinetic knowledge has a similar dimension as the revision of the value for $k_1$ in the seventies [*Howard and Evenson*, 1977], which radically changed the then existing view of ozone chemistry in the stratosphere. Based upon the kinetic information available today, all the investigated peroxy radicals, except for $CH_3C(O)O_2$ which reacts about 3 times faster, have values of $k_5$ of $10^{-11}$ $cm^3$ $s^{-1}$ or less. According to the photochemical model discussed by *Mihelcic et al.* [2002], $CH_3O_2$ and other aliphatic peroxy radicals alone represent about 50% of $RO_2$. We thus find it difficult to conceive that the majority of the peroxy radicals would react at such a fast rate with NO. Another argument comes from the ozone budget. Quadrupling of $k_{1,5}$ would lead to four times larger ozone production rates, which are ruled out by the aircraft studies in BERLIOZ (see below).

[50] As was first discussed by *Parrish et al.* [1986], an overestimation of $PO_3$ and $RO_x$ from PSS may be explained by the presence of unknown oxidants XO that convert NO to $NO_2$.

$$\text{(R9)} \qquad XO + NO \rightarrow NO_2 + X$$

[51] Whether this process leads to a real ozone production or not depends on the origin of XO, which might be produced under consumption of $O_3$, as it is the case for halogen radicals.

$$\text{(R10)} \qquad O_3 + X \rightarrow XO + O_2$$

[52] This important question can be examined by comparing the different estimates of $PO_3$ to the ozone budget derived in the plume of Berlin on the basis of airborne measurements conducted during BERLIOZ. Briefly, the DO-128 aircraft operated by FZ-Karlsruhe [*Corsmeier et*

*al.*, 2002] flew at different altitudes along the transport vector of the Berlin plume and measured the turbulent and advective fluxes of ozone. The data were used to solve the continuity equation for ozone, yielding a photochemical production rate of 6.5 ppb $h^{-1}$ in the plume downwind of Berlin [*Corsmeier et al.*, 2002]. Another aircraft (Eco-DIMONA; operated by MetAir in cooperation with FZ-Jülich) transected the plume at two altitudes and at two distances from Berlin in a quasi-Lagrangian experiment. From the traverses close to and 50 km away from Berlin an increase of ~10 ppb $O_x$ (the sum of $O_3$ and $NO_2$) [cf. *Guicherit et al.*, 1988] was observed in a transport time of 160 min, corresponding to a rate of change around 4 ppb $h^{-1}$. When including meaningful estimates for losses due to deposition, dilution and chemical reactions in the $O_x$ budget, a production rate of $PO_3 = 7 \pm 2$ ppb $h^{-1}$ was needed to explain the observed increase of $O_x$ within the plume [*Konrad*, 2000], in excellent agreement with the estimate from the DO-128. The NO mixing ratio obtained in the plume from the airborne measurements averaged 1.4 ± 0.4 ppb. Thus the production rate required for closing the budget requires a peroxy radical mixing ratio of 6 ± 2 ppt.

[53] From the excellent agreement of the ozone budget with the radical measurements by MIESR and CA (cf. Figures 11 and 12) it is concluded that the unknown NO to $NO_2$ conversion process which is responsible for the observed enhancement in the Leighton ratio and $PO_3$ does not lead to a net $O_3$ production. The process must proceed with a first order rate coefficient of approximately 0.01 $s^{-1}$.

[54] A known process that converts NO to $NO_2$ is the production and destruction of $NO_3$:

$$\text{(R11)}\quad NO_2 + O_3 \Rightarrow NO_3 + O_2 \qquad k_{11} = 1.2 \times 10^{-13}\exp(-2450/T)\,cm^3\ s^{-1}$$

$$\text{(R12)}\quad NO_3 + NO \Rightarrow 2NO_2 \qquad k_{12} = 1.5 \times 10^{-11}\ cm^3\ s^{-1}$$

$$\text{(R13)}\quad NO_3 + hv \Rightarrow NO + O_2 \qquad J_{13} < 0.025 s^{-1}$$

$$\text{(R14)}\quad NO_3 + hv \Rightarrow NO_2 + O \qquad J_{14} < 0.16 s^{-1}$$

[55] In order to estimate the maximum effect of $NO_3$ on the $NO_2$/NO ratio, we neglect photolysis and other reactions of $NO_3$ [for details, see *Geyer*, 2001], which is a reasonable assumption at the highest NO concentrations. In this simplified system, the net effect of $NO_3$ chemistry is equivalent to a conversion of NO to $NO_2$ with a rate given by (reaction (R9)), which is always less than 1% of the rate of reaction (R7) for the conditions in BERLIOZ and thus influences $PO_3$ by less than 3%. In reality, the effect is much smaller because of the competition of $NO_3$ photolysis with reaction (R12), the formation of $N_2O_5$ and reactions of $NO_3$ with other trace constituents.

[56] Iodine monoxide was proposed as an NO oxidant [*Chameides et al.*, 1990], although its participation in the atmospheric reaction cycle was later found to be unlikely [*Chatfield and Crutzen*, 1990; *Cantrell et al.*, 1996; *Crawford et al.*, 1996]. *Harder et al.* [1995] and *Carpenter et al.* [1998] discussed the possibility that BrO radicals might be responsible for unexplained NO to $NO_2$ conversion for measurements made in maritime air masses at the west coast of Europe. In order to explain the deviations in the Leighton ratio at Pabstthum, BrO mixing ratios of 15 to 40 ppt would be required. Such high BrO mixing ratios are difficult to imagine in the continental boundary layer outside of the polar arctic.

## 5. Conclusions

[57] Ambient measurements of a comprehensive set of inorganic trace gases, peroxy radicals and physical parameters, including the photolysis frequency of $NO_2$ made during the BERLIOZ campaign at Pabstthum, a relatively unpolluted site about 50 km N-NW of Berlin, are discussed. An important aspect was the assurance of data quality through external quality control and by instrument comparison at the site. Most important, four independent instruments deployed for $NO_2$ agreed within 5%, thus ruling out principal problems with the measurement of $NO_x$ by photolytic conversion/chemiluminescence.

[58] The relatively high NO concentrations observed in many nights showed a strong anti correlation with $O_3$ and wind speed and are best explained by emissions from the surrounding soil and vegetation, although contamination by the radical measurements cannot be completely ruled out at all instances.

[59] The data were used together with peroxy radical measurements from accompanying papers to investigate the often observed overestimation of the ozone formation rate by the PSS approach. It could be shown, that the large deviation is not a special feature of the BERLIOZ data set but is also observed elsewhere in Europe and North America. It was also shown that a very high accuracy of the individual measurements is required in order to calculate significant values for $PO_3$. Due to the high confidence in the data, it is strongly suggested that an as yet unknown process exists in the atmosphere that converts NO to $NO_2$. Most important, by comparison of $PO_3$ with the ozone budget in the plume of Berlin that was independently derived from airborne measurements, it could be shown that the unknown process which converts NO to $NO_2$ does not lead to a net production of ozone. In the search for the unknown oxidation process, it is important to note that the most prominent correlation of XO is with the peroxy radicals themselves (Figure 10). The large disagreement of PSS with the direct measurements of peroxy radical concentrations and with the budget of $O_3$ points out that PSS is not suitable to determine ozone production rates.

[60] **Acknowledgments.** We gratefully acknowledge the financial support by the German Minister for Research and Development (BMFT) as part of the Tropospheric Research Focus (TFS) grant 07TFS 31/HA.3 and of EUROTRAC-TOR (grant 07 EU 723). The measurements at Tenerife were kindly supported by the European Commission DG-XII as part of the project OCTA (EV5V-CT91-0042).

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