

Introduction to Special Section: Photochemistry Experiment in BERLIOZ

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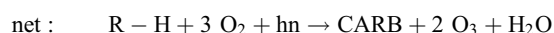
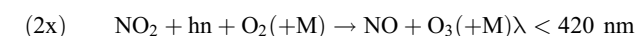
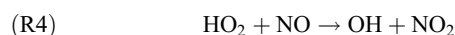
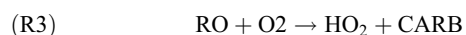
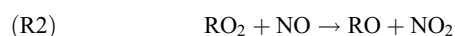
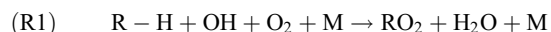
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[1] PHOEBE was conducted during the Berlin Ozone Experiment (BERLIOZ) between 5 July and 7 August 1998 near the city of Berlin. It aimed at a quantitative understanding of the fast radical chemistry in rural and suburban air by simultaneous measurements of the major free radicals (OH, HO₂, RO₂, and NO₃) and the chemical compounds and physical parameters that control the radical concentrations. Interpretation of the measurements involved models of different complexity. The methods deployed and the results are discussed in the subsequent publications of this special section. This paper outlines the aims of PHOEBE, describes the observational site at Pabstthum, and briefly summarizes the different measurements and instrument comparisons as well as the main results of the accompanying publications. *INDEX TERMS*: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0394 Atmospheric Composition and Structure: Instruments and techniques; *KEYWORDS*: field campaign, free radicals, modeling, measurements, overview

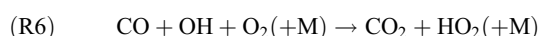
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1. Introduction

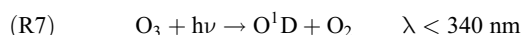
[2] The transition region between urban and rural areas is important in understanding the fast photochemistry that leads to the build up of high concentrations of ozone and other photooxidants during so-called summer smog episodes. As is schematically outlined in reactions (R1)–(R5), hydrocarbon oxidation by hydroxyl radicals (OH) leads to formation of peroxy radicals (RO₂ and HO₂), which oxidize NO to NO₂, thereby regenerating the OH. Photolysis of the NO₂ then generates the oxygen atoms required to produce ozone [Chameides and Walker, 1973; Crutzen, 1979]. In this simplified view, the net effect of the radical chain in the presence of sufficient NO is that hydrocarbons are oxidized to carbonyl compounds (CARB, i.e., aldehydes and ketones) and O₃ [cf. Chameides et al., 1992]



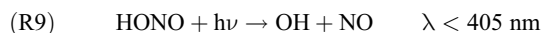
Additional HO₂ is produced from the oxidation of CO:



Production of OH radicals in the troposphere occurs mainly via photolysis of O₃ ((R7) and (R8)) [Levy, 1971]



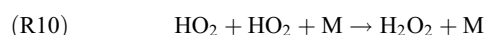
Another potentially important source for OH, particularly in polluted air, is the photolysis of HONO which is formed either in the tail pipe of motor vehicles [Kessler and Platt, 1984] or upon emission in the atmosphere via heterogeneous reactions [Stockwell and Calvert, 1983].



Since (R9) occurs at much longer wavelengths than (R8), it can produce OH during the early morning, when (R8) is still rather ineffective. Thereby, HONO photolysis is thought to provide an important trigger for photochemical smog formation in the urban and suburban environment [Harris et al., 1982; Platt, 1986; Jenkin et al., 1988; Calvert et al., 1994; Harrison et al., 1996; Volz-Thomas and Kolahgar, 2000]. Other sources of OH and peroxy radicals include the ozonolysis of olefinic VOC [cf. Paulson and Orlando, 1996; Kroll et al., 2001; Siese et al., 2001], and the reaction

of NO₃ radicals with organic compounds at night [Wayne *et al.*, 1991; Mihelcic *et al.*, 1993; Carslaw *et al.*, 1997; Platt *et al.*, 1990; Salisbury *et al.*, 2001].

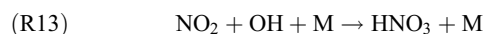
[3] During daytime, the concentration of OH and the production rate of ozone both depend on the UV flux (i.e., on the photolysis frequencies JO¹D, JNO₂, JHONO, JHCHO, ...) and on the concentrations of H₂O, O₃, CO, NO_x, and VOCs. The role of NO_x in the budgets of HO_x (OH and HO₂) and ozone is ambivalent: At low NO_x concentrations, where recombination reactions of the peroxy radicals ((R10) + (R11)) constitute the major radical loss, NO controls the recycling of HO_x and is the rate limiting factor in ozone production [Crutzen, 1979].



At high-NO_x levels, radical losses by recombination of peroxy radicals become insignificant and HO₂ is almost completely recycled to OH in reaction (R4). Due to photolysis of the carbonyl compounds formed in reaction (R3), more radicals can be produced from the hydrocarbon oxidation mechanism than are initially consumed in (R1), depending on the VOC to NO_x ratio and VOC reactivity [Jeffries and Tonnesen, 1994].



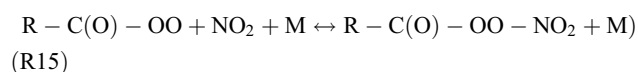
This effect is counteracted by the reaction of OH with NO₂, which becomes the predominant sink of HO_x in the high-NO_x regime and thus effectively limits the production of RO₂ and HO₂.



The net effect of NO_x on the radical balance and ozone formation depends on the NO/NO₂ ratio, which is controlled by the photolysis rate of NO₂(R5) and by the concentrations of peroxy radicals and O₃ via reactions (R2), (R4), and (R14).



The radical chemistry in the high-NO_x regime is further complicated by the photolysis of HONO (R9). Another complication in the understanding of the radical budget is the formation of alkyl nitrates and peroxyacyl nitrates, e.g., PAN. Alkyl nitrates are formed as by-products in (R2). The branching ratios tend to increase with the size of the organic rest and are higher for secondary and tertiary RO₂ [Atkinson *et al.*, 1982, 1983, 1984, 1987; Becker and Wirtz, 1989]. The net effect is a decrease in the local ozone formation rate. Similarly, the production of peroxyacetyl nitrate (PAN) and its homologues by reaction of acylperoxy radicals with NO₂ (R15) removes peroxy radicals and NO_x from the active pool. Thermal decomposition of the PAN compounds establishes equilibrium, but the net effect on the local radical balance depends on temperature and history of the air mass.



[4] Because of their short chemical lifetimes, free radicals (OH, HO₂, and RO₂) are largely decoupled from transport processes and can thus be investigated with zero dimensional chemistry models, provided that the chemical and physical parameters which control the local radical concentration, e.g., UV radiation, NO_x, and VOC, are quantified. This is strictly the case only if the radicals and other parameters are measured with a time resolution given by the atmospheric lifetimes of the radicals, e.g., between less than 1 s for OH and a few seconds to minutes for the peroxy radicals. Until now this is an unsolved challenge for many atmospheric trace gases, in particular for hydrocarbons which in urban air can constitute of more than 100 different compounds [Ciccioli *et al.*, 1992]. The interpretation of the radical measurements thus relies on assumptions about stationarity and homogeneity of the investigated air masses. These conditions are best achieved if the measurements are made at sufficient distance from sources or sinks and if the different measurements are made as close together as possible.

[5] The fast photochemistry of the troposphere has been investigated by measurements of the concentrations of the free radicals (OH, HO₂, and RO₂) and of those chemical and physical parameters that are thought to control the radical concentrations. Besides airborne missions in the free troposphere [Brune *et al.*, 1998; Mauldin *et al.*, 1998; Wennberg *et al.*, 1998], a strong emphasis has been on ground based studies, mostly in the planetary boundary layer (PBL) [cf. Perner *et al.*, 1987; Platt *et al.*, 1988; Eisele *et al.*, 1994, 1996, 1997; Poppe *et al.*, 1994; Cantrell *et al.*, 1996, 1997; Armerding *et al.*, 1997; Carpenter *et al.*, 1997; McKeen *et al.*, 1997; Mount and Williams, 1997; Penkett *et al.*, 1997; Brandenburger *et al.*, 1998; Holland *et al.*, 1998; Jefferson *et al.*, 1998; Carslaw *et al.*, 1999; Ehhalt, 1999; Haughustaine *et al.*, 1999; Kanaya *et al.*, 1999, 2000; Volz-Thomas and Kolahgar, 2000; Brauers *et al.*, 2001; Carroll *et al.*, 2001; Savage *et al.*, 2001]. These field experiments qualitatively confirmed fundamental aspects of the free radical chemistry, such as the principal dependencies of OH on the ozone photolysis frequency JO¹D and the concentration of NO_x.

[6] The quantitative comparison of measurements and models does not show a coherent picture. There is a general tendency of photochemical models to overestimate OH and peroxy radicals. Exceptions are the ALBATROSS, POP-CORN, and SCATE campaigns and the MLOPEX-2 campaign in spring, where modeled and measured OH were found to agree within the experimental uncertainties for clean air conditions [Eisele *et al.*, 1996; Jefferson *et al.*, 1998; Ehhalt, 1999; Brauers *et al.*, 2001], and some campaigns conducted in forested areas (e.g., AEROBIC, PROPHET, and SLOPE) where OH was found to be significantly underestimated by the models [Volz-Thomas and Kolahgar, 2000; Carslaw *et al.*, 2001; Creasey *et al.*, 2001; Tan *et al.*, 2001]. It is also noted that in some of the earlier studies, the comparison was somewhat limited by the lack of measurements for several trace gases that are of importance to OH formation or loss, e.g., part of the VOC. Very little information exists so far on the behavior of OH radicals in highly polluted atmospheres, except of the LAFRE campaign [George *et al.*, 1999].

[7] The PHOEBE campaign was planned to investigate the radical chemistry in an environment covering suburban

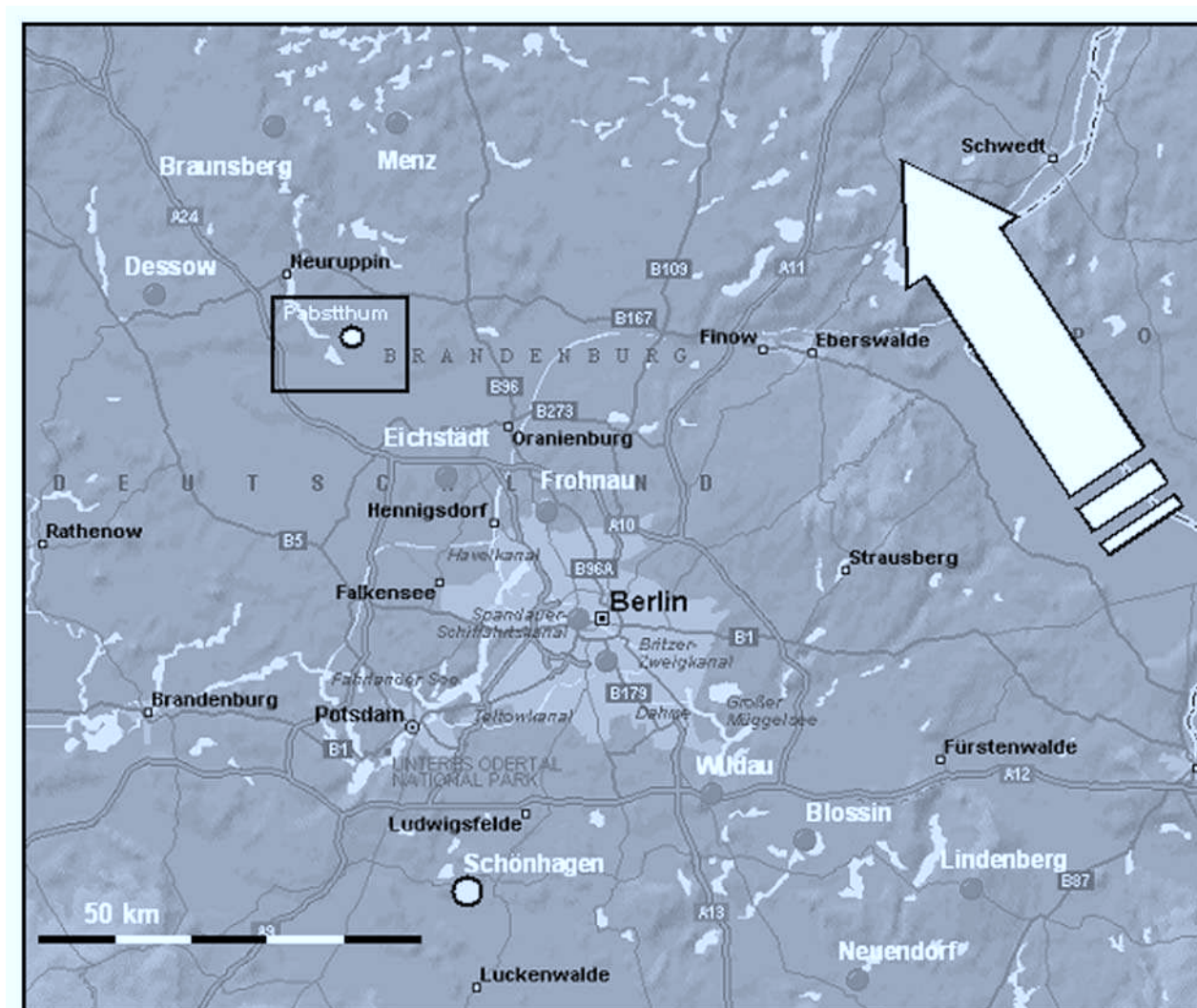


Figure 1. Map of the area around Berlin with the surface sites of BERLIOZ indicated by the red dots and the airfield Schönhagen by the yellow dot. The red lines denote motorways and major roads. See color version of this figure at back of this issue.

to rural conditions. It was a major activity of the Berlin Ozone Experiment (BERLIOZ) [Becker *et al.*, 1999] which took place between 5 July and 7 August 1998 including 1 week for intercomparison and quality control of the different analytical instruments. The overall aim of the BERLIOZ was to analyze the transport and chemical processes responsible for photooxidant formation and the contribution of groups of precursor substances to the ozone formation in the Berlin area. For this purpose, many speciated hydrocarbons and carbonyl compounds, O_3 , PAN, NO, NO_2 , HNO_2 , HNO_3 , and NO_3 radicals (e.g., JNO_2 and JO^1D) were measured at different ground based sites by in situ techniques, along with measurements of meteorological parameters and photolysis frequencies.

[8] A map of the area around Berlin with the BERLIOZ sites is shown in Figure 1. The sites had been lined up along an axis extending from ca. 70 km SE to 80 km NW of Berlin, according to the predicted main wind direction during episodes with large photochemical activity. In

addition to the surface sites, which were operational during the whole BERLIOZ period, 6 ozone LIDAR systems, 5 tethered balloons and 6 aircraft were deployed during intensive operational periods (IOPs). Some of the ground based measurements, i.e., carbonyl compounds, carboxylic acids, and the measurements of peroxy radicals by MIESR (see below) were also confined to the IOPs. The technical equipment, the achieved data, estimates of the precursor emissions and trace gas budgets are described in [Corsmeier *et al.*, 2002; Junkermann *et al.*, 2002; Moortgat *et al.*, 2002; Platt *et al.*, 2002; Winkler *et al.*, 2002]

[9] The emphasis of PHOEBE was on the understanding of the local balance of the free radicals. (OH , HO_2 and RO_2 and NO_3). For this purpose, measurements of the free radicals were performed at a selected site, Pabstthum, together with a large suite of comparatively stable chemical compounds, e.g., odd nitrogen compounds (NO , NO_2 , NO_y , nonsoluble NO_y , PAN), hydrocarbons and oxygenated

organic compounds (VOC), peroxides, ozone, CO, photolysis frequencies and meteorological parameters.

[10] Specific questions addressed by PHOEBE were:

1. How do the concentrations of free radicals depend on the primary production, i.e., JO^1D , and on the concentrations of NO_x and VOC?

2. What is the influence of other sources (e.g., HONO photolysis and ozonolysis) on the radical concentrations?

3. How well do state of the art photochemical models reproduce the measured radical concentrations?

4. Is the photostationary state (PSS) approach a suitable tool to determine the local ozone production rate PO_3 ?

5. What are the main sources of free radicals at night and how large is the influence of NO_3 radicals on the oxidation capacity of the atmosphere?

[11] In this paper we describe the experimental setting of PHOEBE, give a summary of the many analytical techniques applied at Pabstthum and the experimental results, including instrument comparisons, and highlight the main scientific conclusions from the publications of this special section. The research groups that participated in PHOEBE are listed in Table 1.

2. Experimental

2.1. The PHOEBE Site at Pabstthum

[12] The PHOEBE site ($12^\circ 56' 25''\text{E}$, $52^\circ 51' 15''\text{N}$, 50 m above sea level) was established about 400 m east of the small village Pabstthum at the western border of a flat grassland of $7.5 \times 4.5 \text{ km}^2$ extension (Figure 2). Selection criteria were the distance from Berlin in order to obtain a good representation of the plume development in conjunction with the other BERLIOZ sites (see Figure 1), as well as the absence of local anthropogenic sources, reasonably flat terrain with unrestricted flow from the direction of Berlin, and logistical requirements such as electrical power and road access for supplying liquid nitrogen and gases.

[13] The area around Pabstthum, which itself consists of only 5 residences, is extremely sparsely populated. Local emissions from traffic, industry and residences in the vicinity of Pabstthum are negligible, except for the motorway A24 in the west about 10 km away. The nearest villages Wall and Radensleben located about 5 and 7 km to the SE and NW, respectively, have less than 500 inhabitants. The closest city is Neuruppin, 12 km in the NW, with 38,000 inhabitants. Berlin (3.4 million inhabitants) is located in southeasterly direction (140°) at a distance of about 50 km (city center).

[14] 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 easterly direction, which was kept clear during the campaign.

2.2. Instrumentation

[15] The instrumentation deployed at Pabstthum is summarized in Table 2 together with information on the time resolution of the measurements and the responsible institutions (cf. Table 1). More detailed information is found in the accompanying papers. The experimental setting of the

Table 1. Institutions Involved in PHOEBE

Acronym	Institution
FZJ	Research Center Jülich, Institut für Chemie und Dynamik der Geosphäre
IUP	University of Heidelberg, Institut für Umwelphysik
IVD	University of Stuttgart, Institut für Dampfkesselwesen
MPI-C	Max-Planck Institute for Chemistry, Mainz
TUD	Technical University of Darmstadt, Institut für Chemie

PHOEBE site is shown in Figures 3 and 4. In order to keep the influence of local surface emissions and deposition at a minimum, the instruments were placed as close together as possible at a height of approximately 10 m.

[16] The instruments for odd nitrogen compounds, O_3 , CO, PAN, HCHO and speciated hydrocarbons were housed inside an air conditioned mobile laboratory. The inlets were mounted 10–11 m above ground on a pneumatic mast, which also carried a photometer for the measurement of J_{NO_2} . The gold converter for NO_y was mounted directly at the inlet. Details are given by Konrad *et al.* [2003] and Volz-Thomas *et al.* [2003]. Air temperature, wind direction and wind speed were also measured at 11 m height on the same mast.

[17] The cryogenic sampler of the MIESR (Matrix Isolation ESR Spectroscopy) was also operated on a pneumatic mast, 11 m above ground, about 10 m NE of the mobile laboratory. The samples were collected over 30 min intervals and analyzed after the campaign at the laboratory in Jülich [Mihelcic *et al.*, 2003].

[18] The LIF (Laser-Induced Resonance Fluorescence) instrument for the measurement of OH and HO_2 radicals was mounted inside a laboratory container which was placed on a 5 m high scaffolding platform. The inlet of the LIF instrument was 10 m above ground. Measurements of photolysis frequencies were made on the LIF container using a scanning spectral radiometer and two filter radiometers (JNO_2 and JO^1D). Another container on the platform housed the sampling devices for the measurement of peroxides, carbonyl compounds and carboxylic acids [Grossmann *et al.*, 2003] and a chemical amplifier for the measurement of peroxy radicals, i.e., the sum of HO_2 and RO_2 [Volz-Thomas *et al.*, 2003].

[19] A DOAS (Differential Optical Absorption Spectroscopy) system for the measurement of NO_2 , NO_3 , O_3 , HCHO and SO_2 was also mounted on the platform. It had a folded light path of a total length of more than 2 km (Multireflection Cell with 15 m base length, 144 reflections) [Alicke *et al.*, 2003]. A second DOAS system (DOAS2) for the measurement of NO_3 , NO_2 , HONO, HCHO, SO_2 , O_3 , and aromatic VOC pointed in easterly direction from a height of 1.5 m at the station to a retroreflector mounted 36 m above the ground at a distance of 6.3 km [Geyer *et al.*, 1999, 2003].

[20] Vertical soundings of O_3 , NO_x , and meteorological parameters were conducted with a tethered balloon up to an altitude of 900 m. A second tethered balloon carried four automatic sampling units for hydrocarbons [Glaser *et al.*, 2003].

[21] The site was in operation from 13 July to 8 August. Most of the continuous in situ measurements, including

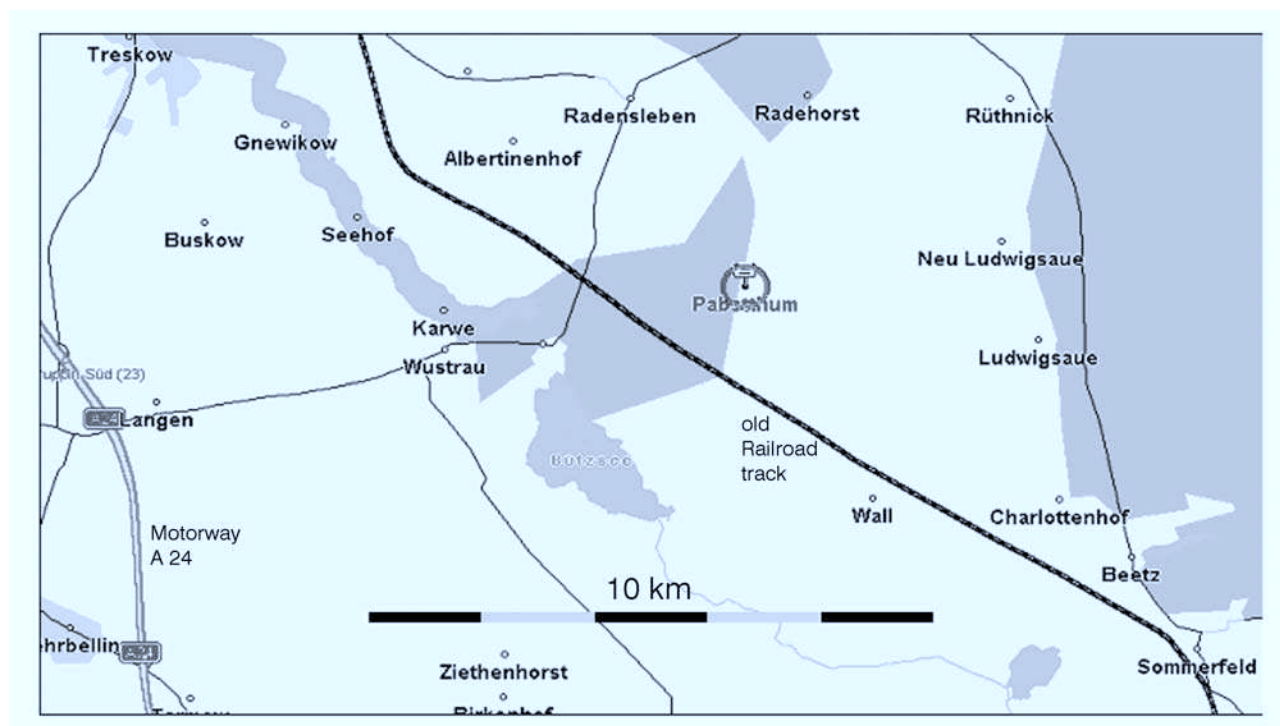


Figure 2. Surroundings of the PHOEBE observatory site Pabstthum (green: forested areas, blue: water bodies). See color version of this figure at back of this issue.

DOAS, LIF and the GCs, were conducted over the entire period and were interrupted only for calibration and maintenance, or during rain fall. The vertical soundings and some other experiments (i.e., MIESR, peroxides, carbonyl compounds and carboxylic acids), however, were limited in the number of samples. These measurements were concentrated on the intensive observational periods (IOPs) which took place on 20 and 21 July and 4 and 5 August upon announcement by the BERLIOZ steering group on the basis of weather forecasts. Thus, the full set of chemical measurements was available only during these time periods, on which the interpretation of the radical chemistry and the modeling work presented in this special section is concentrated.

3. Meteorological Situation

[22] The meteorological situation during BERLIOZ was dominated by a westerly monsoon regime, which lasted unusually long. Winds between 180° and 360° prevailed more than 80% of the time (Figures 5 and 6), while southeasterly winds from the direction of the greater Berlin area (120° – 160°) occurred only at about 3% of the time. This was not expected from the long term wind rose of Berlin exhibiting a secondary maximum at southeasterly directions with a probability of about 9% during July (E. Reimer, personal communication).

[23] Because of this situation, the PHOEBE site was under the influence of marine air for most of the time. The nearest larger cities in the west sector are Magdeburg (110 km, SW), Hamburg, (150 km, WNW), and Halle/Leipzig (170 km, SSW). The Ruhr Valley and the Frankfurt/Mannheim area are more than 400 km in the west and SW, respectively. The city plume of Berlin with photosmog

conditions was only observed on a few occasions, i.e., on 20, 21, and 23 July. On the first 2 days of this period an IOP was called by the BERLIOZ steering group. During the second IOP (3–5 August), the wind direction was NW so that Pabstthum was not under the influence of the Berlin plume, which was then to be detected by the southeasterly BERLIOZ sites.

3.1. Synoptic Situation on 20 July 1998

[24] Behind a strong low pressure system moving from the North Sea to the northern part of Scandinavia, a weak high-pressure system developed over Poland during the night of 19 and 20 July. At the same time warm air originating in the subtropics moved north over SW Germany, thereby pushing a warm front towards NE. The edge of the warm front reached Berlin during the early afternoon of 20 July with little weather activity (Figure 7). The arrival of the warm air was accompanied by low level stratiform clouds, which dissolved shortly after 8 UTC without any precipitation. The advection of warm air and the enhanced irradiance under clear skies led to a pronounced increase in temperature relative to the previous days. The maximum temperature of slightly above 30°C was 6°C higher than during the previous days.

[25] The surface wind at Pabstthum (10 m above ground) was calm during the night, increased after sunrise, and turned to southeasterly directions between 0500 and 0530 UTC. During the day the wind direction remained at about 160° until 18 UTC allowing the advection of air from the southwestern part of the greater Berlin area.

[26] Local profiles of potential temperature at Pabstthum [Glaser *et al.*, 2003] showed the vertical development of the mixing layer from <100 m in the early morning to above

Table 2. Instrumentation Deployed at Pabstthum

Parameter	Instrument	Time resolution	Institution ^a	Reference
<i>Odd Nitrogen Compounds</i>				
NO	Chemiluminescence (770 ALppt, EcoPhysics)	1 min	FZJ	<i>Volz-Thomas et al. [2003]</i>
NO _x	CLD 770 ALppt + PLC 760 (EcoPhysics)	1 min	FZJ	<i>Volz-Thomas et al. [2003]</i>
NO ₂	Differential optical absorption spectroscopy (DOAS 1 and 2)	30 min	IUP	<i>Alicke et al. [2003]</i>
NO ₂ ^b	Matrix isolation and ESR spectroscopy (MIESR)	30 min	FZJ	<i>Mihelcic et al. [2003]</i>
NO _y	CLD 770 ALppt + Au-converter	1 min	FZJ	<i>Volz-Thomas et al. [2003]</i>
NO _y -HNO ₃	CLD 770 ALppt + Au-converter + Denuder	1 min	FZJ	<i>Volz-Thomas et al. [2003]</i>
HNO ₂	DOAS 1	30 min	IUP	<i>Alicke et al. [2003]</i>
PAN	GC-ECD (Meteorologieconsult)	6 min	FZJ	<i>Volz-Thomas et al. [2003]</i>
<i>Other</i>				
O ₃	DOAS	30 min	IUP	<i>Alicke et al. [2003]</i>
O ₃	UV Absorption (TE-49)	1 min	FZJ	<i>Volz-Thomas et al. [2003]</i>
H ₂ O ₂ , ROOH	Enzyme catalyzed fluorescence	23 min	MPI	<i>Grossmann et al. [2003]</i>
CO	IR Absorption (TE-48)	1 min	FZJ	<i>Volz-Thomas et al. [2003]</i>
CN	Condensation Nuclei Counter (TSI)	1 min	FZJ	<i>Volz-Thomas et al. [2003]</i>
SO ₂	DOAS	30 min	IUP	<i>Alicke et al. [2003]</i>
<i>Organic Compounds</i>				
NMHC: C ₅ -C ₁₀	In situ GC (Airmotec HC1010)	20 min	FZJ	<i>Konrad et al. [2003]</i>
NMHC: C ₂ -C ₁₀	In situ GC (HPGC/Cryogenic sampling)	85 min	FZJ	<i>Konrad et al. [2003]</i>
H ₂ CO	Fluorescence (AeroLaser, AL4001)	1 min	FZJ	<i>Volz-Thomas et al. [2003]</i>
H ₂ CO	DOAS	30 min	IUP	<i>Alicke et al. [2003]</i>
Carbonyl comp. ^b	Derivatization, GC/ECD	1 h	TUD	<i>Grossmann et al. [2003]</i>
Carboxylic acids ^b	Capillary Electrophoresis-LIF	1 h	TUD	<i>Grossmann et al. [2003]</i>
Aromatics, Phenols	DOAS	30 min	IUP	<i>Alicke et al. [2003]</i>
<i>Free Radicals</i>				
OH	LIF	90 s	FZJ	<i>Holland et al. [2003]</i>
HO ₂	LIF	90 s	FZJ	<i>Holland et al. [2003]</i>
HO ₂ ^b	MIESR	30 min	FZJ	<i>Mihelcic et al. [2003]</i>
RO ₂ ^b	MIESR	30 min	FZJ	<i>Mihelcic et al. [2003]</i>
RO _x (HO ₂ + RO ₂)	Chemical amplifier (CA)	72 s	MPI-C	<i>Volz-Thomas et al. [2003]</i>
NO ₃	DOAS	30 min	IUP	<i>Geyer et al. [1999, 2003]</i>
NO ₃ ^b	MIESR	30 min	FZJ	<i>Mihelcic et al. [2003]</i>
<i>Meteorology and Radiation</i>				
T, rH, P, wind vector	Psychrometer, wind vane, cup anemometer (Thiess)	1 min	FZJ	<i>Volz-Thomas et al. [2003]</i>
Global radiation	Pyranometer (Kipp&Zonen)	1 min	FZJ	<i>Volz-Thomas et al. [2003]</i>
JO ¹ D, JNO ₂	2π sr filter radiometers	10 s	FZJ	<i>Holland et al. [2003]</i>
JNO ₃	2π sr filter radiometer	10 s	IUP	<i>Geyer et al. [1999, 2003]</i>
J _{i,j} (actinic flux)	2π sr spectral radiometer (Bentham)	90 s	FZJ	<i>Holland et al. [2003]</i>
<i>Vertical Profiles (Tethered Balloon)</i>				
O ₃	Chemiluminescence (GFAS, OS-B-2)	10 s	IVD	<i>Glaser et al. [2003]</i>
NO ₂ and NO _x	Luminol chemiluminescence (Scintrex, LMA-4)	10 s	IVD	<i>Glaser et al. [2003]</i>
NMHC ^b	Adsorption tubes, GC/FID	3 h	IVD	<i>Glaser et al. [2003]</i>
T, rH, P, wind vector	Meteorological Sonde (Atmos. Instr. Res. Inc.)	10 s	IVD	<i>Glaser et al. [2003]</i>

^aSee Table 1.^bOff-line samples collected only during IOPs.

900 m (the ceiling altitude of the balloon) at 11 UTC lasting until late afternoon. The analysis by *Corsmeier et al. [2002]* for the entire BERLIOZ area and including the aircraft measurements confirmed the well defined planetary boundary layer (PBL) with southeasterly wind directions and a sharp transition to southwesterly winds in the free troposphere. According to the aircraft data, the PBL rose between 6 and 12 UTC to approx. 900 m and developed further to 1.4 km. In the late afternoon, the vertical extent of the southerly wind regime decreased again to approx. 1 km around 18 UTC. In the evening, the westerly wind regime proceeded downward by the combined action of the diurnal change in the heat balance and the shear-induced turbulence at the top of the PBL. Due to the latter, transport conditions

were not as well defined as intended for the BERLIOZ experiment.

3.2. Synoptic Situation on 21 July 1998

[27] Another low pressure system moved slowly NE ward from Scotland on 20 July (Figure 7). Advection of hot air ahead of the system lead to temperatures well above 30°C in Berlin on 21 July. Starting sunny in the morning clouds developed during the day while a frontal system that had originated in the morning west of Berlin moved eastward creating some precipitation in isolated showers and thunderstorms. Ahead of the convergence the wind direction turned towards SE. During the day the winds moved on to westerly directions just behind the frontal system bringing in slightly

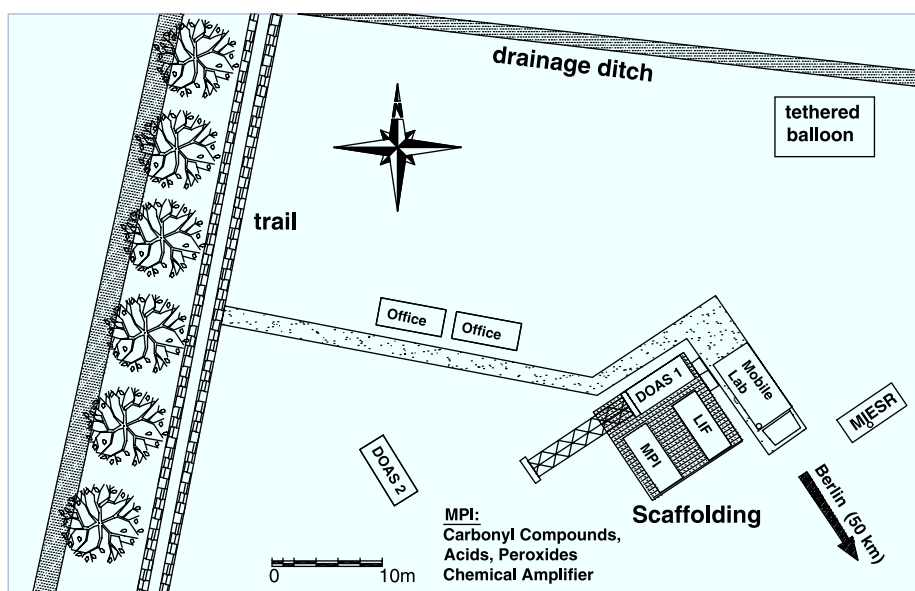


Figure 3. Schematic arrangement of the individual measuring systems at the observatory site.

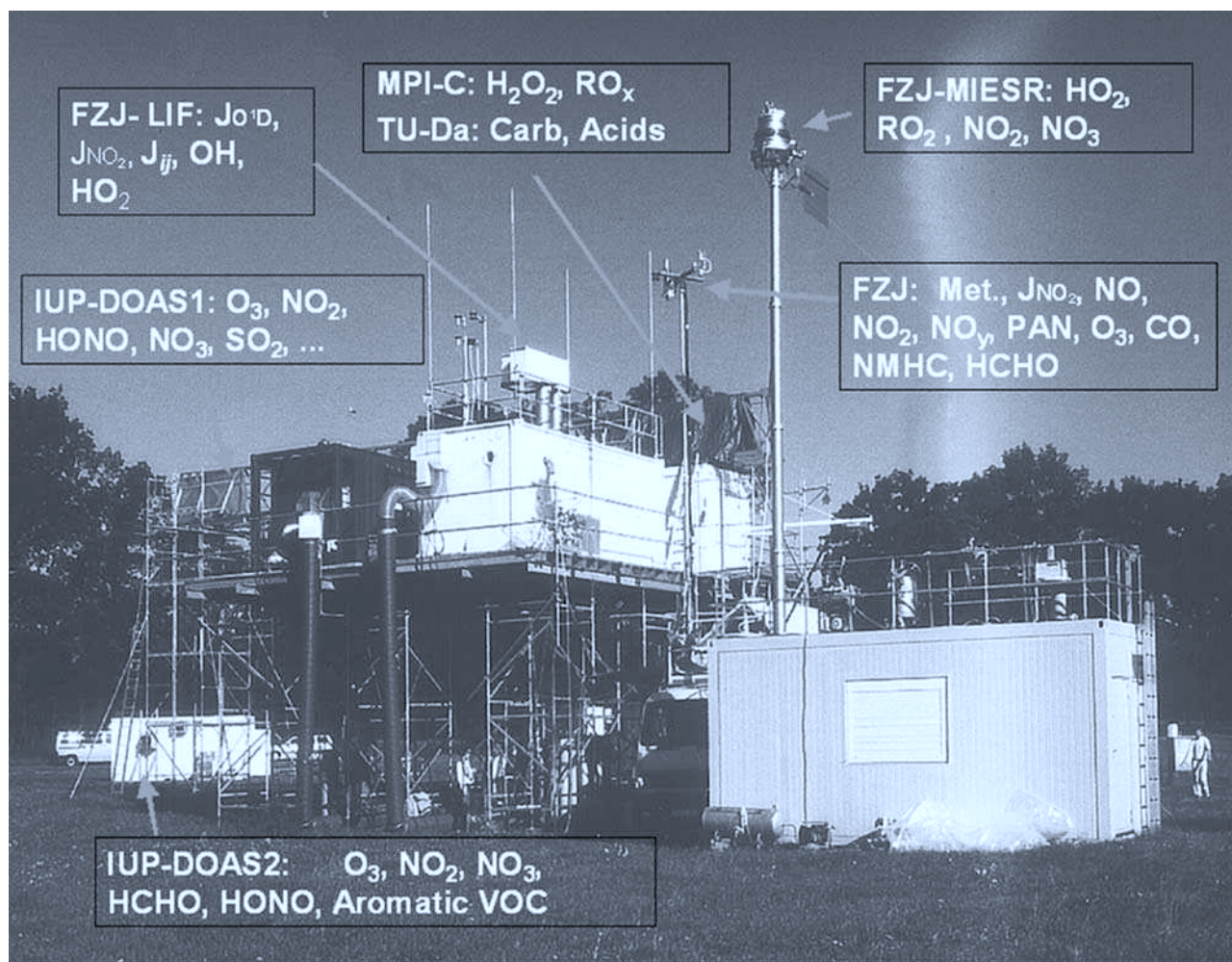


Figure 4. Photograph of the observatory site viewed from east. See color version of this figure at back of this issue.

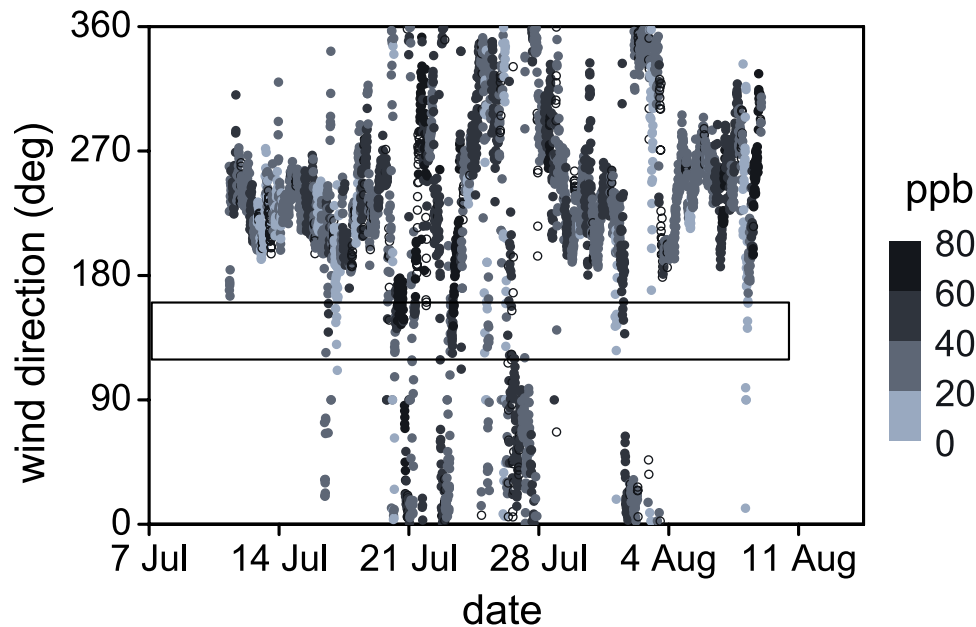


Figure 5. Time series of the wind direction at Pabstthum during the BERLIOZ campaign (10 min averages). The box indicates the sector for winds coming from the greater Berlin area. Colors denote the O_3 mixing ratio (black circles: missing O_3 values). See color version of this figure at back of this issue.

drier and colder air masses than before. The wind speed was generally lower than on 20 July and decreased further except for some isolated gusts in the greater Berlin area.

[28] At Pabstthum, wind from SE was observed shortly after 6 UTC for about 2 hours. After 8 UTC, the wind turned to SW and west throughout the whole boundary layer. Wind speed at the surface was low with 2–4 m/s. In contrast wind speeds at 200 m above ground were much higher reaching

more than 10 m/s. A mixing layer depth of only 200 m was observed in the morning increasing to about 500 m at 12 UTC [Glaser *et al.*, 2003]. Cloudiness increased after 11 UTC diminishing gradually the insolation.

3.3. Synoptic Situation on 3 and 4 August

[29] The general meteorological situation was characterized by a pronounced trough over western Europe at 500

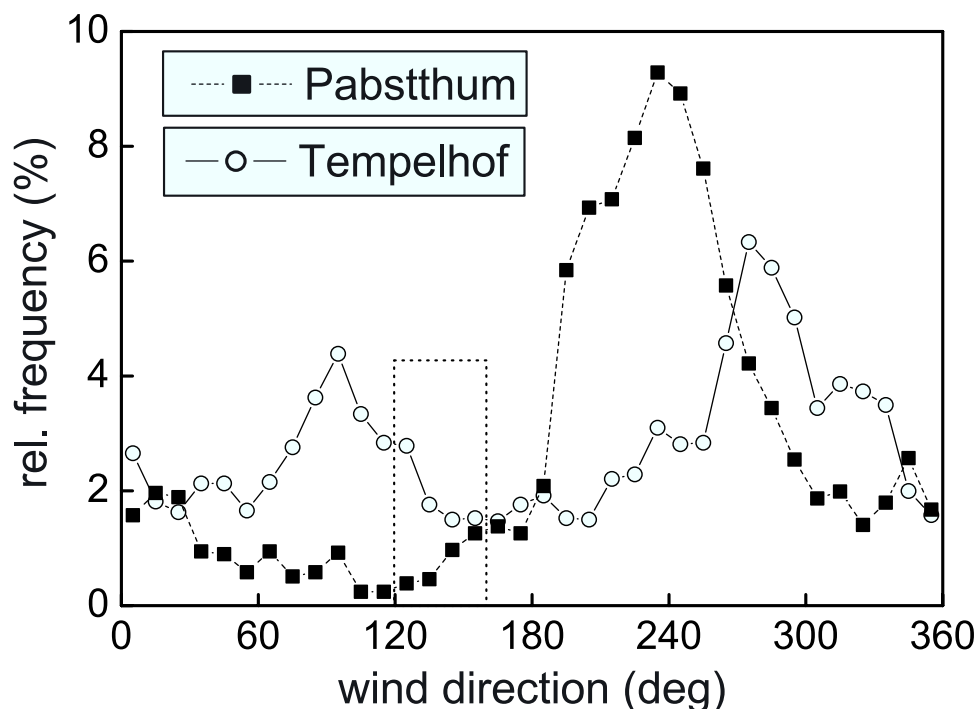


Figure 6. Frequency distribution of the wind direction at Pabstthum during BERLIOZ (squares) compared to the long-term distribution for summer at Berlin-Tempelhof (open circles).

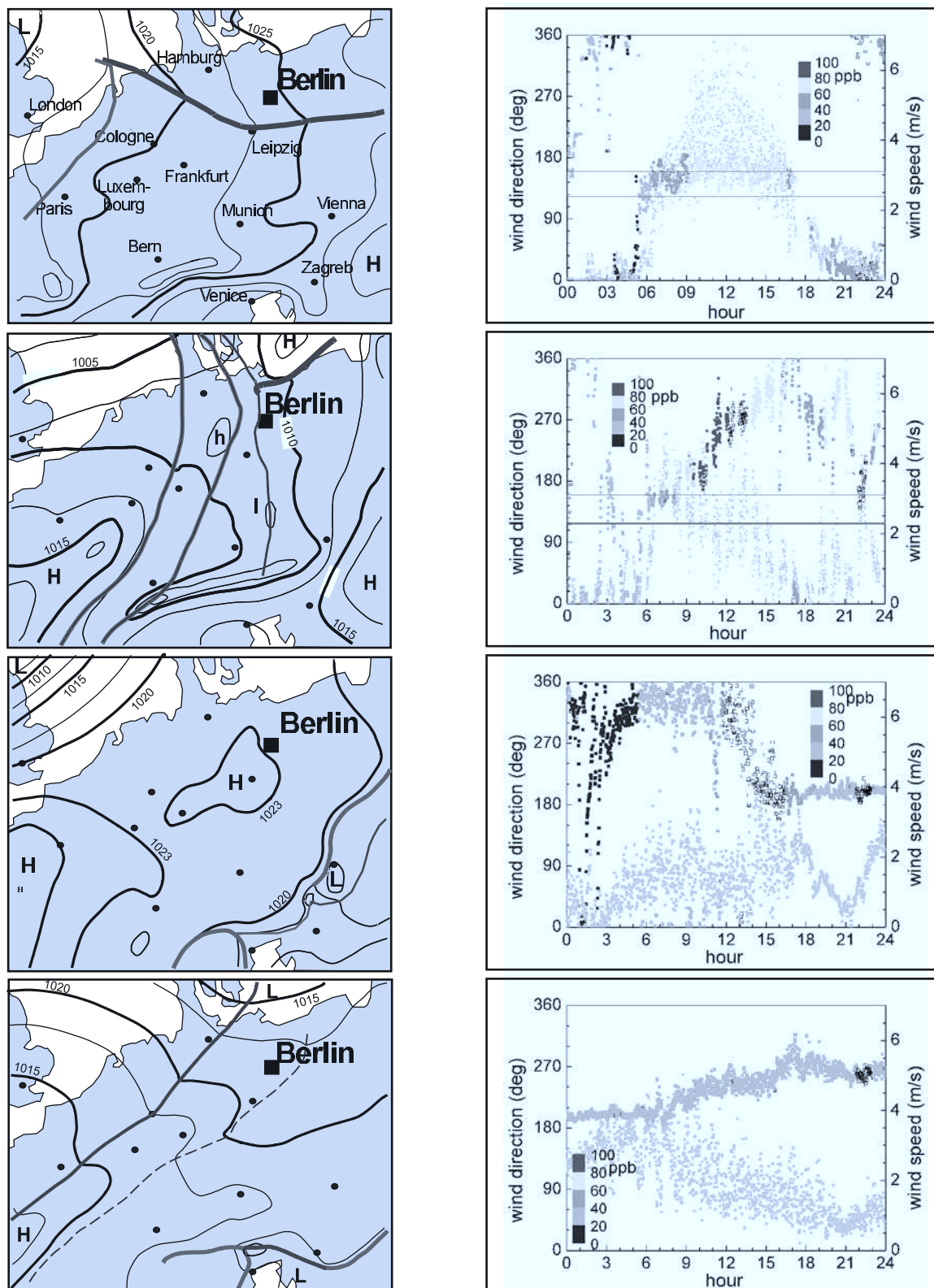


Figure 7. Meteorological surface charts for 12 UTC (left) and surface wind (at 10 m above ground) at Pabstthum (right) for 20 July (top), 21 July, 3 August, and 4 August (bottom). The color code in the wind direction denotes the O_x mixing ratio (black circles: missing O_x values; gray dots: wind speed). See color version of this figure at back of this issue.

hPa moving slowly eastward (Figure 7). An intense cutoff low developed on the 3 August and moved into the Gulf of Genoa. Westerlies with high wind speeds in the free troposphere prevailed over Central Europe. A high-pressure ridge that stretched from the Azores to northern Scandinavia on 3 August, moved southward and covered most of the middle and northern parts of Europe, before it was replaced by frontal systems moving from the North Sea to Poland on 4 August.

[30] On the southern edge of the high pressure, winds from northerly directions were observed at 2 and 3 August over the BERLIOZ region, turning south after noon on 3 August behind a weak front transporting warm air quickly from mid-Atlantic ocean to the BERLIOZ region. The balloon profiles [Glaser *et al.*, 2003] showed that surface winds prevailed throughout the boundary layer. After the passage of the cold front between 6 and 9 UT on 4 August, the wind direction changed to SW and to west in the afternoon behind an occlusion. Moderately warm air originating at subpolar regions was advected with the frontal systems.

[31] The surface wind speed on average did not exceed 2 m/s on 3 August but was highly variable with gusts up to 4 m/s. During to the warm front passage the speed decreased but increased before midnight of the 3rd ahead of the first cold front reaching about 3.5 and 4.5 m/s during gusts around 9 UT on 4 August. After the passage of the first and the second cold front speed decreased continuously. During night between 4 and 5 August, when measurements of NO₃ radicals were made, surface winds were calm between 0.5 and 1 m/s. Under decreasing cloud cover, a stable surface layer developed during the night. In the early morning, a shallow fog layer developed at Pabstthum.

4. Main Results From the Accompanying Papers

4.1. Data Quality and Instrument Comparisons

[32] Quality assurance was an important aspect in BERLIOZ. It served the purpose to assess the accuracy of each measurement and to ensure the consistency of calibrations of different instruments that measured the same quantity during the campaign. Intercomparisons were performed at different times. Photolysis frequency instruments, which participated in BERLIOZ, were compared in advance against reference techniques during the field experiment JCOM97 in summer 1997 at Jülich [Kraus *et al.*, 1998; Kraus *et al.*, 2000]. Most other in situ instruments (VOC, NO_x, CO, O₃, PAN, HCHO) were brought together 1 week before the campaign at the airfield Schönhagen, where the measurements of all participants were formally calibrated against certified standards and compared to reference instruments in ambient air [Kanter *et al.*, 2002; Volz-Thomas *et al.*, 2002]. Even more intensive, albeit informal, comparisons were made at Pabstthum where most of the free radicals (HO₂, HO₂ + RO₂, NO₃) and longer-lived compounds (O₃, NO_x, HCHO) were measured with different techniques [Geyer *et al.*, 1999; Platt *et al.*, 2002; Volz-Thomas *et al.*, 2003].

4.1.1. Radicals

[33] Hydroxyl was measured by only one technique, laser-induced fluorescence (LIF), at Pabstthum [Holland *et al.*, 2003]. The instrument and its calibration has been

compared previously against an absolute laser absorption spectrometer (DOAS) in a different campaign (POPCORN) where good agreement had been found [Hofzumahaus *et al.*, 1998]. The same calibration method, the 185 nm photolysis of water vapor in synthetic air yielding OH and HO₂, was applied during BERLIOZ where the estimated 2σ-calibration error was 20% for both radicals.

[34] At Pabstthum the LIF instrument was also used for the measurement of HO₂ concentrations, which were calibrated with the same radical source as for OH. On 2 days (20 and 21 July 2001) HO₂ was measured additionally by MIESR, an absolute technique with an estimated accuracy of 5% [Mihelcic *et al.*, 2003]. The correlation of the temporally overlapping measurements was linear ($R^2 = 0.88$) and showed a good agreement with a slope of 1.03, well within the combined uncertainty of both instruments [Platt *et al.*, 2002].

[35] Measurements of speciated peroxy radicals (HO₂, CH₃COO₂, and the sum of all other organic peroxy radicals RO₂) were performed by MIESR, each with an accuracy of 5% [Mihelcic *et al.*, 2003]. The sum of all peroxy radicals (HO₂ + RO₂) was also recorded by a chemical amplifier with a calibration uncertainty of 20% [Volz-Thomas *et al.*, 2003]. The comparison of both techniques showed good agreement, the chemical amplifier data being about 7% lower than the MIESR measurements, again well within the estimated calibration errors.

[36] Simultaneous NO₃ measurements were achieved in the night of 4 and 5 August by MIESR and the DOAS2, which was operated with a single-folded light path over a distance of 6.3 km. Despite of relatively low concentrations, the comparison of the DOAS and MIESR data sets showed a tight linear correlation ($R^2 = 0.98$). The systematic deviation of 17% is within the combined systematic errors of both measurement techniques [Geyer *et al.*, 1999], although the influence of spatial inhomogeneity cannot be excluded completely.

4.1.2. Photolysis Frequencies

[37] A scanning spectroradiometer was deployed at Pabstthum to measure absolute spectra of the solar actinic flux from which photolysis frequencies of different species (O₃, NO₂, HCHO, H₂O₂, HONO, CH₃OOH, CH₃CHO) were derived [Holland *et al.*, 2003]. The actinic flux calibration was performed using certified UV lamps traceable to national standards (PTB, Germany). The spectra were evaluated using the quantum yield of Matsumi *et al.* [2002]. In a previous campaign JO¹D determined by the spectroradiometer had been compared against a chemical JO¹D actinometer. Agreement was found within 14% which could be explained by the uncertainties of both measurement techniques [Müller *et al.*, 1995]. The spectroradiometer and two independent chemical JNO₂ actinometers were compared during JCOM97. All three instruments agreed within 7% over a large range of solar zenith angles (<80°) [Kraus *et al.*, 1998, 2000; Junkermann *et al.*, 2002].

[38] A number of commercial fixed-bandwidth filter radiometers (Meteorologieconsult, Glashütten) were used to measure JNO₂ at most BERLIOZ sites. During JCOM97, all filter radiometers (N = 11) showed consistent calibrations within 4% (2σ) and agreed on average within 4% with two different chemical actinometers [Kraus *et al.*, 1998]. During BERLIOZ, two of the filter radiometers and the

spectroradiometer measured simultaneously at Pabstthum. The agreement was on average within 2.5% for solar zenith angles less than 70° [Holland et al., 2003]. No independent comparison was possible for JO¹D, since the additional filter radiometer deployed for JO¹D at Pabstthum was calibrated against the spectroradiometer measurements.

4.1.3. NO_x, O₃, CO, and PAN

[39] As outlined by Kanter et al. [2002], the O₃ monitor deployed at Pabstthum agreed within 5% with a reference instrument that was calibrated against the NIST traceable primary standard of the Eidgenössische Materialprüfungs- und Forschungsanstalt (EMPA, Dübendorf, CH). For quality assurance of CO, two canister samples were collected at Pabstthum and measured against certified standards traceable to NOAA CMDL, Boulder (3–8% disagreement with the reference). The dynamic PAN calibration systems [Pätz et al., 2002] used by the different investigators agreed within 10% [Kanter et al., 2002].

[40] For NO₂, NO_y, and PAN, the instruments described in this paper served as the reference in BERLIOZ. The NO standard used at Pabstthum for calibration of all four CLDs agreed within 1% with the BERLIOZ reference standard (NIST traceable via EMPA). The data quality of the NO₂ measurements was investigated by comparison of the simultaneous measurements made at Pabstthum by CLD/PLC, DOAS, MIESR, and with the balloon borne LMA4 instrument (cf. Table 2). Although the comparison was not organized in a strictly blind fashion, the different instruments had been calibrated independently and the data were not harmonized before the comparison. On average, the deviation between the four techniques was less than 5% with slightly higher values determined by the spectroscopic methods [Volz-Thomas et al., 2003].

[41] The agreement for NO_x (NO and NO₂), between the balloon borne LMA4 instrument employing conversion of NO to NO₂ on Cr₂O₆ and the ground based CLD/PLC instrument was similarly good as for the NO₂ measurements. A direct comparison of the NO concentrations was not possible as the LMA4 on the tethered balloon measured NO_x and NO₂ sequentially and thus at different heights [Volz-Thomas et al., 2003].

4.1.4. VOC

[42] The characterization and harmonization of the different in situ GC systems (10 different laboratories with almost 20 instruments) deployed in BERLIOZ was a major task of the quality assurance activities. Because of the many new systems deployed and the involvement of groups with varying experience in field measurements, the activities involved several comparisons of standard mixtures before a final assessment of instrument performance was made by a comparison in ambient air at Schönhagen [Volz-Thomas et al., 2002].

[43] Non methane hydrocarbons (NMHC) were determined at Pabstthum by in situ gas chromatography with two different systems, namely an Airmotec HC1010 and a custom made system built around a HP5890 (referred to as HP-GC). The HC1010 is appropriate for measuring C₅–C₁₀ HC with a time resolution of 20 min, whereas the HP-GC is suitable for C₂–C₁₀ HC with an 80–90 min measuring cycle. The HP-GC had been elected as the reference instrument for the overall quality assurance in BERLIOZ [Volz-Thomas et al., 2002]. A comparison of the two GCs and

tests performed with the inlet system are described by Konrad et al. [2003] and Konrad and Volz-Thomas [2000].

[44] The DOAS system was also set up to measure several aromatic hydrocarbons, as well as phenols and cresols. While some of these compounds were indeed found at significant levels at Eichstädt, the concentrations at Pabstthum remained always below the detection limit of the DOAS system so that a comparison with the GCs was not possible.

4.1.5. Formaldehyde

[45] Several commercial monitors (AeroLaser) that utilize fluorescence for detection of HCHO following the Hantzsch reaction were deployed at the different BERLIOZ sites. Calibration of the monitors was based on a common liquid standard provided by the University of Wuppertal. The comparison at Schönhagen [Kanter et al., 2002] was formally satisfying, although somewhat hampered by very low concentrations. At Pabstthum, HCHO was also measured by DOAS [Alicke et al., 2003]. The mixing ratios measured by DOAS (max. 7.7 ppb) were systematically larger by a factor 1.3 on average and by a factor 1.7 during high photochemical activity [Grossmann et al., 2003]. An even larger discrepancy between Hantzsch and DOAS was observed at the BERLIOZ sites Eichstädt and Blossin (see Figure 1). Grossmann et al. [2003] discuss the possible reasons for the discrepancy in the light of results from other comparisons and conclude that none of the two measurements at Pabstthum can be proven wrong on the basis of the existing information and that the unresolved discrepancy of about a factor of two must be included in the uncertainty of [HCHO] for model simulations of the radical budgets (see below). Further comparison of the different methods for the measurement of HCHO under atmospheric conditions certainly remains an important task.

4.2. Observational Results

4.2.1. OH Radicals

[46] OH radical concentrations were measured by LIF for the time period from 20 July to 6 August with a typical time resolution of 90 s [Holland et al., 2003]. The variability of OH was mainly controlled by changes in the solar UV responsible for the photochemical formation of OH [Holland et al., 2003]. Daily maxima of OH were usually observed at midday and showed values in the range of $(4\text{--}8) \times 10^6 \text{ cm}^{-3}$. The shape of the diurnal OH profiles followed closely the variations of JO¹D with a linear correlation coefficient of $R \sim 0.9$. During the early morning and late evening hours, however, OH concentrations as high as $1.5 \times 10^6 \text{ cm}^{-3}$ were measured even when JO¹D was essentially zero. This behavior can be attributed to the radical production by photolysis of HONO and HCHO. These precursors were found to be efficient photochemical sources of OH under polluted conditions like in the morning of 20 and 21 July [Alicke et al., 2003]. At sunset the observed OH may be explained as a result of reactions of O₃ and NO₃ radicals with alkenes [Geyer et al., 1999, 2003].

[47] NO_x was found to be another important parameter that controls OH. This is seen in the JO¹D-normalized OH data which exhibit a nonlinear NO_x dependence with a maximum around 3 ppb NO_x [Holland et al., 2003]. Towards lower NO_x levels the OH concentrations decline due to the decreasing conversion of HO₂ into OH by

reaction with NO (R4), whereas towards higher NO_x levels the OH concentrations decrease due to increasing depletion of OH by reaction with NO₂(R13). In comparison to the field campaign POPCORN, which took place in a clean rural environment [Plass-Dülmer *et al.*, 1998], the OH data from BERLIOZ are about a factor of 2 lower for the same values of JO¹D and NO_x [Holland *et al.*, 2003].

[48] At night, OH concentrations were usually below the detection limit of the LIF when short integration times (90 s) were applied. Averaging the data over time intervals of 20 min yielded significant OH concentrations of $(1.9 \pm 0.8) \times 10^5 \text{ cm}^{-3}$ in the night of 20 and 21 July, which could be explained by the nocturnal production of OH from the reactions of biogenic monoterpenes with O₃ and NO₃ radicals [Geyer *et al.*, 2003]. Averaging all nocturnal OH data measured at Pabstthum between 2100 and 0300 UT, yielded an experimental upper limit of $5 \times 10^4 \text{ cm}^{-3}$ for nocturnal OH [Holland *et al.*, 2003].

4.2.2. HO₂ Radicals

[49] HO₂ radicals were measured by the LIF technique following the conversion of HO₂ into OH in the measurement system by added NO [Holland *et al.*, 2003]. Two independent detection channels were run in parallel to measure HO₂ and OH simultaneously from 20 July to 6 August. Additional HO₂ concentrations were measured by MIESR on 20 and 21 July during daytime [Mihelcic *et al.*, 2003] and in the night of 4 and 5 August 1998 [Geyer *et al.*, 2003].

[50] The HO₂ concentration showed daytime maxima due to photochemical formation [Holland *et al.*, 2003]. The highest value ($8 \times 10^8 \text{ cm}^{-3}$, i.e., 32 ppt) was observed at noon on 21 July, a day which was characterized by exceptionally high VOC mixing ratios [cf. Konrad *et al.*, 2003]. On other days the daily maxima were in the range of $(2\text{--}4) \times 10^8 \text{ cm}^{-3}$ (8–16 ppt). HO₂ exhibited a much less pronounced dependence on the solar UV than OH. HO₂ was strongly influenced by NO, which efficiently converts the peroxy radicals into OH by reaction (R4). In the morning hours (0400–1000 UT) when NO usually exhibited a morning peak, the HO₂ concentration was typically close to or below the detection limit.

[51] After sunset HO₂ usually remained at significant levels above the detection limit ($1 \times 10^7 \text{ cm}^{-3}$) and had an average nighttime value of $3 \times 10^7 \text{ cm}^{-3}$ (~1 ppt). On some occasions HO₂ even increased after sunset as a result of HO₂ production by the reaction of biogenic VOCs with NO₃ and O₃ [Geyer *et al.*, 2003]. The highest nocturnal HO₂ value ($1 \times 10^8 \text{ cm}^{-3}$, i.e., 4 ppt) was observed in the night from 20 to 21 July when very high mixing ratios of organic species were encountered (e.g., up to ~0.5 ppb α-pinene). From midnight to sunrise the HO₂ concentrations usually decayed and reached values near the detection limit in the early morning as mentioned above.

4.2.3. RO₂ Radicals

[52] Measurements of speciated peroxy radicals (HO₂, CH₃COO₂) and of the sum of all other organic peroxy radicals (RO₂) were performed by MIESR at daytime on 20 and 21 July and at nighttime between 4 and 5 August [Mihelcic *et al.*, 2003]. In addition continuous measurements of the total sum of all peroxy radicals (HO₂ + RO₂) were performed by a chemical amplifier from 12 July to 3 August [Volz-Thomas *et al.*, 2003]. In general the variations

of the diurnal profiles of RO₂ and HO₂ showed a great similarity. Like HO₂ the RO₂ radicals were often close to the detection limit in the morning due to elevated NO mixing ratios. The daily maxima of RO₂ occurred typically 1–2 hours after local noon and reached the highest value, about 20 ppt (i.e., ~55 ppt of HO₂ + RO₂), on 21 July 1998 [Mihelcic *et al.*, 2003; Volz-Thomas *et al.*, 2003]. The concentration of CH₃COO₂ never exceeded the limit of detection (2 ppt) of the MIESR. The sum of other organic peroxy radicals measured by MIESR during daytime was about the same as the concentration of HO₂. This result is consistent with ratios of (HO₂ + RO₂)/HO₂ determined from the chemical amplifier and LIF technique. At noon of 20 and 21 July the ratio had a value around 2, but was higher (~3) in the morning and evening hours [cf. Platt *et al.*, 2002].

[53] At night the RO₂ radicals had much higher concentrations than HO₂. For example the highest value of HO₂ + RO₂ was 22 ppt, whereas the maximum HO₂ value was 4 ppt [Geyer *et al.*, 2003]. During many nights a significant increase of HO₂ + RO₂ was observed after sunset as a result of the reaction of NO₃ radicals with biogenic monoterpenes. In these cases the HO₂ + RO₂ concentration started from typically 3–4 ppt and reached a maximum of about 6 ppt between 2000 and 2200 UT. For the rest of the night RO₂ generally decreased together with HO₂ and reached a minimum at sunrise when NO started to increase [Geyer *et al.*, 2003].

4.2.4. NO₃ Radicals

[54] Nitrate radicals were measured by the DOAS technique along a 12.6 km light path running at an average height of 18 m above the ground between the Pabstthum site and a reflector at 6.3 km distance [Geyer *et al.*, 2003]. Since NO₃ is rapidly photolyzed during daytime, measurements were performed continuously from 17 July to 8 August between dusk and dawn only. In the night from 4 to 5 August NO₃ measurements were also performed by MIESR at the Pabstthum site and found to be in reasonable agreement with DOAS [Geyer *et al.*, 1999].

[55] The mixing ratios obtained by DOAS exceeded the detection limit of 2.4 ppt in 15 nights. Nighttime maxima were usually of the order of 10 ppt [Geyer *et al.*, 2003]. In one night the NO₃ mixing ratio reached 70 ppt due to an exceptional high production rate of nitrate radicals by the reaction of NO₂ with O₃. Similar time series of NO₃ were measured at the BERLIOZ sites Lindenberg, Blossin, and Eichstädt, where other DOAS instruments were operated. A correlation of the nighttime levels of NO₃ was observed among all four measurement sites [Platt *et al.*, 2002].

[56] At Pabstthum the average nighttime profile of NO₃ started to rise above the detection limit around sunset and reached a maximum between 2000 and 2200 UT, followed by a continuous decay reaching levels below the detection limit at sunrise [Geyer *et al.*, 2003]. This time profile was found to have a positive, linear correlation with the concentration of HO₂ + RO₂ which also exhibited a nighttime maximum before midnight. For example, in the night of 4 and 5 August the correlation coefficient was $R^2 = 0.83$. The observed correlation can be described generally by a chemistry model showing that the nighttime HO₂ and RO₂ radicals were largely formed by the reaction of NO₃ with biogenic VOCs at Pabstthum [Geyer *et al.*, 2003].

4.2.5. VOC

[57] More than 60 hydrocarbons (NMHC) in the range of C_2 – C_{10} were identified and quantified with the two GC systems deployed at Pabstthum [Konrad *et al.*, 2003]. The data sets from both GC systems were combined to join the high time resolution of the HC1010 with the high precision and the larger number of measurable compounds on the HP-GC. This was achieved by interpolation between two data points of the HP-GC with the pattern given by the HC1010. For compounds that could not be reliably measured with the HC1010, patterns of compounds with similar reactivity were used.

[58] Air masses with the lowest photochemical age as estimated from the toluene/benzene ratio and the highest hydrocarbon mixing ratios were observed on 20 and 21 July when air was advected from the direction of Berlin. Alkanes were the most abundant hydrocarbons (~60%) on a molecular basis, followed by alkenes and aromatics. The reactivity of the hydrocarbons towards OH, however, was dominated by the alkenes (>60%), with the biogenic hydrocarbons isoprene and α -pinene constituting the major fraction even during the time when the site was under the influence of air from the greater Berlin area.

4.2.6. Oxygenated VOC

[59] Up to 30 different aldehydes and ketones ($\geq C_2$) were identified and quantified at Pabstthum during the IOPs using a novel analytical technique (derivatization with PFBHA on cartridges, followed by GC-ECD analysis in the laboratory [Schlowski *et al.*, 1997]). HCHO was measured continuously by both, DOAS and a commercial Hantzsch monitor (see above).

[60] Carboxylic acids (C_1 – C_9) were sampled with a new optimized scrubber system. The samples were analyzed by sequential reaction with dicyclohexylcarbodiimide and 4-aminofluoresceine, followed by capillary zone electrophoresis (CEP) and detection by LIF [Kibler *et al.*, 1999]. These measurements were made during the IOPs only.

[61] Grossmann *et al.* [2003] discuss the diurnal variation of the oxygenated compounds and the correlation between primary and the secondary species that were observed at Pabstthum. The C_2 – C_{10} aldehydes, which originate primarily from anthropogenic hydrocarbon degradation processes, showed maximum mixing ratios from 0.6 ppb (C_2) to 0.1 ppb (C_5). The C_6 , C_9 and C_{10} alkanals exhibited strong fluctuations, thus giving evidence of biogenic emissions. The primary unsaturated carbonyl compounds (methylvinylketone and methacrolein) and the secondary oxidation products of isoprene (hydroxyacetone and glycolaldehyde) showed excellent correlation. Also, diurnal profiles of glyoxal, methylglyoxal, biacetyl, benzaldehyde, and pinon-aldehyde were obtained.

[62] Formic and acetic acid varied between 0.6 and 2.6 ppb. The mixing ratio of the other acids decreased from 0.1 to 0.2 ppb for C_3 to a few ppt for the C_9 monocarboxylic acids. The measurements highlight the importance of carbonyl compounds for accurately determining the total VOC reactivity. In some cases, important information on the chemical mechanism is derived from the observed correlation between precursors and oxidation products.

4.2.7. PAN

[63] The PAN concentrations measured at Pabstthum were similar as on the other BERLIOZ sites, with maximum

mixing ratios around 1 ppb observed on the afternoon of 20 and 21 July. Because of the high temperatures on these days, PAN was an important source of peroxy radicals [Konrad *et al.*, 2003] despite the low concentrations. On the other days with westerly winds, PAN usually remained around a few hundred ppt [Volz-Thomas *et al.*, 2003].

4.2.8. Peroxides

[64] The hydroperoxides show pronounced diurnal variations with peak mixing ratios in the early afternoon. The maximum mixing ratios were observed on 21 July (1.4 ppb H_2O_2 , 0.64 ppb methylhydroperoxide, and 0.22 ppb hydroxymethyl-hydroperoxide). The increase of H_2O_2 in the morning originated mainly from vertical transport from the residual layer and changes in advection. A secondary maximum sometimes observed in the late afternoon indicates the formation from ozonolysis of biogenic alkenes. The H_2O_2/HNO_3 ratio is used as indicator for distinguishing between NO_x and VOC limitation of photochemical ozone production at Pabstthum [Grossmann *et al.*, 2003].

4.2.9. Odd Nitrogen Compounds and Photostationary State of NO_x

[65] As observed in several other campaigns, the measured NO/NO_2 ratio was found to be significantly larger than that calculated from either the box models (see below) or from the so-called photostationary state, i.e., by assuming quasi steady state between the NO_2 photolysis rate and the oxidation rate of NO provided by reactions with O_3 , HO_2 , and RO_2 . The PSS approach was shown to severely overestimate the local ozone formation rate as determined from the measured NO and radical concentrations and the accepted rate coefficients [Mihelcic *et al.*, 2003; Volz-Thomas *et al.*, 2003]. Faster rate coefficients for the reaction of RO_2 with NO, as discussed by Frost *et al.* [1998], are not considered a likely explanation, because the discrepancy exists also at high NO concentrations where the peroxy radical concentrations are at or below the detection limit of the MIESR. Moreover, the budget of ozone in the plume as derived from the aircraft measurements in BERLIOZ [Corsmeier *et al.*, 2002] does not allow for much larger formation rates than those calculated from the measured RO_2 concentrations and the accepted rate coefficients. Therefore, an unknown oxidation process must exist in the atmosphere for NO. While similar suggestions have been made before [Parrish *et al.*, 1986; Volz-Thomas *et al.*, 1997; Carpenter *et al.*, 1998], the high data quality achieved in PHOEBE precludes the possibility of analytical errors being responsible for the observed discrepancy. Furthermore, the comparison with the ozone budget gives evidence that the unknown process does not lead to a net formation of O_3 . The MIESR data from BERLIOZ and several other campaigns conducted at Schauinsland in southern Germany and at Tenerife suggest that ozone formation rates do not exceed values of 10 ppb/h [Mihelcic *et al.*, 2003].

4.3. Model Simulations

4.3.1. Daytime Chemistry

[66] The measurements were used to calculate the radical concentrations with photochemical box models of different complexity, i.e., the Master Chemical Mechanism (MCM) [Jenkin *et al.*, 1997] and the condensed mechanism RACM [Stockwell *et al.*, 1997]. Both models predict the concentrations of OH, HO_2 and RO_2 quite well in the high- NO_x

regime [Konrad *et al.*, 2003; Mihelcic *et al.*, 2003]. An important conclusion is that the photolysis of HONO accounts for most of the HOx production in these air masses during early morning [Alicke *et al.*, 2003].

[67] On the other hand, both models significantly overestimate the OH concentrations at low NO_x (<5 ppb). The disagreement is up to 60% for the MCM and 80% for RACM. The agreement for HO₂ and RO₂ is much better. Ozonolysis of mostly biogenic olefins is an important source of RO₂ and HO₂ in the late afternoon.

[68] Qualitatively, the results from Pabstthum confirm earlier exercises, in which constrained models were also found to over predict OH concentrations [e.g., Perner *et al.*, 1987; Platt *et al.*, 1988; Poppe *et al.*, 1994; Eisele *et al.*, 1994, 1996; McKeen *et al.*, 1997; Carslaw *et al.*, 1999; George *et al.*, 1999; Hauglustaine *et al.*, 1999; Savage *et al.*, 2001]. The sensitivity studies conducted in PHOEBE demonstrate that missing hydrocarbon reactivity, as argued in several earlier studies, is not the sole reason for the overestimation of OH. This conclusion is possible from the specific RO₂ measurements made in PHOEBE [Mihelcic *et al.*, 2003]. Increasing the VOC reactivity leads to a pronounced over prediction of the RO₂ concentration by the model. The concentrations of all radicals can be brought into reasonable agreement with the measurements when a sink term is introduced in the models, corresponding to a first order loss of approximately 1 s⁻¹ for OH or 0.02 s⁻¹ for HO₂, and by increasing the total biogenic VOC reactivity by approximately 20% [Konrad *et al.*, 2003].

4.3.2. Nighttime Chemistry

[69] The simultaneous observations of NO₃, RO₂, HO₂, and OH during several nights were interpreted with a chemical box model by Geyer *et al.* [2003]. For most of the nights the model results and ambient observations of RO₂ and HO₂ are in good agreement, whereas the modeled OH concentrations are just within the upper limit of the measurements (5×10^4 cm⁻³). In one night (20 and 21 July), when very high mixing ratios of VOCs were encountered, the model yielded a maximum nocturnal OH level of $(4.1 \pm 0.7) \times 10^5$ cm⁻³, significantly higher than the measured value of $(1.60 \pm 0.85) \times 10^5$ cm⁻³. The overestimation by the model could point to a missing nocturnal sink of OH.

[70] Reactions of NO₃ with VOCs, mainly with biogenic monoterpenes, were shown to constitute a considerable source of organic peroxy radicals at night.

[71] Generally a positive linear correlation of the mixing ratios of RO₂ and NO₃ was observed and modeled during the campaign. The model analysis shows that this dependence can be attributed to the role of NO as a sink for both radicals. In addition, the production rate of RO₂ increased with increasing NO₃ concentration during nights, when VOCs were of minor importance for the NO₃ removal. While Carslaw *et al.* [1997] also found a positive correlation of RO₂ and NO₃ at the eastern coast of England, Mihelcic *et al.* [1993] observed a negative correlation for a clean, forested site where the NO₃ losses were dominated by reactions with VOCs.

[72] The contribution of OH to the nocturnal oxidation of VOCs, CO, and CH₄ was modeled to be 15% of that of NO₃ for the situation at Pabstthum. This corresponds to a contribution of 2.6% by nighttime OH to the 24 hour integral of the total atmospheric oxidation capacity. Since

the model tends to overestimate the measured OH levels at night, the contribution is even smaller and therefore negligible during BERLIOZ.

5. Conclusions

[73] The measurements made during BERLIOZ at Pabstthum comprise the most complete data set collected so far in the PBL on atmospheric free radicals, as well as the physical parameters and chemical compounds that are thought to control the radical concentrations. Most radicals, i.e., HO₂, RO₂, and NO₃, were measured with two different analytical techniques. The good agreement gives high confidence in the accuracy of the data. The situation is similar for the stable compounds, e.g., excellent agreement (<5%) was observed between four different methods for the measurement of NO₂, more than 50 hydrocarbons and 30 carbonyl compounds were identified and quantified, and quantitative experimental information was obtained on the relevant photolysis rates that control radical production. For the concentration of HCHO, significant differences of up to a factor of two were observed between DOAS and the in situ measurement, which could not be resolved.

[74] Although the city plume was observed only for a few hours, the measurements covered the entire range of chemical conditions from continental background (<1 ppb NO_x) to suburban air with up to 30 ppb of NO_x.

[75] The interpretation of the data set in the accompanying papers leads to important conclusions regarding our understanding of the radical chemistry:

1. The NO/NO₂ ratio is 25% lower than predicted by photochemical models and by the PSS approach.
2. The photochemical ozone production rate does not seem to exceed values of 10 ppb/h. The production rates derived from PSS are much larger and must be regarded with great caution.
3. The large overestimation of OH by the models at low NO_x mixing ratios suggest a yet unidentified loss process for HO_x radicals. The RO₂ data show that missing VOC reactivity is not the sole reason.
4. Nighttime chemistry initiated by NO₃ radicals and ozonolysis plays an important role in the degradation of many VOCs and is an important source for peroxy radicals at night.
5. HONO is an important source for OH in polluted air in the morning.

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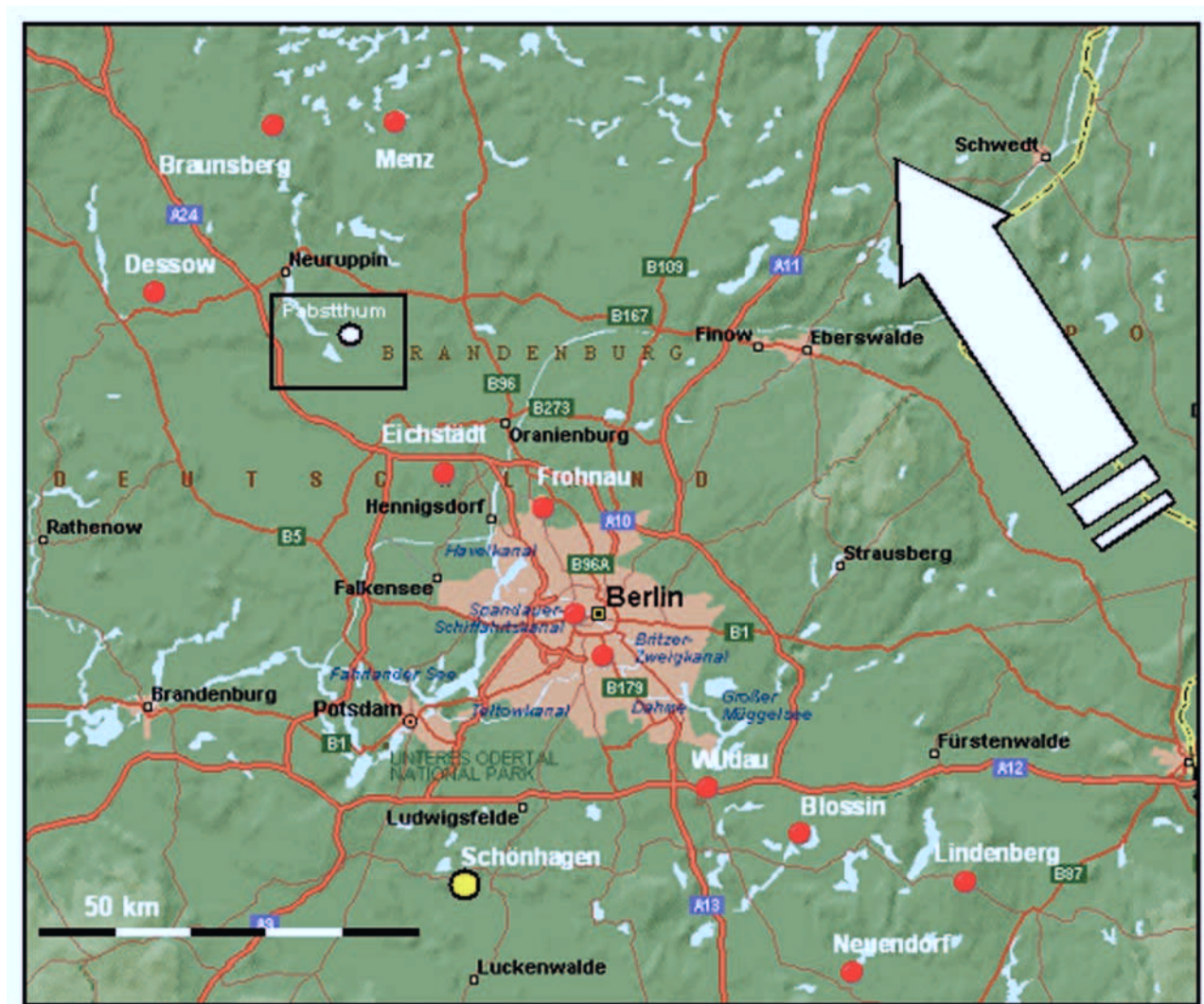


Figure 1. Map of the area around Berlin with the surface sites of BERLIOZ indicated by the red dots and the airfield Schönhagen by the yellow dot. The red lines denote motorways and major roads.

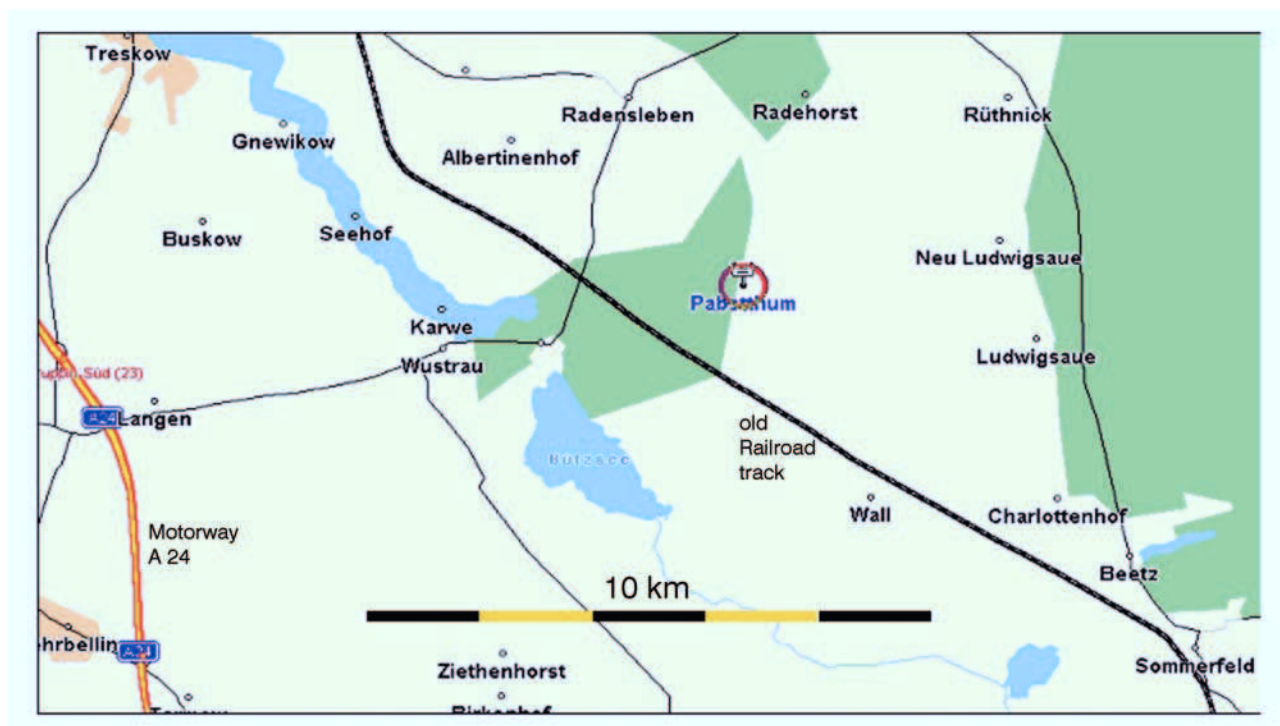


Figure 2. Surroundings of the PHOEBE observatory site Pabstthum (green: forested areas, blue: water bodies).

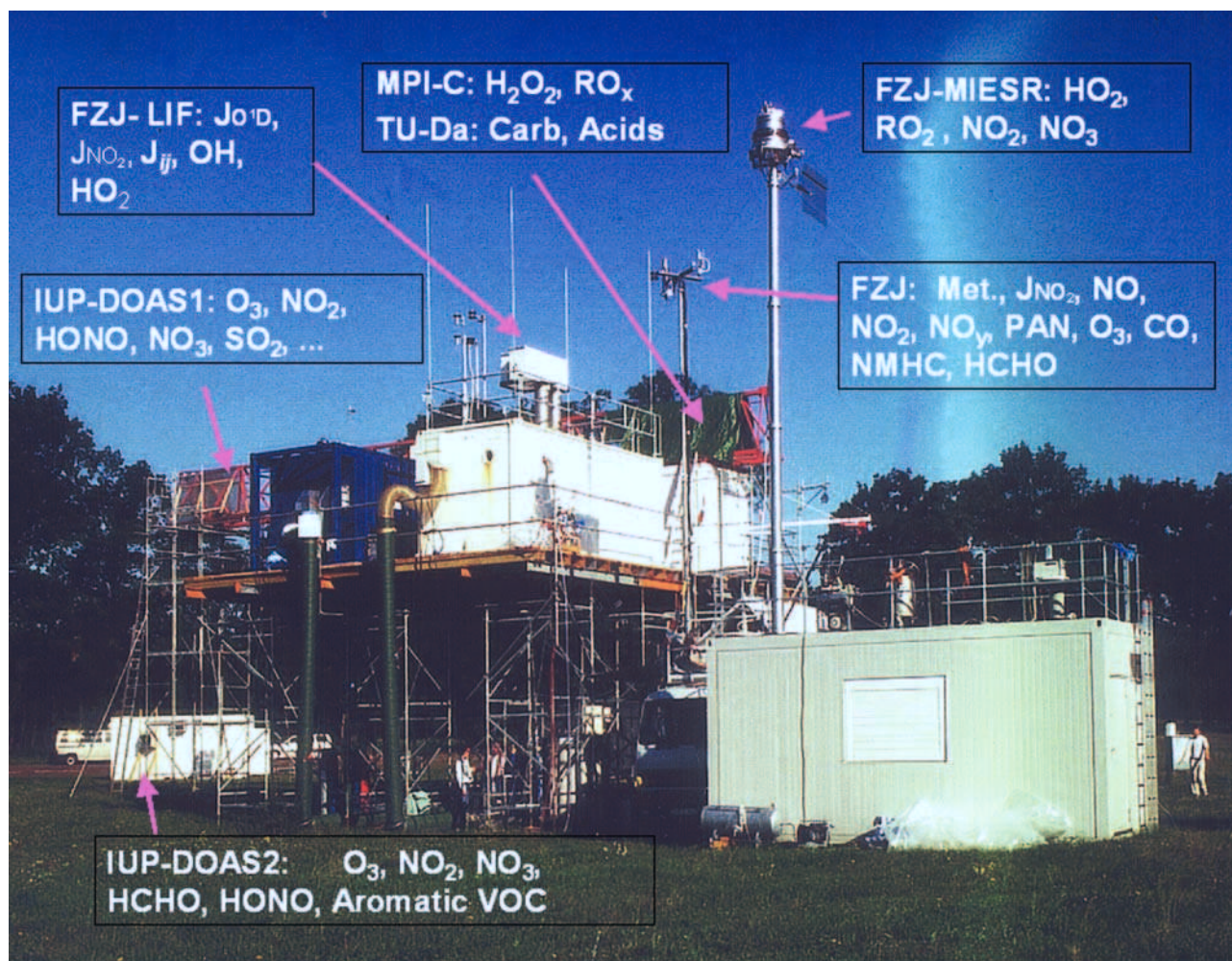


Figure 4. Photograph of the observatory site viewed from east.

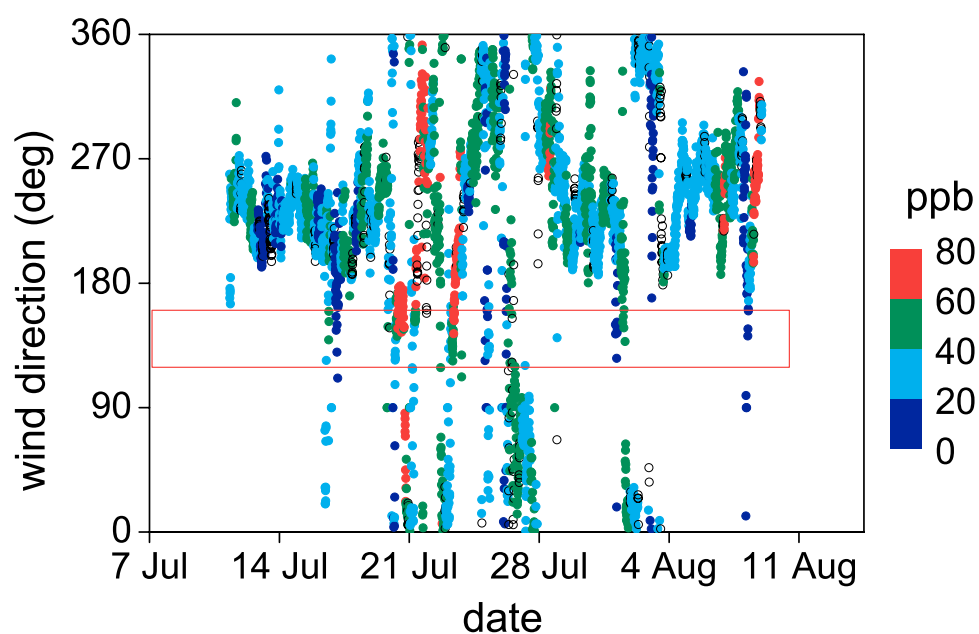


Figure 5. Time series of the wind direction at Pabstthum during the BERLIOZ campaign (10 min averages). The box indicates the sector for winds coming from the greater Berlin area. Colors denote the O_x mixing ratio (black circles: missing O_x values).

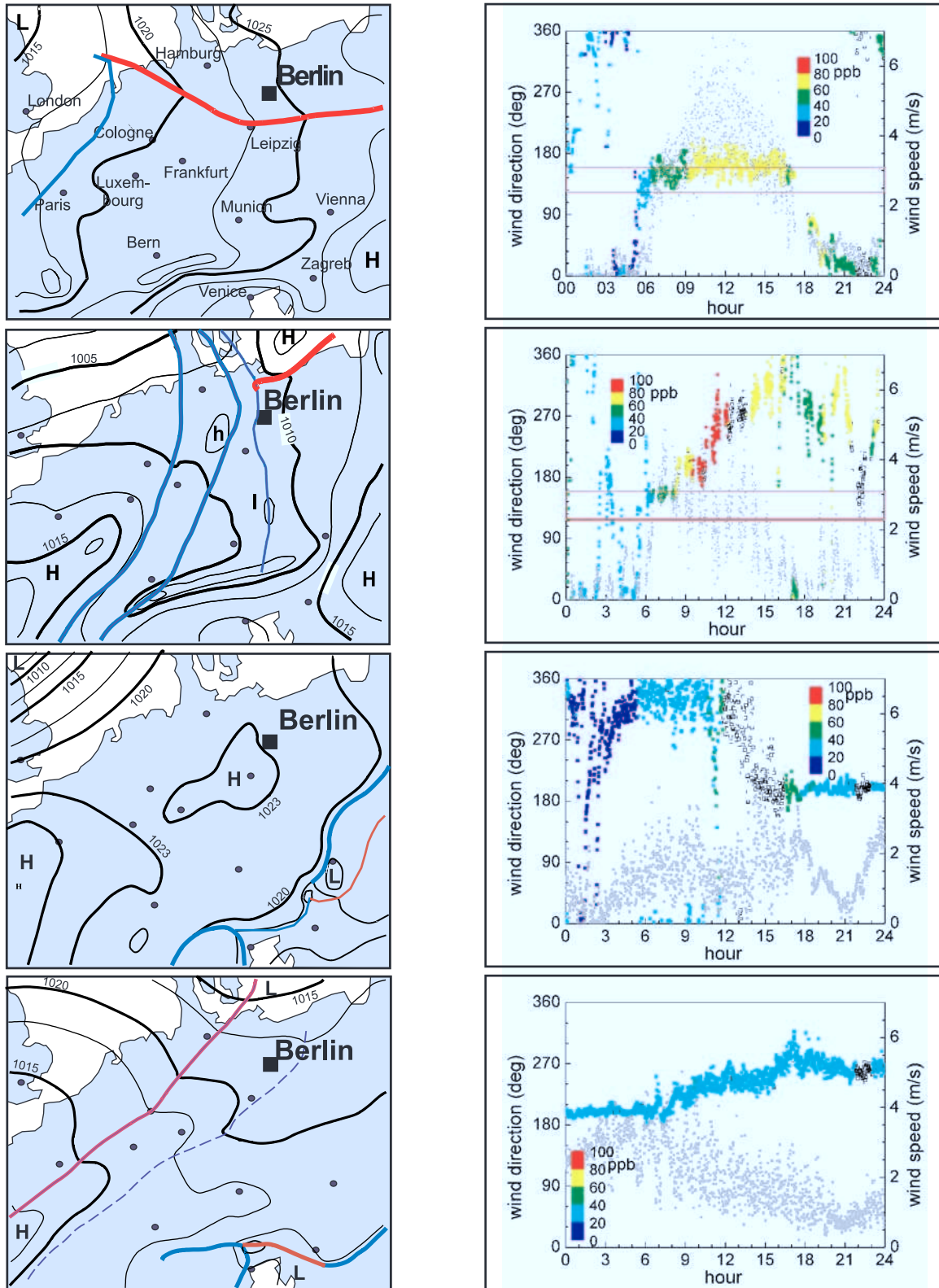


Figure 7. Meteorological surface charts for 12 UTC (left) and surface wind (at 10 m above ground) at Pabstthum (right) for 20 July (top), 21 July, 3 August, and 4 August (bottom). The color code in the wind direction denotes the O_x mixing ratio (black circles: missing O_x values; gray dots: wind speed).