

# POPCORN: A Field Study of Photochemistry in North-Eastern Germany

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**Abstract.** The intensive field study POPCORN (Photo-Oxidant Formation by Plant Emitted Compounds and OH Radicals in North-Eastern Germany) was carried out in a rural area of North-Eastern Germany during August 1994. An overview of the objectives, measurements and major results of this campaign is presented. Measurements of a set of relevant atmospheric trace compounds, including the hydroxyl radical, along with meteorological data were performed to increase the understanding of OH radical chemistry and photo-oxidant formation. Additionally, plant emissions and the exchange of trace gases between a maize field and the atmosphere were investigated. Budgets of selected trace gases were calculated to assess the relative importance of local sources, chemistry or transport. Intercomparisons between measurement techniques were a central issue of POPCORN and included measurements of OH, hydrocarbons, formaldehyde, photolysis frequencies and vertical fluxes. OH radical concentrations were measured simultaneously by LIF (Laser Induced Fluorescence) and DOAS (Differential Optical Absorption Spectroscopy). Both methods showed good agreement. Maximum OH concentrations were around  $10^7 \text{ cm}^{-3}$  and the diurnal cycles closely followed the rate of primary production via ozone photolysis. Generally, the trace gas composition during POPCORN was characterized by relatively low concentrations of most compounds, e.g. CO: 85–200 ppb, ethane: 0.6–2 ppb, and moderate  $\text{NO}_x$  levels: 0.5–5 ppb (at nighttime). Concentrations of individual biogenic volatile organic compounds (VOC) were mostly well below 100 ppt. However, formaldehyde and acetaldehyde which partly originate from biological sources were observed at mixing ratios of some ppb.

**Key words:** field campaign, photo chemistry.

## 1. Introduction

The formation of potentially harmful photo-oxidants in the troposphere, e.g. the budget of ozone in non-urban areas, is one of the central issues in tropospheric chemistry. Understanding photo-oxidant formation requires a detailed understanding of the OH radical chemistry since it determines the turnover of most atmospheric constituents and by this controls their atmospheric lifetimes and the pro-

duction of secondary pollutants. The first step in the formation of many secondary photochemical pollutants is the reaction of an organic molecule with an OH radical. The details of the reaction pathways following this initial step predominantly depend on the concentrations of NO and NO<sub>2</sub>, although a number of other trace components also have some impact. Ideally, a study of the formation of photo-oxidants should therefore include measurements of the OH radical, VOC – and NO<sub>x</sub> concentrations.

Furthermore, the concentration of OH radicals in the troposphere depends in a complex way on a large number of parameters. Thus a study aimed at a better understanding of the OH related chemistry of the troposphere requires the simultaneous measurement of a very large set of parameters ranging from concentrations of trace substances and photolysis rates to detailed meteorological observations.

Because measurements of OH radicals require substantial efforts the number of studies of photochemical processes with emphasis on OH chemistry in the troposphere is limited (Crosley, 1997; Ehhalt *et al.*, 1991; Poppe *et al.*, 1994; Thompson, 1995). This is especially true when studies including a comprehensive set of measurements of trace gases are considered. Tables I and II provide an overview of some recent field studies in non-urban areas and list the main parameters measured, site and time, and the basic objectives. Several of the studies included a large number of measurements of different parameters, however, they were always limited to a subset of parameters which were thought to be most relevant for the specific objectives of the investigation. Additionally, some of the studies used long-path differential optical absorption spectroscopy (LP-DOAS) and had to struggle with the interpretation of spatially inhomogeneous trace gas patterns (Perner *et al.*, 1987; Eisele *et al.*, 1994; Poppe *et al.*, 1994; Mount *et al.*, 1997). These field studies have provided large data sets to test the understanding of local photochemistry and thus are very valuable for tropospheric chemistry.

Measurements of tropospheric OH in the 1980's using DOAS techniques have been reported (Hübler *et al.*, 1984; Platt *et al.*, 1988; Perner *et al.*, 1987). These studies revealed first experimental proof for the existence of free OH radicals in the troposphere and gave insights in their diurnal variations and levels related to ambient trace gas composition and meteorological parameters. However, precision and time resolution of these measurements were mostly too limited to study short time fluctuations in OH concentrations and their relations to changes in production and loss rates. With the improvement of OH measurement techniques (Eisele and Tanner, 1991; Brune *et al.*, 1995; Holland *et al.*, 1995; Wennberg *et al.*, 1995). sensitivities in the range of several 10<sup>5</sup> cm<sup>-3</sup> at time resolutions down to 10 s were achieved. However, these instruments are not absolute instruments and face the problems of calibration, wall losses and artifacts and thus require careful calibration and characterization. In addition, improved DOAS methods (Hausmann *et al.*, 1997; Dorn *et al.*, 1995; Brauers *et al.*, 1995; Armerding *et al.*, 1994) have been developed which combine the advantages of an absolute method with a measurement in a more confined volume.

Table 1. Recent field studies of photochemistry in nonurban continental areas

Field study <sup>a</sup>	Year	Month	ASL	Location	Objectives
Denseibach <sup>b</sup>	1983	5	480 m	Rural site Germany	OH chemistry
Schäfersland <sup>c</sup>	1984	6	1300 m	Mountain site Germany	OH chemistry
Jülich <sup>e</sup>	1987	7	100 m	Rural/industrialized Germany	OH chemistry
Jülich <sup>e</sup>	1988	5/6	100 m	Rural/industrialized Germany	OH chemistry
Jülich <sup>d</sup>	1990	7/8	100 m	Rural/industrialized Germany	OH chemistry
SCAPE <sup>e</sup>	1990	9	1037 m	Mountain site forested	VOC/NO <sub>x</sub> limitations to O <sub>3</sub> production factors controlling carbonyls/carboxylic acids
ROSE <sup>f</sup>	1990	6/7	91 m	Forested Alabama	RO <sub>x</sub> chemistry; photooxidant formation
MLOPEX <sup>g</sup>	1988	5/6	3400 m	Mountain site marine Hawaii	Photochemistry at low NO <sub>x</sub>
MLOPEX <sup>2h</sup>	91/92	- m	3400 m	Mountain site marine Hawaii	HO <sub>x</sub> radical chemistry; seasonal effects
Pullman <sup>i</sup>	1992	10/11	780 m	Rural, Washington, U.S.A.	Intercomparison of 2 OH techniques
Fritz Peak <sup>j</sup>	1991	7/8	≈2800 m	Mountain site Colorado	Intercomparison of 2 OH techniques
TOHPF <sup>k</sup>	1993	8-10	≈2800 m	Mountain site Colorado	Intercomparison of 4 OH techniques OH chemistry
POPCORN <sup>l</sup>	1994	8	53 m	Rural site Germany	OH chemistry; photooxidant formation Biogenic impacts Intercomparison of 2 OH techniques

<sup>a</sup> Where available, the name of the field study is given, otherwise, the name of the site is given. Added are the year of the study and references providing an introduction and overview. <sup>b</sup> Perner *et al.*, 1987; <sup>c</sup> Poppe *et al.*, 1994; <sup>d</sup> Poppe *et al.*, 1996; <sup>e</sup> Shenandoah cloud and photochemistry experiment, Keene *et al.*, 1995; <sup>f</sup> Rural Oxidants in the Southern Environment, Cantrell *et al.*, 1992; <sup>g</sup> Mauna Loa Observatory Photochemistry Experiment, Ridley and Robinson, 1992; <sup>h</sup> Mauna Loa Observatory Photochemistry Experiment 2, Atlas and Ridley, 1996; <sup>i</sup> Campbell *et al.*, 1995; <sup>j</sup> Eisele *et al.*, 1994; <sup>k</sup> Tropospheric OH Photochemistry Experiment, Mount and Williams, 1997; <sup>l</sup> Photo-Oxidant Formation by Plant Emitted Compounds and OH Radicals in North-Eastern Germany, this issue; <sup>m</sup> several months year round.

Table II. Recent field studies of photochemistry in nonurban continental areas, see Table I for references. Generally most field studies had trace gas measurements of NO<sub>x</sub>, O<sub>3</sub>, and CO. Some studies had also SO<sub>2</sub> and CH<sub>4</sub> measurements

Field study	HOx	Peroxides	NO <sub>y</sub>	VOC <sup>a</sup>	OVOC <sup>b</sup>	Radiation
Denuselh, 1983	OH	-	-	C2-C4 > C4	HCHO CH <sub>3</sub> CHO	J(O <sub>1</sub> D) J(NO <sub>2</sub> )
Schauinsl, 1984	OH	-	-	C2-C4 > C4	HCHO CH <sub>3</sub> CHO	J(O <sub>1</sub> D) J(NO <sub>2</sub> )
Jülich 1987	OH	-	-	C2-C4 > C4	HCHO CH <sub>3</sub> CHO	J(O <sub>1</sub> D) J(NO <sub>2</sub> )
Jülich 1988	OH	-	NO <sub>y</sub> , PAN	C2-C4 > C4 C <sub>5</sub> H <sub>8</sub>	HCHO CH <sub>3</sub> CHO	J(O <sub>1</sub> D) J(NO <sub>2</sub> )
Jülich 1990	OH	-	NO <sub>y</sub> , PAN	C2-C4 > C4 C <sub>5</sub> H <sub>8</sub>	HCHO CH <sub>3</sub> CHO	J(O <sub>1</sub> D) J(NO <sub>2</sub> )
SCAPE 1990	-	H <sub>2</sub> O <sub>2</sub>	NO <sub>y</sub>	C2-C4 > C4	Aldehydes ketones Org. acids alcohols	UV radiation
ROSE 1990	HO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	NO <sub>y</sub> , PAN HNO <sub>3</sub>	Propane > C4	Aldehydes ketones Org. acids alcohols	Eppley J(NO <sub>2</sub> )
MLOPEX 1988	-	H <sub>2</sub> O <sub>2</sub>	NO <sub>y</sub> , PAN HNO <sub>3</sub>	C2-C4 > C4	HCHO	Eppley J(NO <sub>2</sub> )
MLOPEX2 91/92	OH	H <sub>2</sub> O <sub>2</sub>	NO <sub>y</sub> , PAN HNO <sub>3</sub>	C2-C4 > C4	Aldehydes ketones Org. acids alcohols	Eppley J(NO <sub>2</sub> )
Pullman 1992	2 × OH	-	-	-	-	UV radiation
Fritz Peak 1991	2 × OH	-	NO <sub>y</sub>	-	HCHO	Eppley
TOHPE 1993	4 × OH	-	NO <sub>y</sub> , HNO <sub>3</sub>	Propane > C4	HCHO CH <sub>3</sub> CHO	Eppley
POPORN 1994	2 × OH	H <sub>2</sub> O <sub>2</sub>	NO <sub>y</sub>	C2-C4 > C4	HCHO CH <sub>3</sub> CHO	J(O <sub>1</sub> D) J(NO <sub>2</sub> )
			PAN HNO <sub>3</sub>	C <sub>5</sub> H <sub>8</sub> terpenes	> C4 OVOCS	Spectro-radiometer

<sup>a</sup> VOC: Volatile organic compounds: Measurements of hydrocarbons in the categories: C2-C4, >C4, isoprene, terpenes.  
<sup>b</sup> OVOC: Oxygenated volatile organic compounds: Aldehydes, ketones, alcohols, and organic acids.

Recently, two informal intercomparisons between DOAS and ion-assisted mass spectrometry together with measurements of ancillary trace gases have been reported by Eisele *et al.* (1994) and Mount *et al.* (1997) (see Tables I and II for details). Generally, for clean air conditions good agreement between both methods was observed. However, both instruments revealed systematic differences during some episodes. These differences were explained in terms of different air mass compositions sampled by both techniques. The ion-assisted mass spectrometry instrument measured OH at a single point close to the ground whereas the long path DOAS system used a 10 km integration path above a forested area. During the Fritz Peak intercomparison in 1991 inhomogeneous air composition, especially with respect to VOCs which have not been measured, were suspected to be the reason for the observed differences (Eisele *et al.*, 1994). During TOHPE in 1993, it was concluded that roughly half of the measurements agreed within 30% and a quarter disagreed due to inhomogeneous trace gas distributions leaving the disagreement for the remaining 25% unexplained (Mount *et al.*, 1997). Further OH-results obtained during TOHPE by FAGE (Fluorescent Assay by Gas Expansion, Mather *et al.*, 1997) and the reactive scrubbing method were rather limited for several reasons and did not allow a conclusive intercomparison (Crosley, 1997). Another informal intercomparison of two OH techniques ( $^{14}\text{CO}$  and FAGE) in October–November 1992 revealed consistent relative patterns of OH measurements, however, both techniques differed on average by a factor of about 3, which has been unexplained yet (Campbell *et al.*, 1995). Only a very limited number of ancillary parameters were reported.

In addition to the OH-chemistry related observations, the POPCORN field study included measurements of trace gas emissions, especially volatile organic compounds (VOC), and deposition rates. Purpose was deriving budgets for these substances and evaluating the impact of the different trace gas sources on the photochemistry of the atmosphere. There are numerous trace gas emission and deposition studies as well as ambient observations of constituents relevant for the photo-chemistry of the lower troposphere reported in literature. However, there are no studies combining emission and deposition studies with OH-measurements. In combination with atmospheric concentration measurements this adds further constraints to the trace gas budgets reducing ambiguities in identifying sources of imbalances in local trace gas budgets.

Specifically, the POPCORN field study addressed four major objectives:

- To study the photochemistry of the rural atmosphere with the emphasis on OH radical chemistry and the formation of photo-oxidants.
- To investigate the fluxes of trace gases between soil or plants and the atmosphere. This part focused on trace gases which are relevant for the photochemistry of the troposphere but also included a few other substances.
- To set up local atmospheric budgets of trace gases.

- To provide a platform for instrument intercomparison. The special focus was an *in situ* intercomparison for OH-radical measurements by LIF and folded long-path DOAS.

This paper will give an introduction and overview of the POPCORN field study, the site, meteorology and measurement program. Some of the main results and conclusions are presented. Details concerning the measurements, results, and their interpretation are published in other contributions to this special issue, except for VOC emission rate measurements from plants which will be published elsewhere.

## 2. The POPCORN Field Study

### 2.1. SITE

In order to achieve the objectives of POPCORN, some conditions were important for the selection of an appropriate site: Low anthropogenic impact from nearby sources, no strong perturbation of planetary boundary layer flow patterns due to ground morphology (e.g. no mountains), a large area with homogenous vegetation surrounding the site, and finally logistic requirements concerning electrical power, cooling water etc. These requirements were met by a maize field at Pennewitt in North-Eastern Germany. A maize field was selected since part of the study focused on the impact of biogenic volatile organic compounds (VOC) on the chemistry of the rural atmosphere. Maize is reported to have VOC emission rates of 1–2  $\mu\text{g g}_{\text{dwt}}^{-1} \text{h}^{-1}$  ( $\mu\text{g}$  of VOC per gram of plant dry weight and hour) (Lamb *et al.*, 1993) and it is grown in large monocultures. The maize field selected for the field study POPCORN is located south of the village of Pennewitt (53.8° N, 11.7° E) with about 50 inhabitants. Pennewitt is about 100 km east of Hamburg (1.6 Mio inh.) (Figure 1). The closest cities to Pennewitt are Schwerin (30 km, direction SW, 130 000 inh.), Wismar (20 km, NW, 57 000 inh.) and the area of Rostock (40 km NE, 250 000 inh.). Within a distance of about 20 km, only few small towns and villages with less than 10 000 inhabitants can be found. No major industry and motorways exist and less than 100 000 people live in this area. Figure 2 shows the villages and traffic lines most close to the site (Warin is about 4 km away). Two small roads on the northeastern and northwestern side of the maize field connect Pennewitt with Warin (2000 inh.) and Mankmoos (200 inh.). There is no through traffic since no other paved roads exist in Pennewitt. Hence, the traffic frequency is quite low with less than about 50 cars per day. The field site is in a mixed land use area with forests, lakes, pasture, and crops (Figure 2). It is at an altitude of 54 m (ASL), altitude variations are less than  $\pm 10$  m in the surrounding area of 2 km radius. Maize is the predominantly cultivated plant in this area with about 250 ha or 20% of the total area. Forest is mainly found north-west of the campaign site. It consists of pine and some deciduous tree species. In total, forests cover approximately 20% of the area (2 km radius).

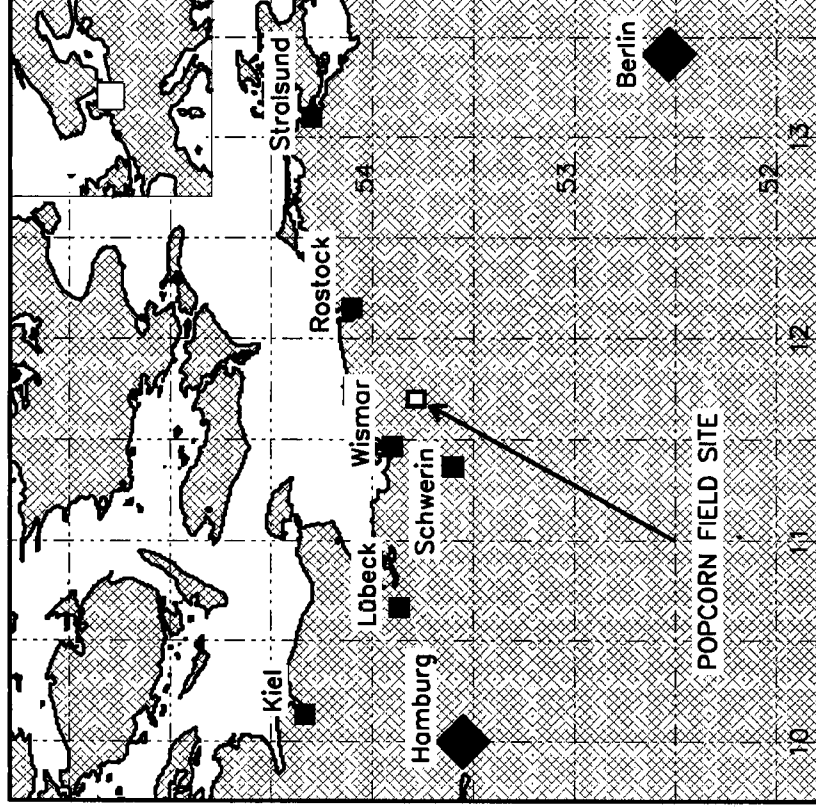


Figure 1. The map shows a part of northeastern Germany and the location of Pennewitt, the POPCORN site. In the insert in the upper right corner the position of the map within Europe is indicated. The open rectangular area marked with an arrow indicates the location and spatial extent of the field site at Pennewitt shown in Figure 2.

The maize field is about 35 ha large and essentially square shaped (600 m × 600 m) (Figure 3A). It is surrounded by pasture and fallow land. The agricultural treatment of the field was a 25 m<sup>3</sup>/ha application of liquid manure before ploughing in March. The crop which was planted April 26 consisted of forage maize (Zea mais). On May 10 lime-nitrate fertilizer (280 kg/ha) was applied and around May 15 a number of herbicides were sprayed (LidoPack 2.6 l/ha, Bucril 0.4 l/ha, and Cato 50 g/ha). In August the maize plants had grown to an average height of 1.2 m (1–1.5 m) which is unusually low for this site and season. The reduced growth of the maize plants is the consequence of a long lasting draught due to an extremely warm summer in Germany which was the warmest and most sunny since the beginning of this century.

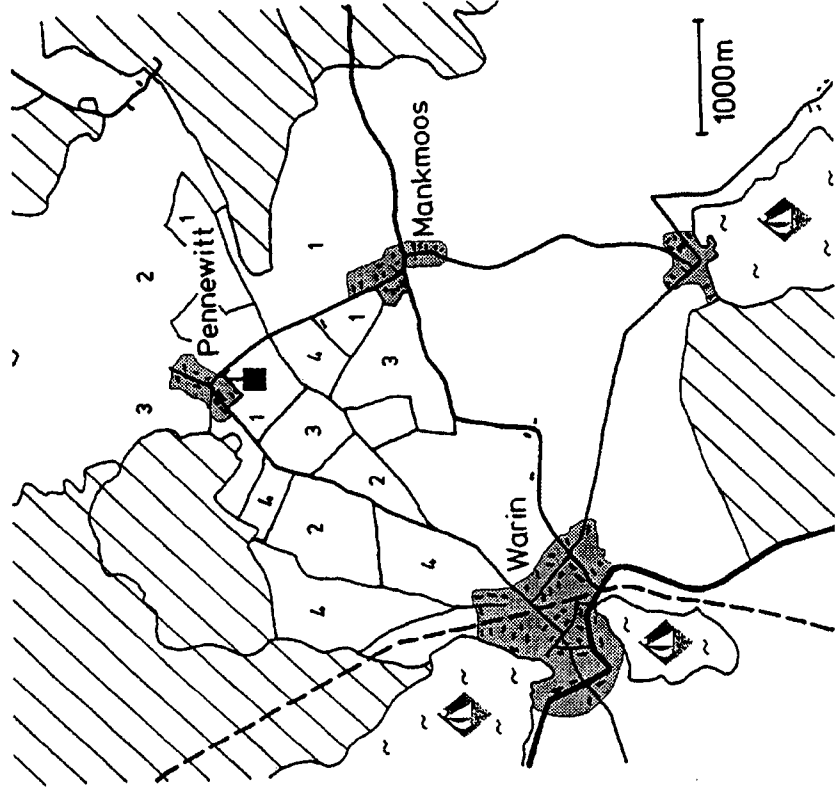
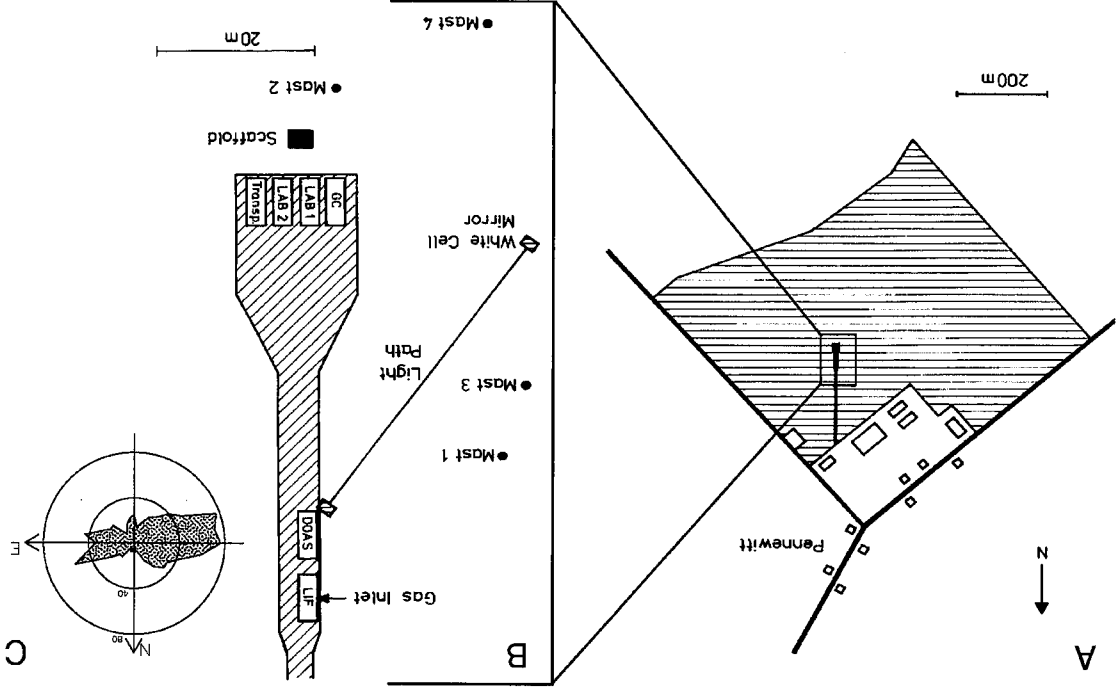


Figure 2. The closer surrounding of the POPCORN site (solid square) south of Pennewitt. The villages (marked by grey area) Pennewitt (50 inh.) and Mankmoos (200 inh.) and the small town Warin (2000 inh.) are connected by minor roads. Thick solid line: through road, dashed lines: rail road tracks. The hatched area indicates forests, the area marked by tilde denote lakes. Additionally, the crops grown on the agricultural areas adjacent to the field site are indicated by numbers: 1: Corn (Maize), 2: cereals, 3: pastures, 4: fallow land.

At the center of the maize field the analytical instruments are installed in six 20 ft. containers (Figure 3). Sampling lines and sampling devices as well as some of the instruments are mounted on masts and scaffolds south or west of the containers. This setup was chosen in order to minimize the risk of contamination due to the containers and operator related activities since the main wind directions were west or, less frequent, east (see wind frequency distribution, Figure 3, and Brauers *et al.*, this issue). Power was supplied from a nearby electrical transformer station. Transportation by vehicles, smoking and other emission related activities were not allowed within the maize field during the measurement campaign.



Figure 3. (A): The maize field (shaded area), location of the measurement equipment (box within the field) and the path cut into the field (solid line) is shown. Adjacent buildings (open rectangles) are not in use or they are small private houses. (B): The location of the measurements and the sampling positions enlarged. The path cut into the maize is represented by the shaded area. The boxes correspond to 20 feet containers housing instruments. The different masts were used to fix sample line inlets, sampling devices, and meteorological instruments. (C): Frequency distribution of the 30-min averages of the wind direction measured during the campaign.



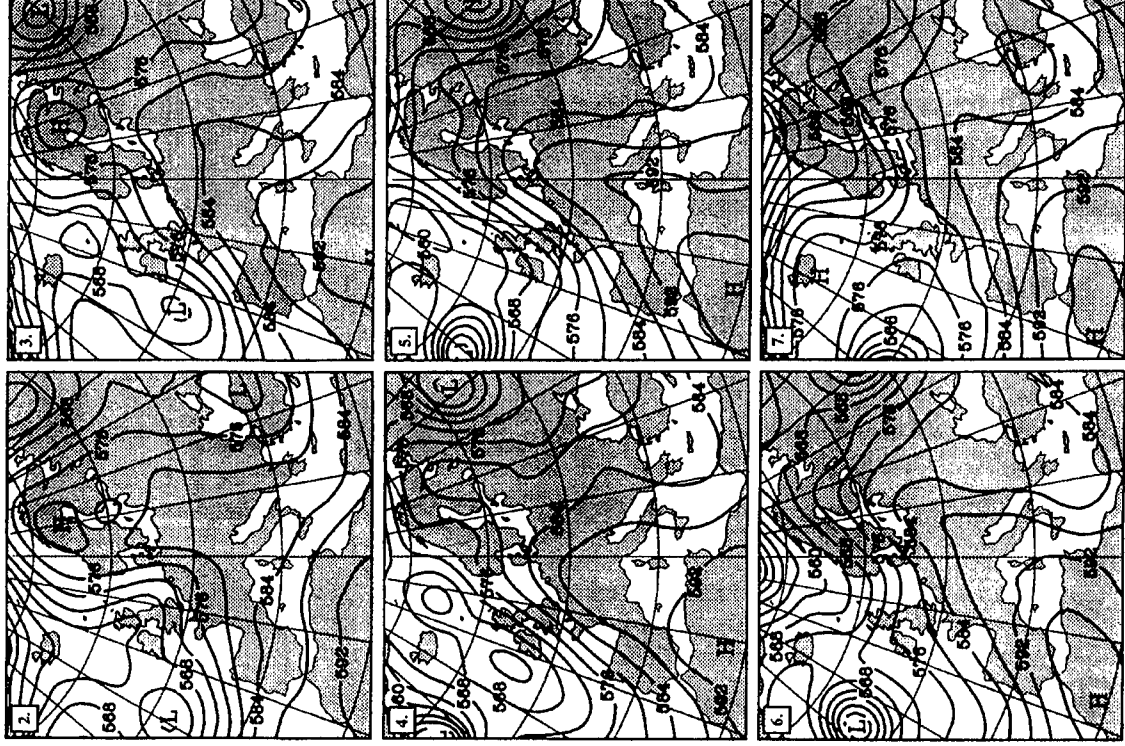


Figure 4. Geopotentials at 500 hPa from August 2-7. All maps are for 0:00 UT (figure provided by D. Melzer, H. Kunz and P. Speth of the Institut für Geophysik und Meteorologie, University of Cologne, Germany, based on the 'Berliner Wetterkarte', August 1994). The number in the upper left corner of the individual maps indicates the day of August 94.

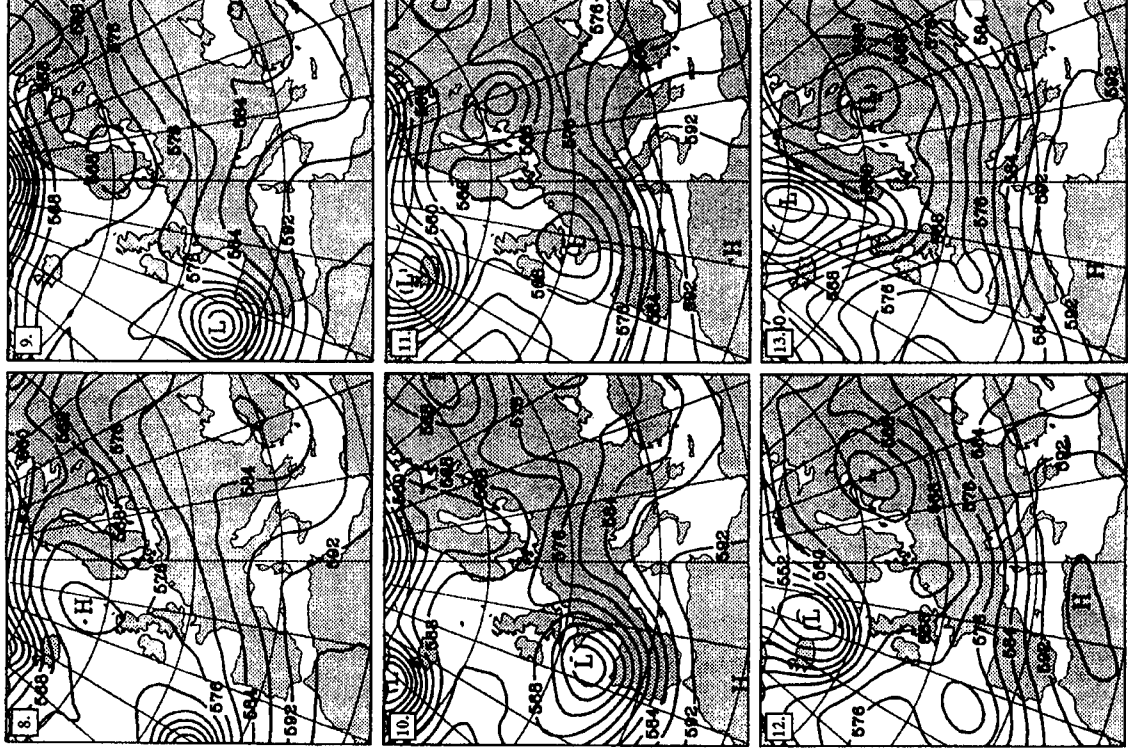


Figure 5. Geopotentials at 500 hPa from August 8-13. All maps are for 0:00 UT (figure provided by D. Melzer, H. Kunz and P. Speth of the Institut für Geophysik und Meteorologie, University of Cologne, Germany, based on the 'Berliner Wetterkarte', August 1994). The number in the upper left corner of the individual maps indicates the day of August 94.

## 2.2. METEOROLOGICAL SITUATION

Two day isentropic backtrajectories (300 K level) were calculated for various geopotential heights (for details see Koppmann *et al.*, this issue). The pattern of trajectories indicates that airmasses were advected from westerly directions most of the time during POPCORN. These air masses passed over Central Europe and Great Britain.

The general meteorological situation changed during the campaign from summer to early autumn conditions. This is demonstrated in the synoptic situation (Figures 4–7) and reflected in the meteorological conditions during POPCORN with temperatures and radiation higher before August 11 (see Figures 3 and 5 in Brauers *et al.*, this issue). The POPCORN campaign can be divided into 6 consecutive episodes (Table III) which can be distinguished by changes in the meteorological conditions. Before August 5, a very hot and dry periode with anticyclonic conditions prevailed for several weeks over Europe (Figure 4, Aug. 2–4). Air masses were of marine origin with continental impacts during the last 2 days. The maximum daily temperature increased from day to day reaching the campaign's maxima of 35 °C. This period was accompanied by nearly clear sky resulting in high values of solar radiation. The wind speed was below 5 m/s. On August 5 at 16:00 UT a cold front passed which is reflected in changes of the wind direction and air pressure (see Figure 1 in Brauers *et al.*, this issue). A cyclonic system west of Great Britain moved south and after August 8 in north-eastern directions bringing subpolar airmasses to the POCORN site (Figures 4 and 5, Aug. 6–10). The solar radiation is reduced due to frequent cloud coverage and temperatures were around 25 °C. On the afternoon of August 10 a thunderstorm developed starting a period with rain and storm. After August 11 the temperatures dropped further, they were below 24 °C all the time with minima down to 10 °C. A cold front passed Pennewitt on August 13 (8:00 UT) with distinct changes in wind direction and air pressure. Between August 13 and 16 a cyclonic system moved from the North Atlantic southeastward across the Baltic Sea and brought very clean arctic air to the POPCORN site (Figures 5 and 6 Aug. 13–16, see also trajectories of August 15–17, Koppmann *et al.*, this issue). A cold front occlusion passed Pennewitt on August 16 (18:00 UT) and air masses were transported over France and southwest Germany to the POPCORN site. In this period an intensive cyclonic system moved in from Great Britain (Figure 6, Aug. 17–19). It moved further east and lost intensity. In the period August 20–24 zonal air mass trajectories developed and persisted until August 23 (Figure 7, Aug. 20–23).

## 2.3. MEASUREMENTS CONDUCTED DURING POPCORN

A summary of the measurements and the sampling positions is given in Table IV. The sampling positions mentioned in Table IV are indicated in Figure 3B. Details concerning sampling and analysis as well as the results are reported in the given references (Table IV). Table V provides an overview of the status of the

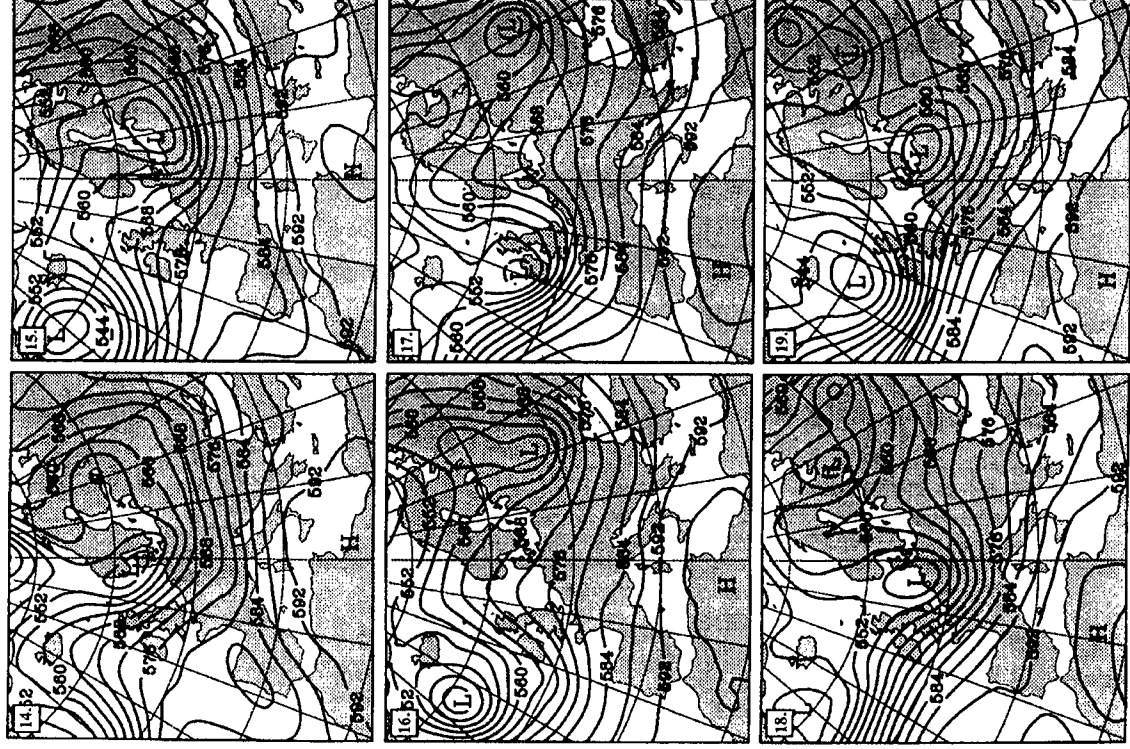


Figure 6. Geopotentials at 500 hPa from August 14–19. All maps are for 0:00 UT (figure provided by D. Melzer, H. Kunz and P. Speth of the Institut für Geophysik und Meteorologie, University of Cologne, Germany, based on the 'Berliner Wetterkarte', August 1994). The number in the upper left corner of the individual maps indicates the day of August 94.

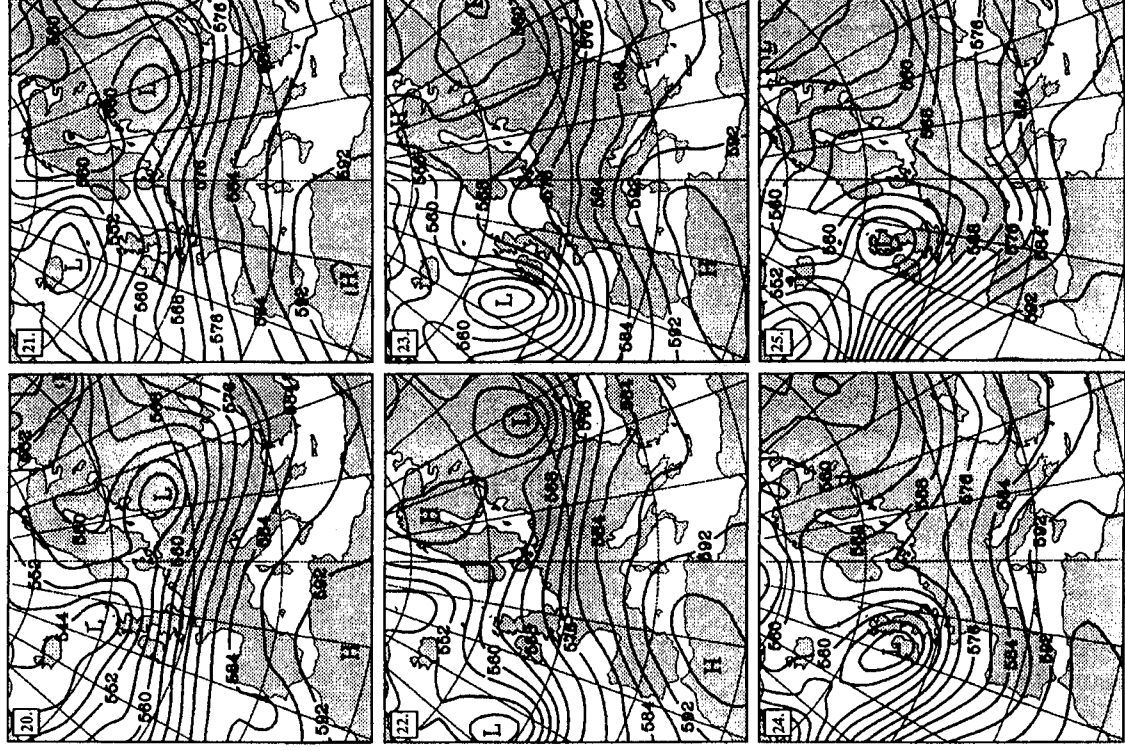


Figure 7. Geopotentials at 500 hPa from August 20-25. All maps are for 0:00 UT (figure provided by D. Melzer, H. Kunz and P. Speth of the Institut für Geophysik und Meteorologie, University of Cologne, Germany, based on the 'Berliner Wetterkarte', August 1994). The number in the upper left corner of the individual maps indicates the day of August 94.

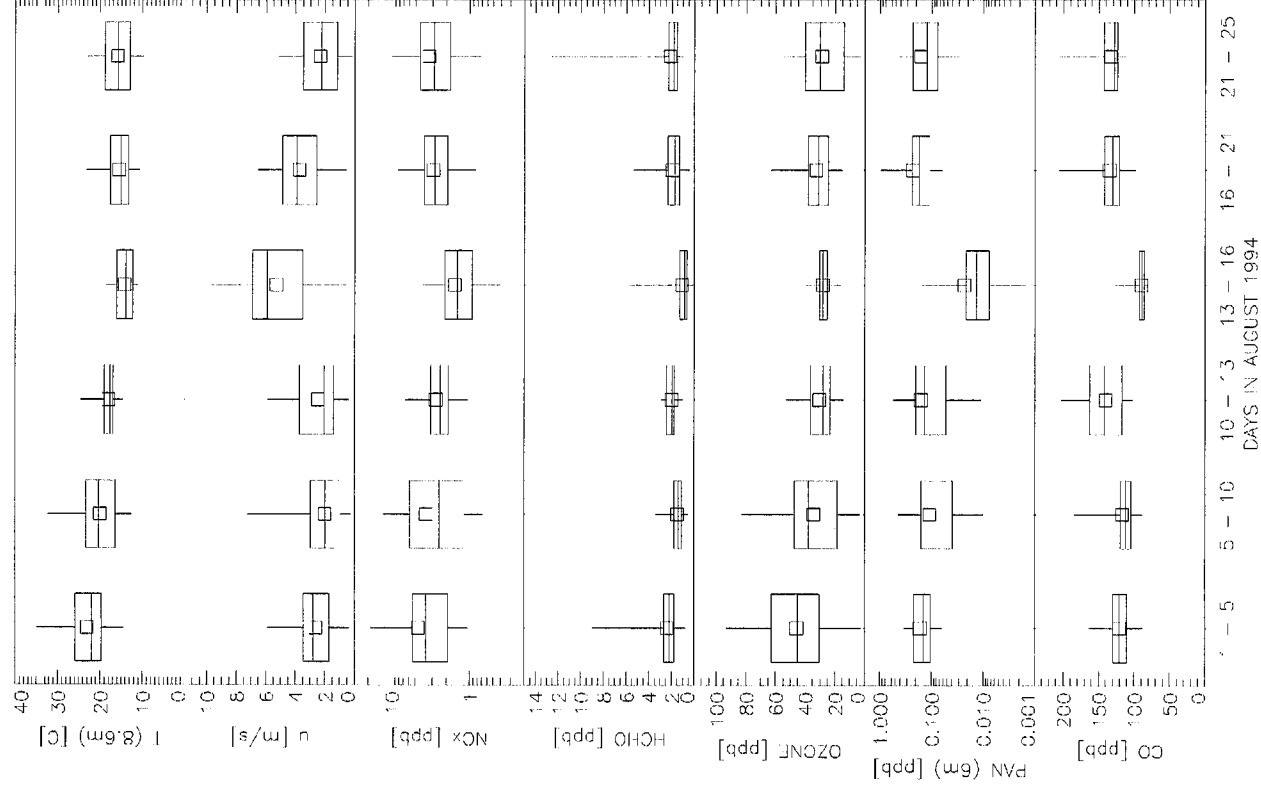


Figure 8. Characteristic air chemistry parameters during the 6 meteorological episodes of POPCORN which were defined in Table III. Shown are mean value (square), and median, 25, and 75 percentiles (boxes), and the range (vertical lines) of the 30-min averages of all data of each episode.

Table III. Meteorological episodes during POPCORN

Episode	Start	End
1	Aug. 1 00:00	Aug. 5 16:00
2	Aug. 5 16:00	Aug. 10 17:00
3	Aug. 10 17:00	Aug. 13 08:00
4	Aug. 13 08:00	Aug. 16 18:00
5	Aug. 16 18:00	Aug. 20 24:00
6	Aug. 21 00:00	Aug. 24 24:00

(quasi-)continuous measurements throughout the POPCORN field study. Seven measurement days, August 8, 9, 10, 13, 16, 17, and 22 named hereafter as *photochemistry intensives* are highlighted. On these days the measurement frequency of OH and aldehydes was enhanced and all ambient air measurements were run at the highest reasonable frequency with interruptions only for calibration and maintenance.

### 3. Results and Discussion

#### 3.1. CONCENTRATION LEVELS OF SELECTED TRACE GASES

During the campaign, the site of the POPCORN field study was marginally to moderately influenced by anthropogenic emissions. Changes in air mass arising from frontal passages (previous section) are easily seen from the time series of a number of trace gases like CO (Koppmann *et al.*, this issue), ozone (Brauers *et al.*, this issue) and PAN (Schrimpf *et al.*, this issue).

An overview of the concentration levels of selected trace gases and the wind speed is shown in Figure 8 for the different meteorological periods (see Table III) encountered during POPCORN. The averaged precursor concentrations of CO, and NO<sub>x</sub> indicate very low impact due to anthropogenic emissions in episode 4 (Aug. 13–16) where clean North Atlantic air masses were encountered. In this episode, also the lowest ozone, formaldehyde and PAN mixing ratios were observed. During the other episodes air masses were advected over Europe for longer times with different anthropogenic impact depending on the emissions along the trajectories. On average the highest CO concentrations were measured in episodes 5 and 6 (Aug. 16–24). The medians of NO<sub>x</sub> mixing ratios were between 1.5 and 3.5 ppb with highest values in episode 1 (Aug. 3–5). PAN and formaldehyde are photochemically produced from hydrocarbons and NO<sub>x</sub> and thus were higher during episodes 1, 5, and 6 characterized by higher precursor concentrations and intensive solar insolation. Ozone concentrations were highest in episode 1 with maxima of up to 90 ppb which most probably were the result of the longlasting anticyclonic conditions that prevailed over Europe at that time.



Table IV. Measurements during POPCORN

Parameter	Technique	Location	Height [m] <sup>a</sup>	Ref.
<i>Oxidized nitrogen species</i>				
NO, NO <sub>2</sub>	CL-phot. conv.	M2	6 or 2	A
NO <sub>2</sub>	WC	M2	6	B
NO <sub>y</sub>	CL-gold conv.	M2	2.9	A
PAN	GC-ECD	M2	2, 6 <sup>b</sup>	C
HNO <sub>3</sub>	filter, IC	M2	2.9	D
<i>Carbon species</i>				
CO	GC-HgO	M2	6	E
C2-C8 HC	GC-FID/ECD	M2	6	E
C6-C20 VOC	GC-MS (FID) <sup>c</sup>	SC	6(2)	F
C6-C10 VOC	GC-FID	SC	2; 6	B
C1-C2 Aldehydes	derivat. HPLC	SC	6	G
C1-C9 Aldehydes	derivat. HPLC	SC	6	H
HCHO	DOAS	DL	3.5	I
CO <sub>2</sub>	IR	M2	2+6	J
<i>Oxidants</i>				
O <sub>3</sub>	UV	M1; SC	2.2, 4.4, 7.0; 5.5	K, A
H <sub>2</sub> O <sub>2</sub>	enzymatic	SC	4.6	L
<i>OH radicals</i>				
OH	DOAS	DL	3.50	I
OH	LIF	LIF	4.50	M
<i>Aerosol properties</i>				
Nr. density	CN counter	M1	1.4	K
Scattering coeff.	nephelometer	M1	1.8	K
<i>Meteorology, Radiation</i>				
Wind speed	Cup anemometer	M1	2.2, 4.5, 7.0	K
u, v, w, u <sub>z</sub>	Ultrasonic anemometer	M3	7.0	K
Temperature	Pt 100	M1	2.2, 4.3, 6.7, 8.6	K
Rel. humidity	Capacitive	M1	8.6	K
Air pressure	Pressure gauge	M1	2.0	K
Global rad.	Solarimeter	M3; LIF	5.0; 3.9	K
J(NO <sub>2</sub> )	Filter radiometer	M3; SC	5.0, 7.2	K, A
J(O <sup>1</sup> D)	Filter radiometer	M3	5.0	K
UV actinic flux	Spectroradiometer	LIF	4.9	N
<i>Flux and tracer measurements</i>				
<sup>222</sup> Rn	$\alpha$ -activity	SC	6 and 2	A
<sup>222</sup> Rn flux	$\alpha$ -activity	Ground	0	A
CO <sub>2</sub> , H <sub>2</sub> O	Eddy-corr.	M4	4.0	D

Table IV. (Continued)

Parameter	Technique	Location	Height [m] <sup>a</sup>	Ref.
<i>Organic compound emissions</i>				
C2-C8 HC	GC-FID	Various	Various	O
C5-C10 VOC	GC-FID	Various	Various	B, H, P
Aldehydes	Deriv. HPLC	Various	Various	H
NO	CL-O <sub>3</sub>	Ground	0	A

*Locations for sampling (see Figure 3):* M1: mast 1; M2: mast 2; M3: mast 3; M4: mast 4; SC: scaffold; DL: DOAS light path; LIF: LIF container;

*References:* A: Rohrer *et al.*, this issue; B: Gomiscek *et al.*, 1995; C: Schrimpf *et al.*, this issue; D: Ibrum *et al.*, private comm.; E: Koppmann *et al.*, this issue; F: Wedel *et al.*, this issue; G: Benning and Wahner, this issue; H: Hewitt *et al.*, 1995; I: Brandenburger *et al.*, this issue; J: Levin *et al.*, private comm.; K: Brauers *et al.*, this issue; L: Lörzer *et al.*, private comm.; M: Holland *et al.*, this issue; N: Kraus and Hofzumahaus, this issue; O: Parusel, 1996; P: Puxbaum *et al.*, 1995; *Remarks:* <sup>a</sup>: The maize plants were at a height of about 1.0 to 1.5 m; <sup>b</sup>: Alternating measurements between the two specified heights were made. <sup>c</sup>: Massspectrometric detection was made until Aug 15, FID thereafter.

*Measurement techniques:* CL: chemiluminescence gas phase; phot. conv.: NO<sub>2</sub> photochemically converted to NO; gold conv.: NO<sub>y</sub> catalytically converted to NO on gold with CO added; WC: wetchemical luminescence; GC: gaschromatography; ECD, FID, MS, and HgO: electron capture, flame ionisation, mass selective, and HgO detectors for GC; IC: ion chromatography; derivat. HPLC: DNPH derivatisation, high performance liquid chromatography; DOAS: differential optical absorption spectroscopy; IR: infrared optical absorption measurement; UV: ultraviolet optical absorption measurement; enzymatic: enzyme catalysed fluorescence; LIF: laser induced fluorescence; CN counter: condensation nuclei counter; eddy-corr.: eddy correlation technique, ultrasonic anemometer.

For a continental site in Central Europe, the CO and NMHC levels were quite low and sometimes close to marine background levels at mid northern latitudes (Koppmann *et al.*, this issue; Wedel *et al.*, this issue). The concentrations of biogenic hydrocarbons such as isoprene and terpenes also were low, rarely exceeding 100 ppt and many of these substances exhibited mixing ratios below 10 ppt (Wedel *et al.*, this issue). NO<sub>x</sub> levels at nighttime generally were below 2 ppb which may be characterized as typical rural concentration levels (Chameides *et al.*, 1992). However, during nocturnal inversions the strong surface source of NO gave rise to mixing ratios occasionally exceeding 10 ppb (Rohrer *et al.*, this issue). On average, NO<sub>x</sub>/VOC ratios were in a fairly high regime of about 3 ppbV/13 ppbC or about 3 ppbV/2.3 ppbC(propylene-equivalent). This implies that during most time of



POPCORN ozone production was VOC limited (Chameides *et al.*, 1992). As can be expected from the relatively low concentrations of precursors, the concentrations of photo-oxidants, e.g. ozone and PAN are quite low, typical diurnal averages are 30–40 ppb and 0.05–0.25 ppb, respectively (Brauers *et al.*, this issue; Schrimpf *et al.*, this issue).

### 3.2. MAJOR FINDINGS FOR THE VARIOUS GROUPS OF TRACE GAS CONSTITUENTS

#### 3.2.1. Volatile Organic Compounds (VOC)

The results of the emission studies of biogenic VOC are not presented in this issue. In general, the NMHC emissions including isoprene and terpenes from maize were small, in total not exceeding some  $10 \text{ ng g}_{\text{dwt}}^{-1} \text{ h}^{-1}$  (Parusel, 1996; Hewitt *et al.*, 1995; Puxbaum *et al.*, 1995).

Nonmethane hydrocarbons were measured with two independently calibrated *in situ* gas chromatographic instruments: one with cryogenic preconcentration and FID/ECD detection for light hydrocarbons (C2–C7) and halocarbons (Koppmann *et al.*, this issue) and one with adsorptive sampling on Tenax TA/Carbotrap and MS/FID detection for C6–C15 hydrocarbons and oxygenated hydrocarbons (Wedel *et al.*, this issue).

The concentrations of typically man made VOC (e.g. alkanes, alkyl benzenes), CO and methane are essentially controlled by advection (Koppmann *et al.*, this issue; Wedel *et al.*, this issue). The ambient levels of biogenic hydrocarbons (isoprene and several monoterpenes) were most probably due to emissions from the trees close to the POPCORN field site since their patterns resemble the emission patterns of these trees (Wedel *et al.*, this issue; Hewitt *et al.*, 1995; Puxbaum *et al.*, 1995). Concentrations of individual biogenic VOC were mostly well below 100 ppt.

#### 3.2.2. Aldehydes

In view of the low concentrations of VOC the formaldehyde mixing ratios are surprisingly high, on average nearly 2 ppb, occasionally exceeding 3 ppb and nearly always above 0.5 ppb. Also higher acetaldehyde levels than expected for a remote rural area are found, on average 1.4 ppb (Benning and Wahner, this issue). Neither formaldehyde nor acetaldehyde show a significant diurnal variation.

Sources for aldehydes are emissions from maize and photo-oxidation of VOC in the atmosphere. Acetaldehyde is most likely to a large extent due to plant emissions. Emissions of maize for formaldehyde and acetaldehyde were measured up to  $2 \mu\text{g g}_{\text{dwt}}^{-1} \text{ h}^{-1}$  (Hewitt *et al.*, 1995). Its yield from photochemical oxidation of atmospheric VOC is only small since the levels of precursor VOC are quite low. During daytime the photo-oxidation of VOC, especially acetaldehyde and methane, can compensate the formaldehyde destruction. During nighttime emission from

vegetation is the only relevant formaldehyde source (Benning and Wahner, this issue).

Formaldehyde concentrations measured by differential optical absorption spectroscopy (DOAS) and the 2,4-dinitrophenylhydrazine coated silica cartridge derivatisation method (DSC) are compared by Benning and Wahner (this issue). They show good agreement within the limits of accuracy and precision of both measurements.

### 3.2.3. $NO_x$

$NO_x$  levels range around some ppb, at noontime they are often below 2 ppb. However, during night time inversion situations, indicated by elevated  $^{222}Rn$  concentrations,  $NO_x$  concentrations strongly increase and frequently exceed 5 ppb, sometimes even 10 ppb while  $O_3$  at ground level approaches zero (Rohrer *et al.*, this issue). This is attributed to substantial nighttime soil emissions of NO in the range of  $40 \text{ ng(N) m}^{-2} \text{ s}^{-1}$ . During night the  $NO_x$  balance is closed. However, the local surface source of NO is not sufficient to explain the observed  $NO_x$  levels during daytime. The most probable additional sources of  $NO_x$  is advection (Rohrer *et al.*, this issue).

### 3.2.4. *OH Radicals*

The most important intercomparison performed during POPCORN is the *in situ* comparison of two independent methods for OH radical measurements. The LP-DOAS system (long path differential optical absorption spectroscopy) is a calibration free absolute method (Brandenburger *et al.*, this issue). The LIF (laser induced fluorescence) has a better sensitivity and higher time resolution, but it needs calibration (Holland *et al.*, this issue). With  $1.5 \times 10^6 \text{ cm}^{-3}$  and  $0.5 \times 10^6 \text{ cm}^{-3}$  the mean  $2\text{-}\sigma$  detection limits of the DOAS and LIF instruments, respectively, were sufficient to allow a realistic intercomparison of the daytime OH-measurements. A large data set of overlapping measurements in conjunction with well defined measurement errors is available from the POPCORN campaign. Both instruments gave essentially identical results (Hofzumahaus *et al.*, this issue) within the stated accuracies of the absorption cross section (DOAS: 7%) and the calibration (LIF: 25%). Only for a certain wind sector (NNW) significant deviations between the two methods exist, possibly due to a local perturbation of the DOAS measurements. It can be concluded that both instruments agreed in their calibrations and accurately can measure the concentrations of OH radicals. Under clear sky conditions OH radical concentrations reached maximum values of  $10^7 \text{ cm}^{-3}$  around noon, night time concentrations were below the detection limit of about  $4 \times 10^5 \text{ cm}^{-3}$ . These diurnal cycles of OH were well correlated with the primary production rate due to ozone photolysis (Holland *et al.*, this issue; Brandenburger *et al.*, this issue). However, during early morning and late afternoon the photolysis of formaldehyde can contribute substantially to the production of OH radicals (Kraus and Hofzumahaus,

this issue; Brandenburger *et al.*, this issue). Occasional observations of OH radical concentrations of some  $10^6 \text{ cm}^{-3}$  in the very early morning could be a hint to a OH production from photolysis of nitrous acid, HONO (Brandenburger *et al.*, this issue; Platt *et al.*, 1980).

### 3.2.5. PAN

During most of the campaign PAN exhibited strong diurnal cycles with maxima in the afternoon and minima late in the night (Schrimpf *et al.*, this issue). The average nighttime PAN deposition velocity was estimated to be  $0.54 \pm 0.06 \text{ cm/s}$  (Schrimpf *et al.*, 1996). Local budgets of PAN predict for daytime generally higher PAN formation rates than the actually observed increase rates. A consequence of the enhanced PAN production due to local emissions of acetaldehyde, an important PAN precursor, is a net export of PAN from the study area. The export rate of 'excess PAN' is in the range of some hundred ppt/h ( $\approx 10^6 \text{ cm}^{-3} \text{ s}^{-1}$ ) and has only little impact on the local  $\text{NO}_x$  concentration. However, the above rate is in the order of the  $\text{HO}_x$  production rate via photolysis and PAN occasionally must have been an important reservoir and transport medium for  $\text{HO}_x$  radicals (Schrimpf *et al.*, this issue).

### 3.2.6. Ozone

During most of the campaign ozone exhibits strong diurnal cycles with maxima in the afternoon and minima late in the night (Brauers *et al.*, this issue; Rohrer *et al.*, this issue). The budget of ozone very strongly reflects the variation of the height of the inversion layer. During conditions of low nighttime inversions the ozone concentrations are reduced drastically, mainly the result of dry deposition. Via the formation of  $\text{NO}_2$  from reaction of NO with  $\text{O}_3$  the soil emissions of NO also contribute to the nighttime loss of ozone. For an inversion layer height of 100 m the NO emissions from soil correspond to an ozone loss rate of about 2.5 ppb/h. During many days a strong increase in the ozone concentration was observed in the morning (Brauers *et al.*, this issue). The formation of ozone from the photo-oxidation of VOC, with on average 3–4 ppb/h (Wedel *et al.*, this issue), is not sufficient to explain the ozone increase of up to 10 ppb/h (Brauers *et al.*, this issue). Most likely, the breakup of the nocturnal inversion layer in the morning results in the advection of ozone rich air from above (e.g. Warneck, 1988).

### 3.2.7. $^{222}\text{Rn}$ Tracer Based Flux Measurements

From measurements of the  $^{222}\text{Rn}$  gradients between 2 and 6 m, the  $^{222}\text{Rn}$  fluxes, and measurements of gradients of NO and PAN, the fluxes of these trace gases could be calculated (Rohrer *et al.*, this issue; Schrimpf *et al.*, 1996). During part of the POPCORN campaign PAN deposition was studied by two methods, the novel  $^{222}\text{Rn}$  method (using the simultaneously measured gradients of PAN and  $^{222}\text{Rn}$ ) and a modified Bowen ratio method with good agreement (Schrimpf *et al.*, 1996).

This gives additional confidence that the novel  $^{222}\text{Rn}$  method which has been used for the first time during POPCORN is a useful and reliable method to determine deposition velocities. Additionally, a study of the diurnal profile of  $^{222}\text{Rn}$  and  $\text{NO}_x$  was used to derive the magnitude of the  $\text{NO}_x$  soil emissions.

#### 3.2.8. Photolysis Frequencies

Photolysis frequencies were determined by absolute UV spectroradiometric measurements in combination with molecular photodissociation data from literature (Kraus and Hofzumahaus, this issue). This includes the photolysis frequencies of  $\text{NO}_2$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , HONO, and HCHO. Additionally, photolysis frequencies for  $\text{NO}_2$ ,  $J(\text{NO}_2)$ , and for the formation of excited oxygen atoms from ozone,  $J(\text{O}^1\text{D})$ , were measured by filter radiometers (Rohrer *et al.*, this issue; Brauers *et al.*, this issue). A comparison between the  $J(\text{O}^1\text{D})$  measurements by filter radiometer and spectroradiometry showed a very good agreement. For  $J(\text{NO}_2)$  slight differences were found and both measurements showed substantial differences compared to the literature values (Kraus and Hofzumahaus, this issue).

#### 4. Conclusion and Perspectives

During the POPCORN campaign a unique data set of atmospheric trace gas concentrations, meteorological data and related measurements was acquired. For the first time, a conclusive intercomparison of in situ hydroxyl measurements by LIF and folded long-path DOAS was performed. Thus, difficulties in the data interpretation due to spatially inhomogenous trace gas concentrations as it was the case in previous intercomparisons (Eisele *et al.*, 1994; Mount *et al.*, 1997) were reduced although not fully eliminated. Even in the POPCORN OH intercomparison with the 2 instruments measuring side by side (horizontal distance between 10 m and 50 m) deviations for a certain wind sector at low wind speeds were observed. Excluding this wind sector, the results obtained by LIF and DOAS agreed very well within the stated uncertainties of the measurements. This agreement was found for all air mass situations and the entire range of trace gas patterns encountered during POPCORN independent of the pollution level of the air masses. Thus there can be confidence in the determined OH concentrations which now can be used to test our current understanding of tropospheric photochemistry.

With known OH concentrations the daytime budgets of reactive trace gases within simple box models could be set up. However, these budgets are not closed since fluxes into and out of the study area were not measured. Based on the current understanding of photochemistry, however, a net transport can be assessed. The uncertainty in identifying transport or gaps and errors in our current knowledge of atmospheric chemistry as source for budget imbalances is considerably reduced for the POPCORN field study since for the OH-radical, one of the most important constituents in determining atmospheric trace gas turnover, reliable measurements exist. For PAN it has been concluded from the discrepancy between the calculated

photochemical budget and the observed changes in concentrations that PAN transport from the study area is needed to balance the substantial gap in the local budget (Schrumpf *et al.*, this issue). This has important consequences on the budget of HO<sub>x</sub> radicals.

Surprisingly for a remote location, ozone formation during the POPCORN field study is VOC and not NO<sub>x</sub> limited. If this holds true for other rural areas in northern Germany or even Central Europe, this has important consequences for air quality control and ozone reduction strategies. The question remains how representative these findings of low VOC/NO<sub>x</sub> ratios are for remote rural areas in Germany or Central Europe and it would be premature to generalize the findings from a single field study. Nevertheless, none of the characteristics of the POPCORN field site indicates that the study area fundamentally differs from other remote rural areas.

Currently further interpretations of the POPCORN data are on the way. Mainly, this concerns detailed photochemical modeling and the comparison of the POPCORN results with model data. In addition, a 3-dimensional model is under development in order to describe the combined effect of transport and chemistry.

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