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Schauinsland Ozone Precursor Experiment (SLOPE96): Scientific background and main results

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Abstract. The Schauinsland Ozone Precursor Experiment (SLOPE) was conducted in June 1996 as part of the former European Experiment on Transport and Transformation of Environmentally Relevant Trace Constituents in the Troposphere Over Europe (EUROTRAC) subproject Tropospheric Ozone Research (TOR) in order to study the photochemical formation of ozone and the degradation of the precursors in the plume of the city of Freiburg on its way to Schauinsland. Chemical and meteorological measurements were made at several surface sites in a valley that channels the airflow to Schauinsland, including vertical profiles at several locations, and aboard a small aircraft. A tracer experiment with SF_6 was made in order to establish transport and dispersion in the valley. Particular emphasis was on the determination of the OH concentration from the decay of hydrocarbons during transport. The relatively high OH concentration of 7×10^6 cm^{-3} in the presence of high NO_x concentrations (3–15 ppb) indicates the potential for unidentified processes in the HO_x budget in the high-NO_x regime which may have important consequences for the ozone budget and smog chemistry in the urban/suburban environment.

1. Introduction

The transition region between urban and rural areas is important in understanding the fast photochemistry that leads to the buildup of high concentrations of ozone and other photooxidants during so-called summer smog episodes. While several experiments have investigated the budgets of ozone and radicals at low and moderate NO_x concentrations, including direct spectroscopic measurements of [OH] [e.g., *Dorn et al.*, 1988; *Eisele et al.*, 1994; *Mount and Williams*, 1997; *Holland et al.*, 1998], little quantitative experimental information exists so far on the ozone balance and the radical concentrations in the high NO_x regime.

The OH concentration and the production rate of ozone both depend in a nonlinear fashion on the UV flux and on the concentrations of NO_x and VOCs. The role of NO_x in the budgets of HO_x ($[HO_x] = [OH] + [HO_2]$) and ozone is ambivalent. At low NO_x concentrations, where recombination of the peroxy radicals constitutes the major radical loss, [NO] controls the recycling of OH and is the rate-limiting factor in ozone production [*Logan et al.*, 1981; *Crutzen*, 1979]. At high NO_x levels, on the other hand, radical losses by recombination of peroxy radicals become insignificant, and HO_2 is almost completely recycled to OH. In the presence of sufficient NO, even more radicals can be produced from the hydrocarbon oxidation mechanism than initially consumed, because of the photolysis of the carbonyl compounds formed in the mechanism [*Jeffries and Tonnesen*, 1994; *Jang et al.*, 1995]. This effect is counteracted by the reaction of OH with NO_2, which becomes the predominant sink of HO_x in the high-NO_x regime and thus limits the production of RO_2 and HO_2. The net effect of NO_x on the radical balance and ozone formation depends on the NO/NO_2 ratio, which is controlled by the UV radiation flux (J_{NO_2}) and by the concentrations of peroxy radicals and O_3. The radical chemistry in the high-NO_x regime is further complicated by the fact that photolysis of nitrous acid (HONO), which is coemitted with NO_x [*Kessler and Platt*, 1984] and/or produced from NO_x via heterogeneous reactions [cf. *Harrison et al.*, 1996], is a potentially important source of HO_x in polluted air, in particular during the morning hours.

In addition to chemistry, the local concentration of trace gases is influenced by transport, dispersion, and deposition. Which of the different processes dominates depends on the chemical lifetime of the species and on the meteorological conditions. While the concentrations of OH and other short-lived radicals are reasonably well described by the local chemical fields, transport usually dominates the local rate of change of the longer-lived trace gases such as ozone. For example, the daily ozone maximum which develops under fair weather conditions results by approximately 70% from downward mixing of ozone from the residual layer to the surface layer, while only the remaining 30% can be related to local chemical formation [*Fiedler*, 1998]. Therefore information about the meteorological conditions like mixing layer height, stratification of the boundary layer, and three-dimensional structure of the wind field is essential for the determination of the contributions of advection and diffusion in an experiment that aims at the budgets of trace gases. This is particularly the case in complex terrain, where thermally induced periodic wind systems [*Atkinson*, 1981; *Whiteman*, 1990; *Barry*, 1992], like slope and valley winds, are important for the ventilation of the valley atmosphere and have a strong influence on the local change of trace gases [e.g., *Carroll and Baskett*, 1979; *Kurita et al.*, 1990; *Millan*,

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1992; *Bischoff-Gauß et al.*, 1998]. In order to separate the contributions of transport and dispersion on the local concentration changes from the chemical transformation processes it is advantageous to analyze the behavior of an artificial inert tracer, in addition to measurements of the chemical composition of the air [e.g., *Wilson et al.*, 1983; *Clements et al.*, 1989; *Allwine*, 1993].

With this in mind, and on the basis of earlier experiments, the following strategy was selected for the Schauinsland Ozone Precursor Experiment (SLOPE96). The steep and narrow valley "Großes Tal" between the city of Freiburg and the Schauinsland observatory was used as approximation of a flow reactor to study the chemical and physical development of the city plume of Freiburg in a quasi-Lagrangian approach by detailed meteorological and chemical measurements, including a tracer experiment with SF_6. The advantage of using a valley for such an experiment is the well-defined transport path, which makes it relatively easy to arrange the measurement systems, and that the exchange of the transported air mass with the surrounding environment is restricted to the vertical dimension. A particular advantage of the Großes Tal for a chemical budget study is its very thin population and the absence of a transit road.

The details of the various measurements and the scientific results are described in subsequent manuscripts of the special section. This paper briefly outlines the history and the layout of SLOPE96 and summarizes the main results and conclusions.

2. History of SLOPE

The field station Schauinsland (47°54′N, 7°48′E; 1230 m above sea level (asl) [*Volz-Thomas et al.*, 1997]) was operated between 1989 and 1996 as part of the European Experiment on Transport and Transformation of Environmentally Relevant Trace Constituents in the Troposphere Over Europe (EUROTRAC) subproject Tropospheric Ozone Research (TOR) [*Kley et al.*, 1997]. It is located in the southern part of the Black Forest mountains (Figure 1) on a saddle about 400 m east of the Schauinsland summit (1284 m asl). The area around the station is characterized by a general decline within about 10 km to the Rhine Valley in the west (250 m asl). The hills and valleys south, west, and northwest of the station are mostly covered with coniferous and deciduous forest. The remaining parts are covered with grasslands, interrupted by small tree and bush stands. The site is shielded from direct influence of local traffic by a ridge. The road to the observatory is closed for public traffic for the last 1.5 km. The nearest settlement (some 100 inhabitants) is about 2 km away, and the next major city is Freiburg (120,000 inhabitants) in the Rhine Valley, about 11 km northwest. Toward northwest the terrain declines with a slope of more than 20% into the narrow valley Großes Tal, in which the SLOPE experiment took place.

Figure 2 shows the summertime wind roses for Schauinsland and for Feldberg, the highest mountain of the Black Forest (1486 m asl, about 10 km southeast of Schauinsland). Although not truly representative of the geostrophic flow, Feldberg is not much influenced by local topography and thus should be representative of the wind field in the upper planetary boundary layer (PBL) in the region, whereas the wind field at the TOR station Schauinsland is strongly influenced by local topography and the vicinity of the Rhine Valley.

While the wind rose of Feldberg shows the expected maximum at southwesterlies (35.6% between 230° and 190°) with secondary maxima in the northeast, the southwesterly component is much less pronounced at Schauinsland, and the northeasterly components are completely absent. Instead, there is a strong peak at northwesterly winds (>40% during daytime), which is due to the up-valley wind system in the Großes Tal. The northwest wind is, in general, associated with low wind speeds (90% <3 m s^{-1}). At night, southeasterly wind directions are more frequent, and the northwesterly component is strongly reduced. In winter (not shown), northwesterly winds are rather seldom, mostly during frontal passages, and there is almost no difference between day and night.

The chemical situation is illustrated by the average diurnal variations of the trace gases in summer in Figure 3. Schauinsland is exposed to very clean air from southwesterly directions. The next larger agglomeration in that direction is Lyon, about 300 km away. The data from the northwest sector show a pronounced diurnal cycle, which is due to the fact that Schauinsland usually resides above the inversion at night. The peak at noon is caused by the breakup of the inversion in the morning and the establishment of the valley wind system in the Großes Tal. The pronounced diurnal variation in the northwest sector is a clear indication for the Rhine Valley being a strong source for pollutants and photooxidants at Schauinsland. As is exhibited by the NO_x and NO_y data in Figure 3, these air masses have been subjected to relatively fresh emissions, for example, from the Rhine Valley and the city of Freiburg, leading to fairly large concentrations of ozone in the course of the day.

The regular appearance of the northwesterly winds at Schauinsland led to the idea of utilizing the valley Großes Tal as an approximation of a flow reactor. A first experiment was conducted in September 1992 with ground-based measurements made in Kappel, a small village at the entrance of the valley, and at Schauinsland (see Figure 4). Both sites were equipped with instrumentation for NO, NO_x, NO_y, O_3, J_{NO_2}, and C_2–C_8 hydrocarbons and meteorological parameters [*Kramp and Volz-Thomas*, 1997].

Similar to the approaches used by, for example, *Calvert* [1976], *Roberts et al.* [1984], *Satsumabayashi et al.* [1992], *Blake et al.* [1993], *Jobson et al.* [1994], and *McKenna et al.* [1995], the OH concentration was estimated by simultaneously integrating the continuity equation (1) for a family of reactive hydrocarbons RH_i,

$$\frac{\partial [RH_i]}{\partial t} = P_{RH_i} - L_{RH_i} - \mathbf{u}\nabla[RH_i] - \nabla(K\nabla[RH_i]) \quad (1)$$

where $\partial/\partial t$ is the local rate of change, P and L are the local production and loss terms, and $\mathbf{u}\nabla[RH_i]$ and $\nabla[K\nabla[RH_i]]$ is the flux divergence due to advection and turbulence.

As has been discussed in several publications [*McKeen and Liu*, 1993; *McKenna*, 1997; *Kramp and Volz-Thomas*, 1997; *Ehhalt et al.*, 1998], the successful application of the so-called hydrocarbon clock relies on the fulfillment of several assumptions: First of all, it is assumed that the reaction with OH (R1) constitutes the major chemical loss process for the hydrocarbons considered.

$$\text{(R1)} \qquad RH + OH + O_2 \rightarrow RO_2$$

In this sense, it must be emphasized that the result does not constitute a positive identification of OH in the atmosphere but rather relies on the wisdom about the role of OH as the major oxidant in the sunlit atmosphere [*Levy*, 1971]. The chemical losses are then given by

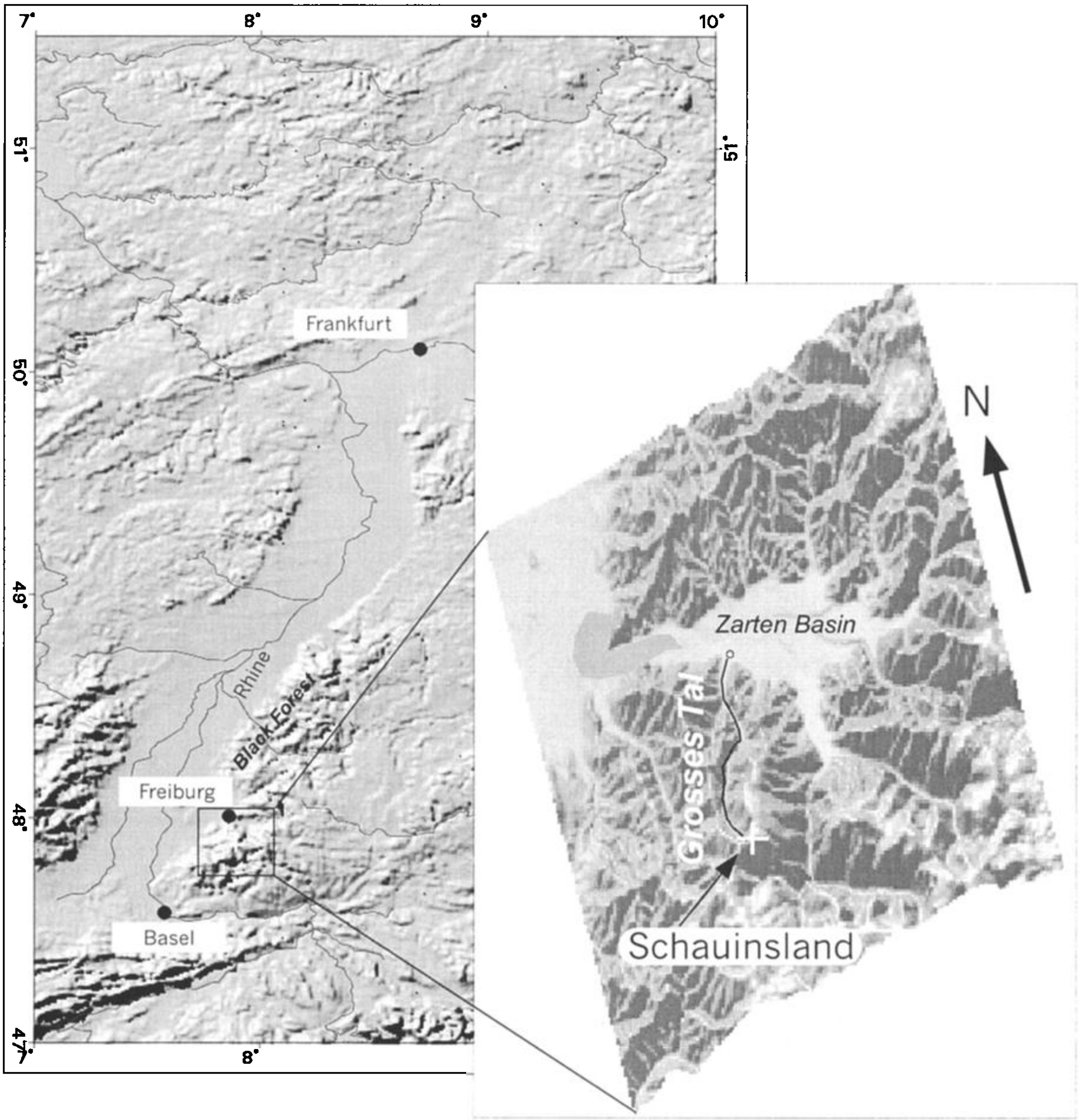

Figure 1. Map of the Upper Rhine Valley and the Black Forest mountains with the location of Schauinsland and the city of Freiburg. The insert gives an enlarged view of the area around Freiburg and the Zarten Basin, with the Großes Tal marked by the solid line.

$$L_{RH_i} = [RH_i] \times [OH] \times k_{1i} \qquad (2)$$

with k_{1i} being the rate coefficients for (R1), which must be known from laboratory measurements. Second, chemical production and emissions of the considered hydrocarbons during transport between the two measurements must be negligible. Last but not least, (1) can only be integrated if the dilution term is equal for all hydrocarbons, such that the term $\nabla(K\nabla[RH_i])$ can be approximated by a first-order loss process with a dilution coefficient k_d. With these assumptions and after transformation into Lagrangian coordinates, we obtain

$$-\frac{d[RH_i]}{dt} = [RH_i] \times ([OH] \times k_{1i} + k_d) \qquad (1')$$

and after integration,

$$\ln([RH_i]_{t_2}/[RH_i]_{t_1}) = -\int_{\Delta t}[OH] \times k_{1i}\,dt - \int_{\Delta t} k_d\,dt$$

$$\approx -[\overline{OH}] \times k_{1i} \times \Delta t - \bar{k}_d \times \Delta t \qquad (3)$$

According to (3) the average OH concentration can be estimated from the slope of a semilogarithmic plot of the ratios of the individual hydrocarbons versus the respective rate coefficients (k_{1i}) with OH. The ratios $[RH_i]_{t_2}/[RH_i]_{t_1}$ are formed from concentration pairs that are measured at Kappel at the time t_1 and at Schauinsland at the time t_2. Precondition for

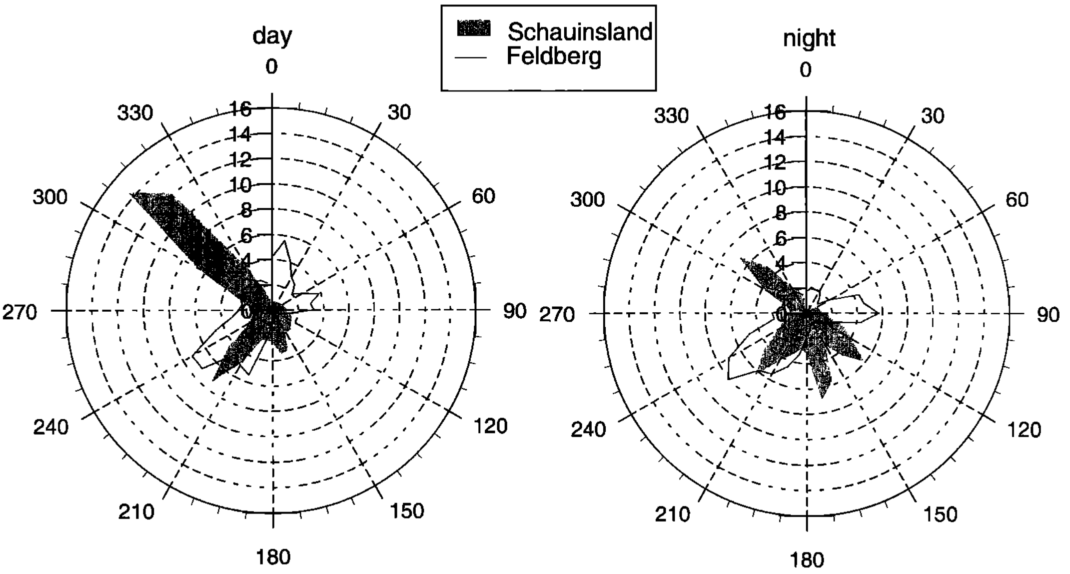

Figure 2. Wind rose at Schauinsland and Feldberg during summer: (left) day and (right) night.

determination of the OH concentration from the slope is the knowledge of the transport time $\Delta t = t_2 - t_1$ between the two points of measurement. The first-order dilution term, which is equivalent to a volumetric dilution factor ($k_d \Delta t = \ln (V_{t_1}/V_{t_2})$), is derived from the intercept with the ordinate. In 1992 the transport time was estimated from the local wind speed at Kappel and Schauinsland and by minimizing the overall variance in the semilogarithmic regressions made for all sets $[\mathrm{RH}_i]_{t1+\Delta t}/[\mathrm{RH}_i]_{t1}$ in the time interval when the valley wind system persisted [*Kramp and Volz-Thomas*, 1997].

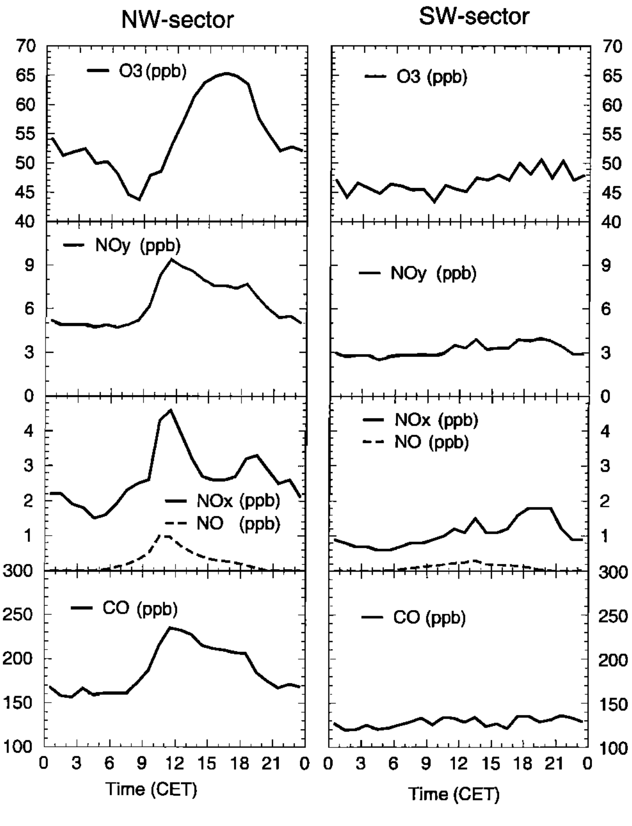

Figure 3. Average diurnal variation of O_3, NO_y, NO_x, and CO in summer for the two main wind sectors observed at Schauinsland.

In view of the large NO_x mixing ratio in the investigated air mass (70 ppb at Kappel and 15 ppb at Schauinsland), the OH concentration (5–8 × 10^6 molecules cm^{-3}) obtained from the hydrocarbon decay was surprisingly large. An analysis of the radical budget showed that the large OH was not sustained by the primary sources, even when including an estimate for HONO photolysis. As a possible explanation, it was postulated that amplification processes during the oxidation of hydrocarbons may lead to the production of more HO_x radicals (in the form of HO_2) than originally consumed in the reaction of the hydrocarbons with OH. In order to close the budget it was calculated that on the basis of the measured hydrocarbons 2 HO_2 radicals had to be formed in the course of the degradation of an initial RO_2 radical. Such a large amplification factor seemed unreasonable, and it was argued that biogenic VOCs other than isoprene, which were not measured in 1992, might have contributed to the HO_x recycling and radical amplification, in addition to the radical production from the ozonolysis of olefinic VOCs, for example, terpenes.

Uncertainties in the 1992 experiment were associated with the assumptions about the general transport path, the transport time, and the influence of mixing processes, in particular after total development of the boundary layer. In order to reduce these uncertainties, tracer experiments with SF_6 were conducted in the following years. The result of the preexperiments confirmed the assumption that the transport of polluted air from Freiburg to Schauinsland indeed proceeded through the valley Großes Tal. Transport time and dilution factor were found to be similar to those derived from the experiment in 1992.

On the basis of these encouraging results, SLOPE96 was planned and conducted in June 1996 with two intensive measuring campaigns (June 4–6 and 27). The different research groups and measurement systems that participated in the campaign are listed in Table 1, and Figure 4 gives a three-

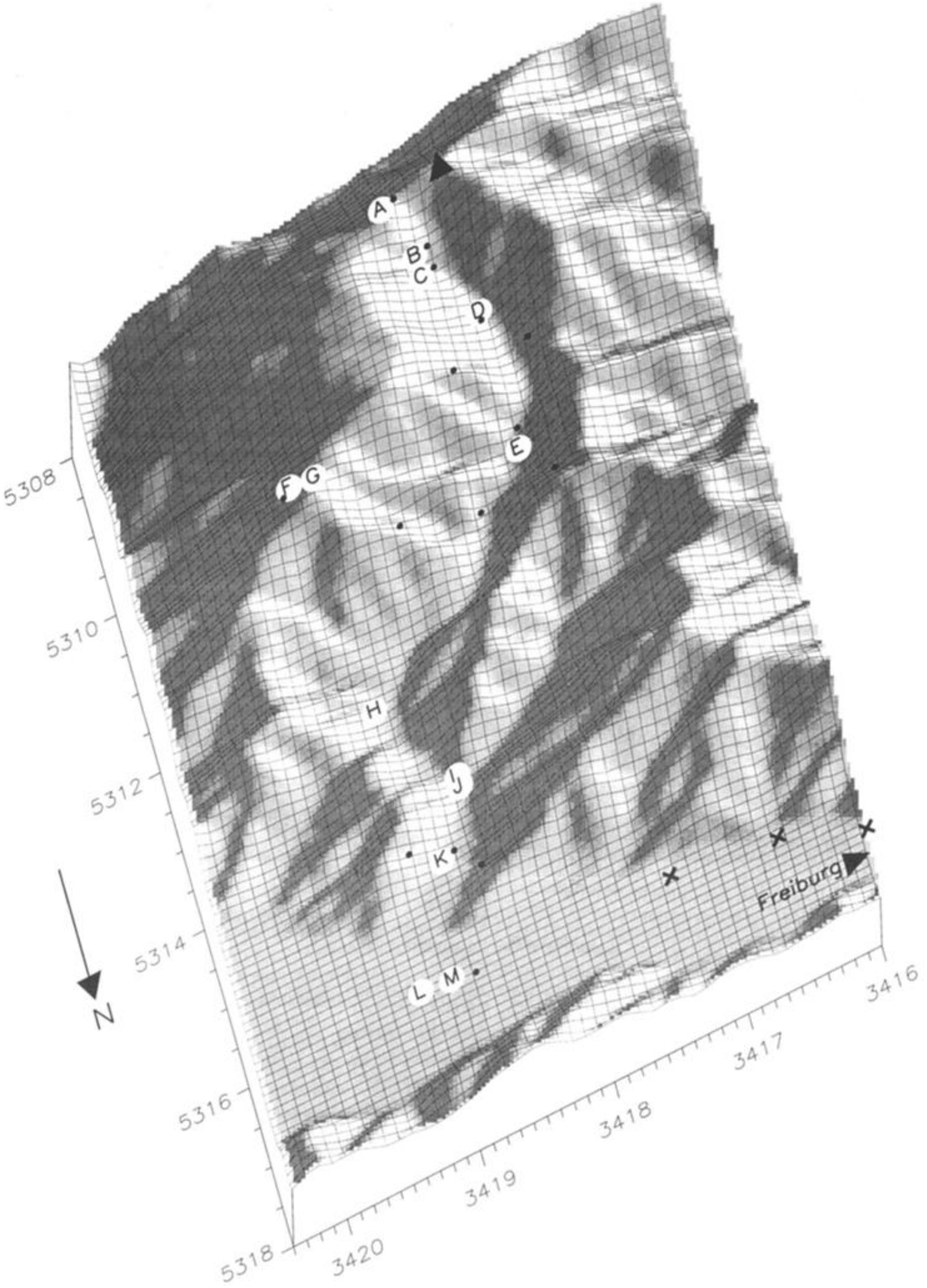

Figure 4. Three-dimensional map of the Großes Tal and parts of the Zarten Basin with the measurement sites during SLOPE96 (for explanation of the sites, see Table 1).

dimensional view of the valley with the measurement sites. Detailed ground-based chemical measurements were made at Kappel and Schauinsland. A relatively dense meteorological surface network was installed to analyze the development of the valley wind systems in the different valleys. Vertical profiles of ozone, NO_2, and meteorological parameters were obtained with remote sensing techniques (four SODARs and two ozone LIDARs) and from three tethered balloons. Airborne measurements of hydrocarbons, ozone, NO_2, and meteorological data were made aboard a small airplane. An inert tracer (SF_6) was released into the city plume of Freiburg to obtain quantitative information on advection and dispersion, and model calculations were carried out to support the interpretation of the meteorological phenomena and the behavior of the tracer. The analysis concentrated on the data from June 5, 1996, when clear air conditions led to the development of necessary up-valley winds, a prerequisite for the transport path from Freiburg via the Großes Tal to Schauinsland.

3. Summary of the Publications on SLOPE96

B. Kolahgar et al. (unpublished manuscript, 1999) describe the experimental methods used for determination of VOCs at the two surface sites and aboard the small aircraft. At each site

Table 1. Participants in SLOPE96 and Description of the Measurements Sites Shown in Figure 4

Symbol (Figure 4)	Height, m asl	Measuring System	Institution	Acronym
A	1230	TOR station Schauinsland (chemistry, meteorology)	Forschungszentrum Jülich—Institut fur Chemie und Dynamik der Geosphäre (ICG2)	ICG2
B	1060	meteorological tower	Uni Paderborn	UPB
F	980	SODAR	Forschungszentrum Karlsruhe—Institut für Meteorologie und Klimaforschung	IMK
G	995	meteorological tower	Uni Freiburg Geologisches Institut	MIF
C	980	meteorological tower	Uni Paderborn	UPB
D	830	ozone-LIDAR, SODAR	Forschungszentrum Geesthacht	GKSS
D	830	tethered balloon (O_3, meteorology)	Forschungszentrum Karlsruhe—Institut für Meteorologie und Klimaforschung	IMK
E	630	IFU measuring container	Fraunhoferinstitut für Atmosphärische Umweltforschung	IFU
H	495	tethered balloon (meteorology)	Uni Freiburg Geologisches Institut	MIF
I	392	launch site for Zeppelin (O_3, meteorology)	Uni Stuttgart—Institut für Statik und Dynamik der Luft- und Raumfahrt	IVD
J	385	tethered balloon (O_3, NO_2, meteorology)	Uni Stuttgart—Institut für Verfahrenstechnik und Dampfkesselwesen	IVD
K	354	mobile laboratory (chemistry, meteorology)	Forschungszentrum Julich—ICG2	ICG2
K		meteorological tower, SODAR	Forschungszentrum Jülich—ASS, Universität Köln, Meteorologisches Institut	ASS MIK
K		ozone-LIDAR	Max-Planck-Institut Hamburg	MPI
L	330	SODAR	Uni Freiburg Geologisches Institut	MIF
M	327	radio sonde	Forschungszentrum Karlsruhe—Institut für Meteorologie und Klimaforschung	IMK
X	327	SF_6 release sites	Forschungszentrum Jülich—ASS	ASS
●		SF_6-sampling sites	Forschungszentrum Jülich—ASS	ASS

a self-built gas chromatographic (GC) system with cryogenic preconcentration was operated in combination with a commercial GC (Airmotec HC1010) that achieves a better time resolution (20 min) but suffers from coelution and memory effects for some compounds. Another Airmotec GC was operated aboard the aircraft (time resolution 10 min). Measurements of (C_8–C_{15}) VOCs were made at the surface sites by GC-MS on samples collected on charcoal adsorption tubes. The data quality was explored on the basis of an instrument comparison using calibration standards and concurrent measurements in ambient air. Particular emphasis of the comparison was to identify those compounds that were measured by the three Airmotec instruments with a comparability of better than 10% to be used for the determination of OH.

The measurements of all systems were combined in order to obtain an estimate of the total VOC reactivity and the VOC/NO_x ratio. During the time when the city plume of Freiburg was transported through the Großes Tal, about 50% of the VOC reactivity was due to biogenic VOCs. The latter included a relatively large fraction from terpenes and from oxygenated compounds.

Pätz et al. [this issue] discuss the ground-based measurements of inorganic compounds and photolysis rates, and the chemical measurements made on the tethered balloons and aboard the aircraft. Again, an instrument comparison was conducted which was used for harmonization of the data sets for ozone and nitrogen oxides. Additional checks were made using situations in which the aircraft was in the vicinity of the Schauinsland station and of the tethered balloon.

From the measurements of NO, NO_2, NO_y, PAN, and HNO_3 at Schauinsland, an estimate of the noontime OH concentration of 1×10^7 cm^{-3} is derived with a simple quasi steady state model. The temporal behavior of the different NO_y compounds is well predicted by the steady state model when dry deposition for HNO_3 is included with a first-order loss term corresponding to a deposition velocity of 2–3 cm s^{-1}. The local ozone production rate as estimated at Schauinsland from the photostationary state of NO_x shows a positive correlation with the product of UV radiation (J_{NO_2}) and precursor concentrations (NO_x) with maximum values around 60 ppb h^{-1}.

M. Möllmann-Coers et al. (unpublished manuscript, 1999) describe the planning and conduction of the tracer experiment. The optimum release sites were found in preexperiments conducted between 1993 and 1995 and with the aid of model simulations with the Karlsruhe Atmospheric Mesoscale Model (KAMM) [*Fiedler*, 1993]. From simultaneous SF_6 and CO measurements made in the samples it is concluded that anthropogenic emissions in the Großes Tal are of negligible importance for the concentrations in the city plume of Freiburg.

Kalthoff et al. [this issue] discuss the results of the meteorological measurements and the tracer experiment. The data from meteorological surface sites and vertical soundings are used to analyze the temporal development of the valley wind system and the mixed layer height within the different valleys. The data show that from 0900 to 1200 central European time (CET) up-valley wind systems existed in the Großes Tal and in the Zarten Basin, leading to the transport of polluted air from Freiburg via the Zarten Basin and the Großes Tal to the Schauinsland mountain. Around midday, however, a larger-scale westerly flow above the Black Forest hills disturbed the up-valley wind system in the Großes Tal. This was of relevance for the interpretation of the temporal behavior of SF_6 and NO_x at Schauinsland.

From the tracer, SF_6, which was released between 0900 and 1030 CET at three sites in the Zarten Basin, the transport time

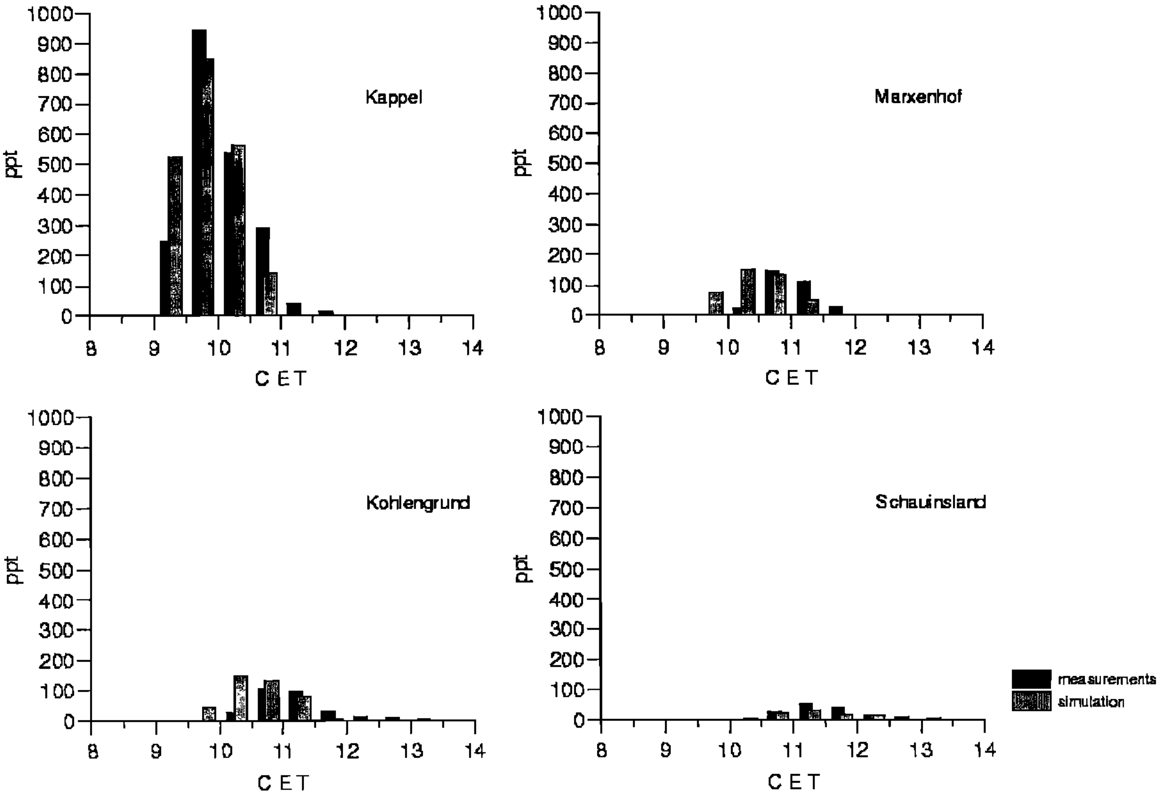

Figure 5. Comparison of the measured SF_6 concentrations in the Großes Tal with the model simulations (Marxenhof: site E, Kohlengrund: site D) [*Fiedler et al.*, this issue].

and dilution rate was calculated (Figure 5). At the entrance of the Großes Tal the peak of 942 ppt appeared between 0930 and 1000 CET. At Schauinsland the SF_6 peak of 79 ppt was detected between 1100 and 1130 CET. The transport time between Kappel and Schauinsland as derived by fitting a modified Gauss function to the observed SF_6 concentrations was 90 ± 5 min, corresponding to a propagation rate of 1.5 m s^{-1}. The SF_6 concentration was reduced during transport between the two sites by approximately a factor of 10.

The NO_x peak appeared between 0900 and 1030 CET at the entrance of the Großes Tal in coincidence with the SF_6 peak. At Schauinsland, however, the NO_x data revealed two peaks. A first but minor peak was detected before 1200 CET, together with the SF_6 peak. The major NO_x peak appeared much later at about 1300 CET. This was caused by the change in wind direction at 1200 CET, which led to advection of polluted air from the Rhine Valley. For this reason, only the data before 1200 CET could be used for calculation of OH concentrations from the hydrocarbon decay during transport in the Großes Tal.

Fiedler et al. [this issue] present model calculations, which support the observed meteorological phenomena and the behavior of the tracer in the investigated area. From the calculations it is concluded that the decrease in the SF_6 concentrations in the Großes Tal resulted from flow splitting of the airflow into a side valley of the Großes Tal, up-slope winds and mountain venting over the mountain ridges, and mixed layer growth during the transport of the tracer from the entrance of the Großes Tal to the Schauinsland (Figure 5). The observed disturbance of the valley wind in the Großes Tal at midday was caused by the formation of a larger-scale westerly flow due to the formation of up-slope winds on the Black Forest slopes of the Rhine Valley. In the course of the morning, these winds reached the edge of the Black Forest slopes and penetrated farther eastward into the Black Forest. As a result of this penetration of the larger-scale westerly flow, the transport of air masses did no longer take place via the valley wind systems from Freiburg via the Zarten Basin and the Großes Tal to Schauinsland, but directly from the Rhine Valley over the Black Forest slopes to Schauinsland.

Volz-Thomas and Kolahgar [this issue] utilized the data obtained on June 5, 1996, for estimation of the average OH concentration during transport between Kappel and Schauinsland. With experimental information about the chemical composition of the background air from the airborne VOC measurements and the dilution factor from SF_6, equation (3) was expanded using a simple mixing scheme:

$$\ln\left(\frac{[\mathrm{RH}_t]_S}{f\times[\mathrm{RH}_t]_K+f'\times[\mathrm{RH}_t]_B}\right)=-k_{1t}\times[\overline{\mathrm{OH}}]\times\Delta t \qquad (4)$$

$[\mathrm{RH}_t]_S$, $[\mathrm{RH}_t]_K$, and $[\mathrm{RH}_t]_B$ are the mixing ratios as measured at Schauinsland (t_2), at Kappel (t_1), and in the air above Kappel (t_1). Δt is the transport time between Kappel (t_1) and Schauinsland (t_2), and $f = 0.1$ is the reciprocal dilution factor. Both quantities are obtained from the SF_6 maxima at Kappel and Schauinsland (see above), and $f' = (1 - f)$ is the fraction at which the background air is admixed to the plume.

The resulting OH concentration of 7 × 10^6 cm^{-3} is 30% lower than that obtained without background correction, that is, using equation (3), still almost a factor of 2 larger than what is calculated with a chemical box model constraint by the measured trace gas concentrations and photolysis rates. The radi-

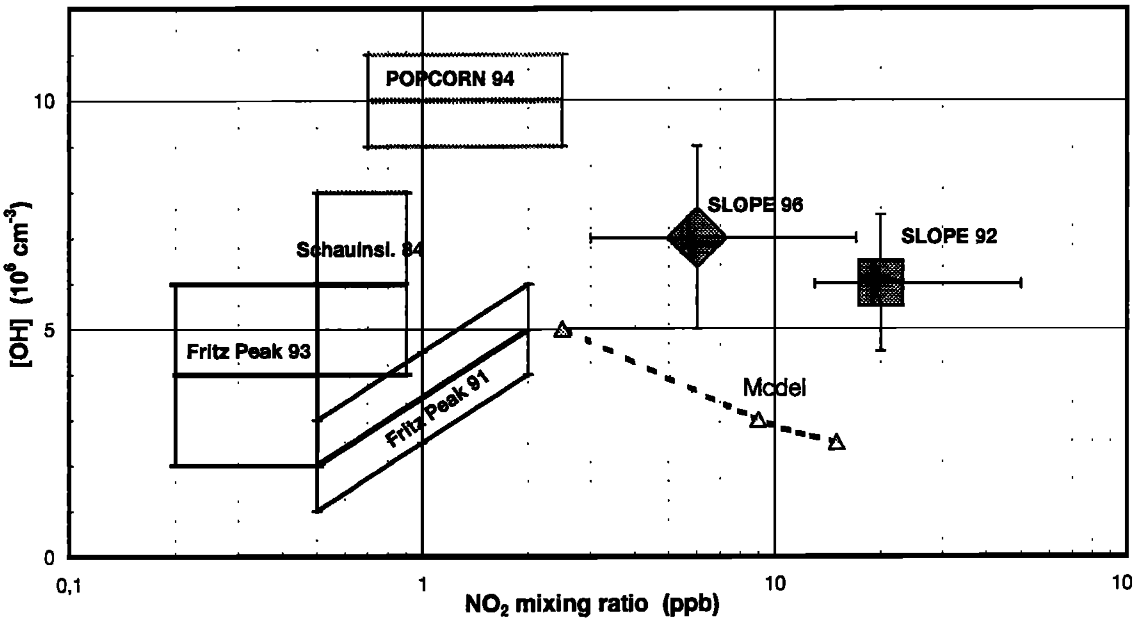

Figure 6. OH concentrations as measured at different locations with different techniques as a function of the prevailing NO_2 mixing ratio (see *Volz-Thomas and Kolahgar* [this issue] for details).

cal budget can be closed within the experimental uncertainties, when an upper limit is adopted for the photolysis of nitrous acid, in addition to the radical production from photolysis of ozone, H_2O_2, and carbonyl compounds as well as ozonolysis of unsaturated VOCs. Biogenic VOCs contribute significantly to the recycling of HO_x and represent, on average, about 50% to the total VOC reactivity measured at the surface sites. The results from SLOPE96, in particular the analysis of the tracer experiment, confirm the assumptions made in the analysis of the earlier experiment conducted in 1992, when noontime OH concentrations of $(6-8) \times 10^6$ cm^{-3} were derived in the presence of NO_x mixing ratios between 70 ppb at the entrance of the valley and 15 ppb at Schauinsland.

A comparison of the results obtained from SLOPE with direct measurements from different studies is shown in Figure 6. As discussed by *Volz-Thomas and Kolahgar* [this issue], the data qualitatively exhibit the theoretically expected dependence of [OH] on the NO_2 mixing ratio with a maximum around 1 ppb of NO_2, but seem to give larger OH concentrations in the high-NO_x regime than what is currently believed.

4. Conclusions

The valley Großes Tal between Freiburg and Schauinsland was used as an approximation of a chemical flow reactor in order to study chemistry and transport in the city plume of Freiburg. Transport and dispersion was quantified from a tracer experiment and detailed meteorological measurements, including vertical profiles at six different locations.

Relatively large concentrations of hydroxyl radicals are estimated from the decay of reactive hydrocarbons in the plume, which may point to as yet unknown processes. The radical budget can be closed, however, within the experimental uncertainties if sources of HO_x from the ozonolysis of alkenes and the photolysis of carbonyl compounds, H_2O_2, and HONO are included at their maximum rates allowed from the measurements or other estimates. Biogenic emissions seem to have a large influence on the total VOC reactivity in the valley, even at times when the city plume passes.

The tracer experiment and the interpretation of the meteorological data also allowed to confirm the validity of the assumptions made for the estimation of [OH] from the experiment in 1992. It seems therefore as if OH concentrations in the high-NO_x regime might indeed be substantially larger than what is currently assumed.

With appropriate nesting (from 5 km to 250 m grid spacing), the transport model KAMM is capable of describing the flow and dispersion of the tracer in the narrow valley, including the observed asymmetry perpendicular to the valley axis. The comprehensive data set collected during SLOPE96 provides a unique opportunity for the testing of chemical transport models. Future work will include modeling studies to investigate the potential causes for the large OH concentrations in the high-NO_x regime.

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