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Ozone and hydrogen peroxide during summer smog episodes over the Swiss Plateau: Measurements and model simulations

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Abstract. As part of the POLLUMET (Pollution and Meteorology in Switzerland) study, measurements of O_3 , NO_2 , and H_2O_2 were made at ground stations, by aircraft, and manned hydrogen balloons to characterize the photochemical processes prevailing during times of high ozone production. During summer smog episodes, elevated ozone concentrations were found over the whole area of the Swiss Plateau, which is a densely populated and industrialized region. However, NO_2 concentrations were generally at a low level in the afternoon. An increase of hydrogen peroxide concentration in the mixing layer during photochemical episodes was observed. To understand better the photochemical processes which control ozone formation over the Swiss Plateau, calculations with the Harvard photochemical model and the Harwell photochemical trajectory model were conducted. A comparison of model results with measurements of the triad O_3 , NO_2 , and H_2O_2 indicates an ozone formation under low NO_x conditions.

1. Introduction

The Swiss Plateau, located between the mountains of the Alps and the Jura, is a large, densely populated and industrialized valley (Figure 1). The topography restricts ventilation and stimulates the development of summer smog episodes. Surface ozone levels exceed regularly the air quality standard (62 ppb, allowed to be exceeded once an hour within a year). In 1989 a coordinated research effort was started to investigate ozone formation over the Swiss Plateau. The program POLLUMET (pollution and meteorology) was centered around several intensive observation periods (IOPs) in the summer months. The objective of the IOPs was to identify the processes regulating ozone concentrations.

Ozone is produced rapidly in polluted air by photochemical oxidation of volatile organic compounds (VOC) in the presence of nitrogen oxides ($NO_x = NO + NO_2$). The production may be limited by the availability of NO_x (low- NO_x regime) or VOCs (high- NO_x regime). One of the key questions related to the occurrence of high-ozone episodes over the Swiss Plateau is whether ozone production is VOC or NO_x limited. Photochemical model calculations by Kleinman [1986, 1991] indicate that peroxides represent a sensitive indicator of low- versus high- NO_x regime. Therefore concurrent measurements of O_3 , H_2O_2 , and NO_2 concentrations should help to determine the regime for O_3 production.

In this study we present measurements of O_3 , H_2O_2 , NO_2

concentrations, and meteorological parameters over the Swiss Plateau from the surface through the mixed layer to the troposphere above the boundary layer. Airborne measurements were made with a manned balloon and a motor glider. The observations are interpreted using photochemical models to determine the regime for O_3 production.

2. Chemistry

The atmospheric oxidation of hydrocarbons (RH) produces ozone in the presence of NO_x :

The mechanism requires the presence of HO_x radicals ($OH + HO_2$). The major sources of these radicals are the photolysis reactions

Loss of NO_x and HO_x is by (R8)–(R11):

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Figure 1. Map of the Swiss Plateau with the Organization for Economic Cooperation and Development grid. Principal urban centers and selected measuring stations are shown. The star indicates the Bernese grid cell.

The NO_x and HO_x radicals are chain carriers in the ozone production (reactions (R1)–(R7)), while the hydrocarbons are consumed. If the NO_x concentration is low, the termination reactions (R8) and (R9) compete with the chain reactions (R2) and (R3), leading to the production of peroxides (low-NO_x regime). If the NO_x concentration is high, (R10) scavenges OH (high-NO_x regime), suppressing the formation of peroxides. Measurements of peroxide concentrations offer thus a diagnostic tool of the photochemical regime.

3. POLLUMET Field Campaigns

Two field studies were conducted in the summer of 1990 (June, July) and 1991 (July, August). There were two types of measurements: (1) routine measurements taken throughout the 2-month period and (2) additional measurements during the 2- to 5-day intensive observation periods (IOP90 from July 23 to July 30, 1990, and IOP91 from July 9 to 11, 1991). Routine data included the Automatic Network of Weather Stations (ANETZ and ENET) and the surface air chemical monitoring network operated by the Swiss federal and cantonal authorities. The IOPs included additional measurements at the Schüpberg ground station, which is situated on a hill in the central part of the Swiss Plateau (see Figure 1), and airborne measurements with a manned balloon in 1990 and with a motor glider in 1991. Table 1 lists the instrumentation aboard the balloon and the motor glider.

IOP90 was timed at the end of a 2-week-long anticyclonic situation and encompassed the Swiss Plateau from the Lake of Geneva in the west to the region of Zurich in the east; for a detailed description of the meteorological situation, see Wanner *et al.* [1993]. IOP91 covered the buildup of a weak anticyclone and was confined to the region of Bern, the central part of the Swiss Plateau; it was aimed to gather a detailed cross section from the Jura Mountains to the Alps.

3.1. Instrumentation

Ground-based measurements of peroxides were made with a dual-channel instrument similar to the one described by Lazrus *et al.* [1986]. Ambient air at a rate of 2 L/min was drawn through a glass coil, 1.5-mm diameter times 50 cm in length, where gas phase peroxides dissolved in bidistilled water. The peroxides form a fluorescent dimer of 4-ethylphenol in the presence of the enzyme peroxidase. The dimer is detected by its fluorescence at 400 nm. To control baseline drifts, the flow injection analysis technique was used. Calibration was routinely performed with aqueous standard

Table 1. Instrumentation of Airborne Platforms

Component	Balloon Cruises (IOP90)	Light Aircraft (IOP91)*
Pressure	Rosemount, capacitive	Rosemount, capacitive
Temperature	Vaisala, capacitive	Meteolabor, thermocouple
Humidity	Vaisala Humicap	chilled mirror
Ozone	UV absorption	UV absorption
NO ₂	Luminex LMA-3	Luminex LMA-3
H ₂ O ₂	enzymatic fluorimetry	enzymatic fluorimetry

*A detailed description of the light aircraft is given by Neininger and Fuchs [1994].

solutions of H₂O₂ assuming a collection efficiency of 100% [Heikes, 1992]. After the coil the liquid sample was split into two channels. The first channel measured H₂O₂ and partly organic peroxides (see below). The second one passed a small column (ID 1.5 mm, length 15 mm) filled with MnO₂-coated Al₂O₃ (grain size 0.5 mm) which specifically destroys H₂O₂ with an efficiency > 97%, CH₃OOH by only 5%, and hydroxymethyl hydroperoxide (HMHP) by 30% at most. The instrument had a detection limit of 0.1 parts per billion by volume (ppbv) and a time resolution of 5 min. Measurements at the beginning of the field campaign in summer 1990 revealed that the signal of the second channel hardly exceeded the detection limit. Because of operational problems we then removed the MnO₂ catalyst and measured with two channels in parallel.

For the balloon cruises and especially for the motor glider we built a special low-weight to low-power diffusion denuder system (DS) with a gas phase flow injection analysis configuration [Dasgupta *et al.*, 1988; Sigg *et al.*, 1992a, b]. The instrument contains an automatic gas phase calibration system. This is a Henry equilibrator, consisting of a 50-cm-long microporous polypropylene tubing (Accurel) immersed in an aqueous H₂O₂ solution which is thermostated to 5°C by Peltier elements. The resulting H₂O₂ partial pressure is calculated using the data of Lind and Kok [1986]. Zero air and calibration gas enter the sample inlet tubing only 5 cm after the inlet point. This configuration accounts for possible H₂O₂ losses in the inlet tubing. Air aspirated continuously by the intake pump is alternately ambient air, zero air, or calibration gas.

The balloon monitor was constructed as a dual-channel instrument with two Nafion tubes in the glass pipe of the diffusion scrubber. Similar to the coil system, one channel passed a small MnO₂ column which removed quantitatively H₂O₂ (>98%) in the liquid stream. Because of operational problems the organic peroxide channel worked only during the third balloon cruise. Because of space and weight restrictions in the pods of the motor glider, only a single-channel instrument could be constructed for that purpose.

The detection limit of the DS under laboratory conditions is 0.05 ppbv and the precision for ambient air with 1 ppb of H₂O₂ is better than 5%. The system is linear in the range 0.1–10 ppbv. Under field conditions, performance cannot be maintained at this high level, mainly due to temperature drifts. The detection limit is at 0.1 ppbv and the precision at 1 ppbv better than 10%. The coil system and the DS have been compared under field conditions and gave agreement within 10% [Sigg and Nefel, 1993]. An interference of 0.4% to ozone has been determined for the DS. The accuracy of the DS critically depends on the Henry constant used to calculate the concentration of the internal calibration source. The reported values in the literature differ by more than 30% [Staffelbach *et al.*, 1993], and the accuracy of the H₂O₂ measurement is no better than the uncertainty in the determination of the Henry coefficient.

The H₂O₂ measurements are subject to interference due to organic peroxides as listed in Table 2. The sensitivity to HMHP and CH₃OOH depends critically on the concentration of peroxidase and 4-ethylphenol as well as the reaction time. The coil system had a reaction time of 40 s, whereas the single-channel DS used in the light aircraft had a reaction time of only 15 s. The peroxidase concentration used was rather low. Because of these operational modes the DS

Table 2. Interference of Methylhydroperoxide (MeOOH) and Hydroxymethyl Hydroperoxide (HMHP) to the H₂O₂ Signal

	Standard Solution	Coil System	Diffusion Scrubber System
H ₂ O ₂	1	1	1
HMHP	0.4–0.6	0.6	0.15–0.3
MeOOH	0.25	0.15	0.02–0.05

Numbers given are H₂O₂ equivalent per unit of organic peroxide.

system showed a quite good discrimination against soluble organic peroxides. Although the coil system showed higher interferences to organic peroxides, initial measurements with the MnO₂ scavenging technique (see above) showed that signals hardly exceeded the detection limit (<1% H₂O₂ equivalent). All reported H₂O₂ data in this paper are therefore given without corrections for organic peroxides. Such a correction would have been difficult because the mixture of organic peroxides is not known.

The ozone monitors on the balloon and the motor glider were miniaturized UV photometers, which were calibrated before and after each study against a MonitorLabs 8910. For the airborne NO₂ measurements only the Luminol instrument (LMA-3, Scintrex/Unisearch) met the requirements of fast response (1 s), high sensitivity (<0.1 ppbv), low-power consumption and low weight [Drummond *et al.*, 1989]. The luminol technique suffers from an ozone and a peroxyacetyl-nitrate (PAN) interference; the ozone interference is about 0.3% of O₃ for zero NO₂ but can vary with luminol solution. PAN interference has been reported to be around 25% of PAN [Kelly *et al.*, 1990]. The baseline of the system is very sensitive to temperature changes, despite a built-in signal processing which is intended to compensate temperature changes. Although ozone interference was corrected, the NO₂ concentrations measured with the small aircraft have still an uncertainty of 1.5 ppbv in the baseline.

The motor glider Stemme S10 VC, owned by the Swiss company MetAir, was described by Neininger and Fuchs [1994]. Chemical and meteorological instruments have been installed in two pods attached below the wings.

At some ground stations, commercially available differential optical absorption systems (DOAS) from the Swedish company OPSIS, which measured O₃, NO₂, and SO₂, were used. For the NO₂ measurements we determined a precision of ±0.2 ppb at an integration time of 1 min. The offset had an uncertainty of ±0.5 ppb.

4. Experimental Data

4.1. Ground-Based Measurements

To put things into perspective, we present the data from the rural station Schüpberg, northwest of the city of Bern, which we consider as representative of the regional pollution over the Swiss Plateau. It is located in a gently hilly agricultural area 100 to 200 m above the lowest and also flattest part of the Swiss Plateau. Figures 2a and 2b show the O₃, NO₂, H₂O₂, and H₂O concentrations registered at this station. Two main differences emerge comparing the data from 1990 and 1991: (1) The water vapor and H₂O₂ concentrations were considerably lower during IOP90 than during

Figure 2. Concentrations of O_3 , NO_2 , H_2O_2 , and H_2O at the rural site Schüpberg. (a) 1990: NO_2 was measured by DOAS (OPSIS analyzer), O_3 with a DASIBI RS1008, and H_2O with a conventional relative humidity instrument (Rotronic). H_2O_2 was measured with the system described in the text. Accuracy: $\text{O}_3 = 3$ ppb; $\text{NO}_2 = 0.5$ ppb. (b) 1991: NO_2 was measured with a Scintrex LMA-3. Because of problems with luminol solutions the offset might reach 2 ppb.

IOP91. H_2O_2 concentrations ranged between 0 to 3 ppb in 1990, while it reached 6 ppb in 1991; (2) IOP90 took place at the end of a period with elevated ozone concentration, while IOP91 covered the buildup of a “summer smog” episode. During such periods of 3–5 days the buildup of ozone concentration usually levels off around 80–100 ppb [Künzle and Neu, 1994].

In 1990 H_2O_2 concentrations increased during the two episodes July 18–23 and 24–26 at a rate of about 0.3 ppb/d.

Because of operational problems we could not follow the full buildup during IOP91.

Mean average NO_2 concentrations in the afternoon at the Schüpberg station fell below 1 ppb. Even more, DOAS instruments of cantonal authorities located in the city of Bern and the semirural area of Worb also recorded values of similar low concentrations. It should be pointed out that in the case of the Swiss Plateau the rural character of a location is relative in view of the dense population. Table 3 summa-

izes the average NO₂ concentrations from July 21 to July 28, 1990, observed for these three types of sites for the afternoon hours from 1300 to 1700 LT; in the case of the city of Bern the time interval was limited to 1600 LT.

4.2. Balloon H₂O₂ Measurements

Figure 3 shows the tracks of the three cruises performed on July 23, 25, and 27, 1990. The balloon started at Attisholz, 25 km northeast of our research station Schüpberg, and led on July 23 and 25 close to Schüpberg, whereas on July 27 the balloon flew in the opposite direction. Figure 4 compares the H₂O₂ measurements of the Schüpberg ground station with those of the balloon flight on July 23. After the start the balloon was transported by the easterly winds close to the ground to the west along the Jura Mountains. Around 1400 LT the inversion layer was crossed and due to the northwesterly winds in the upper layer the direction changed to southeast. There existed a marked difference in H₂O₂ concentration between the lower and the upper layer of air. As long as the balloon flew in the lower layer, from 1130 to 1400 and before landing at 1630 LT, similar concentrations as in Schüpberg were observed, whereas in the upper layer, concentrations 2 to 3 times as high were measured. At 1500 LT the balloon was exactly over the Schüpberg site. Because of technical problems, O₃ could not be measured during the whole cruise and the measurement signal exhibited considerable noise. Nevertheless, it can be seen that the ozone concentration did not show a shift going from the lower to the upper layer. Ozone concentration at Schüpberg agreed with the balloon measurements in the boundary layer (see Figure 2a). The double-layer structure is not a local but a larger-scale feature. Trajectory calculations of the Deutsche Wetterdienst model for 900, 850, and 700 hPa over a 48-hour period exhibited a counterflow situation. While concentrations of ozone in both layers were similar at around 90–100 ppb, those of hydrogen peroxide were very different.

The second balloon cruise on July 25 (Figure 5) showed a fairly regular increase of the hydrogen peroxide concentration from 0.5 to 2 ppb during the day, although the height of the flight track varied between 500 and 2000 m mean sea level (msl). The mixing layer extended up to 1600 m msl. A sharp rise in the H₂O₂ concentration was observed around noon above a small forested hill (Büttenberg), where thermal upwelling carried the balloon up by 200 m. A second sharp rise was observed as the balloon landed in a forest of beech and Norway spruce; the concentration during descending stayed almost constant at 1.9 ppb but jumped to 4 ppb as soon as the basket of the balloon dove into the top of the trees. After we transported the basket out of the forest to a meadow, the concentration dropped to 1.6 ppb. This points to a local phenomenon, which could be explained with

Figure 3. Tracks of the three balloon cruises on July 23, 25, and 27. Axis labels are Swiss kilometer coordinates.

peroxide production from the oxidation of biogenic alkene emissions [Hewitt and Kok, 1991; Lee et al., 1993].

The third flight on July 27 (Figure 6) followed along the Jura Mountains in the northeastern direction until the city of Olten, a region with a lot of traffic and industry, before it turned east into a rural area. This day the inversion layer stayed rather low at around 1200 m msl. Hydrogen peroxide concentrations were the highest of all three flights, both in the boundary layer and above the inversion layer. Although the Schüpberg ground station also showed the highest value of these days, it still was 40% less than at the landing site of the balloon. Again, there is a marked difference in concentration between the upper and the lower layer. During this flight the organic peroxides could be measured. It is seen that the concentration expressed as H₂O₂ equivalents remains below 0.3 ppbv. Therefore due to the good discrimination between H₂O₂ and organic peroxides of the DS system the contribution to the H₂O₂ signal is minor, even though the concentration of organic peroxides might be as high as that of H₂O₂.

4.3. Motor Glider Measurements, 1991

Flights were conducted twice daily (midday and late afternoon) in the Bernese region, along a track extending from the Jura mountain Chasseral and the high-Alpine research station Jungfrauoch. Figure 7 depicts the vertical profile of this flight track together with the H₂O₂ concentration. Vertical soundings were not over a fixed location, but ascents form the Bernese region to Jungfrauoch. Figure 8 presents the sequence of such vertical profiles during IOP91 of temperature, potential temperature, water vapor mixing ratio, O₃, NO₂, and H₂O₂. The temperature and water mixing ratio profiles indicate a multilayered lower troposphere. It is interesting to note that there is no correlation between ozone and hydrogen peroxide concentrations above the inversion layer. The second flight of July 10 shows, for instance, a strongly enhanced layer of H₂O₂ between 1500 m msl and 2500 m msl which is not followed by a change in ozone concentration. The same feature can be observed on July 12 around 3500 m msl. A close flyby at the high-Alpine research station Jungfrauoch, which was equipped with a H₂O₂ monitor, showed in that case comparable concentrations for the top layer, confirming the reliability of the motor glider measurements [Lehmann et al., 1992]. Figure 9 shows the correlation of H₂O₂ with dew point for all data above the

Table 3. Average NO₂ Concentrations Between 1300 and 1700 LT from July 21 to 28, 1990, at a Rural (Schüpberg), Semirural (Worb), and Urban (Bern, Only 1300–1600 LT) Site

Station	Characterization	NO ₂ , ppb	σ_c
Schüpberg	rural	0.84	0.9
Worb	semirural	1.1	0.93
Bern	urban	3.5	1.5

Figure 4. Comparison of balloon H_2O_2 data with measurements at Schüpberg on July 23. MESZ is local time.

mixing layer. For comparison, calculated steady state hydrogen peroxide concentrations for the free troposphere for 20 and 200 ppt NO_x are depicted as given by *Daum et al.* [1990]. The calculated concentrations do not take into account wet and dry deposition processes and thus represent upper limits. It is seen that several data sets are falling into that range, e.g.: (1) the high H_2O_2 concentration layer on July 10 (flight 2); July 11 (flight 2); July 12 (flight 1), the top layer with a low dew point but also the range between 1200 and 3500 m msl with a much higher dew point; and July 12 (flight 2).

The values below this range may have two reasons.

1. The system has not yet built up to a steady state. For some measurements near water vapor saturation conditions existed and therefore variable amounts of H_2O_2 may have been previously removed by aqueous phase reactions; for example, July 9 was fairly cloudy and a front moved over the Swiss Plateau.
2. The NO_x level is higher than 200 ppt, thus suppressing peroxide production. Because the NO_2 measurements with the motor glider exhibited a large uncertainty below 1.5 ppb, this could not be examined.

Figure 5. Balloon results from July 25.

Figure 6. Balloon results from July 27.

Concentrations increased between the two daily flights, most pronounced in the mixing layer, and also increased over the 4-day period from July 9 to 12. A statistical summary of the hydrogen peroxide measurements divided into values within and above the mixed layer is given in Table 4. In Table 5 we give an estimate of the H₂O₂ increase in the mixed layer due to photochemical production between the two daily flights. On July 10 a strong inversion layer around 1200 m msl was present between the two flights and prevented, to a high degree, air exchange between the planetary boundary layer (PBL) and aloft. The observed increase of 1.1 ppb of the median in the PBL is therefore attributed to photochemical production. On July 11 and 12 the mixing layer grew from 1200 m msl to over 2200 m msl between flights. Entrainment of air will therefore increase the H₂O₂ concentration in the mixed layer. We assume that the median H₂O₂ value of the first flight above the mixed

layer corresponds to the reservoir concentration which is mixed into the PBL during the rise of the mixing height. The photochemical contribution to the increase of hydrogen peroxide in the mixed layer is estimated as the difference between the concentration in the 500- to 2200-m column between the first and the second flight.

The measurements at the Schüpberg site yielded peak H₂O₂ concentrations of 4–6 ppb on July 10–12, exceeding the flight data. We could not find an instrumental artifact to explain this difference. Water soluble organic peroxides produced from biogenic VOC emissions might be the cause of this observation. The Schüpberg station is situated in an agricultural area and no strong anthropogenic VOC sources are nearby.

The NO₂ profile from the July 12 flight exhibits characteristic features of many of the airborne measurements. The late morning flight shows, below the inversion layer, concentrations up to about 10 ppb, whereas above it, they drop below 2 ppb. During the afternoon the concentration below the inversion layer, which by then had risen to 2200 m msl, had also decreased mostly below 1 to 2 ppb. As mentioned earlier, an overestimation of up to 1.5 ppb is possible.

Figure 7. Vertical profile of the first flight of July 11. Size of symbol is proportional to H₂O₂ concentration.

5. Model Calculations and Comparison With Experimental Data

5.1. Model Description

For further interpretation of the data we used 1-dimensional (vertical) boundary layer simulations with the Harvard photochemical model and the Harwell photochemical trajectory model (HPT-M). The Harvard model has been used extensively for simulation of tropospheric chemistry observations [e.g., Fan *et al.*, 1994]. The version used here is based on recent compilations of kinetic and photochemical data [Atkinson, 1990; DeMore *et al.*, 1992; Atkinson *et al.*, 1993]. The UV radiation field is computed with a six-stream code for the Rayleigh scattering atmosphere at 47°N in July

Figure 8. Vertical profiles of (a) temperature, potential temperature, water vapor mixing ratio, and (b) O_3 , NO_2 , and H_2O_2 from motor glider measurements in the region of Bern between July 9 and 12, 1991. Shaded segments represent height of layers.

Figure 8. (continued)

Figure 9. H₂O₂ as a function of dew point for all motor glider flights. Data included are above mixing layer given in Table 4. Solid curves are computed H₂O₂ concentrations for the free troposphere by Daum *et al.* [1990] assuming NO_x concentrations of 20 and 200 ppt. Areas indicated are (1) flight 2, July 10, layer with high H₂O₂ concentration; (2) flight 1, July 12, 1200–3500 m msl; (3) flight 1, July 12, above 3500 m msl; (4) flight 2, July 12.

(solar declination is 22°), assuming clear-sky conditions and an O₃ column of 330 Dobson units (DU) [Hilsenrath *et al.*, 1979]. The planetary boundary layer is represented by six layers of different spacing, and transport between layers is simulated with eddy diffusion coefficients (Figure 10). The maximum diurnal depth of the mixed layer was taken as 1300 m, based on data from IOP90 [Künzle and Neu, 1994]. Temperature and water mixing ratios in the different layers were adapted to the observations. A number of gases are removed to the surface with specified dry deposition velocities (Table 6).

The Harwell photochemical trajectory model HPT-M [Derwent and Jenkin, 1990] is a two-layer trajectory model for the boundary layer. Chemistry is restricted to the lower layer (mixed layer); the upper layer is treated as an inert reservoir entraining in the lower layer in the daytime. The depth of the lower layer varies diurnally from 300 m at night to 1300 m in the afternoon. The chemical mechanism de-

Table 5. Estimation of Observed H₂O₂ Increase in the Mixed Layer due to Photochemical Production and Calculated Values

Flight Observed*	July 10 1.1	July 11 1.2	July 12 2.0
Model calculation†	0.6	0.6	0.5
Day	day 3	day 4	day 5

*Average height of ground level is 600 m msl.

†Differences are taken from 1000 and 1600, because local time is solar time plus 2 hours.

scribed by Derwent and Jenkin [1990] was slightly modified using the new compilation of rate constants for the inorganic reactions [Atkinson *et al.*, 1993]. The photolysis rates of NO₂, H₂CO, and O₃ to O(¹D) were adopted from the Harvard model.

Emissions of NO_x, fractionated hydrocarbons, and CO were specified with 50 km × 50 km resolution from the inventory developed by the Organization for Economic Cooperation and Development (OECD) [Lübker *et al.*, 1989]. This inventory, compiled for the year 1980, has been updated for Switzerland by the Federal Office for the Environment, Forests and Landscape (BUWAL) for the summer 1990 [Rosset and Kerr, 1993]. Natural organic emissions were not included in the emission inventory. Anthropogenic VOC emissions (ng C/m² s) over the Swiss Plateau in summer are about 5 times higher than biogenic VOC emissions, which are mainly terpenes [Andreani-Aksoyoglu and Keller, 1994].

5.2. Trajectory Studies

The July 24–26, 1990, period was characterized by anticyclonic conditions, clear skies, and slow easterly winds, lending some justification for a 1-dimensional modeling approach. Episodes with high ozone levels are often related to such meteorological situations. We considered a boundary layer column arriving at Schüpberg (Bern) on the evening of July 26 and estimated the transport history of that air column over the past days using trajectory analyses from Neu [Künzle and Neu, 1994] over Switzerland and from the Deutsche Wetterdienst over Germany. It appears from these analyses that the boundary layer column over Schüpberg on July 26 had originated over southeast Germany three days before. We computed the photochemical evolution of the boundary layer column along this 3-day trajectory assuming

Table 4. Statistical Summary of H₂O₂ Concentration (parts per billion by volume) Above and in the Mixing Layer (ML) of All Motor Glider Measurements Between July 9 and 12, 1991

Flight, LT	Mixing Layer Height, m msl	Above ML			Within ML		
		Median	50% Range*	Range	Median	50% Range*	Range
July 9, 1359–1536	1200	1.9	1.9–1.9	1.4–2.0	1.6	1.4–1.8	1.1–2.2
July 9, 1710–1935	1600	1.5	1.2–1.9	0.8–2.9	1.5	1.2–1.8	0.8–2.4
July 10, 1039–1344	1500	1.6	1.3–1.9	1.0–2.5	0.6	0.4–0.8	0.3–2.7
July 10, 1738–1943	1500	2.2	2.0–2.4	1.7–5.4	1.7	1.5–1.9	1.3–2.4
July 11, 0946–1242	1200	2.6	2.2–3.0	1.2–4.2	2.0	1.6–2.4	0.2–3.6
July 11, 1528–1841	2300	3.0	2.8–3.2	2.6–3.5	3.6	3.2–4.0	2.2–4.7
July 12, 1040–1228	1200	2.2	1.2–2.9	1.1–4.1	1.3	1.2–1.7	0.4–2.7
July 12, 1502–1629	2200	2.9	2.2–3.6	2.1–3.6	3.9	3.7–4.2	2.0–4.3

*Range of the middle half of the data.

Figure 10. The six model levels, the diurnally varying exchange coefficients, and mixing height used in the Harvard photochemical model.

clear skies and specifying temperature, humidity, and boundary layer height from meteorological data along the trajectory. Figure 11 shows the time series of surface ozone computed with the HPT-M for July 24–26, together with observations at rural sites along the trajectory of the air column. The model is successful at reproducing the observed daily maxima. Concentrations of NO₂ at Schüpberg in the model were around 1 ppb, in agreement with measurements (Figure 2, Table 3).

We defined the transition between the NO_x- and the VOC-limited regimes for O₃ production by conducting simulations with emissions modified by fractional increments from the base case (taken as 100%). We chose for this purpose an idealized trajectory starting over the Lake of Constance at 1800 LT and reaching the area of Bern at late afternoon of the following day. Initial concentrations are given in Table 7. The resulting isopleths of ozone and H₂O₂ concentrations after one day are shown in Figure 12. We see that the H₂O₂ concentration is a sensitive indicator of photochemical regime, decreasing rapidly as ozone production evolves from low-NO_x to high-NO_x regimes. The base case in the HPT-M is on the ridge of the transition region between NO_x- and VOC-limited O₃ production; in the

Figure 11. Calculation of the ozone concentration along a trajectory from the Thüringerwald, Munich, to Lake of Constance, Zürich, into the region of Bern on July 24–26, 1990. Symbols correspond to ground-based measurements along the trajectory: solid circles, Brotjackriegel; crosses, Stuelegg; asterisks, Friedrichshafen; open circles, Haselberg; open triangles, Hohenrain; diamonds, Bleichenberg; squares, Langenthal; pluses, Schupberg; solid triangles, Payerne.

Harvard model the base case is more squarely in the low-NO_x regime. This difference between the two models appears to reflect principally the more rapid dilution of NO_x emissions in the Harvard model during daytime and the reduced O₃ deposition due to restricted dilution during nighttime. H₂O₂ concentrations in the models are in the range of the observed values, although this agreement reflects in part the initial conditions; the simulated increase in day-to-day peak concentration in the mixed layer is in agreement with observations. For this calculation a low-deposition velocity, 0.5 cm/s, as for ozone was used. There have been few measurements of H₂O₂ dry deposition velocities; however, the limited studies suggest that it is higher in a manner similar to that of HNO₃. Therefore the computed increases of H₂O₂ reflect upper limits. Higher-deposition rates of 2 cm/s decrease H₂O₂ production by ~0.3 ppb for the Harvard model and 0.5 ppb for the HPT-M, respectively. In this case, the HPT-M would predict no net peroxide production over 24 hours. However, at Schüpberg, increas-

Table 6. Dry Deposition Velocities (centimeters per second) Used in the Harvard and HPT Models

Species	Multiday Calculation		Trajectory, Day/Night
	Day, 0600–1800 ST*	Night, 1800–0600 ST	
O ₃	0.6	0.12	0.5
H ₂ O ₂	2.0	0.4	0.5
CH ₃ O ₂ H	0.5	0.1	0.2
Other peroxides	0.2	0.04	0.2
NO ₂	0.4	0.08	0.15
Peroxyacetylnitrates (PAN)	0.2	0.04	0.2
Aldehydes	0.2	0.04	0.2
HNO ₃	†	†	2.0

*ST, solar time.

†Deposition velocities are calculated by means of the resistance analogy with R_c (surface resistance) = 0; 24-hour average deposition velocity is 1.2 cm/s, during daytime 5 cm/s.

Table 7. Initial Concentrations in parts per billion (ppbC VOC) for the Multiday Calculations of the Harvard Model and for the Trajectory Calculations of Both Models

Species	Multiday Calculations	Trajectory
O ₃	40	78
NO ₂	0.7	0.7
NO	0.08	0.08
CO	200	250
H ₂ O ₂	1.0	1.6
CH ₃ O ₂ H	0.4	0.4
PAN	0.6	0.6
HNO ₃	0.07	5.1
CH ₄	1700	2000
VOC	11.2	11.2

The values for the latter are the concentrations after the initialization run over southern Germany.

Figure 12. Ozone (solid curves) and H₂O₂ (dashed) isopleths as a function of NO_x/volatile organic compound (VOC) emissions relative to the base year 1990 calculated from (a) the HPT-M and (b) the Harvard photochemical model. Concentrations are in parts per billion by volume. In parentheses are the differences between initial and final concentrations (23 hours). For the Harvard model, concentrations are given for the lowest layer.

ing hydrogen peroxide concentrations were observed during two periods of easterly winds.

Figure 13 shows the dependence of the calculated NO₂ concentration at the time of the ozone maximum from the HPT-M (cross section of Figure 12 at the 100% VOC level). In the low-NO_x regime the NO₂ concentration dependence from the emissions is weaker than in the high NO_x regime. The turning point happens around 150% NO_x/100% VOC. Our NO₂ measurements with the DOAS instrument are in agreement with the low-NO_x branch of this curve (see Table 3).

Flight measurements in 1991 yield information across the Bernese area and the temporal development between morning and afternoon. To understand the photochemical activity, we performed model simulations with the Harvard model under the approximation of a stationary column over that area. Emissions of the grid cell in the central part of Switzerland (indicated in Figure 1); which is representative of average emissions of the Swiss Plateau, were chosen. The simulation was conducted for 8 days with diurnally varying emissions [Sigg and Neftel, 1993] and mixing height (Figure 10). The initial concentrations chosen are given in Table 7. H₂O₂ and O₃ concentrations show steadily increasing con-

centrations and strongly varying values in the lowest layers, as can be seen in Figure 14. The increase of the ozone concentration slows down after a few days. Even after 8 days, the concentration does not surpass 100 ppb, in agreement with observations [Künzle and Neu, 1994].

The physical and chemical interplay concerning the production of H₂O₂ can be clearly seen in the model. In the afternoon a thoroughly mixed boundary layer leads to a small vertical concentration gradient. During the night, H₂O₂ decreases due to deposition, particularly in the lowest layer. With the onset of the vertical mixing in the morning, H₂O₂ is mixed down, which produces a sharp increase at ground level. Net production of H₂O₂ takes place in the morning, when NO_x concentrations are relatively low. This H₂O₂ mixes down over the course of the day, producing the daily net increase of H₂O₂ of about 0.3–0.5 ppb. The rise of H₂O₂ from morning to afternoon in the model is about half of observed values (Table 5). It is also interesting to note that on July 11 and 12, hydrogen peroxide concentrations decrease with height opposite to the model behavior. This points to a pronounced peroxide production near the surface. The photochemical regime for ozone production appears therefore to be more NO_x limited than indicated by the models based on the standard emission inventory.

6. Summary and Conclusions

The important results of the observations were the following: (1) H₂O₂ concentrations ranged between 1 and 6 ppb. Elevated local concentrations could be due to biogenic VOC emissions. During the buildup of a regional O₃ smog episode, increasing hydrogen peroxide concentrations were observed. (2) Peak ozone concentrations in this highly industrialized and densely populated area level off at around 80–100 ppb. (3) Ground-based mean NO₂ concentrations in the afternoon in rural and semirural areas are below 1.5 ppb.

Two photochemical trajectory models were used to calculate ozone and hydrogen peroxide production over the Swiss Plateau. Calculated isopleths from the Harvard photochemical model show a low-NO_x type ozone production, whereas for the HPT-M it is in the transition range. However,

Figure 13. Calculated NO₂ concentration from the HPT-M expressed as a function of NO_x emission at 100% VOC emission.

Figure 14. Base-case 8-day run with the Harvard model. Results for O₃ and H₂O₂.

hydrogen peroxide production in the mixing layer is underestimated. This points to an underestimation of the VOC/NO_x emission ratio (e.g., due to the neglect of biogenic hydrocarbons, underestimation of anthropogenic VOC, or overestimation of NO_x emissions) and indicates a NO_x-limited regime for ozone production.

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