

Photochemical Smog in the Munich Metropolitan Area

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Abstract

Photochemical smog and the formation of photooxidants have become common in the Munich metropolitan area, in particular during the summer season. Maximum mixing ratios of ozone and PAN reach 120 ppb and 3 ppb, respectively, until present. As the major source of precursor emission is automobile exhaust, with NO being the dominant primary NO_x species, O₃ is reduced in the vicinity of traffic, with higher levels forming downwind towards more remote areas. Some typical examples of photosmog episodes are presented and discussed. The annual variation of ozone and superimposed short-term fluctuations are synchronous throughout the area, with absolute ozone levels increasing from the central parts of the city towards rural and forested areas in the surroundings.

Zusammenfassung

Photochemischer Smog im Großraum von München

Die Bildung von Photooxidantien und das Auftreten von photochemischem Smog ist im Großraum von München immer häufiger zu beobachten, insbesondere während der Sommermonate. Zur Zeit werden maximale Mischungsverhältnisse von 120 ppb für Ozon und 3 ppb für PAN gemessen. Als Hauptquelle der Vorläufersubstanzen kann der Kraftfahrzeugverkehr angenommen werden, wobei NO die Hauptkomponente der Stickoxide darstellt. Ozon wird bei hohem Verkehrsaufkommen abgebaut, so daß höhere O₃-Konzentrationen im ländlichen Umland von München zu finden sind. In der vorliegenden Arbeit werden einige Beispiele für Smog-Episoden diskutiert. Die jährliche Variation von Ozon sowie überlagerte kurzzeitige Fluktuationen verhalten sich synchron im gesamten Bereich, wobei die absoluten Ozonkonzentrationen vom Innenstadtbereich zum Stadtrand und zu den umgebenden Waldgebieten zunehmen.

Introduction

Photochemical smog occurs when immissions of nitrogen oxides, carbon monoxide and hydrocarbons are exposed to intense solar radiation. Thereby secondary substances are formed, such as ozone, aldehydes, peroxyacyl nitrates (PANs) and aerosol particles. The precursor gases are predominantly related to all kinds of combustion sources, with traffic exhaust being dominant in many densely populated areas. Photochemical smog was first observed and studied in the Los Angeles basin (Haagen-Smit 1950, Haagen-Smit et al. 1953, Finlayson and Pitts 1976, Rodes and Holland 1981, Hoggan et al. 1982). Ozone mixing ratios of more

than 500 ppb were observed, which is about 50 times more than the natural tropospheric ozone level as documented in early ozone measurements of the nineteenth century (Volz and Kley 1988, Anfossi et al. 1991, Sandroni et al. 1992).

Today, photochemical smog is a common feature of many metropolitan areas throughout the world. Ozone levels of up to about 300 ppb have been recorded in Tokyo, San Francisco, Osaka, Sydney or Athens, while peak levels between 100 and 200 ppb have become common in most major cities in the US and Europe as well (Fankhauser 1976, Stewart et al. 1976, Ball 1976 a, b). Since the life time of ozone in the free troposphere is of the order of days to weeks, high ozone levels are not confined to the

polluted metropolitan areas. Ozone is rather advected to remote regions further downwind, where, in the absence of direct emissions of NO, ozone levels are often higher than in the vicinity of the sources. This is illustrated, along with other findings, by the results presented in this paper.

Scheme of Main Photosmog Processes

All ozone in the atmosphere is formed by photochemistry.

In the stratosphere and mesosphere, the dominating three-body reaction

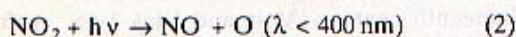


is initiated by UV-photolysis of O₂ yielding O atoms.

This photolysis restricted to wavelengths below 242 nm leads to the buildup of the ozone layer in the middle atmosphere.

In the troposphere, however, the solar spectrum is limited to wavelengths greater than about 290 nm. Nevertheless considerable tropospheric ozone formation is observed in many areas of the world. In Bavaria, for instance, results of regular radiosonde soundings at Hohenpeißenberg (about 50 km SW of Munich, see map in Figure 1) clearly indicate a continuous growth of tropospheric ozone, by about 2 percent/year, throughout the whole troposphere (Wege et al., 1989, Wege and Vandersee 1991). Compared to the "clean" troposphere, whose ozone mixing ratios range between 10 and 20 ppb (10⁻⁹ by volume) resulting from the steady-state equilibrium between stratospheric influx and ground-level decomposition (Fabian and Pruchniewicz, 1977) average ozone levels have more than doubled.

This formation of a secondary and continuously growing tropospheric ozone layer is due to photosmog reactions initiated by photolysis of NO₂



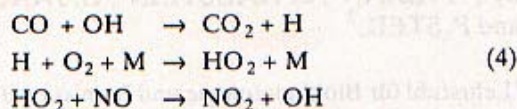
yielding oxygen atoms which can react to form O₃ according to (1). As O₃ rapidly reacts with NO



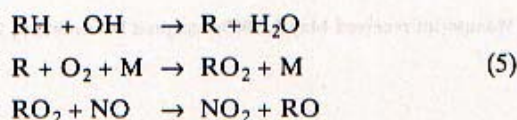
the resulting equilibrium number density of O₃ is limited to $[\text{O}_3] = j_1 [\text{NO}_2] / k_3 [\text{NO}]$, wherein j_1 and k_3 denote the photolysis rate of (2) and the rate coefficient for reaction (3), respectively.

However, the oxidation chains of carbon monoxide (CO) and nonmethane hydrocarbons (RH) by

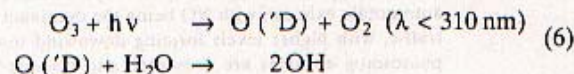
hydroxyl radicals lead to the formation of peroxy radicals, which convert NO to NO₂ without consuming O₃ and thus shift the equilibrium towards higher ozone levels:



and



As the two-step production of OH is initiated by ozone photolysis



ozone is necessary to initiate photosmog reactions which in turn can build up considerably higher ozone levels. The threshold for this ozone production is determined by the ratio $[\text{NO}]/[\text{O}_3] = 2 \times 10^{-4}$ (Warneck 1988) which is permanently exceeded in large areas of North America and Europe, as a result of anthropogenic emissions of NO_x, mainly from automobile exhaust.

Besides converting NO to NO₂, RO₂ radicals formed in the hydrocarbon oxidation chains (5) can get accommodated on aerosol surfaces, thereby contributing to aerosol growth and thus increasing atmospheric turbidity.

Further smog products such as aldehydes are formed in reactions of RO₂ with oxygen. Aldehydes are unstable and rapidly react with OH. In the presence of NO₂, peroxyacetyl nitrates (PANs) are formed. (See for instance Schurath 1976, Seinfeld 1989, Becker and Löbel 1985.) Their dominant representative is peroxyacetyl nitrate (PAN, CH₃COO₂NO₂) whose main precursor is acetaldehyde (CH₃CHO). With increasing order, abundances of the different PANs usually decrease. Mixing ratios of peroxypropionyl nitrate (PPN, C₂H₅COO₂NO₂) for instance, the next higher one based on propionylaldehyde (C₂H₅CHO), were found to be only about 10 percent of those of PAN (Kourtidis et al. 1993). Due to the absence of natural sources, PANs are key substances of photochemical smog.

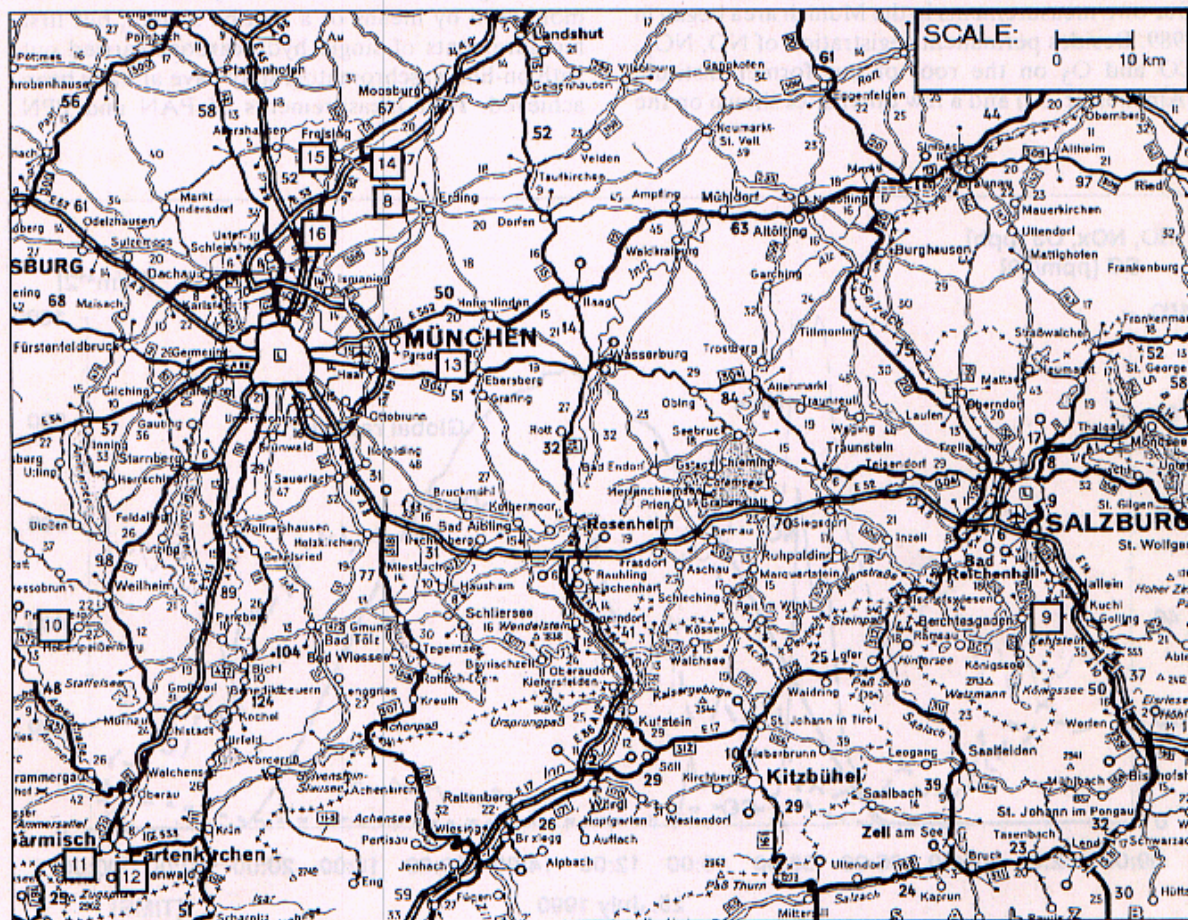


Figure 1 Map of Munich (upper part) and the Munich metropolitan area (lower part) depicting the measurement sites.
 1 Amalienstraße 52, 2 Englischer Garten, 3 Stachus, 4 Lothstraße, 5 Bayerstraße, 6 Olympiaturm, 7 Theresienstraße,
 8 Notzing, 9 Berchtesgaden, 10 Hohenpeißenberg, 11 Garmisch-Partenkirchen, 12 Wank, 13 Ebersberger Forst, 14 Schwaig,
 15 Weihenstephan, 16 Neufahrn

Measurements of Photooxidants and their Precursors in the Munich Area

Since 1980, the Bavarian environmental protection agency (Bayerisches Landesamt für Umweltschutz, LFU) has been operating a network of 10 stations in the city of Munich. Besides SO_2 which is not discussed here, CO has been measured at all 10 sites. NO and NO_2 regular data are available for 4 and 5 stations, respectively, from 1980 onwards, while ozone measurements were added later.

A comprehensive statistical analysis covering the 1980 to 1987 time period yielded average concentrations of CO, NO and NO_2 in Munich of 2.25, 0.077 and 0.048 mg/m^3 , respectively. During this time, CO showed a significant decrease of 4.8 %/year, while NO and NO_2 concentrations significantly increased, by 15.5 %/year and 10.0 %/year, respectively. No statistical analysis of ozone data was carried out so far (Mayer and Haustein 1988).

Our own measurements in the Munich area began in 1989. Besides permanent registration of NO, NO_2 , CO and O_3 on the roof of our former institute (Amalienstr. 52) and a few other sites shown on the

map in Figure 1 most measurements were carried out on a campaign-like basis, at different locations and times. Both a van and a caravan equipped with instruments for monitoring various pollutants and relevant meteorological parameters were used. These measurements were carried out within projects aimed for studying the impact of pollutants on human health and investigations related to the new Munich airport. They were not directly designed for systematically studying the processes of photochemical formation and monitoring the distribution of pollutants. (First interim reports of these projects are given by Jakobi et al. 1993, Rappenglück and Fabian 1993, Suppan and Fabian 1993, Fabian et al. 1993.)

Commercial instruments were applied for measuring NO, NO_2 (chemiluminescence), O_3 (UV-absorption), CO (IR-absorption) and PAN (Luminoltechnique), all instruments having been calibrated in regular intervals. Total hydrocarbons were monitored by means of a Horiba system, but first measurements of single hydrocarbons carried out with on-line-gaschromatography have already been achieved. First measurements of PAN and PPN

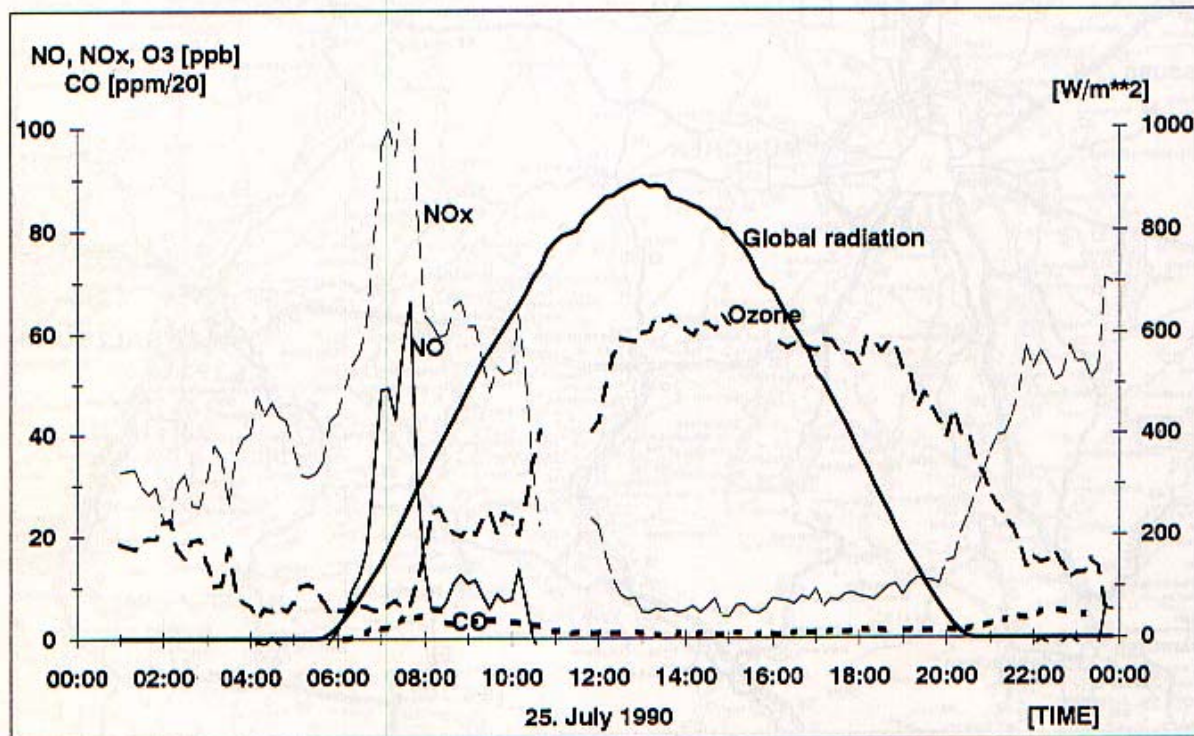


Figure 2 Diurnal variation of NO, total NO_x , CO, O_3 and Global radiation measured on July 25, 1990 on the roof station of the institute, Amalienstr. 52, in the Munich downtown area, about 30 m above street level. See 1 in Figure 1.

carried out in Munich during 1989/90 by gaschromatography have already been published (Kourtidis et al. 1990, Rappenglück 1990, Kourtidis et al. 1993). They show average PAN volume mixing ratios of 0.4 ppb and highest values around 3 ppb for the investigated time period. They also show PPN levels continuously being about 7% of those of PAN clearly demonstrating that peroxyacetyl nitrate is by far the dominating species of the PANs. No further measurements of PPN have, to our knowledge, since been carried out in Munich.

In the following chapter we present some characteristic examples of photochemical smog episodes observed in the Munich metropolitan area during the 1989–1992 period.

Results

Figure 2 illustrates the typical diurnal variation of ozone and its precursors in the boundary layer. The measurements were taken on the roof of our former

institute building, Amalienstraße 52, 30 m above street level, in the center of Munich (see map in Figure 1). 10-minute-averages of NO, total NO_x and CO reflect the typical emission pattern of traffic, which peaks during the morning and evening hours. During the course of the clear and sunny day (see curve of global radiation) ozone builds up leading to a broad maximum by in-situ photochemical production, advection and influx from higher levels due to turbulence and convection, which all calm down during late afternoon/evening. Ozone loss, predominantly via reaction (3), leads to very low ozone levels at night.

PAN was not measured during that time period. Its diurnal variation, however, would have been similar to that of O₃. This is illustrated by results of an earlier measurement shown in Figure 3, with ozone and PAN building up during 2 consecutive days of intense sunshine following a day of highly variable cloudiness (see curve of global radiation).

Kourtidis et al. (1990) have shown that a close correlation between O₃ and PAN exists, with

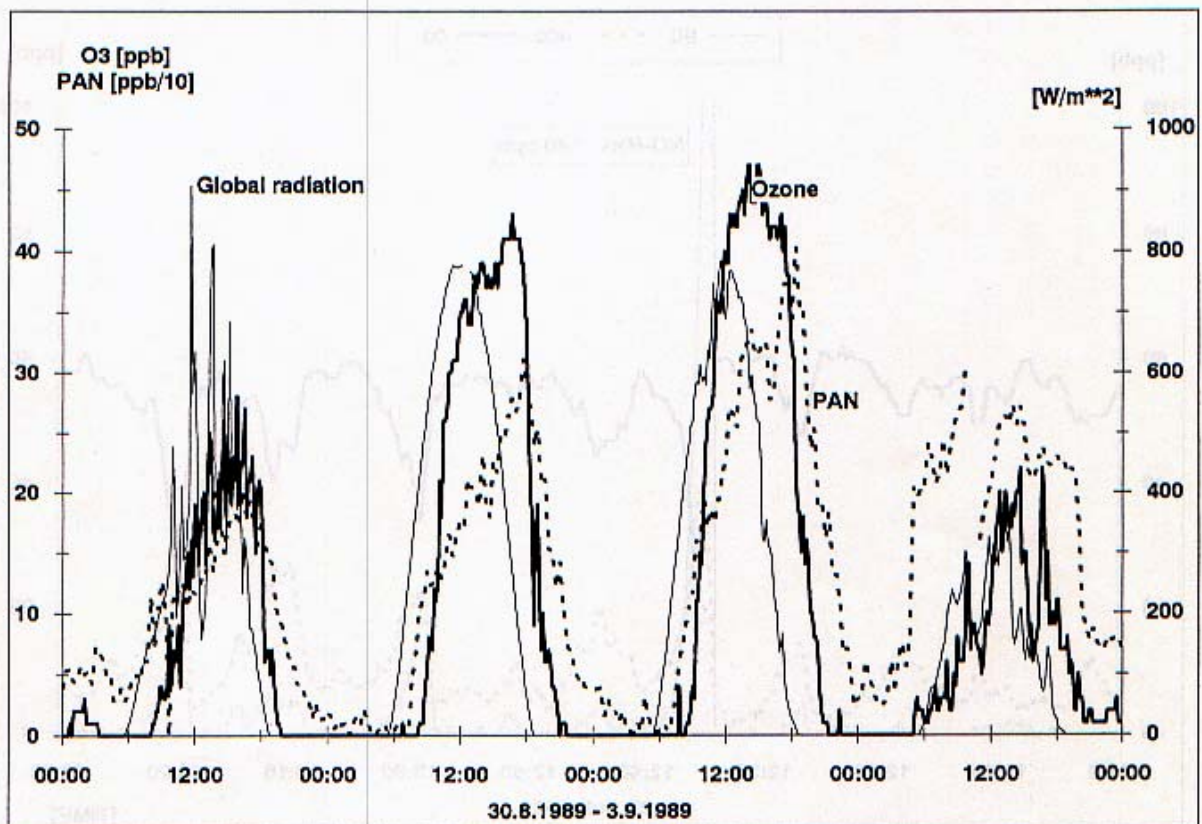


Figure 3 Diurnal variation of Ozone, PAN and Global radiation as measured between August 30 and September 3, 1989 at street level in the downtown area of Munich. PAN volume mixing ratios are scaled by 10, (Rappenglück 1990)

O_3/PAN ratios decreasing towards higher PAN concentrations.

According to evaluations of the Bavarian environmental protection agency (LFU), automobiles contribute about 80 percent to all NO_x emissions in Bavaria (1989). Thus in the Munich metropolitan area, automobiles are by far the dominant source of photo-smog precursors, NO_x , CO and unburnt hydrocarbons. Since NO_x is almost exclusively emitted as NO which rapidly reacts with O_3 via (3), the primary effect of automobile exhaust is a depletion of ozone. This is illustrated by Figure 4 showing 10-second-values of NO, NO_2 and O_3 measured at street level in front of the institute building, Amalienstr. 52. This high-resolution record shows the NO puffs of passing cars, the corresponding, almost instantaneous decreases of ozone and the buildups of NO_2 due to reaction (3), which has a time constant of about 50 sec based on ozone values of about 50 ppb measured during that time.

During the same photo-smog episode, total NO_x and O_3 were measured simultaneously at street level, on

the roof of the institute, and in the backyard, a park-like quadrangle surrounded by 4 to 5-storey building structures. 10-minute averages displayed in Figure 5 show, besides the characteristic diurnal pattern, highest NO_x levels in the street with an average frequency of 4 cars/minute, lowest in the backyard, and intermediate values on the roof. Correspondingly, the ozone record shows the lowest values in the street at most times, whereas in the backyard protected against direct NO emission, the highest ozone mixing ratios were found.

While the measurements at street level and in the backyard were discontinued during night, the permanent registration on the roof top shows a secondary maximum of O_3 (and NO_x) shortly after midnight of July 25. This is a common feature, which occurs when disturbances of the boundary layer cause turbulent mixing and thus influx of ozone from above the inversion. According to Winkler (1980) this turbulent mixing is caused by a boundary layer jetstream which often develops close to the ground level inversion.

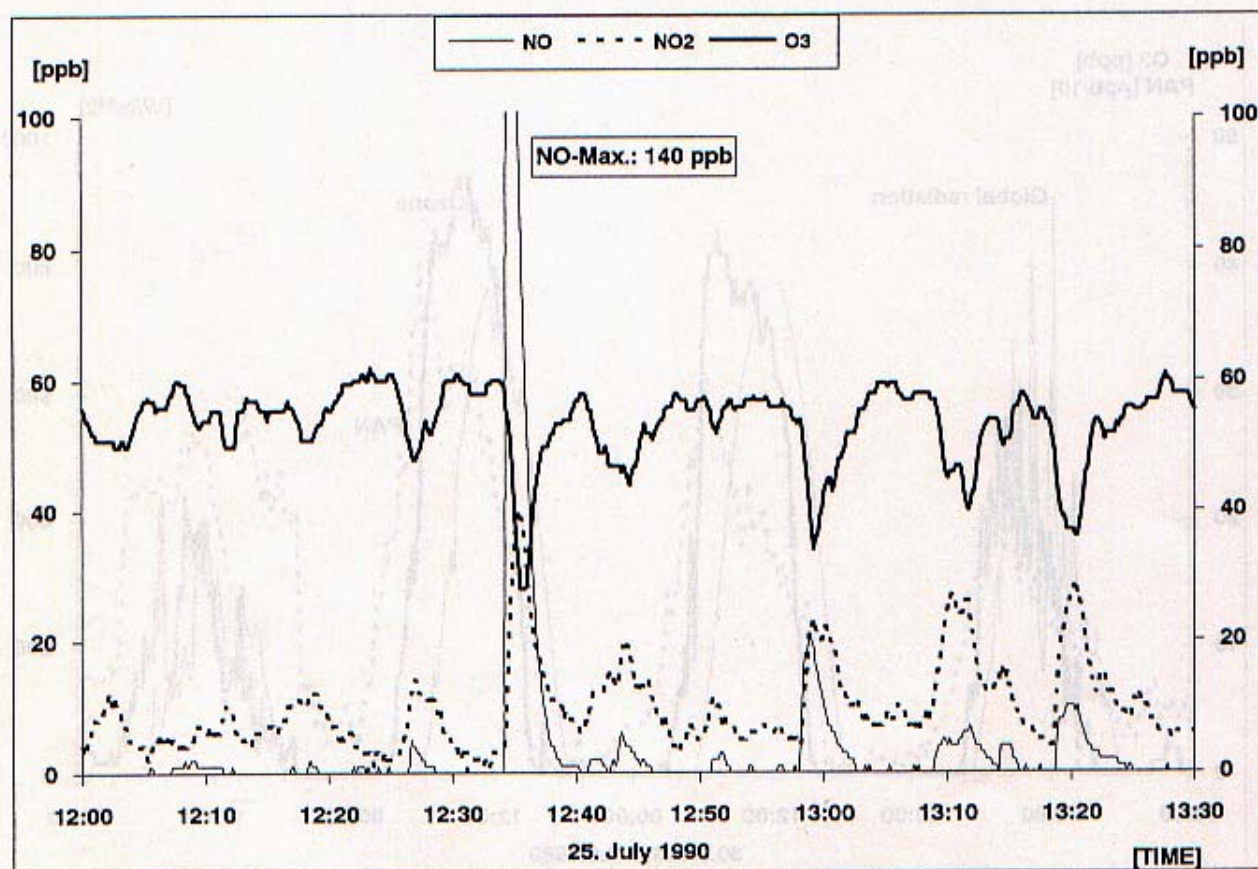


Figure 4 10-sec-means of NO, NO_2 and O_3 measured on July 25, 1990 at street level in front of the institute building, Amalienstr. 52, in downtown Munich.

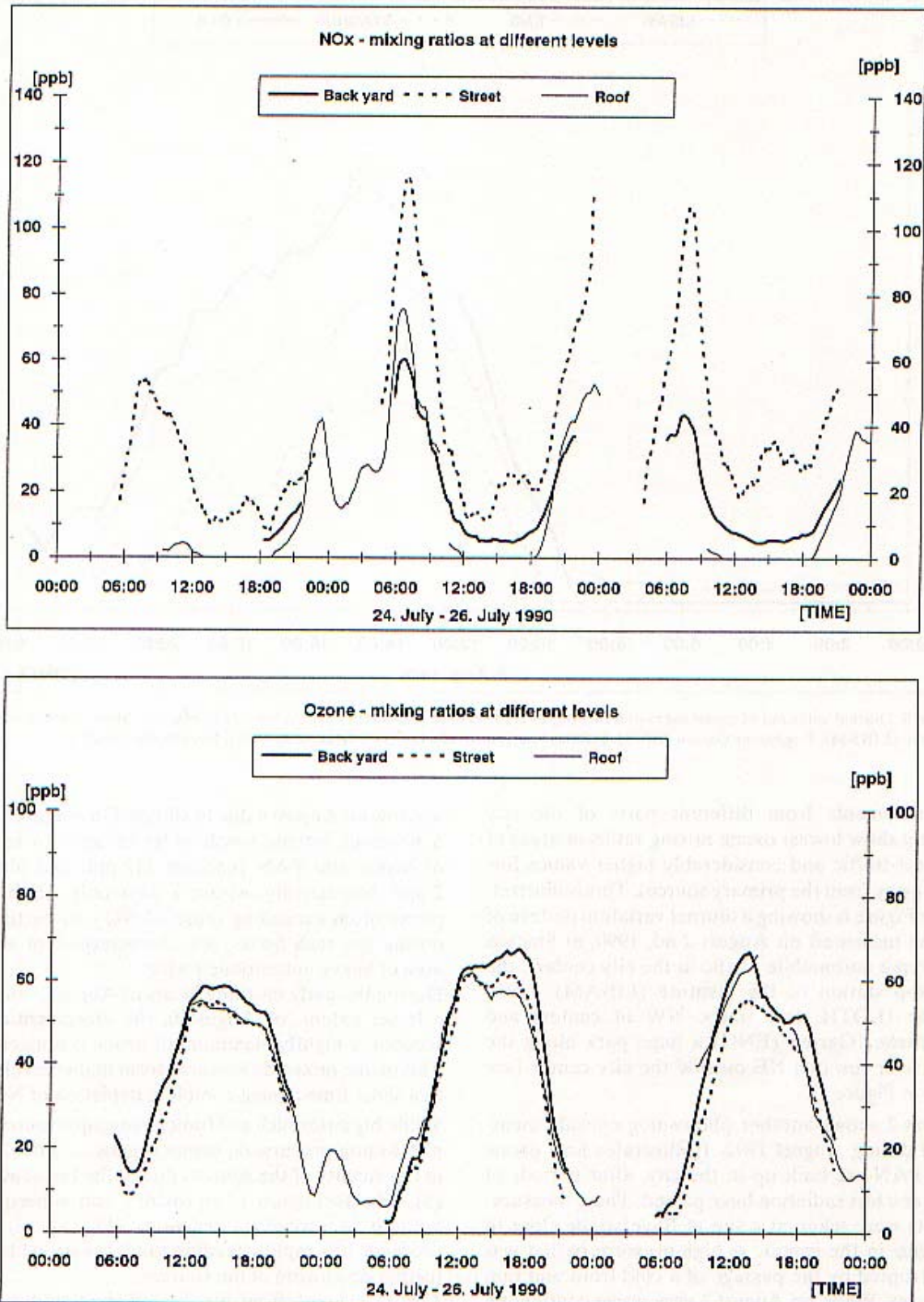


Figure 5 Diurnal variation of NO_x (upper panel) and O₃ (lower panel) measured between July 24 and July 26, 1990 at 3 different locations of the institute-building, street level, roof and backyard.

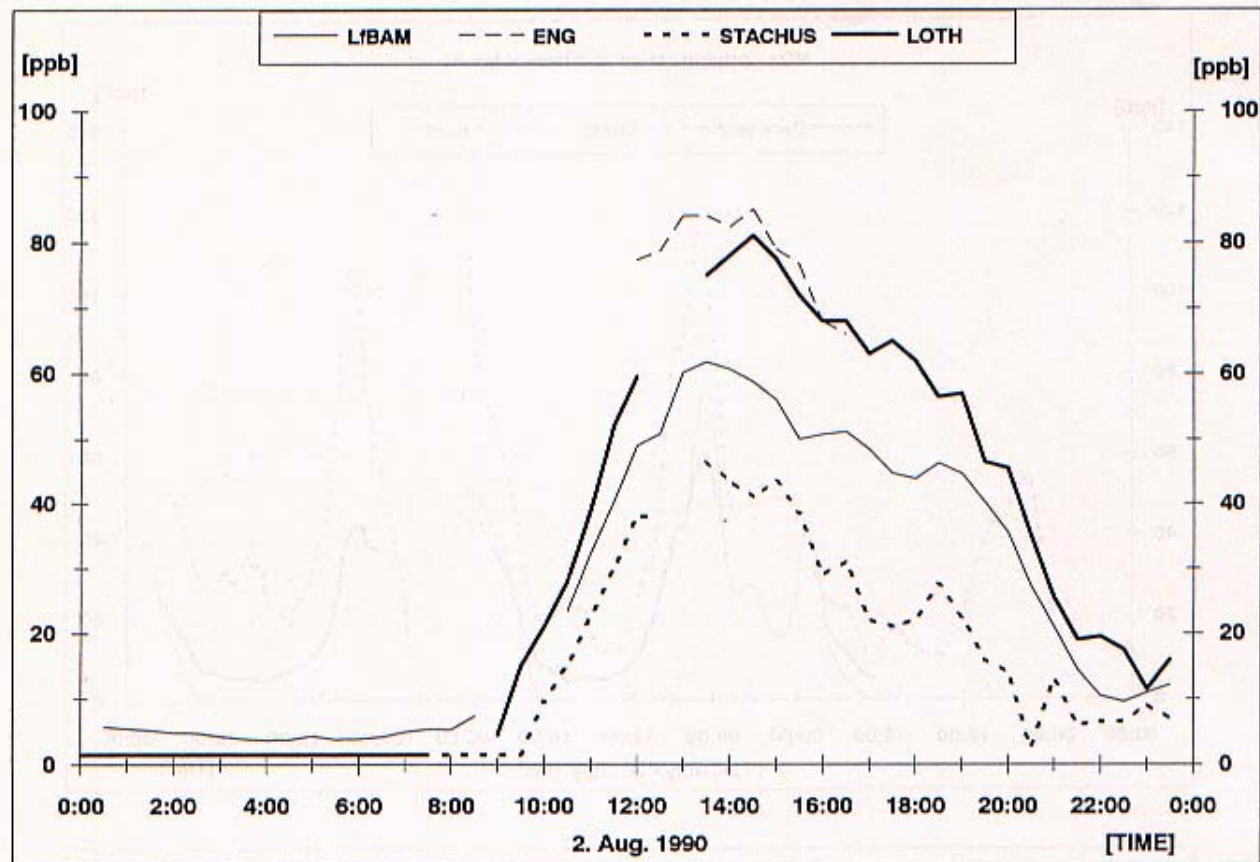


Figure 6 Diurnal variation of ozone measured on August 2nd, 1990 at 4 different sites on the city of Munich: Street level in front of institute (LfBAM), Englischer Garten (ENG), Stachus and Lothstraße (LOTH) (Haustein, 1992). See map in Figure 1.

Measurements from different parts of the city clearly show lowest ozone mixing ratios in areas of highest traffic and considerably higher values further away from the primary sources. This is illustrated in Figure 6 showing a diurnal variation pattern of ozone measured on August 2nd, 1990, at Stachus (extreme automobile traffic in the city center), the rooftop station of the institute (LfBAM), Lothstraße (LOTH, less traffic NW of center) and Englischer Garten (ENG) a huge park along the Isar river towards NE outside the city center (see map in Figure 1).

Figure 7 shows another photo-smog episode measured during August 1992. It illustrates how ozone and PAN are built up in the city, after periods of rain and less radiation have passed. These measurements were taken at a site at Bayerstraße close to Stachus in the center. A high-pressure period was interrupted by the passage of a cold front and rain showers. While on August 3 very warm continental air had prevailed, cool air advected after the cold front had passed around midnight. Global radiation

was low on August 4 due to clouds. On August 5 and 6, however, intense sunshine led to rapid formation of ozone and PAN reaching 112 ppb and almost 2 ppb, respectively, within 2 days only. High NO peaks often exceeding those of NO₂, in particular during the rush hours, are characteristic of a city area of heavy automobile traffic.

During the early morning hours of August 5 and, to a lesser extent, of August 6, the aforementioned secondary nightly maximum of ozone is noticeable. This ozone mixed downwards from higher levels led to a short-time almost complete depletion of NO.

While big cities such as Munich are major sources of photo-smog precursors, ozone is generally depleted in the vicinity of the sources due to the fast reaction (3). The formation of peroxides and subsequent buildup of ozone via reactions (4), (5), (2), (1) proceeds less rapidly leading to higher ozone levels further downwind of the sources.

This is evident from air quality data of the Los Angeles area, where photo-smog has been observed since the forties already, and the distribution of

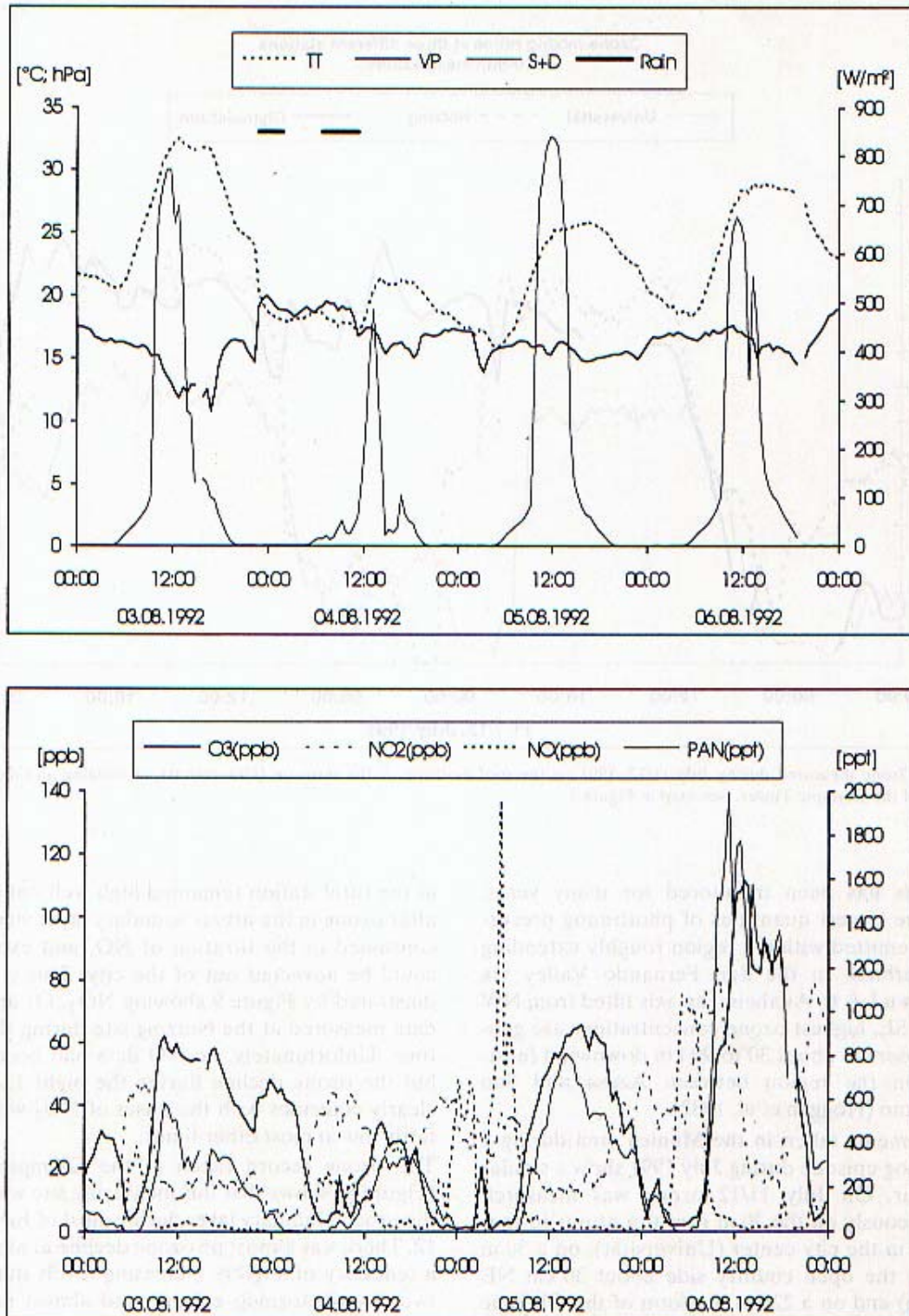


Figure 7 Photosmog episode of August 3–6, 1992: Meteorological parameters (upper panel) temperature (TT) [°C] vapor pressure of water (VP) [hPa] Global radiation (S+D) [W/m²] and time intervals of rain. Mixing ratios of pollutants (lower panel). The measurements were taken in a U-shaped backyard open towards NE at Bayerstraße 28, center of Munich. See 5 in Figure 1.

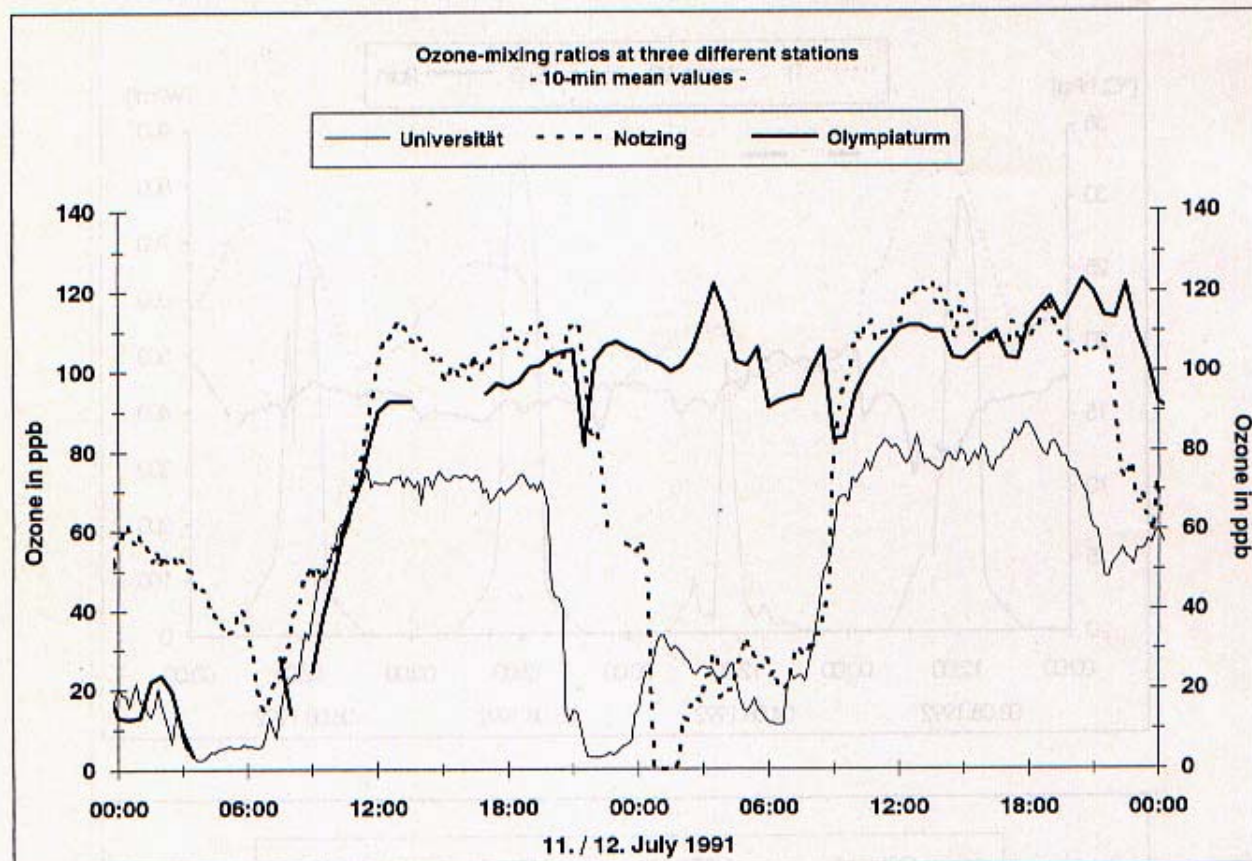


Figure 8 Ozone measured during July 11/12, 1991 on the roof platform of the institute (Universität), at Notzing and on a 200 m-platform of the Olympic Tower. See map in Figure 1.

pollutants has been monitored for many years. While the largest quantities of photochemical precursors are emitted within a region roughly extending from Burbank in the San Fernando Valley via Downtown LA to Anaheim, an axis tilted from NW towards SE, highest ozone concentrations are generally observed about 30 to 90 km downwind (eastwards) in the region between Azusa and San Bernardino (Hoggan et al. 1982).

Measurements taken in the Munich area during a photochemical episode during July 1991 show a similar behaviour. On July 11/12 ozone was measured simultaneously on the 30 m roof top of our former institute in the city center (Universität), on a 30 m tower in the open country side about 30 km NE (Notzing) and on a 220 m platform of the Olympic Tower (Olympiaturm, see map in Figure 1). While ozone in the city did not exceed 70 ppb during both days, up to about 120 ppb were measured at the Notzing site. Furthermore, the afternoon decline in the city began at 3 p.m. already, while ozone levels

at the rural station remained high well until 9 p.m., after ozone in the urban boundary layer was mostly consumed in the titration of NO, and excess NO could be advected out of the city. This is further illustrated by Figure 9 showing NO₂, O₃ and PAN data measured at the Notzing site during the same time. Unfortunately, no NO data had been taken, but the ozone decline during the night 11/12 July clearly coincides with the onset of NO₂ which was fairly low at most other times.

The ozone record taken at the Olympic Tower (Figure 8) shows that this measuring site was above the urban boundary layer during most of July 11 and 12. There was almost no ozone decline at night, with a tendency of slightly increasing levels during the two-day photochemical episode and almost matching the maximum ozone mixing ratios measured at the Notzing site.

Figures 10 and 11 show comparisons of ozone records taken in the center of Munich with those of more remote stations in southern Bavaria, during

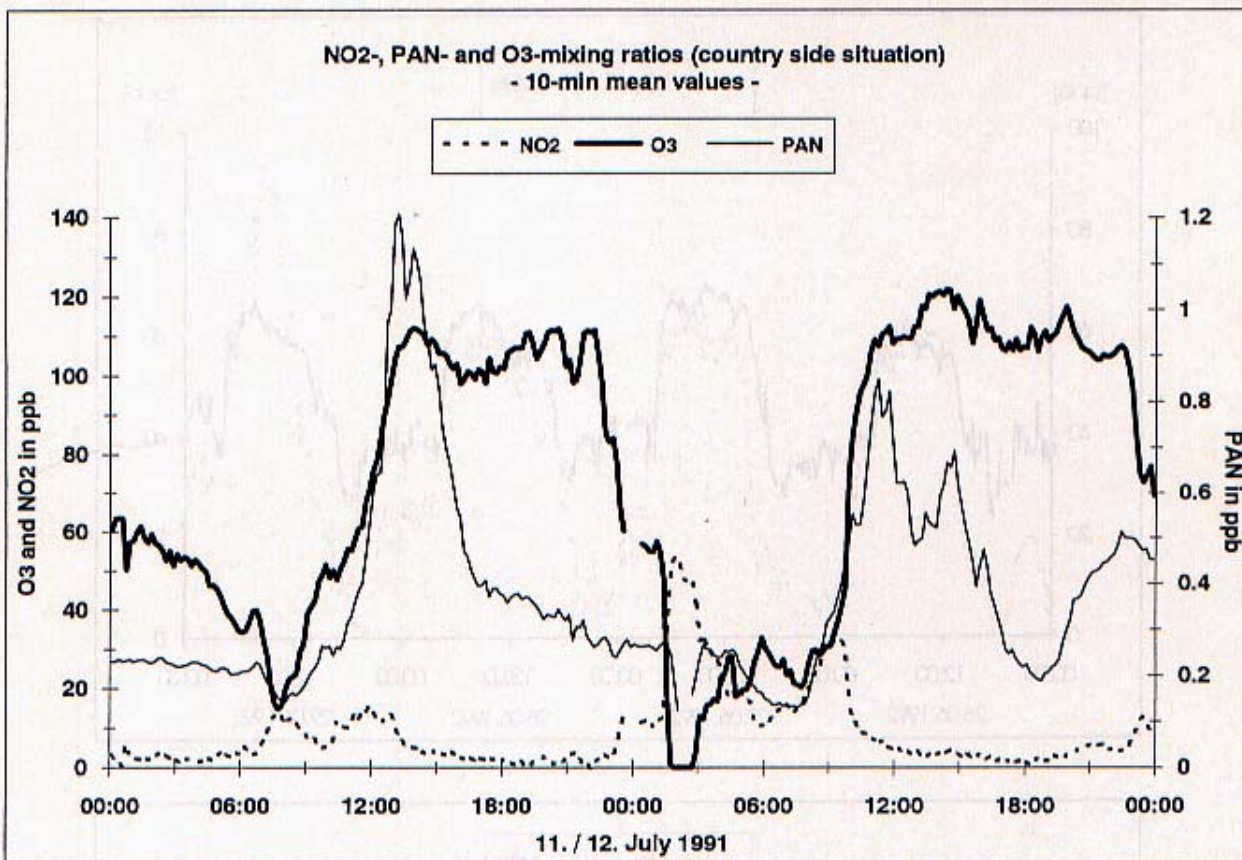


Figure 9 Same measurement period as shown in Figure 8: NO₂, O₃ and PAN at the rural station (Notzing). See 8 in Figure 1.

photosmog episodes in June 1992 and July 1990, respectively. Ozone records taken simultaneously close to Berchtesgaden (see map in Figure 1), about 100 km SE of the city center, and in the downtown area, on the roof of the meteorological institute (Theresienstraße, see Figure 1), show slightly higher maximum values at the Berchtesgaden site (except for June 29), but considerably less ozone depletion at night. This is due to very low NO_x at Berchtesgaden, which was down to almost detection limit during this time and thus is not shown in the lower part of Figure 10. It is interesting to note that extremely high PAN levels, of up to 3 ppb, were measured at Berchtesgaden during this photosmog episode.

A similar comparison of simultaneous ozone records taken during the episode June 24 to 26, 1990, comprises ozone data of the 3 city stations Stachus (STA), Amalienstraße (AMA) and Lothstraße (LOTH) street levels, and those of Garmisch-Partenkirchen (GAP, about 80 km S/SW of the city

center) and the Wank summit directly above Garmisch-Partenkirchen (WANK, 1800 m a.s.l.).

Close to the emission sources ozone maxima are lower and ozone minima are even more reduced compared to more distant stations with less direct emission of NO. At 1800 m altitude (WANK), far above the boundary layer, ozone remains high with almost no diurnal variations. Thus the average ozone exposure in a mountain forest is much larger than in areas of direct precursor emission, in the valleys with heavy traffic etc. This is also confirmed by measurements taken in the ozone networks of Vorarlberg, St. Gallen and other parts of Austria and Switzerland (Wunderli and Gehrig 1990, Baudepartement des Kantons St. Gallen, Amt für Umweltschutz 1991, Umweltinstitut des Landes Vorarlberg 1991).

The examples shown in this chapter demonstrate that photochemical smog episodes do occur in the Munich metropolitan area, with ozone mixing ratios up to about 120 ppb. This is twice the MIK value of

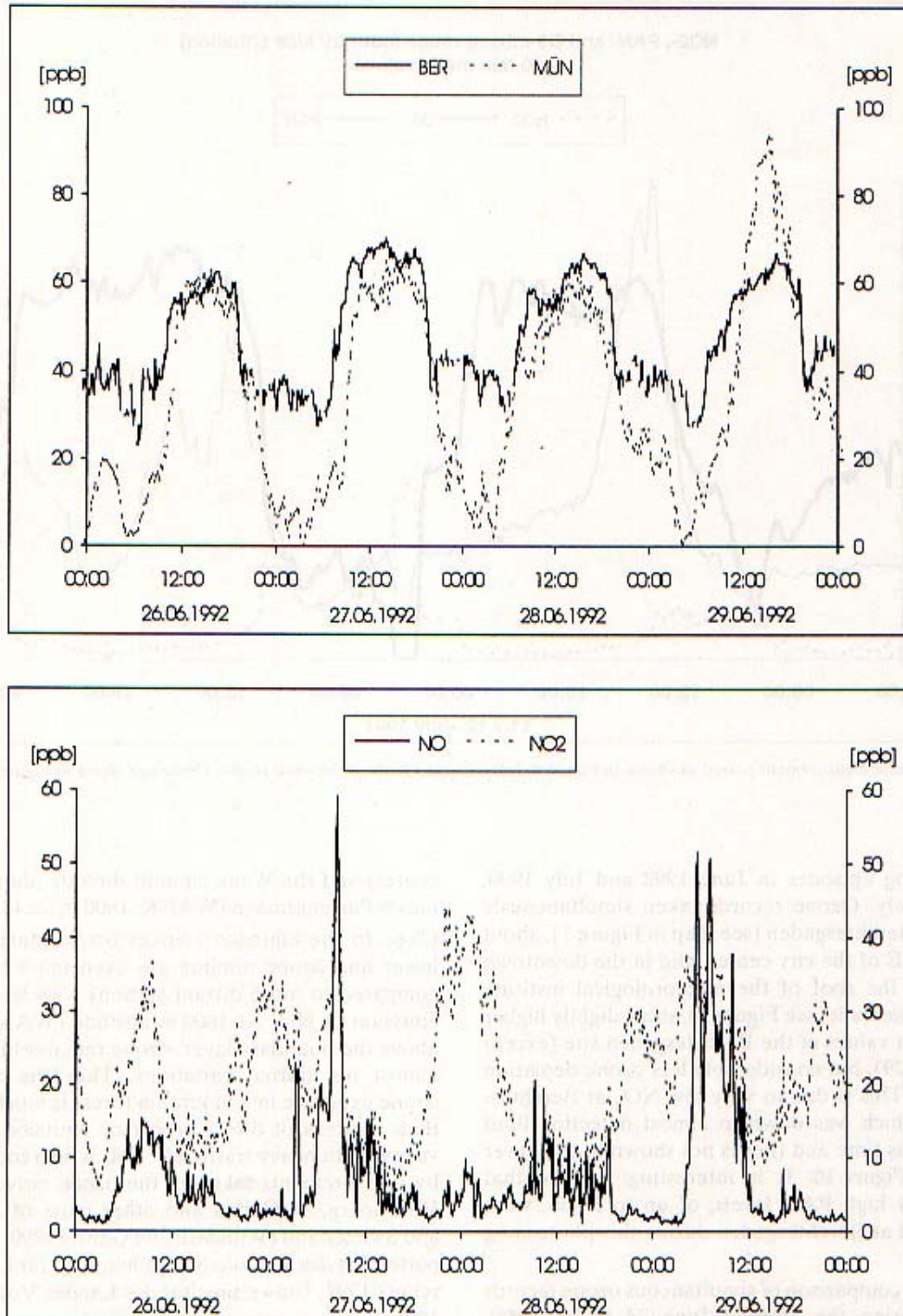


Figure 10 Photochemical episode of June 26–29, 1992. Comparison of ozone mixing ratios measured in the city of Munich, Theresienstraße (MÜN) and close to Berchtesgaden (BER) (Upper panel). See map in Figure 1. The lower panel shows NO and NO₂ mixing ratios measured at the city station (Theresienstraße, MÜN). The NO_x values found at the Berchtesgaden site were so low, close to detection limits, that they are not displayed in Figure 10.

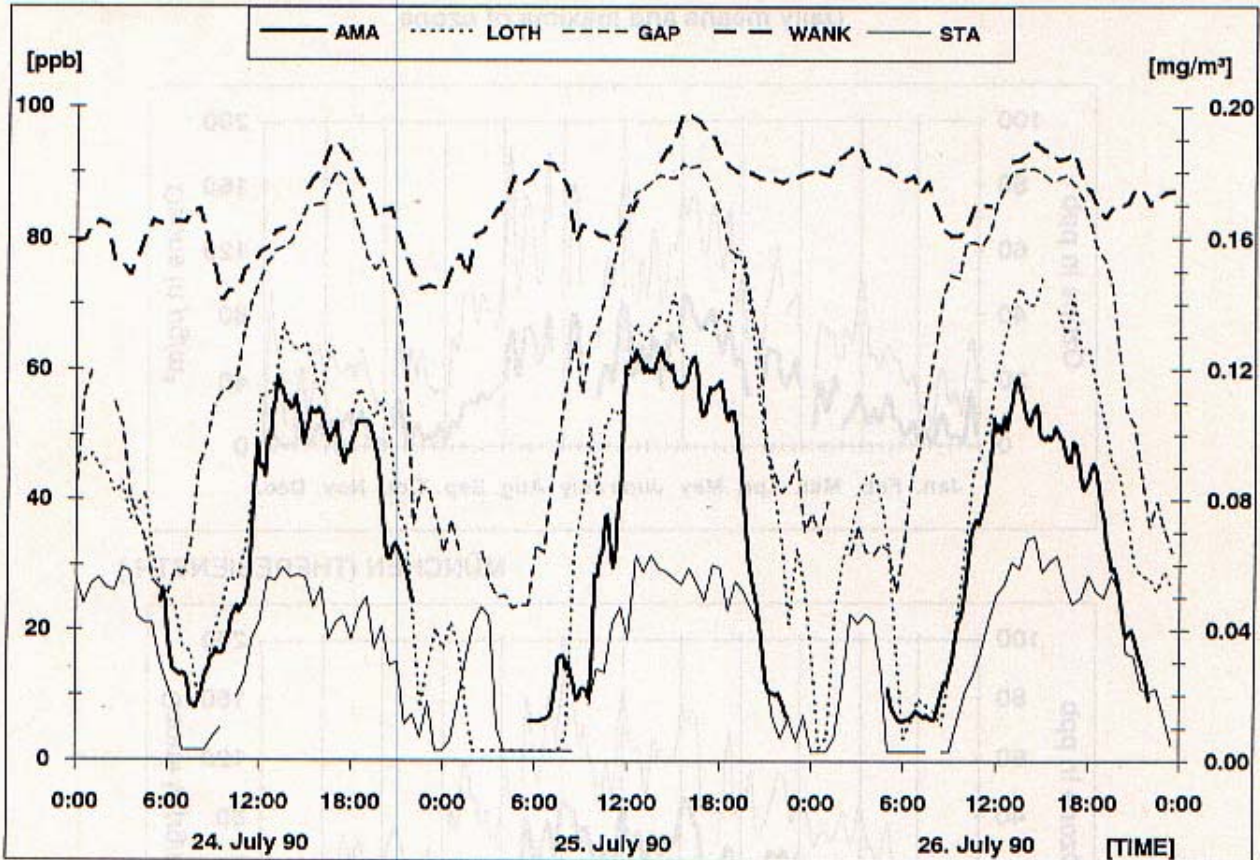


Figure 11 Ozone measured during July 24 to 26, 1990 at 3 city sites Amalienstr. (AMA), Lothstraße (LOTH) and Stachus (STA) as compared to measurements taken at Garmisch-Partenkirchen (GAP) and Wank summit (WANK, 1800 m a.s.l.) (Haustein, 1992). See map in Figure 1.

60 ppb set by VDI-guideline no. 2310 as the upper limit for 30 minutes exposure (VDI 1989). The MIK value is exceeded on many days during the spring and summer months, and in view of the fact that the steady tropospheric ozone increase as observed at Hohenpeißenberg is still going on unabated, even more severe photosmog episodes must be envisaged for future years.

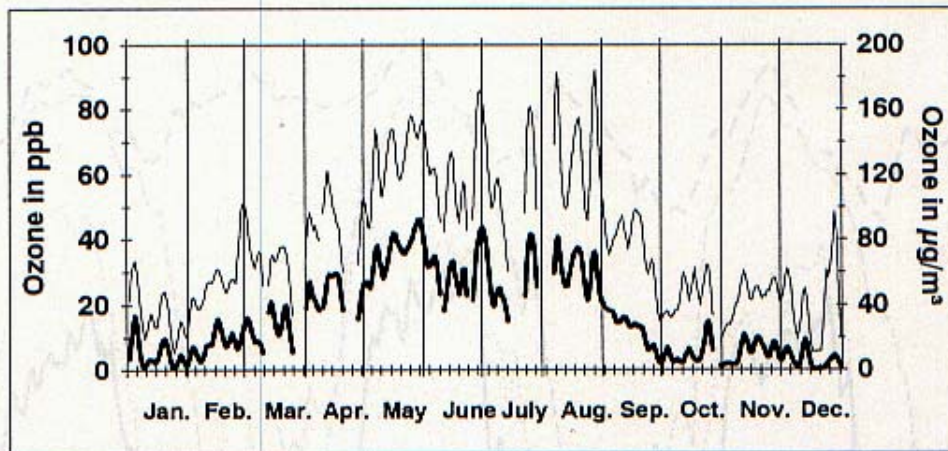
For locations in the vicinity of direct precursor emission ozone levels will be reduced at times, in particular at night, while in the surrounding rural and forest areas up to 20 percent higher ozone concentrations can occur.

The annual variation of ozone as shown in Figure 12 depends on solar radiation and thus season, precursor mixture and air mass, as well as natural intrusion of ozone from the stratosphere. As the latter process is most efficient in spring, a broad annual maximum from May until August develops, while ozone levels are generally low during winter, except for a few weaker photosmog episodes.

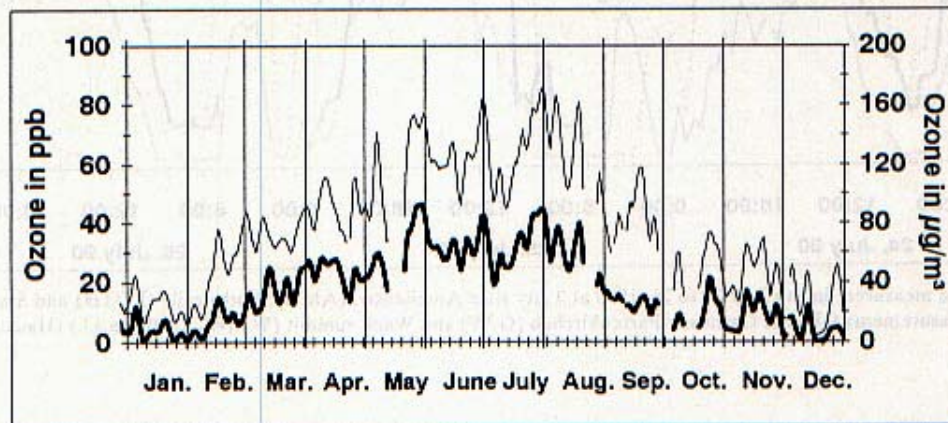
This annual variation is demonstrated by the daily means and maxima as obtained from continuous registrations on the roof of the meteorological institute in the city center, at our rural station Schwaig (30 km NE of the city center, see map in Figure 1) and at our forest station Ebersberger Forst (15 km E of the city center). As the curves for the whole year 1992 clearly show, not only the annual variation but also the fine structure reflecting the different weather situations, air masses and radiation changes are strikingly synchronous at the three sites. They differ with respect to the absolute mixing ratios only, with lowest values in the city center and highest ones at the forest site.

For PAN no such continuous registration exists so far. Our first quasi-continuous registration obtained at our monitoring station in the center of Neufahrn, a small city 15 km NE of Munich, is shown in Figure 13. Due to several failures of the instrument during the first year of operation, wide gaps occur in the display of daily means of PAN. Nevertheless

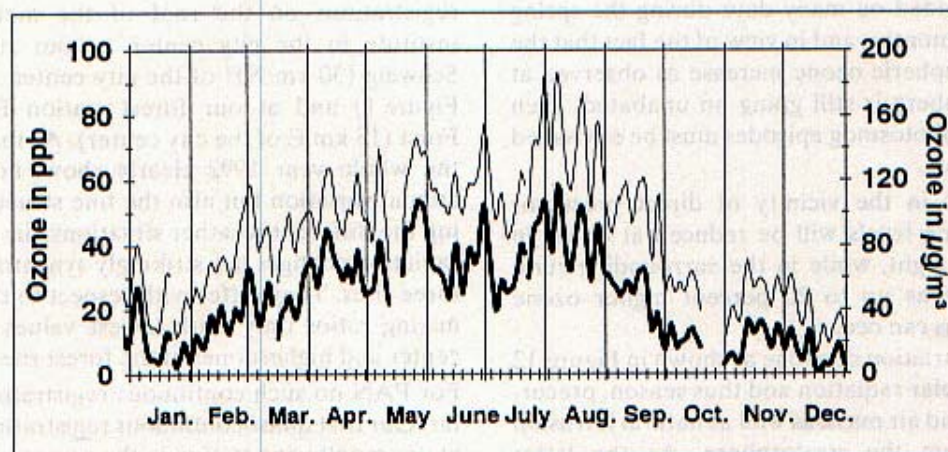
Daily means and maxima of ozone



MÜNCHEN (THERESIENSTR.)



SCHWAIG



EBERSBERGER FORST

Figure 12 Ozone diurnal averages and maxima measured during 1992 in the center of Munich (Theresienstr., upper panel), at a rural site (Schwaig, 30 km NE of city center) and a forest site (Ebersberger Forst, 15 km E of city center, measured above the canopy layer, lower panel). The heavy lines follow daily means, the thin lines daily maxima (1 hour-averages) at the three sites.

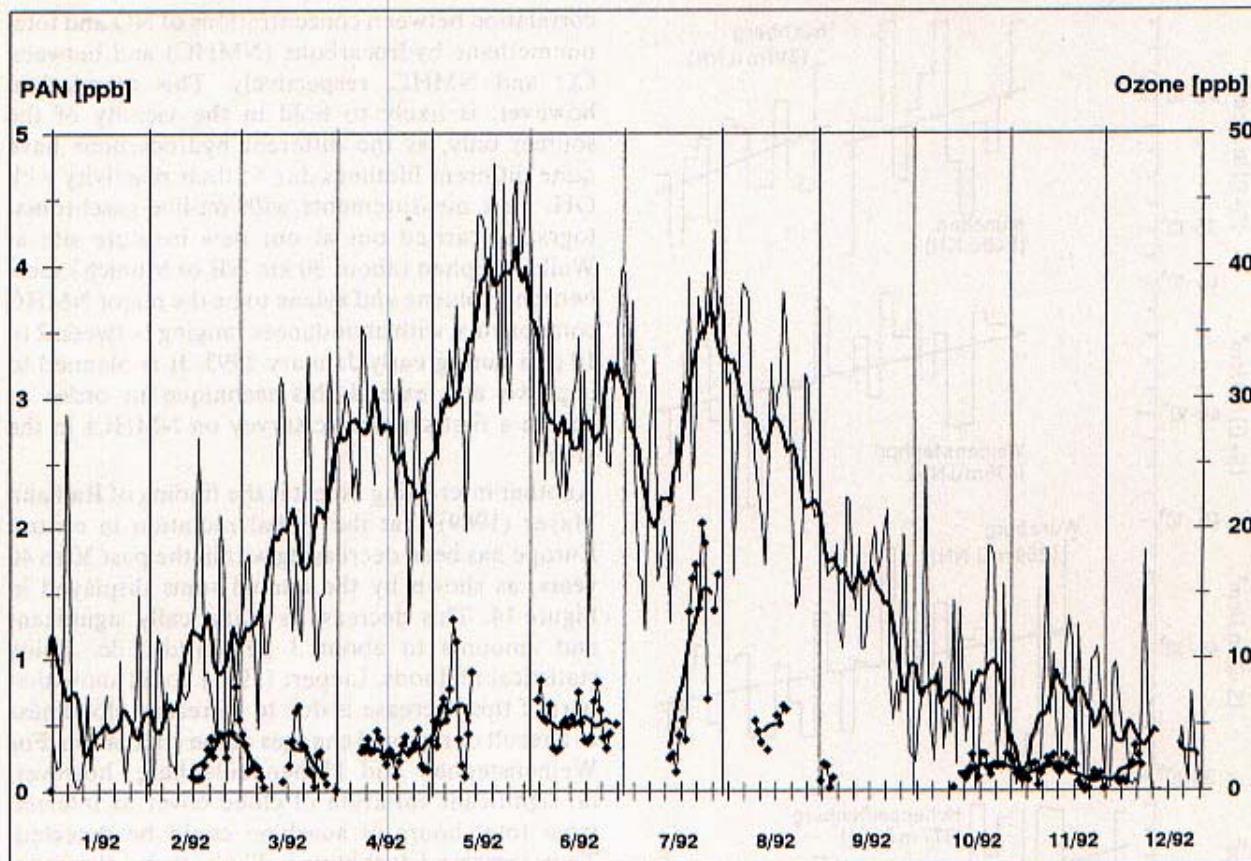


Figure 13 Ozone and PAN diurnal averages measured during 1992 at Neufahrn, a small city 15 km NE of Munich. (See map in Figure 1.) The thick lines are 10-day running averages computed from the daily means.

highest mixing ratios during the summer months and lower values during fall and winter are obvious. The ozone daily means obtained at the same site are plotted for comparison. They show almost the same annual variation and short-term fluctuations as the records of the three stations displayed in Figure 12. Maximum PAN mixing ratios measured so far in the Munich area do not exceed 3 ppb which is comparable to PAN levels observed in other metropolitan areas in Europe such as Paris, Cologne, Copenhagen or London (Penkett et al. 1975, Grennfelt et al. 1982, Tsalkani et al. 1987, Becker et al. 1985).

Concluding Remarks

Results presented in this study show that photochemical smog episodes do occur in the Munich metropolitan area, in particular during the summer

season. Maximum ozone and PAN mixing ratios reach 120 ppb and 3 ppb, respectively, until present. The annual variation of ozone and superimposed short-term fluctuations are synchronous throughout the area. From this we conclude that the ozone level in the boundary layer is largely controlled by air mass and radiation conditions rather than local emissions. These have a slight effect only with respect to absolute ozone values, which are lowest in the central parts of the city and increase towards the rural and forested areas in the surroundings.

This definitely has consequences in view of ozone abatement strategies: Simple local traffic bans in restricted areas are unlikely to result in ozone reductions, they may locally even lead to higher ozone levels. If traffic bans are to be executed with the aim of reducing ozone, they must be maintained at least on a regional scale.

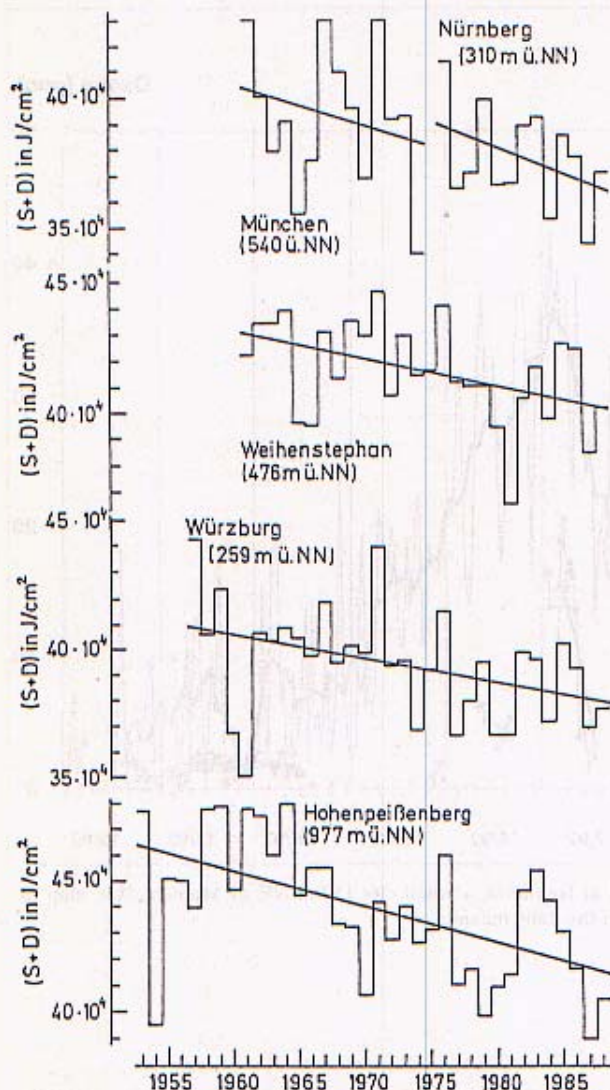


Figure 14 Annual sums of Global radiation from different stations in Germany. The average trends range between -2.2 and -5.0 percent/decade (After Rall and Mayer, 1989).

One of the major uncertainties in the quantitative assessment of photochemical and oxidant formation is the almost complete lack of knowledge on the hydrocarbon distribution in Southern Bavaria and its seasonal variation. Sources and distributions of NO_x are fairly well known (Schmid 1993), but except for a few pilot studies (Bayerisches Landesamt für Umweltschutz 1991, Riemschneider 1992), almost nothing is known on hydrocarbon sources, distributions and budgets.

Haustein (1992) found, during extended survey campaigns in the central part of Munich, a close

correlation between concentrations of NO and total nonmethane hydrocarbons (NMHC) and between CO and NMHC, respectively. This correlation, however, is likely to hold in the vicinity of the sources only, as the different hydrocarbons have quite different lifetimes due to their reactivity with OH . First measurements with on-line-gaschromatography carried out at our new institute site at Weihenstephan (about 30 km NE of Munich) show benzene, toluene and xylene to be the major NMHC components, with abundances ranging between 2 to 10 ppb during early January 1993. It is planned to improve and extend this technique in order to enable a first systematic survey on NMHCs in the area.

Another interesting aspect is the finding of Rall and Mayer (1989) that the global radiation in central Europe has been decreasing within the past 30 to 40 years, as shown by the annual sums displayed in Figure 14. This decrease is statistically significant and amounts to about 3 percent/decade. Using statistical methods, Liepert (1991) could show that part of this decrease is due to increased cloudiness as a result of regional changes of the circulation. For Weihenstephan and Hohenpeißenberg, however, no significant variation of cloud cover as inferred from total hours of sunshine could be detected. Thus increased turbidity is likely to be the main cause of the observed decrease of global radiation in southern Bavaria.

The Hohenpeißenberg ozone data show that tropospheric ozone and thus photochemical activity in southern Bavaria have continuously been increasing since the sixties. (Wege and Vandersee 1991.) As gas-to-particle conversion and aerosol growth proceed in photochemical reactions, these must consequently be considered as the most likely causes of increased turbidity. Detailed model studies are needed to investigate these processes, which may be important for the regional climate.

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