

Peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN) and PAN/ozone ratio measurements at three sites in Germany

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ABSTRACT

PAN and PPN have been measured for some months at a rural site (Lindau) and an urban site (Munich) and during 3 short campaigns at a forest site (National Park Bayerischer Wald) in 1988–1990. PAN was measured concurrently with ozone most of the time, while some concurrent measurements of nitrogen oxides and meteorological parameters have also been made. Monthly mean values of PAN at Lindau were highest during April. A strong positive correlation between PAN and O₃ was found during months with high solar radiation, suggesting significant ozone production in the boundary layer at all three sites. The ozone/PAN ratios were lower at higher PAN concentrations at all sites. Influence of wind direction and speed on PAN levels, and dependence on the general weather type are also reported for the Lindau site. These data suggest significant transport from the former East Germany. PPN has also been detected, its concentration in Lindau and Munich being around 11 % and 7 % of that of PAN, respectively.

1. Introduction

Peroxyacyl nitrates (PANs) are a group of organic nitrogenous compounds produced by the atmospheric photooxidation of non-methane hydrocarbons (NMHCs) and oxides of nitrogen (NO_x). The most abundant members of the group are peroxyacetyl nitrate (PAN, CH₃C(O)O₂NO₂) and peroxypropionyl nitrate (PPN, C₂H₅C(O)O₂NO₂), the latter normally found at concentrations about 10 % those of PAN. Both compounds are strong eye irritants, lachrymators, phytotoxic, and possible mutagens and skin cancer agents (Mudd, 1966; Taylor, 1969; Stephens, 1969; Peak and Belser, 1969; Shepson et al., 1986; Lovelock, 1977). PAN can be used as an indicator of photochemical activity in the troposphere (Stephens, 1969; Nieboer and Van Ham, 1976;

Nielsen et al., 1981; Penkett and Brice, 1986). Further, it has been found to play an important role in the transport of NO_x over long distances (Singh and Hanst, 1981; Singh et al., 1985). The main decomposition pathway for PAN is thermal loss by



and subsequent removal of the peroxyacetyl radical by NO or other reactive species (RO₂, HO₂)



In the absence of sunlight and reactive compounds, PAN can remain in equilibrium with NO₂ and the peroxyacetyl radical for some time. The equilibrium is such that PAN is relatively stable at the cooler temperatures above the boundary layer, but is unstable close to the surface. Thus, PAN will release NO₂ if it is transported from cooler to warmer temperatures.

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In recent years, PAN has been measured in a variety of locations in different seasons. The main body of data available consists of short-term measurements in urban environments, mostly carried out during the summer season, while some data from other seasons and from rural and remote atmospheres have also been reported (Nieboer and Van Ham, 1976; Nielsen et al., 1981; Peake and Sandhu, 1983; Brice et al., 1984; Corkum et al., 1986; Fahey et al., 1986; Singh et al., 1986; Tsalkani et al., 1987). Only limited data are available on PPN levels (Singh and Salas, 1989; Ridley et al., 1990b; Shepson et al., 1992a; Walega et al., 1992). PAN has also been measured in concentrations from a few ppt to a few hundred ppt in the free troposphere (Singh and Salas, 1983; Rudolph et al., 1987; Bottenheim and Gallant, 1989; Ridley et al., 1990a; Singh et al., 1990).

In this study, PAN and ozone relationships from measurements made at three sites in Germany, an urban one (Munich), a rural one (Lindau) and a forest one (National Park Bavarian Forest) are reported. The Munich measurements and the Lindau ones cover extended periods of time, and all 4 seasons are represented, while the Bavarian Forest ones were made during summertime (24 days) and autumn (8 days). In addition, nitrogen oxides, global solar radiation and wind direction and speed were monitored for a fraction of the time. Monthly mean PAN levels and diurnal variation of PAN, as well as dependence on wind direction and speed and General Weather Type (GWT) are also reported for Lindau, while an extensive report concerning PAN levels and dependence on various meteorological parameters in Munich has already been made (Rappenglück, 1990) and will be presented elsewhere. The GC system employed allowed the measurement of PPN at times when its levels exceeded the detection limit. These PPN measurements are also reported. A total of approximately 7500 air samples were analysed in Lindau, 11500 in Munich and 1500 in the Bavarian Forest, PPN exceeding our detection limit 339, 388 and 15 times, respectively.

PAN has already been measured in some sites in (former) West Germany. Löbel et al. (1980) report measurements carried out in the city of Bonn during the summer of 1975, and Bruckmann and Eynck (1979) report PAN measurements made in the city of Essen during the period June–

September 1978. Helmig et al. (1990) report PAN measurements at three heights in a forest site (Eggegebirge) for a more extended period, January 1988–January 1989.

The Lindau measurements (May–August 1988, November 1988–April 1989) were made on the roof of the two-storey building of the Max-Planck-Institut für Aeronomie (MPAE). Lindau ($51^{\circ}06'N$ $10^{\circ}20'E$, 140 m ASL elevation, Fig. 1) has 2000 inhabitants and is located in central Germany, in the Federal State of Niedersachsen, some 20 km from the border to the former GDR. Munich (1.27 million inhabitants) lies in the southern part of the FRG ($48^{\circ}20'N$ $11^{\circ}55'E$). The measurements were made during two periods, June–September 1989 (I) and December 1989–April 1990 (II). During

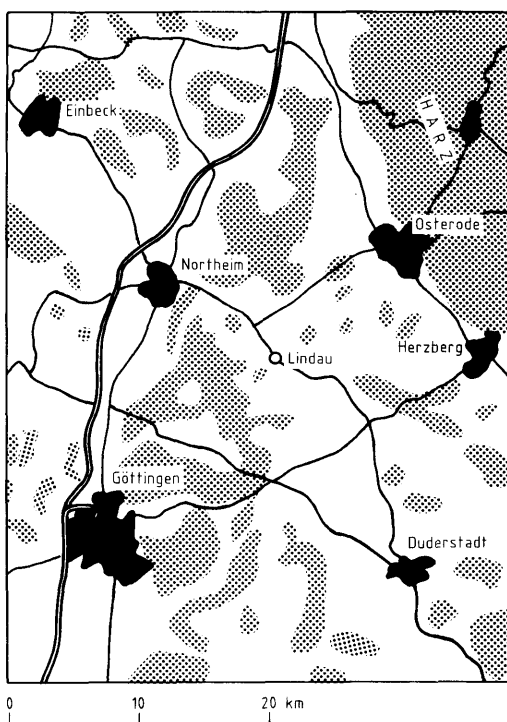


Fig. 1. The Lindau area. The shadowed areas represent forests, the black ones towns, and the white ones are mostly agricultural areas. Göttingen has 120,000 inhabitants, Northeim 30,000, the rest fewer than 20,000. 140 km N lies Hannover with 550,000 and 65 km SW Kassel with 200,000. 15 km NE are the Harz mountains (1142 m), and 14 km W passes the Würzburg–Hannover highway with direction NNE.

period (I) they were made at 4 m above ground, at the site of the Max-Planck-Institut für Extraterrestrische Physik, approximately 5 km from the center of Munich at NNE. During period (II) the analytical instrumentation had been transported to the center of Munich, and air was sampled from the roof of a 5-storey building (sampling height: 38 m above ground). The measurements in the National Park Bayerischer Wald (Bavarian forest) were made at the Schachtenau site (48°57'N 13°25'E, 807 m ASL elevation). The National Park is part of central Europe's largest continuous forest, and lies in the eastern part of Bavaria, attached to the Czechoslovakian border. The forest consists of 86% spruce (mean height 28 m, needles down to 14 m) and 14% beech, with an average density of 712 stems/ha. The site has been described in detail elsewhere (Enders et al., 1991). There are two small villages 2.5 and 4 km SE and a small town with a few thousand inhabitants 10 km to the south. The main road in the area, with not much traffic, passes south of the site. The PAN, O₃ and NO_x measurements reported here from the forest site were made below canopy, at 2-m height. Some PAN measurements at different heights (below, within and above canopy) were also made during the third campaign and have been reported elsewhere together with terpene, peroxide, organic acid and ammonia

measurements made by other groups (Enders et al., 1991). A detailed description of the meteorological situation during the third campaign can also be found in the above mentioned paper. Time series of PAN, O₃, NO and NO₂ during the three campaigns can be found in Kourtidis (1991).

2. Experimental

PAN and PPN measurements were made using a PACKARD 438A gas chromatograph equipped with an ECD. A 10% Carbowax 400 on Chromosorb WHP 80/100 mesh column (glass, i.d. 2 mm, 40 cm long) kept at 40°C separated PAN from PPN with retention times of approximately 4 and 5 minutes respectively (Fig. 2). The ECD was kept at 100°C and the flow rate of the carrier gas (N₂ 5.0, purity > 99.999%, passed through a Molecular Sieve 5Å filter) was around 40 ml/min. The ECD was operated within a signal range of 25 to 40 kHz. This is a much higher signal than the one recommended by the GC manufacturer for ideal sensitivity (around 5 kHz), but in our case we found that the sensitivity of our system was greater at higher signals. The sensitivity to PAN at a 20 kHz signal was around 100% greater than at a 10 kHz one. The identity of PAN in the air samples was established

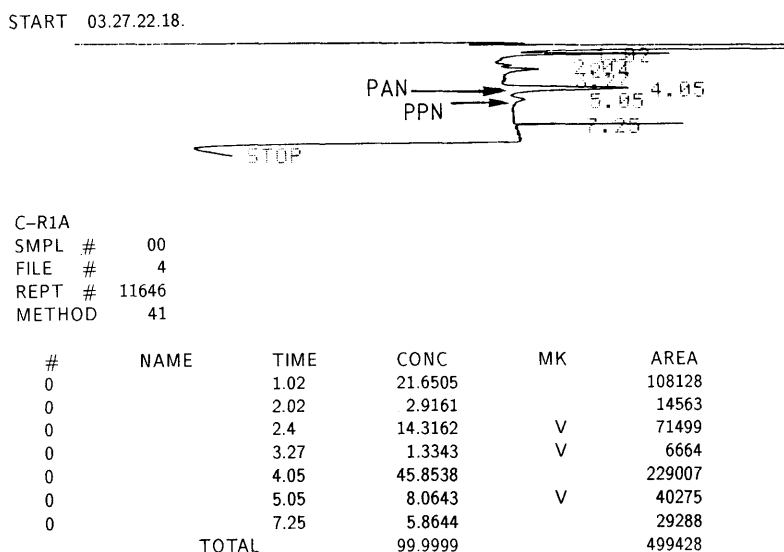


Fig. 2. An ambient air chromatogram of PAN and PPN recorded at Lindau on 27 March 1989.

by retention time measurement. Various other tests were made to confirm the identification of the peak. We observed (a) disappearance of the peak by passing the air through a KOH scrubber, (b) decrease of the peak area, and finally disappearance of the peak by increasing the temperature of a stainless steel tubing connecting a bag with a PAN/zero air mixture in the ppb range with the sample loop and (c) by employing helium as a carrier gas and coupling the GC with a mass spectrometer, a peak at $m/e = 46$ was observed at the retention time of PAN. The identity of the PPN peak was established by comparing the relative retention time of the peak (reference compound: PAN) to the ones reported for PPN by other investigators. Calibration was performed every 3–4 weeks, using PAN standards only. We assumed an identical response to PPN, since their electron ionization efficiencies are virtually identical, and a number of investigations showed identical ECD responses for both compounds (Darley et al., 1963; Singh and Salas, 1989; Walega et al., 1992). Ambient air was sampled continuously through a 1/4" OD Teflon tube and automatically injected every 20 min using two computer-controlled pneumatic valves which activated a 6-port valve. The sample loop (stainless steel, 1/8" OD) had a volume of 1.63 ml. Sample line lengths were 7–8 m for the Lindau and the forest measurements, and the first four months of the Munich ones. The residence time of the sampled ambient air in the tubing was around 7 seconds for these measurements. During the second period of the Munich study, ambient air was first drawn through a 25 m long, 3-cm i.d. Teflon tube by a turbo pump, and then was subsequently further pumped from a glass distributor to the analytical instrumentation. In this case the residence time in the tubing was around 10 s. A Shimadzu CR-1 computing integrator was used to record the data.

Calibration was performed by diluting synthesized PAN solutions in n-heptane. The standards were synthesized using the method of Nielsen et al. (1982). The absolute PAN content in the standards was determined by FTIR spectroscopy or by $\text{Na}_2\text{S}_2\text{O}_3$ titration in a KI solution. Storage of the solutions at -20°C to -30°C prevented fast decay of PAN, but after six months of storage the PAN content was found to be almost halved. The dilution procedure was as follows:

μl aliquots of the PAN/n-heptane solution were injected through an injection port into a 29-lt STP calibration bag (Linde Gas). The bag was at that moment getting filled with zero air (5.0, purity > 99.999 %) entering the bag through the injection port. This way the PAN/n-heptane solution was flushed by the zero air stream into the bag. This procedure of injecting the standard ensured good mixing. 0.1–0.2 ml of H_2O were injected into the bag to humidify the air. After the bag had been filled, it was connected to the 6-port sampling valve through the Teflon tubing used for the ambient air sampling, and an injection was made with the same automated procedure as for the ambient air analysis. The whole procedure, from the injection of the PAN standard until the start of the analysis lasted less than 5 min. A blank injection was also made with the same procedure at the beginning of the calibration. 2 to 4 analyses at various mixing ratios followed, so that a 3 to 5-point calibration curve was obtained, for mixing ratios usually in the range 1–20 ppb (occasionally 0.4–20 ppb). The response was linear within this range. The detection limit was normally around 50 ppt. In some cases, especially in the Munich measurements, baseline noise raised the detection limit to higher levels (up to 120 ppt). The GC was calibrated on-site during the second and the third campaign at the Bavarian Forest. No on-site calibration was made during the first campaign. In that case, the GC was calibrated at MPAE prior to the campaign, and then transported to the Bavarian Forest. The column was not removed during transportation and no other modifications were made. At the end of the campaign, the GC was recalibrated in Lindau. These two calibrations gave responses to PAN that differed by about 10%. The absence of on-site calibration during this campaign might induce an additional error to these measurements. The estimated accuracy of the PAN measurements is $\pm 20\%$ ($\pm 30\%$ for PAN below 1 ppb) and the precision $\pm 10\%$. The assumption of identical response may induce a small additional error to the PPN measurements. For the computation of PAN monthly means and monthly averaged diurnal variations, data below the detection limit were assigned a value of 1/2 the limit.

The ozone measurements were made with a commercial Dasibi 1008 RS UV ozone analyzer. The detection limit of the analyzer is 2 ppb and the

uncertainty $\pm 10\%$. The instrument has a resolution of 20 seconds. The 60 values of a 20-min interval (-10 min to $+10$ min from the PAN analysis) were averaged for comparison with the PAN measurements.

Nitrogen oxides were measured with a Scintrex/Unisearch LMA-3 NO_2 analyzer. The analyzer was coupled with a CrO_3 converter (LNC-3, of the same manufacturer) which oxidises NO to NO_2 . The measurement principle of the analyzer is based on the chemiluminescence of the reaction of NO_2 with a luminol solution. The analyzer has a detection limit of 5 ppt. Kelly et al. (1990) report that the instrument response is not linear for $\text{NO}_x < 2$ ppb. PAN and ozone interfere with the measurement. The PAN and ozone interferences were not tested in this work. Many investigations of these interferences were made by various groups (Fehsenfeld et al., 1990; Kelly et al., 1990, references therein). They all report equivalent responses in the range 24–25% for PAN and 0.33–1% for ozone. These interferences do not pose any problem for polluted air where $\text{NO}_x > 10$ ppb, since for the usually encountered PAN and ozone concentrations they will likely be negligible. They must be taken into account, though, for measurements in relatively clean air such as those in the Bavarian Forest. Since concurrent PAN and ozone measurements were available at the latter site, the instrument readings were corrected according to the formula $[\text{NO}_x] = [\text{NO}_{x(\text{LMA}-3)}] - 0.006[\text{O}_3] - 0.24[\text{PAN}]$. The

analyser was calibrated by dynamical dilution of commercially available NO and NO_2 mixtures in 101 pressurized cylinders (AGA Edelgas). The stability of NO and NO_2 in the cylinders was monitored by cross-referencing of 4 different cylinders. The calibration range was 1–50 ppb. The CrO_3 converter efficiency varied from 100% within the limits of experimental uncertainty ($\pm 4\%$). More details on the calibration can be found in Wendt (1991).

3. Results and discussion

3.1. Measurements at Lindau

A summary of the PAN and ozone measurements is given in Table 1. The year 1988 was characterized by a smaller frequency of easterly weather situations than the long-term average, with a consequently smaller transport of pollutants from the east. Additionally, the winter months of 1988/89 were exceptionally mild, so although solar radiation facilitated PAN production, the prevailing conditions did not favour the transport of pollutants (e.g., PAN and/or its precursors) from a distance. This is also demonstrated by the fact that SO_2 concentrations measured in the Federal State of Niedersachsen this winter at the LÜN (: Niedersachsen Air Quality Monitoring System) stations (LÜN Jahresbericht, 1988; LÜN Jahresbericht, 1989) were lower than the long-term average. In both

Table 1. Mean and maximum PAN and ozone concentrations (in ppb) in Lindau and the National Park Bavarian Forest (NPBW)

Date	Site	PAN	PAN _{max}	N(n)	Ozone	Ozone _{max}
May 1988	Lindau	0.564	1.230	29(0)	—	—
June 1988	Lindau	0.197	0.952	186(37)	—	—
July 1988	Lindau	0.268	1.049	552(12)	18.5	53
August 1988	Lindau	0.419	0.962	305(11)	19.1	69
November 1988	Lindau	0.264	0.957	490(23)	9.1	25
December 1988	Lindau	0.162	1.136	635(55)	8.3	28
January 1989	Lindau	0.337	1.260	1169(9)	—	—
February 1989	Lindau	0.447	2.921	823(6)	—	—
March 1989	Lindau	0.596	3.411	1956(3)	—	—
April 1989	Lindau	1.140	4.712	1479(0)	17.9	48
19 June–1 July 1988	NPBW	0.133	0.684	751(36)	19.1	48
30 May–11 June 1989	NPBW	0.294	0.886	391(30)	21.9	51
19–28 September 1989	NPBW	0.241	1.055	506(29)	11.5	42

N is the number of analyzed samples and n is the % of analyses below detection limit.

1988 and 1989, the frequency of days with midday temperature inversions in the 1000 m layer was lower than the average of the last 10 years (LÜN Jahresbericht, 1988; LÜN Jahresbericht, 1989). The above-mentioned features of these two years may have resulted in PAN concentrations measured in Lindau during this study that are lower than the ones from previous years. The monthly means of PAN and ozone are displayed in Fig. 3 together with ozone data from four neighbouring stations where the record is complete, the latter taken from LÜN Jahresbericht 1988/1989. A PAN monthly maximum of 1.14 ppb was observed in April 1989, and a monthly minimum of 0.16 ppb in December 1988. The maximum daily mean observed was 3.2 ppb and the maximum of one single analysis was 4.7 ppb, both observed in April 1989. The high PAN concentrations observed in April can be attributed to a combination of many factors. The solar radiation is quite intense at this time of the year, leading to a substantial PAN production, and the temperatures are lower than the summer ones, so the destruction of PAN is slower than in summer. Additionally, part of this maximum might be due

to the consumption of NMHCs accumulated in the atmosphere during the winter months (Penkett and Brice, 1986). NMHCs' concentrations measured in England at a height of 1500–3000 m were found to be much higher during winter and early spring than in summer (Lightman et al., 1990). From ethane total column abundances measured in Switzerland, the ratio of maximum (spring) to minimum (fall) C_2H_6 concentration in the troposphere was found to be 1.88 ± 0.12 (Ehhalt et al., 1991). Recently published results from measurements over the north Atlantic ocean show background spring/winter ratios for various NMHCs ranging from 1.8 for ethane to 18.4 for n-pentane (Penkett et al., 1993). This behaviour is not confined to Europe only, but seems to be characteristic of the Northern hemisphere, as NMHCs' measurements in other places have shown (Singh and Salas, 1982; Hov et al., 1984).

PAN exhibited its well-known diurnal variation, with early afternoon maxima and night-time minima. During periods when intense solar radiation was absent, its concentration remained stable throughout the day. Monthly averaged diurnal variations of PAN are displayed in Fig. 4.

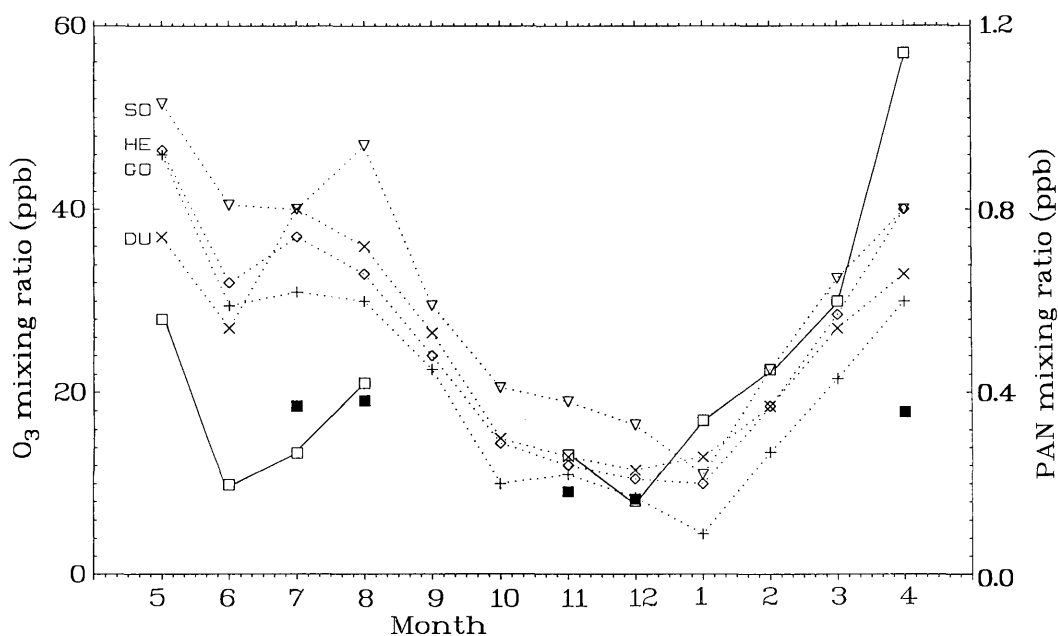


Fig. 3. PAN and O₃ monthly means in Lindau (□ = PAN, ■ = O₃) and ozone monthly means in four neighbouring stations (GO = Göttingen, HE = Herzberg, DU = Duderstadt, SO = Solling) in 1988/1989.

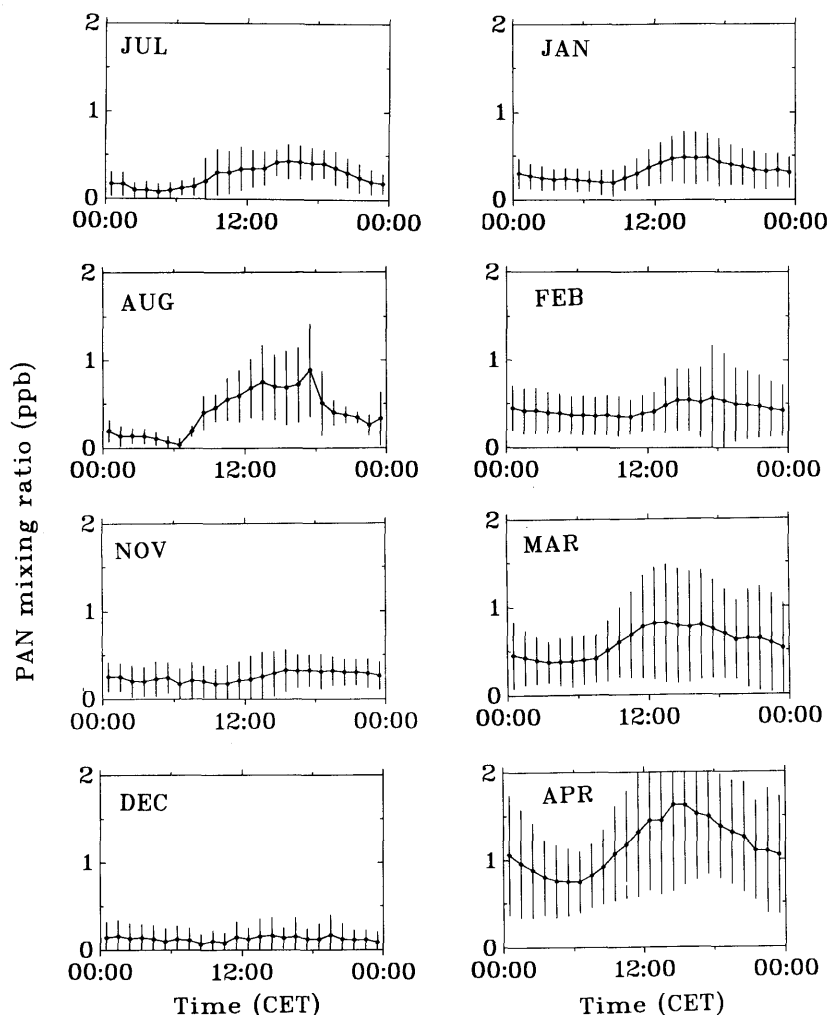


Fig. 4. PAN monthly averaged diurnal variation in Lindau. The vertical lines represent the standard deviation of the measurements.

During March and April 1989, concurrent measurements of wind direction and velocity were made in Lindau (Fig. 5). NO_2 and NO were also measured for 41 days during this period. Nitrogen dioxide and nitrogen monoxide daily means were in the range 2–20 ppb (usually around 10 ppb) and 0–10 ppb (usually around 1.5 ppb), respectively, with no correlation between concurrently measured NO_x and PAN during day or night. This is due to the different diurnal patterns of NO_x and PAN.

The lowest PAN concentrations were encountered

in the west wind sector, thus the contribution of the Würzburg–Hannover highway to high PAN mixing ratios in Lindau is low. Transport from the east is evident in Fig. 5, PAN concentrations being high for winds from the SE, and increasing with wind speed for the whole NE to SE sector. The NO_2/NO ratio also increased from a mean value of 4.5 for winds < 2 m/s to a mean value of 8 for winds > 2 m/s, so the loss of PAN through removal of the peroxyacetyl radical from the equilibrium (1) via reaction with NO is expected to have decreased. A division of the data set into day

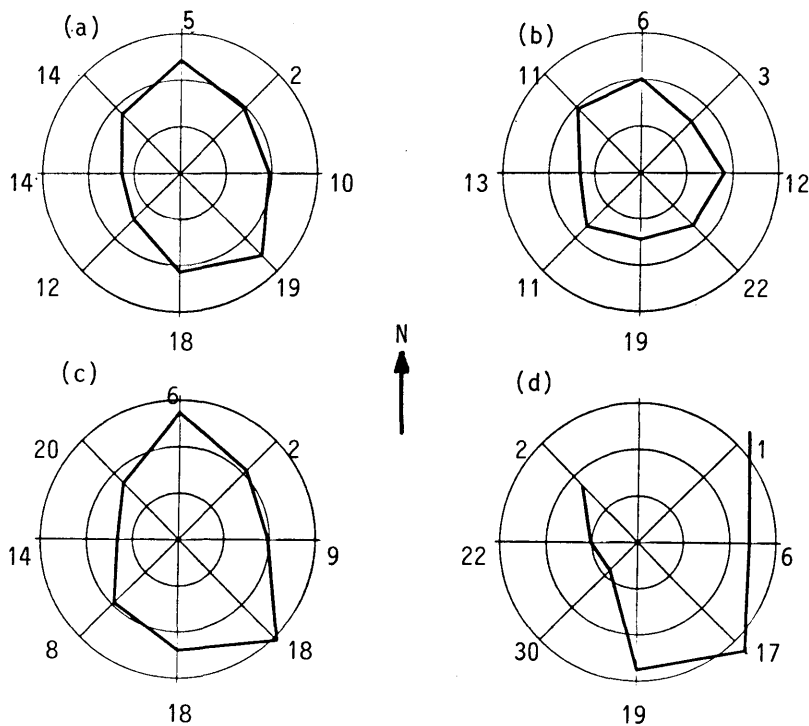


Fig. 5. Mean PAN concentrations for the eight main wind directions, (a) for all winds and (b, c, d) for three different wind speed ranges (0–2 m/s, 2–5 m/s and > 5 m/s, respectively) at Lindau (March and April data only). The number at each sector is the % frequency of winds coming from this direction. The radius of the outer circle is 1.5 ppb.

and night measurements does not affect the characteristics of the PAN wind roses. The same features arise in Fig. 6, where daily mean PAN concentrations and the General Weather Types (GWT) in Europe as defined from Hess and Brezowsky (1977) are considered for the whole period of measurements at Lindau. The GWT indicates the main tropospheric wind flow over Europe and is published for each day from the German Meteorological Office in *Die Grosswetterlagen Europas*. For temperatures of 8°C in Lindau at the time of the measurements and NO_2/NO ratios between 4.5 and 8, by taking $k_1 = 1.95 \times 10^{16} \text{e}^{-13543/T} \text{ s}^{-1}$ and $k_{-1}/k_2 = 0.5$ (Atkinson and Lloyd, 1984 and references therein) from

$$-\frac{d}{dt} \ln[\text{PAN}] = k_1 \left\{ 1 - \frac{1}{1 + (k_2[\text{NO}]/k_{-1}[\text{NO}_2])} \right\}$$

(Cox and Roffey, 1977), PAN lifetimes in the range

25–38 h are deduced. The above-mentioned PAN maxima can thus be attributed to transport from the former GDR. No NMHC measurements in GDR are available to our knowledge, but our measurements suggest that their concentrations

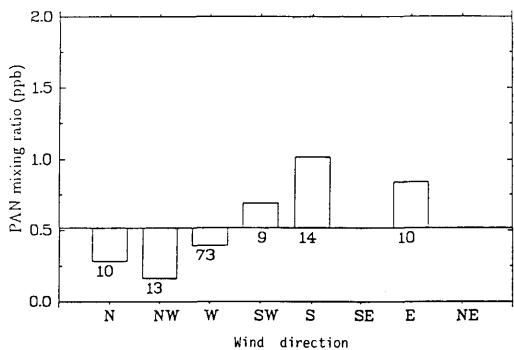


Fig. 6. Mean PAN daily concentrations at Lindau for different General Weather Types. The horizontal line is the mean of all daily means. The numbers are the number of days of each GWT.

must be higher than in (former) West Germany. The use of lignite as a primary energy source and the absence of efficient filters in the power plants of GDR results in the emission of large quantities of NMHCs into the atmosphere. In the large area around the triangle formed by the cities of Halle, Leipzig and Bitterfeld (around 170 km SE of Lindau) some of the most important chemical factories of East Germany are located. They produce various kinds of fuels, nitrogen fertilizers, chemicals and plastics. Many coking plants are operated in this area. During the process of the conversion of lignite to coke, around 400 m³ of gas containing around 4.5% of gaseous NMHCs, 4% CO and 13% CH₄ are emitted per tonne of used lignite (Römpps Chemie-Lexikon). The results of Schmidt (1993) concerning the wind direction of observed ozone maxima in the period May–August 1989 at various LÜN stations in the proximity of Lindau further support our results. Nine out of ten stations experienced O₃ maxima when the air was coming from the direction of the above mentioned triangle.

3.2. Measurements at the National Park Bavarian Forest

In the Bavarian forest site, the highest PAN value measured was 1.05 ppb, so concentrations considered to be phytotoxic (>10 ppb for 4 h) have not been encountered during this study. The area receives relatively clean air, with NO₂ usually around 1–2 ppb and NO around 100–300 ppt. The PAN mixing ratios (Table 1) are in reasonable agreement with the ones reported for forest sites in Europe by other investigators. Perros et al. (1988) report average concentrations around 300 ppt in September 1986 and 400 ppt in June 1987, measured in a forest site in France (Donon). Helmig et al. (1990) report an average of 100 ppt at 1 m height in a forest site in Germany (Eggebirge) during the period 21.–27.6.1988.

PAN and ozone levels measured in the Bavarian Forest, generally follow the solar radiation fluxes, and additionally, the two substances follow extremely parallel fluctuations on most days (Fig. 7). PAN daily maxima usually coincided

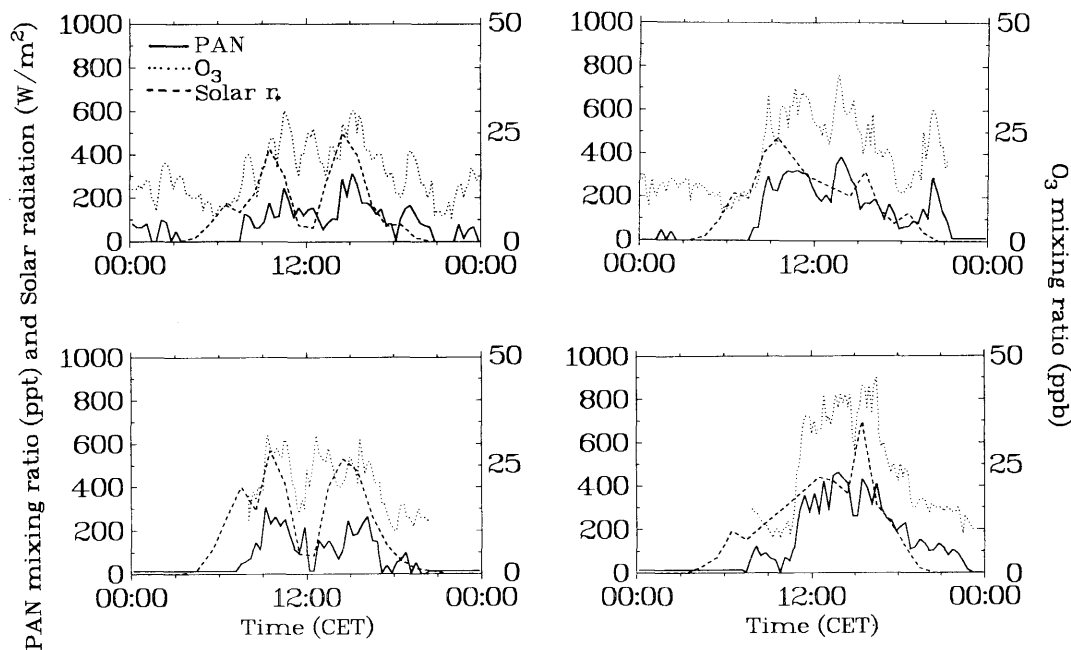


Fig. 7. Diurnal variations of PAN (1 analysis every 20 min) and ozone (10-min means) below canopy and hourly averaged solar radiation at 50 m (provided by LfBAM) for 4 consecutive days (from top left to bottom right: 26 June–29 June 1988) during the forest measurements.

with, or had around a 1 h difference from the solar radiation maxima, and higher PAN concentrations were observed on days with high solar radiation. These features may indicate that there is some local production of PAN from biogenic HC's emitted from the forest. α -pinene and β -pinene measurements made by the Technical University of Munich concurrently with our PAN measurements on 19 September 1989 showed concentrations of these two substances around 800 ppt at 6:00, declining to less than 100 ppt at 12:00 (Enders et al., 1991). The photochemical oxidation of these and other biogenic HC's will yield PAN precursors (methyl glyoxal and biacetyl) which will ultimately produce PAN, as model calculations and measurements showed (e.g., Brewer et al., 1984; Trainer et al., 1991).

The rôle of transport in determining the PAN concentrations observed at the site is demonstrated by the correlation observed between PAN mixing ratios and wind speed during the most photochemically active part of the day (10:00–16:00). Higher wind speeds were associated with higher PAN concentrations. During the first campaign, for example, PAN mixing ratios were around 390 ppt for winds of 4 m/s and 120 ppt for winds of 1 m/s during daytime. The square of the linear correlation coefficient between PAN and wind velocity was $r^2 = 0.52$ (0.999 confidence), and the good correlation was not due to a positive correlation of wind speed and solar radiation, since the square of the linear correlation coefficient for the latter two was only $r^2 = 0.006$. Higher wind speed will result in better mixing of outside air with air inside the forest during stable night-time conditions, when the nocturnal boundary layer is established. During day-time, though, the effect of the wind speed on PAN downward fluxes will not suffice to account for the observed difference, if one assumes that the PAN downward fluxes will behave similarly to the calculated ozone ones (Enders et al., 1991). It seems that if PAN is not rapidly advected into the forest from source regions, its concentrations will remain low due to dry deposition losses within and below the canopy. Measurements of PAN above (41 m), inside (21 m) and below (2 m) the canopy made during the third campaign resulted in averages of 497 ppt, 450 ppt and 421 ppt, respectively, showing dry deposition losses of PAN within the canopy (Enders et al., 1991).

3.3. PAN/ozone ratios

During the winter months, when concurrent PAN and O_3 measurements were made in Lindau and Munich, the ozone levels were independent of the PAN ones. This behaviour is attributed to slow photochemistry, and has also been observed by Singh et al. (1985) at a mountain site receiving clean continental air. From the late spring till the late summer, PAN and ozone are well correlated ($r^2 = 0.15$ – 0.67) at all three sites. The square of the linear correlation coefficient r^2 and the coefficients a and b of the regression line $[O_3] = a + b \cdot [PAN]$ for the cases of good correlation are given in Table 2. The confidence level for r is 0.999. PAN below detection limit has been excluded. This correlation is an indication of a common way of production for ozone and PAN. As already mentioned, both can be produced photochemically from the photooxidation of various NMHCs, which yield peroxy radicals. These facilitate ozone production through conversion of NO to NO_2 . One of these radicals, the peroxyacetyl radical, can also produce PAN through (1). Ozone is also transported from higher altitudes, and can be produced by $NO_x/CO/CH_4$ photooxidation, which is not the case for PAN. Dry deposition is a destruction pathway for both, and at low humidity and low NO/NO_2 ratios in the stable nocturnal boundary layer it is believed to be their dominant loss process (Shepson et al., 1992a, b). It is unclear, though, whether dry deposition loss is more efficient for PAN or ozone, since earlier

Table 2. Square of the linear correlation coefficient (r^2) and regression line coefficients (a), (b) for PAN and O_3 according to $[O_3] = a + b[PAN]$. NPBW denotes the Bavarian Forest

Date	Site	a	b	r^2
July 1988	Lindau	6.9	42.5	0.62
August 1988	Lindau	2.0	41.9	0.67
April 1989	Lindau	4.9	9.6	0.53
June 1989	Munich	9.3	25.8	0.18
July 1989	Munich	4.4	20.6	0.48
August 1989	Munich	7.7	17.6	0.34
September 1989	Munich	-2.3	17.4	0.61
April 1990	Munich	7.4	16.8	0.15
19 June–1 July 1988	NPBW	12.2	50.7	0.52
30 May–11 June 1989	NPBW	18.0	36.7	0.52
19–28 September 1989	NPBW	2.9	40.9	0.66

measurements (Hill, 1971; Garland and Penkett, 1976) determined a $V_d(\text{O}_3)/V_d(\text{PAN})$ ratio roughly $5\text{--}6 \times$ higher than the one of 0.42 ± 0.19 reported recently by Shepson et al. (1992b). Another destruction pathway for ozone is NO titration. PAN can also be lost by removal of the peroxyacetyl radical from the equilibrium (1) via reaction with NO at high NO/NO₂ ratios.

During the months when ozone and PAN are well correlated, a ratio of 37–51 ppb ozone for each ppb of PAN is derived from the slope of the regression line for Lindau (July and August) and the Bavarian forest. This is in agreement with the ratio of 50 observed by Brice et al. (1984) in rural Harwell, UK. In Munich, a smaller ratio of 17–26 ppb O₃/ppb PAN was observed, in accordance with other observations at urban environments (14–26 in the studies referenced at the end of this paragraph). A very low ratio of 9.6 was observed during April at Lindau. The low ratio and the high PAN concentrations during April are indicative of the presence of large amounts of NMHCs in the troposphere over Lindau this time of the year, since ozone/PAN ratios encountered in urban air are lower than the ones at rural/remote environments or the free troposphere (Altshuller, 1983; Singh et al., 1985; Ridley et al., 1990b; Singh et al., 1990; Shepson et al., 1992a).

The increasing ratio for air masses with growing

distance from sources is due to two principal factors, namely the decreasing concentrations of the PAN precursors, and the increasing opportunity for PAN loss due to thermal decomposition. In Fig. 8, the individual O₃/PAN ratios for all the Munich measurements are displayed. It can be seen, that for PAN above around 2 ppb, the O₃/PAN ratios are below 25. As the PAN mixing ratios decrease, the scatter of the O₃/PAN ratios increases, and so do the highest ratio values. For PAN < 30 ppt, values as high as 800 were encountered. It seems that for air masses where substantial PAN production takes place, i.e., air masses with high NMHC's abundances, the O₃/PAN ratios will move in a relatively narrow range of 15–25. As the NMHC's deplete, PAN destruction will dominate production, the range of the O₃/PAN ratios will broaden, and, on the average, higher ratios will be encountered. The Lindau and Bavarian Forest O₃/PAN data exhibit a similar behaviour when plotted against PAN concentrations.

Although no correlation was observed between the individual measurements of nitrogen oxides and PAN at all 3 sites, higher concentrations of NO_x coincided with lower O₃/PAN ratios. This is demonstrated in Fig. 9 for NO_x below and above 4 ppb for the period of the third campaign at the Bavarian Forest site. A decrease of the ratio with

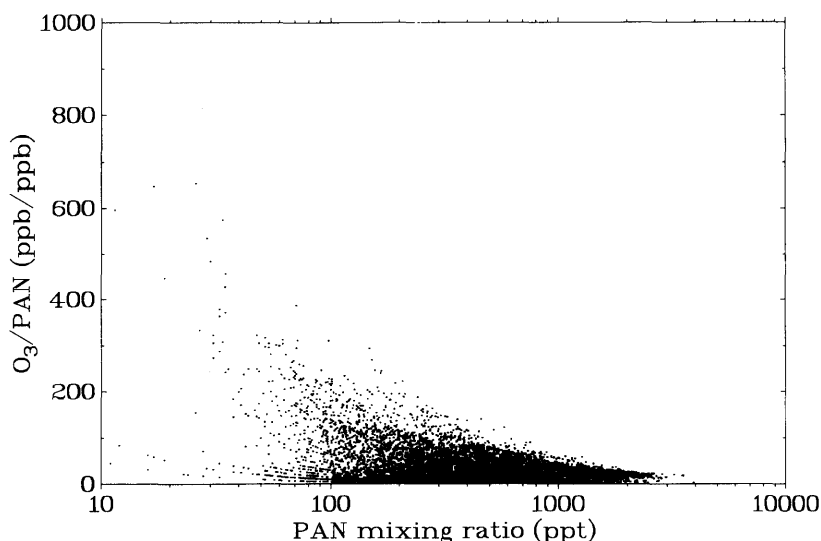


Fig. 8. Measured O₃/PAN ratios in Munich. See also text.

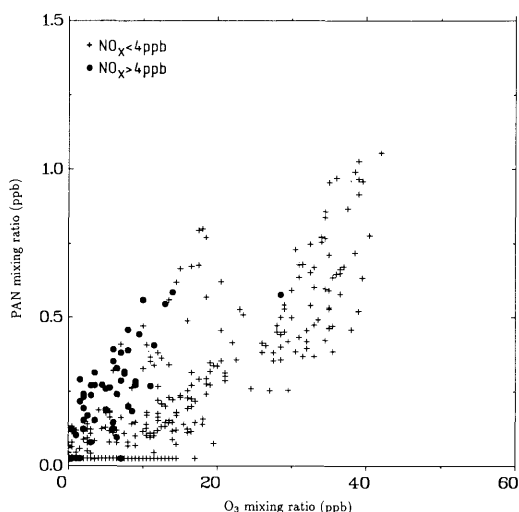


Fig. 9. PAN and ozone relationship in Bayerischer Wald for the period 19–28 September 1989 for NO_x mixing ratios above and below 4 ppb. Undetected PAN values are displayed as $1/2$ of the detection limit.

increasing NO_x for a given PAN concentration was also observed in Munich during June 1989 (Kourtidis et al., 1990). The Lindau data behave similarly, too. This is in agreement with the points made above concerning the O_3 /PAN ratio behaviour.

3.4. PPN measurements

The PPN peak was recognized by the integrator 339 times in Lindau, 244 of them during April 1989, when PAN concentrations were also high, and 388 times in the period June 1989–February 1990 in Munich. In March and April 1990, we stopped the integrator after the elution of the PAN peak because of high baseline noise, so no PPN measurements are available for this period. The highest concentrations encountered were 0.73 ppb in Lindau and 0.37 ppb in Munich. During days when both were recognized, PPN exhibited a diurnal variation similar to that of PAN. Fig. 10 shows the average diurnal variation of PPN during April 1989 in Lindau. Undetected values have been calculated at $1/2$ the detection limit. PPN diurnal behaviour was similar to that of PAN, levels starting to rise after 6:00, peaking between 15:00 and 17:00 in the afternoon, and then declining. PAN and PPN were well correlated (Fig. 11), with a square of the linear correlation coefficient (r^2)

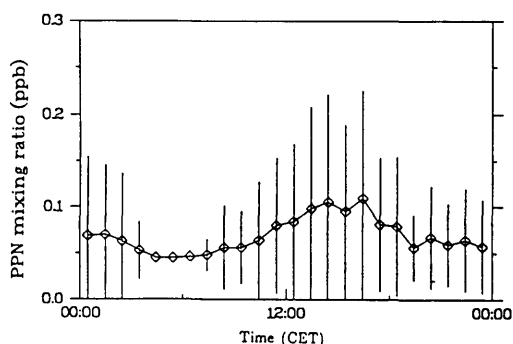


Fig. 10. Average PPN diurnal variation during April 1989 in Lindau.

between the individual measurements of 0.55 and 0.46 (Lindau and Munich, respectively). Each cross corresponds to 20 individual measurements grouped in order of increasing PAN. The horizontal lines represent the span of the involved PAN values, and the vertical ones the standard deviation of the PPN values (of the PPN/PAN ratio, on the other part of the same Figure). On average, PPN was present in concentrations around 11% and 7% (Lindau and Munich, respectively) of those of PAN. This is in agreement with ratios reported by other investigators (Ciccioli et al., 1986 [9%]; Singh and Salas, 1989 [3–14%]; Ridley et al., 1990b [16%]).

Ridley et al. (1990b) report a decline of the PPN/PAN ratio with decreasing PAN at lower PAN concentrations, which is not evident in our data. Shepson et al. (1992a), report PPN/PAN ratios that are independent of the PAN concentration. Further, while the first group reports PPN/PAN ratios that are higher during day-time, the ratios reported by the second group are higher during night-time. The latter was also the case for our measurements. The ratio PPN/PAN was lowest at the time of the PAN daily maximum. During night-time, PAN concentrations are lower than the day-time ones, so we could, at least partly, attribute the increase in PPN/PAN ratios at lower PAN concentrations observed in our data to the diurnal behaviour of the ratios. The thermal lifetimes of PAN and PPN are only slightly different (Roberts, 1990), so the variation must have other causes, that is, differences in the production rates or the deposition velocities. It is not clear, at the moment, whether PPN production becomes

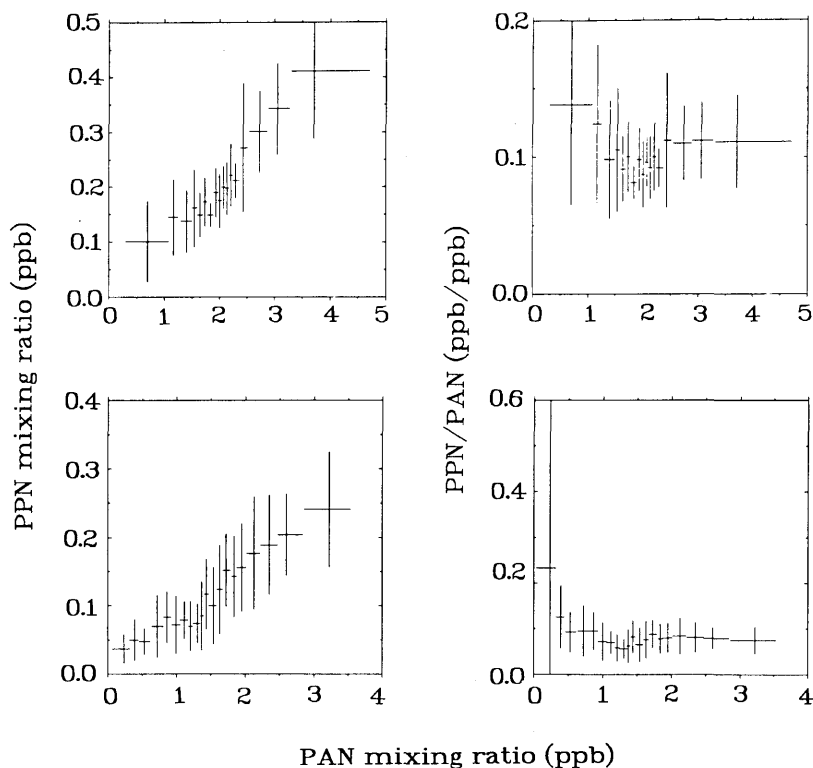


Fig. 11. PAN and PPN relationship, and the relationship of the PPN to PAN ratio with PAN at Lindau ($[PPN] = -0.014 + 0.109[PAN]$, above) and Munich ($[PPN] = 0.006 + 0.074[PAN]$, below). See also text.

more or less important as the air mass ages. The results of Shepson et al. (1992a) show an increase of the PPN/PAN ratio as the air mass moved downwind from urban Toronto to suburban Stouffville. The results of Singh and Salas (1989) and Ridley et al. (1990b), on the other hand, show a decrease of the ratio from urban to rural/remote sites. The present results, show a smaller ratio in urban Munich than in rural Lindau. The direct precursors of PAN and PPN, acetaldehyde and propionaldehyde respectively, have similar reactivities, but their own precursors (e.g., n-butane and 1-butene, respectively) do not. n-butane reacts slower with OH than 1-butene. One would expect, accordingly, that if the air mass moves away from sources of these compounds, 1-butene would deplete faster and the PPN/PAN ratio would decrease. PAN has other precursors than acetaldehyde, too (e.g., acetone, methyl vinyl ketone, methyl glyoxal and methacrolein). The results of

the present work and the ones of Shepson et al. (1992b) suggest that PPN might have other precursors beside propionaldehyde. To confidently interpret the PPN/PAN ratio behaviour at Lindau and Munich, though, concurrent measurements of the precursors of the two compounds are necessary.

In the Bavarian Forest, PPN was above our detection limit $9 \times$ during the first campaign, with concentrations 8.5 % of the ones of PAN, and $6 \times$ during the last campaign, with concentrations 5.3 % of the PAN ones.

4. Conclusions

PAN and ozone have been measured for some months at an urban (Munich) and a rural (Lindau) site in Germany, and for some days in a forest site (National Park Bayerischer Wald). A maximum of

PAN and a low O_3 /PAN ratio was observed at Lindau during April 1990. Transport of PAN and/or its precursors from the former GDR is indicated from meteorological observations. A good linear correlation between PAN and ozone concentrations was found for all sites in months with intense solar radiation, with O_3 /PAN ratios being lower at high PAN concentrations. PPN was also detected in some samples at concentrations around 10% of those of PAN. The PPN/PAN ratio was higher at low PAN concentrations.

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