

Peroxyacetyl Nitrate (PAN) Measurements During the POPCORN Campaign

W. SCHRIMPF, K. LINAERTS, K. P. MÜLLER, R. KOPPMANN and
J. RUDOLPH

Abstract. During the POPCORN campaign between 3 and 24 August 1994 we measured peroxyacetyl nitrate (PAN) in a rural area of Mecklenburg-Vorpommern (North-Eastern Germany) above a corn field. A total of about 5000 PAN measurements were carried out within the three weeks of the campaign. Measured PAN mixing ratios ranged from below the detection limit of 10 ppt up to an afternoon maximum of 1 ppb. The mean value of all data was 140 ppt. The daily mean PAN mixing ratios were typically in the range of 50 to 250 ppt, but during a clean air episode PAN mixing ratios of well below 40 ppt were observed. The characteristic relative diurnal variation of the PAN mixing ratios with a late night/early morning minimum and an afternoon maximum persisted during these episodes. The daily averages of the PAN mixing ratios showed clear episodic variations which coincided with the duration of typical synoptic episodes of two to six days duration. Based on the measurements of the various parameters determining the PAN formation and destruction rates, the local budget for PAN was calculated. During daytime the calculated net photochemical formation rate of PAN was nearly always significantly higher than the observed change of the PAN concentration. This demonstrates that substantial amounts of PAN (often in the range of several hundred ppt/h) were exported from the corn field. The resulting removal of NO_x to some extent effects the budget of nitrogen oxides (NO_x), but the export of odd oxygen radicals in the form of PAN during daytime often amounted up to 30–50% of the OH-radical formation by ozone photolysis. Thus the importance of PAN as reservoir and transport medium for odd oxygen radicals can be very substantial and may have a significant impact on the budget and distribution of odd oxygen radicals.

Key words: peroxyacetyl nitrate, rural measurements, odd oxygen radicals, photochemistry.

1. Introduction

Peroxyacetyl nitrate (PAN), a product of the photochemical oxidation of non-methane hydrocarbons (NMHC) in the presence of nitrogen oxides NO_x , is a crucial component of photochemical smog and plays an important role in tropospheric photochemistry. Three aspects are of special interest:

1. PAN is not emitted into the troposphere by anthropogenic or biogenic processes. Because it has no other source than its production by photochemical reactions it is a better indicator of photochemical smog than ozone (O_3) which is also transported from the stratosphere. Moreover in urban and rural areas O_3 shows a smaller diurnal variability on a higher 'background' concentration level than PAN

due to the larger importance of vertical transport on ozone concentrations in the planetary boundary layer (Rappenglück *et al.*, 1993; Bottenheim *et al.*, 1994).

2. PAN's thermal decomposition to yield free radicals and nitrogen dioxide (NO_2) can result in an acceleration of photochemical ozone production and the development of photochemical smog at elevated temperatures (Carter *et al.*, 1981).

3. The thermal decomposition rate of PAN shows a strong temperature dependence (Atkinson *et al.*, 1992; Bridier *et al.*, 1991). At low temperatures PAN acts not only as a temporary reservoir for photochemically active RO_x radicals but also as a reservoir for atmospheric odd nitrogen (Singh and Hanst, 1981). At temperatures below 283 K the thermal lifetime of PAN is several days and thus allows export of photochemical air pollution by long-range transport (Nielsen *et al.*, 1981).

Among the aims of the POPCORN campaign was the investigation of the influence of NO_x as well as locally emitted volatile organic compounds (VOC) including NMHC on the photochemical production of O_3 and RO_x in rural areas. Because of the aspects mentioned above regional measurements of atmospheric PAN levels in a rural environment are essential for the understanding of observed O_3 , NO_x and RO_x concentrations. A large number of PAN measurements in rural areas – mainly at Northern mid-latitudes – have been performed (Roberts, 1990 and references therein; Shepson *et al.*, 1992a; Hartsell *et al.*, 1994; Bottenheim *et al.*, 1994) since it has been identified as an important component in photochemical smog in the 1960s (Stephens, 1969). Rural measurements show daily mean values typically between 0.1 and 0.8 ppb with daytime maxima up to 4 ppb. Highest values of the daily means are most frequently observed in late spring. PAN shows a strong diurnal cycle with a maximum in the afternoon and a minimum around dawn. The diurnal variation is largest in summer while it becomes nearly insignificant in winter. The objectives of the PAN measurements during POPCORN included studies of the dry deposition of PAN by a gradient method. Details of this part of the POPCORN campaign are presented in another paper (Schrimpf *et al.*, 1996).

2. Experiment

During the POPCORN campaign PAN was measured with an optimized gas chromatograph (GC) equipped with an electron capture detector (ECD). The instrument was situated inside a container (Plass-Dülmer *et al.*, this issue). The complete measurement system is described in detail in a previous paper (Schrimpf *et al.*, 1995). The column oven temperature was 299 K, the ECD temperature 303 K and two short megabore capillary columns of different polarity were used for a two-dimensional sample separation. This way PAN could be separated completely from all other atmospheric trace components within 3 minutes. The measurement frequency was one chromatogram every 5 minutes, the detection limit 10 ppt (3σ), the measurement precision better than 5%, and the measurement accuracy better than 10%.

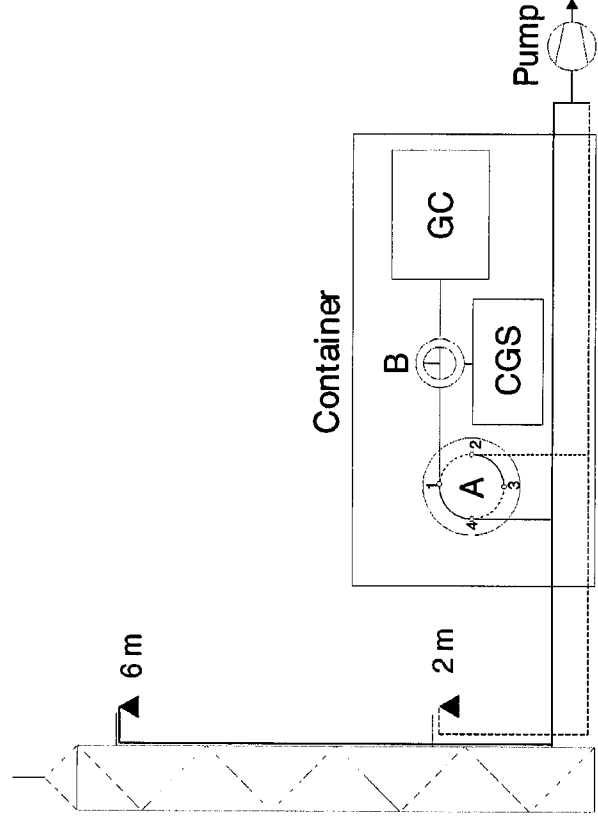


Figure 1. Setup of the inlet system for PAN measurements during the POPCORN field campaign. A represents the automatic four-way-valve, B the manual three-way valve, CGS the calibration gas source and GC the gas chromatograph. The three-way-valve (B) is in the position 'measurement mode'. The possible positions of the four-way-valve (A) are indicated by dotted and solid lines.

The measurements were made in the center of a maize field of about 35 ha area (600 m \times 600 m) near Pennewitt, a village of about 200 inhabitants in North-Eastern Germany. This remote site is located about 100 km east of Hamburg and about 20 km from the Baltic Sea. Within about 20 km distance only small villages with less than 10,000 inhabitants can be found. Only about 100,000 people live in this area and there are no major roads or industrial plants.

The instrument was housed in an air conditioned container. Air was sampled through two identical inlet lines (both of 6 mm ID \times 20 m Teflon tube) which were fixed at 2 m and 6 m height on a mast about 10 m south of the container. Details of the surroundings of the location, set up of the instruments and inlet lines are given by Plass-Dülmer *et al.* (this issue). Both inlet lines were constantly purged by a pump at a flow rate of 8 m³/h (Figure 1).

This way the PAN residence time inside the inlet lines was less than 0.5 s. For the special requirements of automated concentration gradient measurements the inlet system was modified to allow measurements at both heights. During the 'measurement mode' the manual three-way-valve (B) was in the position shown in Figure 1. A small flow of about 50 cm³/min was passed permanently through the four-way-valve (A) and the sample loop of the gas chromatograph (GC). The four-way-valve (A) was switched automatically every 5 min so that alternately ambient

air from 6 m and 2 m height was sampled and analyzed. Instrument calibration was performed utilizing a diffusion source for generating PAN calibration gas which is also described in detail by Schrimpf *et al.* (1995). A constant flow of nitrogen was passed over a PAN/*n*-hexane solution which was kept at 258 K. The PAN mixing ratio of the calibration gas was determined by hydrolysis at the field site and subsequent measurement of the formed nitrite ion concentration (Nicksic *et al.*, 1967; Stephens, 1967) in our laboratory with a photometric technique. This determination of the PAN concentration in the calibration gas was performed about twice a week and showed within the three weeks no systematic change, only statistical variations of less than 3%. The calibration gas was dynamically diluted with PAN-free air to obtain PAN mixing ratios in the range of expected ambient mixing ratios (50 ppt – 5 ppb). In the 'GC calibration mode' the inlet system was operated with the manual three-way-valve (B) turned to the 90° (clockwise) position. This way the diluted calibration gas was passed through the sample loop of the GC and thus a defined amount of PAN could be injected. During the POPCORN campaign GC calibrations were performed during four nights. The mean calibration factor calculated from the GC calibration signal and the absolute determination of the calibration gas showed only statistical variations with an error of the mean of about 3.5%.

3. Results and Discussion

3.1. OVERVIEW OF THE MEASURED PAN MIXING RATIOS AND CONCENTRATION GRADIENTS

Figure 2 shows all measurements of the PAN mixing ratio during the POPCORN campaign.

Gaps in the data set are mainly caused by the nighttime GC calibration procedures. The total number of ambient air measurements is about 5000. The observed mixing ratios cover a range from less than 10 ppt (detection limit) up to nearly 1 ppb (Table I) which is comparable with other observations at rural areas (Roberts, 1990 and references therein; Shepson *et al.*, 1992a; Hartsell *et al.*, 1994; Bottenheim *et al.*, 1994).

However, in comparison with these PAN measurements the mean values and medians during POPCORN (Table I) are at the lower limit of the typical mean values (0.1–0.6 ppb) reported in the literature. Table I also shows that on the average the mixing ratios at 6 m height $c(\text{PAN})_{6m}$ are higher than those at 2 m height $c(\text{PAN})_{2m}$. This indicates the existence of a systematic PAN concentration gradient. During the night the mixing ratios at 6 m height were up to 80% higher than at 2 m height. During daytime the relative concentration difference between 6 m and 2 m was mostly in the range of about 10%. Assuming a gradient which decreases exponentially with increasing height, we can estimate the effect of the measuring height on the PAN mixing ratios from PAN flux and gradient measurements (Schrimpf *et al.*, 1996). For daytime the effect is small, we can expect that

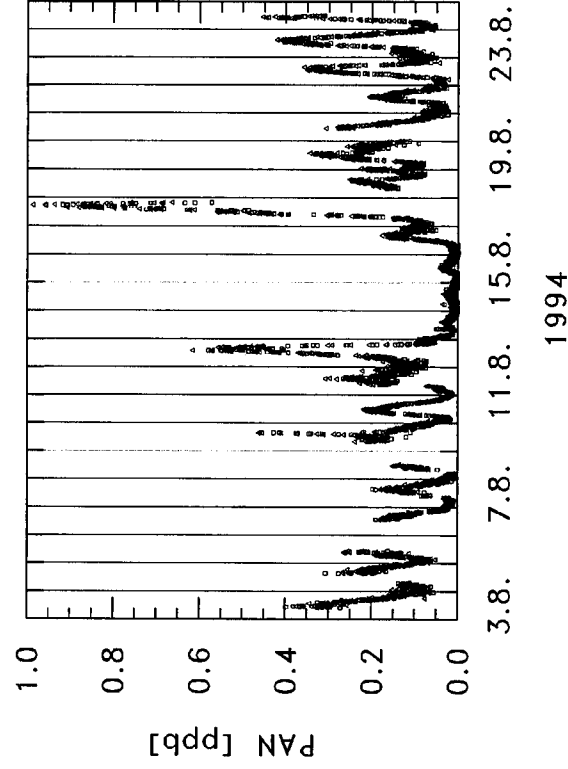


Figure 2. Time series of the PAN mixing ratio at 6 m height (triangles) and 2 m height (squares) during POPCORN. The vertical lines indicate midnight (UT). Local time is UT + 2h.

the difference between 6 m and 50 m altitude is generally about 5%, occasionally even less. However, during night the estimated differences are larger, mostly in the range of 20%, sometimes up to 50%. Assuming a nocturnal inversion layer of 100 m the PAN mixing ratio measured at 6 m height is about 15–25% lower than the mean value for the inversion layer. The exact magnitude of the differences between measurements at 6 m height and the upper region of the mixed layer depends on details of the micrometeorological situation. Nevertheless, from our observations we can conclude that during daytime the PAN mixing ratios measured at 6 m height differ only marginally from the average for the mixed layer. The differences estimated for nighttime are around 15–25%, but still small compared to the overall variability of the PAN mixing ratio at night. In order to simplify the presentation of the results and their discussion in the following part of the paper only the PAN measurements at 6 m height are considered. As discussed above, they generally represent the mean values for the mixed layer reasonably well.

3.2. DAY-TO-DAY VARIATION

In order to examine the day-to-day variation of the PAN mixing ratio we calculated the arithmetic mean, median, minimum and maximum for each day of the campaign (Figure 3).

Table 1. Statistical overview of the data sets obtained from the measurements in 2 m and 6 m height

	PAN (2 m) [ppb]	PAN (6 m) [ppb]
Minimum	<0.010	<0.010
Maximum	0.918	0.986
Mean	0.134	0.141
Standard deviation (1σ)	0.135	0.138
Error of mean	0.003	0.003
Median (50% percentile)	0.104	0.112
5% percentile	0.010	0.010
16% percentile	0.018	0.021
84% percentile	0.221	0.232
95% percentile	0.380	0.388

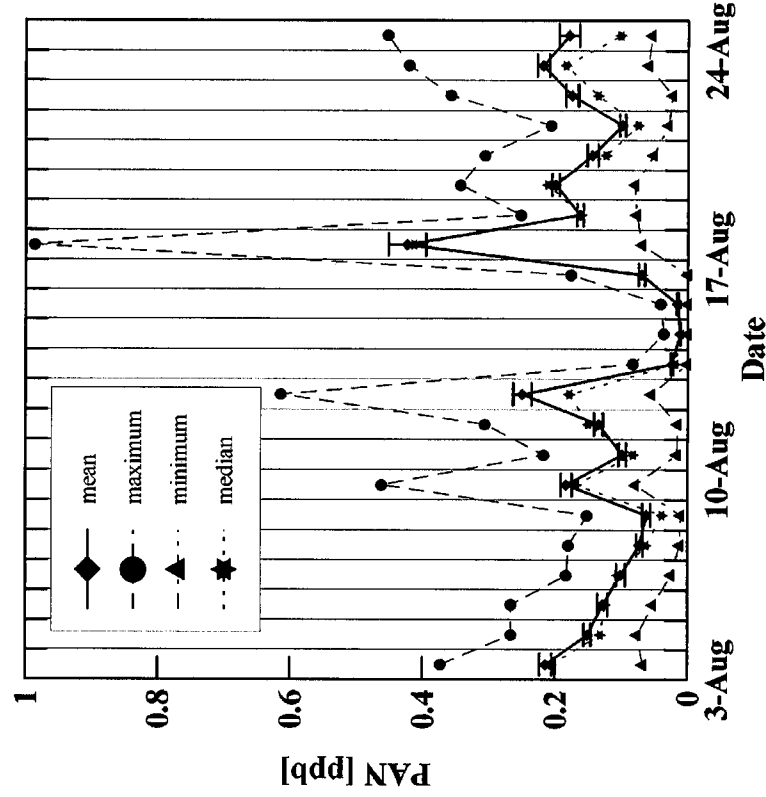


Figure 3. Variation of the daily mean, median, minimum and maximum PAN mixing ratio at 6 m height during POPCORN. The error bars show the standard deviation of all measurements during the 24 h interval. The time axis is also Universal Time (UT).

Table II. Statistical overview of the daily mean, median, minimum and maximum PAN mixing ratios. All mixing ratios are given in ppb

	Daily mean	Daily median	Daily minimum	Daily maximum
Minimum	0.011	0.011	<0.010	0.035
Maximum	0.432	0.413	0.079	0.986
Mean	0.141	0.125	0.039	0.303
Standard deviation (1σ)	0.092	0.088	0.029	0.209
Error of mean	0.020	0.019	0.006	0.046
Median (50% percentile)	0.139	0.124	0.040	0.266
5% percentile	0.015	0.014	<0.010	0.043
16% percentile	0.068	0.047	<0.010	0.160
84% percentile	0.209	0.182	0.073	0.441
95% percentile	0.248	0.211	0.078	0.606

In addition a statistical overview of these quantities which characterize the day-to-day variability of the PAN mixing ratio is given in Table II.

The daily minima were observed in the early morning hours while the maxima were mostly measured in the late afternoon. As can be seen from Table II the minima were always below 80 ppt. Throughout the campaign they showed only a small day-to-day variability on an absolute scale. In contrast the daily maxima were highly variable during POPCORN and ranged from values as low as 35 ppt up to about 1 ppb. The daily mean values of the PAN mixing ratio were most of the time in the range of 50–250 ppt which is in good agreement with the literature cited above. According to the descriptions of the measurement site, the air mass trajectories and the meteorological conditions (Plass-Dülmer *et al.*, this issue; Koppmann *et al.*, this issue; Brauers *et al.*, this issue), five distinctly different periods can be distinguished. These periods are separated from each other by 'transition days' mostly characterized by heavy rain, thunderstorms or cold front passage events. In general the PAN mixing ratios observed during POPCORN follow this episodic distinction. The main characteristics of these episodes are summarized in Table III.

Episode III shows very low PAN values, during episode IV highest PAN values were observed and during episodes I, II and V nearly the same 'typical' PAN mixing ratios were measured. The most important difference between these periods is the air mass origin and the extent of continental influence on the air masses. During most of these periods the lifetime of PAN, τ_{PAN} , was in the range of 0.5 up to 4 hours. Therefore the PAN levels observed during the different meteorological conditions were strongly influenced by the advected amount of PAN precursors and the recently formed PAN in the air mass.

Table III. Overview of the PAN mixing ratios for different episodes during POPCORN

Episode	I	II	III	IV	V
Date	08/03-08/05	08/06-08/11	08/13-08/15	08/17	08/19 08/24
Air Mass Origin ^a	Great Britain/Irish Sea	Belgium/Normandy	North Polar Region	Spain/France	Great Britain/Irish Sea
Main Influence ^a	maritime and continental	maritime and continental	maritime	continental	maritime and continental
Max. Temperature ^b	307 K	299 K	292 K	296 K	296 K
Mean Horiz. Wind Speed ^b	< 4 m/s	< 4 m/s	4 - 9 m/s	< 4 m/s	< 4 m/s
Cloud Cover ^b	very low	low	high	low	low
Maximum PAN	0.373 ppb	0.461 ppb	0.082 ppb	0.986 ppb	0.453 ppb
Minimum PAN	0.052 ppb	0.010 ppb	< 0.010 ppb	0.069 ppb	0.023 ppb
Mean PAN	0.165 ppb	0.108 ppb	0.016 ppb	0.246 ppb	0.169 ppb
Maximum τ^d	96.54 h	99.02 h	99.07 h	96.41 h	97.72 h
Minimum τ^d	0.44 h	1.12 h	4.71 h	3.37 h	1.72 h
Mean τ^d	11.12 h	18.29 h	17.13 h	15.55 h	22.72 h
Mean NO ₂ ^c	3.55 ppb	3.15 ppb	1.36 ppb	3.36 ppb	2.58 ppb
Mean CO ^a	123 ppb	118 ppb	93 ppb	144 ppb	134 ppb
Mean O ₃ ^b	52 ppb	35 ppb	28 ppb	47 ppb	31 ppb

^a Data by Kopppmann *et al.* (this issue);

^b data by Brauers *et al.* (this issue);

^c data by Rohrer *et al.* (this issue);

^d calculated from Equation II.

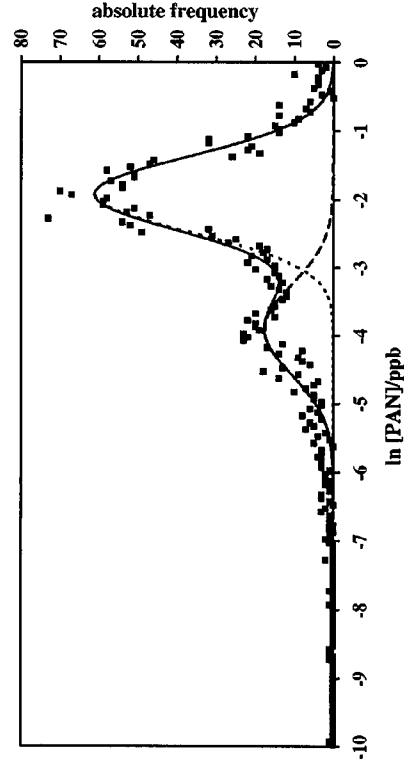


Figure 4. Frequency distribution of the natural logarithm of the PAN mixing ratio in ppb measured in 6 m height throughout the POPCORN campaign. The given absolute frequency is the number of observations for intervals of $\ln [\text{PAN}]/\text{ppb}$ with a width of 0.05. The correlation coefficient of the least-squares fit of the sum of two Gaussian distribution functions is 0.98. Squares: observed frequency, dotted line: Gaussian distribution function #1, dashed line: Gaussian distribution function #2, solid line: sum of the two Gaussian distribution functions.

3.3. FREQUENCY DISTRIBUTION AND CORRELATIONS WITH OTHER PARAMETERS

Frequency distributions of the concentration of atmospheric pollutants often show a log-normal distribution (Larsen, 1969; Bencala and Seinfeld, 1976; Ott, 1990; Bottenheim *et al.*, 1994). This is not surprising since atmospheric dilution of emitted pollutants as well as their chemical degradation show an exponential evolution with time. In Figure 4 the absolute frequency is depicted as a function of the natural logarithm of the PAN mixing ratio in ppb.

The distribution is characterized by two maxima. Such a bimodal lognormal distribution has not yet been reported for PAN. A least-squares fit of the sum of two Gaussian functions allows to determine the maxima and the standard deviation for each mode. They are given together with the corresponding mixing ratios in Table IV.

A fit to log-normal distribution functions which included a PAN concentration offset interpreted as 'background concentration' showed no significant improvement of the correlation coefficient. Also included in Table IV are separate fits to log-normal distributions for day- and nighttime measurements. As expected, nighttime values are on average lower than the daytime mixing ratios. Still, the results show two maxima in both groups.

The air masses investigated from 13 August to 15 August differ from those encountered during the rest of the campaign (Koppmann *et al.*, this issue). During this period two day isentropic backward trajectories show an air mass origin in the North polar region and the air masses had moved across the North Sea to Pennewitt

Table IV. Maxima and 1σ range of the frequency distribution of PAN

Mode 1				
	Maximum		1σ range	
	ln[PAN]	PAN, [ppt]	ln[PAN]	[PAN], ppt ^a
All data	-3.91	20	1.56	4 / 95
Daytime	-3.81	22	0.72	11 / 46
Nighttime	-4.52	11	1.21	3 / 37
08/13-08/15	-3.98	19	1.40	4 / 76
not 08/13-08/15	-	-	-	-

Mode 2				
	Maximum		1σ range	
	ln[PAN]	PAN, [ppt]	ln[PAN]	[PAN], ppt ^a
All data	-1.92	147	1.30	40 / 540
Daytime	-1.59	204	1.05	71 / 583
Nighttime	-2.30	100	0.79	46 / 221
08/13-08/15	-	-	-	-
not 08/13-08/15	-1.90	150	1.22	44 / 507

^a These values give the upper and lower limit of the 1σ range in ppt.

(Koppmann *et al.*, this issue). The air masses during the other periods had mostly moved from Great Britain or the Normandy across the Channel and Northern Germany to the measurement site. A distinction between these two groups of measurements resulted in the observation of one log-normal distribution for each group (Table IV). The frequency distribution maximum of the measurements during the low-PAN period was about 19 ppt, the maximum for the rest of the measurements was about 150 ppt. Thus the two modes observed in the frequency distribution of the PAN mixing ratios are due to air masses of completely different origin with substantially different levels of PAN precursors (cf. Koppmann *et al.* (this issue), Rohrer *et al.* (this issue) and Plass-Dülmer *et al.* (this issue)).

The impact of the pollution level and origin of the air masses is evident from the plot of PAN versus CO mixing ratios (Figure 5a). For both modes of the distributions a clear dependence between CO and PAN concentrations is visible. It is also evident that in addition to the precursor levels the lifetime of PAN plays an important role in determining the PAN concentrations. This is clearly visible from the correlation between PAN mixing ratios and the NO/NO₂ ratio (Figure 5b). With increasing NO/NO₂ ratios the lifetime of PAN decreases (see also chapter 5) which is reflected in the decrease of the PAN mixing ratios with increasing NO/NO₂ ratio. The effect of temperature is less obvious. From the temperature dependence for the thermal decay rate of PAN a decrease of the PAN mixing ratio with increasing temperature would be expected. However, temperature is also

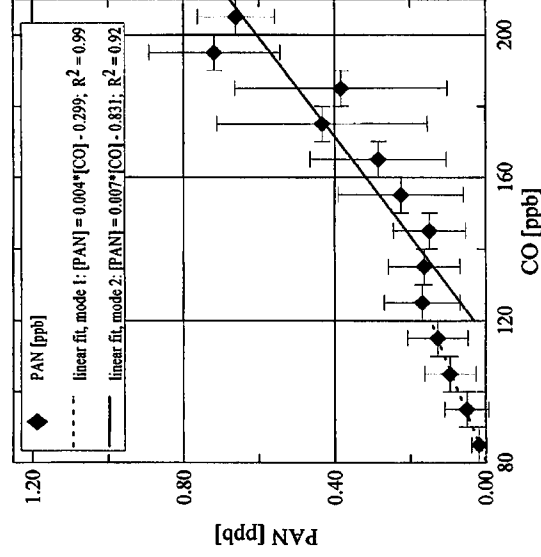


Figure 5a. Plot of PAN mixing ratios versus CO mixing ratios.

related to solar radiation and thus for conditions of high photochemical activity (high solar radiation) one can expect high temperatures (see also Brauers *et al.* (this issue)). This dependence is clearly visible in the plot of PAN mixing ratios versus temperature (Figure 5c). Below 296 K the PAN mixing ratios increase with increasing temperature. Above this temperature they remain more or less constant. The PAN mixing ratios are also closely correlated with the ozone concentrations, both during day- and nighttime (Figure 5d). The very high correlation at night results from the similar deposition velocities for PAN and ozone, since at night deposition was the main loss process for PAN and ozone. The correlation during daytime is due to the related photochemical formation mechanisms.

The frequency distribution of PAN indicates also the existence of a third maximum at -0.3 corresponding to about 750 ppt (Figure 4). Although statistically insignificant this mode can be attributed to the high daytime values during 12 and 17 August. It should be noted that the main features of the frequency distribution of the CO mixing ratios show very similar features with two distinct modes at low and medium mixing ratios and one less pronounced mode at higher mixing ratios (Koppmann *et al.*, this issue).

3.4. DIURNAL VARIATION

Throughout the POPCORN campaign we observed distinct diurnal cycles of the PAN mixing ratio with highest values in the afternoon and lowest values in the early morning. Nearly all rural PAN measurements in summer that are described in the literature show a similar behaviour (Roberts, 1990; Shepson *et al.*, 1992a; Hartsell

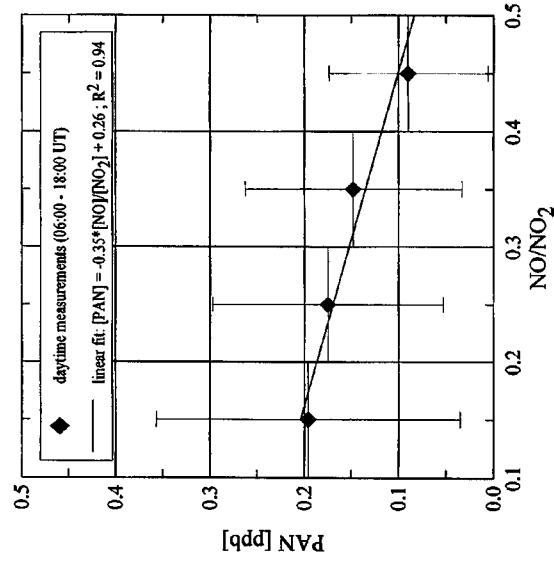


Figure 5b. Plot of PAN mixing ratios versus the NO/NO₂ ratios.

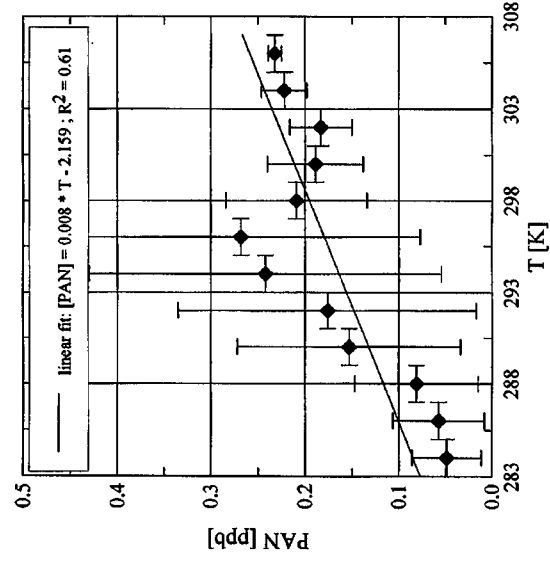


Figure 5c. Plot of PAN mixing ratios versus temperature.

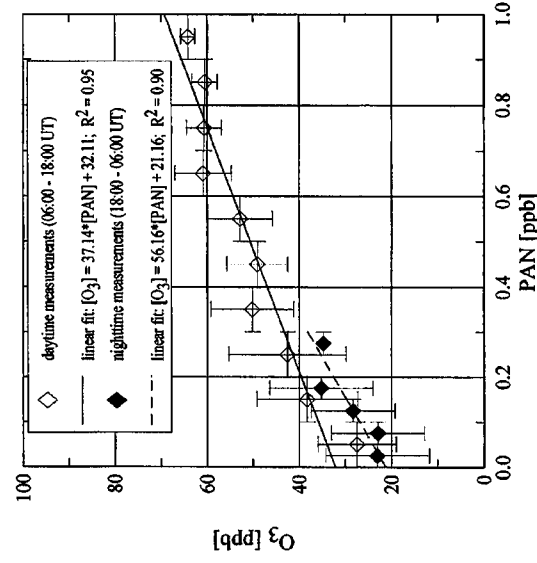


Figure 5d. Plot of PAN mixing ratios versus ozone concentration.

Table V. Characteristic periods of the relative mean diurnal cycle of the PAN mixing ratio

Time of day [UT]	Qualitative variation	Mean relative variation [%/h]
04:30-07:30	Moderate PAN increase	+9
Sunrise		
07:30-11:30	Strong PAN increase	+30
11:30-14:30	Moderate PAN increase	+3
14:30-20:30	Strong PAN decrease	-13
Sunset		
20:30-4:30	Moderate PAN decrease	-5

et al., 1994; Bottenheim *et al.*, 1994). The diurnal cycle is generally explained by a PAN increase in the morning due to photochemical PAN production and transport of PAN from above the nocturnal inversion layer. The decrease in the afternoon is due to thermal decomposition predominating the decreasing photochemical production. A further decrease during the night results from dry deposition at the ground below the nocturnal inversion layer. The mean diurnal cycle of the PAN mixing ratio (Figure 6) can be divided into five typical periods (Table V).

This 'typical' diurnal variation is in excellent agreement with other PAN measurements at rural sites in summer (Roberts, 1990; Shepson *et al.*, 1992a; Hartsell *et al.*, 1994; Bottenheim *et al.*, 1994). The increase in the morning does not neces-

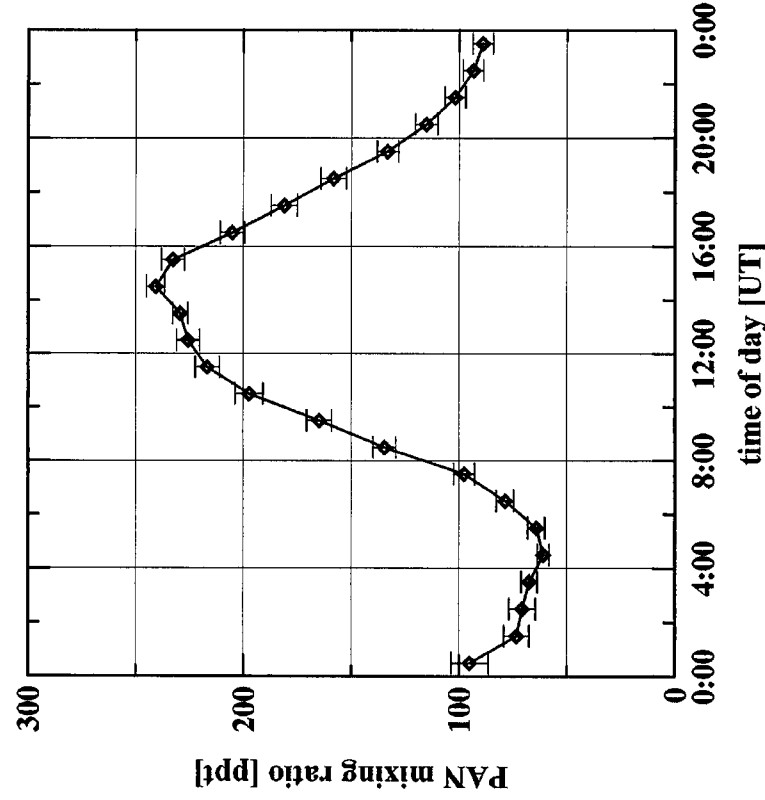


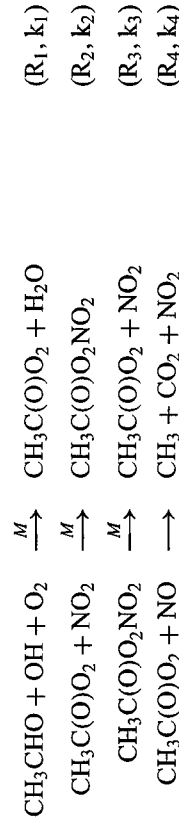
Figure 6. 'Relative mean diurnal cycle' of the PAN mixing ratio during POPCORN. PAN mixing ratios were normalized by its daily mean. The arithmetic mean and the error of the mean were calculated for 1 h intervals. The error bars show the error of the mean. The time axis is Universal Time (UT).

sarily require vertical mixing of PAN from above the inversion layer at the break-up of the nocturnal inversion layer. In view of the high acetaldehyde and OH concentrations (Benning and Wahner, this issue; Holland *et al.*, this issue; Brandenburger *et al.*, this issue) photochemical production of PAN is in general sufficient to explain the observed increase. The PAN decrease in the afternoon can be reasonably well explained by thermal decomposition predominating the photochemical production of PAN. The large impact of dry deposition on the PAN mixing ratios during the night has been investigated in a previous paper (Schrimpf *et al.*, 1996).

3.5. PHOTOCHEMISTRY OF PAN

During the POPCORN campaign the concentrations of the PAN precursors, acetaldehyde and NO_2 , as well as those of NO and the OH radicals were measured.

This allows to determine the in situ formation and destruction rates of PAN. The main reactions determining the PAN formation and decomposition are:



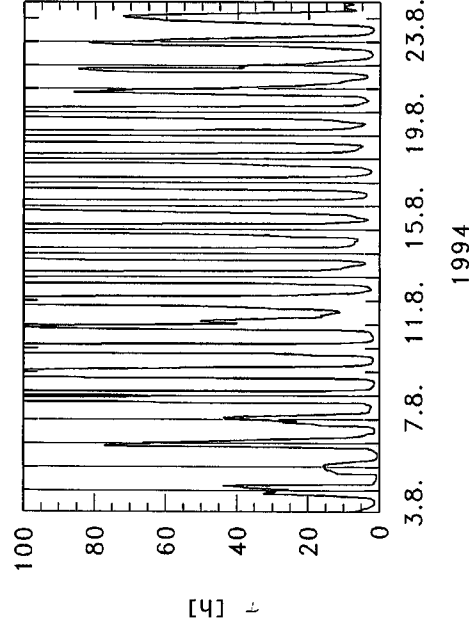
This set of equations neglects the loss of peroxyacetyl radicals as a result of reactions with peroxy radicals. However, for the NO_x mixing ratios of several ppb which were typically observed during POPCORN (Rohrer *et al.*, this issue), these reactions are of marginal importance compared to R_2 and R_4 . It should be noted that there exist other formation mechanisms for the peroxyacetyl radical than R_1 (e.g. photolysis of acetone). However, there are no measurements of the relevant potential precursors available for the POPCORN campaign. Thus the given set of reactions may underestimate the actual formation rate of PAN. However, the acetaldehyde concentrations observed during POPCORN are generally quite high (1–2 ppb, Benning and Wahner (this issue)) and it seems reasonable to assume that R_1 is the dominant formation pathway for peroxyacetyl radicals. The chemical lifetime τ is defined as the inverse of the destruction rates D_i ($\tau = D_i^{-1}$). The chemical processes that lead to a PAN removal in the troposphere are mainly the thermal decomposition of PAN (R_3) at a rate constant k_3 and the subsequent reaction of the formed peroxyacetyl radical by reaction with NO (R_4). The competing degradation by reaction with OH are not relevant in the planetary boundary layer (Talukdar *et al.*, 1995). The chemical loss rate of PAN (D_{ch}) can thus be described by Equation (1).

$$D_{\text{ch}} = k_3[\text{PAN}] - k_2[\text{CH}_3\text{C}(\text{O})\text{O}_2][\text{NO}_2] \quad (1)$$

Assuming a quasi stationary state between the PAN and the peroxyacetyl radical concentration we can derive the chemical lifetime of PAN τ_{PAN} from Equation (2):

$$\tau_{\text{PAN}} = \left[k_3 \left(1 - \frac{1}{1 + \frac{k_4[\text{NO}]}{k_2[\text{NO}_2]}} \right) \right]^{-1} \quad (2)$$

The reaction rate constants and their pressure and temperature dependence are sufficiently well determined (Bridier *et al.*, 1991; Atkinson *et al.*, 1992). The NO/NO_2 ratio has been monitored during POPCORN (Rohrer *et al.*, this issue) as well as the temperature (Brauers *et al.*, this issue). This way the chemical lifetime



1994

Figure 7. Temporal variation of the PAN lifetime. The solid line gives the 1 hour running average of the PAN lifetime calculated according to Equation (1) and (2). Values above 100 hours around midnight were excluded from the data set.

of PAN could be calculated throughout the campaign. Figure 7 shows the 1-hour running average of the temporal variation of the PAN lifetime.

The chemical lifetime of PAN shows clear diurnal cycles with minima around noon and maxima around midnight. This can be explained by the higher temperatures and NO production from NO₂ photolysis during daytime ($\text{NO}/\text{NO}_2 > 0.1$) and the lower temperatures and low NO mixing ratios at night ($\text{NO}/\text{NO}_2 < 0.1$; Rohrer *et al.* (this issue)). Due to the very strong exponential temperature dependence of the thermal decay rate of PAN, the lifetime is dominated by the temperature variations. Therefore and because of the strongly different NO/NO₂ ratio it is useful to distinguish between the lifetime during the day and at night. The mean lifetime during the day (zenith angles below 90°) was 8.6 hours while it was 41.2 hours at night (zenith angles above 90°). This result shows that on the average thermal decomposition of PAN was of minor importance for the observed PAN decrease during the night. During the night the lifetimes calculated according to Equation (2) often exceed 100 hours. Under these conditions this loss is less than 1%/h and thus has no detectable influence on the nighttime mixing ratios of PAN. As mentioned above, under these conditions dry deposition is the dominant removal mechanism for PAN in the inversion layer (Schrimpf *et al.*, 1996). From the deposition velocity of PAN and estimates of the height of the nocturnal inversion layer a mean PAN lifetime due to dry deposition at night of about 5 hours is obtained (Schrimpf *et al.*, 1996). From reactions R₂ and R₃ it is evident that PAN acts not only as a reservoir for NO₂ but also for odd oxygen (RO_x). Neglecting the effect of transport we can estimate the rate of removal or release of NO₂ and RO_x by the formation or degradation of PAN from the diurnal variations of the PAN mixing

ratios. The largest rates of change were observed on 9, 12, 17, 19 and 22–24 August. The increase in the morning and noon hours (8:00–13:00 UT) exceeded 150 ppt/h, corresponding to 1×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$, even values around 300 ppt/h (2×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$) were frequently observed, occasionally a few values as high as 600–750 ppt/h ($4\text{--}5 \times 10^6$ molecules $\text{cm}^{-3} \text{s}^{-1}$) were found. But there were also days when the increase rates in the morning were generally well below 20 ppt/h, e.g. in the period from 13–15 August. On average the PAN increase rate in the morning was roughly 30 ppt/h (2×10^5 molecules $\text{cm}^{-3} \text{s}^{-1}$). The decrease rate in the afternoon (15:00–20:00 UT) was slightly smaller, on average about 20 ppt/h, seldom exceeding 300 ppt/h (2×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$) and never above 450 ppt/h (3×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$).

At first sight the diurnal cycles suggest that PAN primarily acts as a reservoir for NO_x and odd oxygen radicals. This would mainly affect the shape of their diurnal cycles. However, the change in the PAN mixing ratios is influenced by local photochemistry, transport, and mixing. Thus the actual affect of the formation or decomposition of PAN cannot be directly deduced from the changes in concentrations alone.

To determine the influence of transport, we calculate the difference between the local net PAN formation rate based on reactions $\text{R}_1\text{--R}_4$ and the observed local change rate in the PAN concentrations. During the day dry deposition has no significant effect on the atmospheric mixing ratios of PAN and neglecting other formation mechanisms for the peroxyacetyl radical than reaction of acetaldehyde with OH radicals we obtain the following Equation (3) describing the formation rate of 'excess PAN' (E_{PAN}) for each volume element:

$$E_{\text{PAN}} = k_2[\text{NO}_2] \left(\frac{k_3[\text{PAN}] + k_1[\text{CH}_3\text{CHO}][\text{OH}]}{k_4[\text{NO}] + k_2[\text{NO}_2]} \right) - k_3[\text{PAN}] - \frac{d[\text{PAN}]}{dt} \quad (3)$$

All substances in this equation were measured during the POPCORN campaign (Rohrer *et al.*, this issue; Benning and Wahner, this issue; Brandenburger *et al.*, this issue) and the reaction rate constants are known (see above). The calculations were made for each 2 h interval when measurements for all substances involved were available. There are slightly more than 100 data points. The results are summarized in Figure 8. The data include essentially no nighttime values, about 80% of the values are from the period between 8:00 and 18:00 UT and 50% from 10:00–16:00 UT. Since there is no significant diurnal variation of the acetaldehyde mixing ratio the formation rate of peroxyacetyl radicals and consequently the amount of 'excess PAN' will, as a first approximation, follow the diurnal cycle of the OH-radical concentration. Indeed, Figure 8 shows a clear diurnal cycle for 'excess PAN' with a maximum around 11 h UT (corresponding to 13 h local time). This coincides with the maximum of the OH-radical concentrations (Brandenburger *et al.*, this issue; Holland *et al.*, this issue).

From Figure 8 it is evident that under these conditions there is nearly always a positive excess formation of PAN which means that the observed rate of change

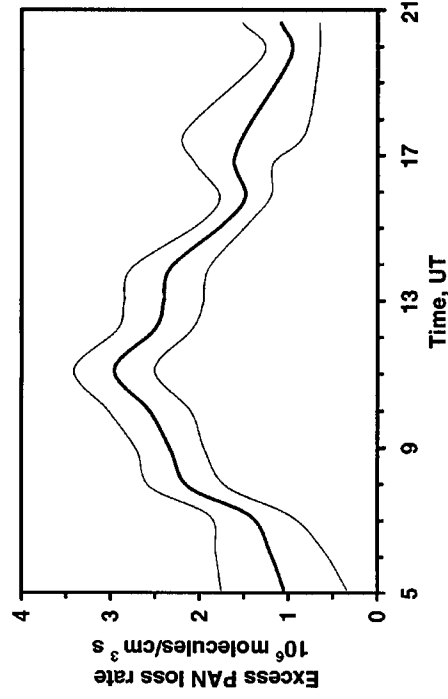


Figure 8. Averaged diurnal variation of the calculated 'excess PAN' loss rate. The thick line represents the 2 h running mean, the thin lines the error of the mean. The total number of data points is about 100, the averages are each calculated from 10–20 values. The larger errors in the morning and in the evening are the result of the lower number of data points during these periods. For consistency only the OH concentration measurement with the DOAS method (Brandenburger *et al.*, this issue) were used.

in the PAN concentrations is generally lower than the change calculated from photochemistry. The average is 264 ppt/h (1.8×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$) with a standard deviation of 230 ppt/h (1.6×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$). The error of the mean is 22 ppt/h (1.5×10^5 molecules $\text{cm}^{-3} \text{s}^{-1}$), the median value 230 ppt/h (1.6×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$).

The most likely explanation for the calculated excess PAN formation are the quite high acetaldehyde mixing ratios observed during POPCORN. They are most probably due to emissions from maize (Benning and Wahner, this issue). In this case the elevated acetaldehyde concentrations will be restricted to the direct vicinity of the maize field and the air masses advected will be lower in acetaldehyde and consequently in PAN. Therefore horizontal or vertical mixing and transport will remove PAN formed photochemically from the POPCORN site and the observed PAN increase rate will be systematically lower than the calculated one.

The evident consequence of this is, that during daytime there is on the average a considerable export of PAN from the observation area. Thus under the conditions of the POPCORN campaign PAN acts as a local sink for both NO_x and peroxy radicals. Consequently, the formation of PAN has an impact on the local NO_x and odd oxygen radical budget. Compared to the observed NO_x mixing ratios of typically several ppb and the diurnal variation of NO_x in the range of a few ppb between morning and noon (Rohrer *et al.*, this issue) a NO_x loss of a fraction of a ppb/h in the form of PAN is not negligible and should be considered in the NO_x budget.

A loss rate of a few hundred ppt/h, corresponding to some 10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$, constitutes a considerable fraction of the primary production of odd oxygen radicals by photolysis which is in the range of several 10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$ during noon (Kraus and Hofzumahaus, this issue). Consequently the formation of PAN has a significant impact on the budget of odd oxygen radicals under the conditions of the POPCORN campaign.

4. Summary and Conclusions

Due to the high sensitivity and measurement frequency of our optimized GC-ECD we obtained an extensive PAN data set of about 5000 measurements ranging from less than 10 ppt up to 1 ppb during the three week period of POPCORN. The data set shows some 'characteristic' features:

1. The daily mean and median PAN mixing ratios were most of the time between 50 ppt and 250 ppt. This is at the lower limit of the range of 'typical' daily mean PAN mixing ratios at rural sites in summer at Northern mid-latitudes. During one period the mean PAN mixing ratios were as low as 16 ppt which is more typical for truly remote sites.
2. In excellent agreement with observations at other rural sites we always observed distinct diurnal cycles of the PAN mixing ratio. The daily maximum was generally in late afternoon, the minimum in the early morning hours.
3. The chemical lifetime of PAN due to thermal decay also showed distinct diurnal cycles with minima as low as 0.5 h around noon and values of up to several hundred hours at night. At night dry deposition generally determines the lifetime of PAN. We estimate that for typical inversion layer heights the PAN lifetime with respect to dry deposition was about 5 hours at night.
4. The PAN mixing ratios during POPCORN showed an episodic behaviour. The episodic variation of the mean PAN level was mainly dependent on the concentrations of available precursors and the air mass history. To a lesser extent temperature, solar radiation and other meteorological parameters determined the mean PAN levels.
5. The frequency distribution of the PAN mixing ratios was bimodal on a logarithmic scale. This result could be explained by two distinctly different air mass histories during different episodes.
6. For the specific conditions of the POPCORN campaign during daytime the formation of PAN resulted in an export of NO_x and peroxyacetyl radicals. This has some effect on the local NO_x budget. Probably more important but is the substantial influence on the budget of odd oxygen radicals. During daytime the export of 'excess PAN' constitutes a loss rate for odd oxygen radicals that corresponds to roughly 30–50% of the OH-radical formation by ozone photolysis.
7. The observed PAN gradient results form dry deposition of PAN. Our results indicate that measurements made at 6 m height above the ground are representative for the mixed layer within reasonable limits. However, measurements at 2 m

altitude are substantially influenced by dry deposition, especially during nighttime. This indicates that PAN measurements made close to groundlevel can be substantially biased towards lower values as a result of the dry deposition of PAN.

In general the data set can thus be stated as representative for rural PAN measurements in late summer at Northern mid-latitudes but during one short episode the PAN mixing ratios are more characteristic for the remote environment. Moreover, the existence of a significant local source for an important PAN precursor, acetaldehyde, has consequences for the impact of PAN on the atmospheric chemistry near the measurement site although the local concentrations of PAN are not significantly elevated compared to other, similar regions.

References

- Atkinson, R., Baulch, D. L., Cox Jr., R. A. Hampton, R. F. Kerr, J. A., and Troe, J., 1992: Evaluated kinetic and photochemical data for tropospheric chemistry: Supplement IV, *J. Phys. Chem. Ref. Data* **21**, 1125.
- Bencala, K. E. and Seinfeld, J. H., 1976: On frequency distributions of air pollutant concentrations, *Atmos. Environ.* **10**, 941-950.
- Benning, L. and Wahner, A., 1998: Measurements of atmospheric formaldehyde (HCHO) and acetaldehyde (CH₃CHO) during POPCORN 1994 using 2,4-DNPH coated silica cartridges, *J. Atmos. Chem.* **31**, 105-117.
- Bottenheim, J. W., Sirios, A., Brice, K. A., and Gallant, A. J., 1994: Five years of continuous observations of PAN and ozone at a rural location in eastern Canada, *J. Geophys. Res.* **99**, 5333-5352.
- Brandenburger, U., Brauers, T., Dorn, H. P., Hausmann, M., and Ehhalt, D. H., 1998: In-situ measurement of tropospheric hydroxyl radicals by folded long-path laser absorption during the field campaign POPCORN in 1994, *J. Atmos. Chem.* **31**, 181-204.
- Brauers, T., Koch, H., Dorn, H. P., and Plass-Dülmer, C., 1998: Meteorological aspects, ozone, and solar radiation measurements during POPCORN 1994, *J. Atmos. Chem.* **31**, 33-52.
- Bridier, I., Caralp, H., Loirat, H., Lescaux, R., Veyret, B., Becker, K. H., Reimer, A., and Zabel, F., 1991: Kinetic and theoretical studies of the reactions CH₃C(O)O₂ + NO₂ \longleftrightarrow CH₃C(O)O₂NO₂ + M between 30 and 760 torr, *J. Phys. Chem.* **95**, 3594.
- Carter, W. P. L., Winer, A. M., and J. N. Pitts, 1981: Effects of peroxyacetyl nitrate on the initiation of photochemical smog, *Environ. Sci. Technol.* **15**, 831.

- Hartzell, B. E., Aneja, V. P., and Lonnemann, W. A., 1994: Relationships between peroxyacetyl nitrate, O_3 and NO_y at the rural southern oxidants study site in Central Piedmont, North Carolina, Site Sonia, *J. Geophys. Res.* **99**, 21033–21041.
- Holland, F., Aschmutat, U., Hefling, M., and Hofzumahaus, A., 1998: Highly time resolved measurements of OH during POPCORN using laser-induced fluorescence spectroscopy, *J. Atmos. Chem.* **31**, 205–225.
- Koppmann, R., Plass-Dülmer, C., Ramacher, B., Rudolph, J., Kunz, H., Melzer, D., and Speth, P., 1998: Measurements of carbon monoxide and nonmethane hydrocarbons during POPCORN, *J. Atmos. Chem.* **31**, 53–72.
- Kraus Al. and Hofzumahaus, A., 1998: Field measurements of atmospheric photolysis frequencies for O_3 , NO_2 , HCHO, CH_3CHO , H_2O_2 and HONO by UV spectroradiometry, *J. Atmos. Chem.* **31**, 161–180.
- Larsen, I., 1969: A new mathematical model for air pollutant concentration averaging time and frequency, *J. Air Pollut. Control Assoc.* **19**, 24.
- Nicksc, S. W., Harkins, J., and Mueller, P. K., 1967: Some analyses for peroxyacetyl nitrate and studies for its structure, *Atmos. Environ.* **1**, 11–18.
- Nielsen, T., Samuelsson, U., Grennfelt, C., and Thomsen, E. L., 1981: Peroxyacetyl nitrate in long-range transported polluted air, *Nature* **293**, 553–555.
- Ott W. R., 1990: A physical explanation for the lognormality of pollutant concentrations, *J. Air Waste Manag. Assoc.* **40**, 1378–1383.
- Plass-Dülmer, Ch., Brauers, T., and Rudolph, J., 1998: POPCORN – A field study of photochemistry in North-Eastern Germany, *J. Atmos. Chem.* **31**, 5–31.
- Rappenglück, B., Kourtidis, K., and Fabian, P., 1993: Measurements of ozone and peroxyacetyl nitrate (PAN) in Munich, *Atmos. Environ.* **27B**, 293–305.
- Roberts, J., 1990: The atmospheric chemistry of organic nitrates, *Atmos. Environ.* **24A**, 243–287.
- Rohrer, F., Brüning, D., Grobler, E. S., Weber, M., and Ehhalt, D. H., 1998: Mixing ratios and photochemical state of NO and NO_2 observed during the POPCORN field campaign at a rural site in Germany, *J. Atmos. Chem.* **31**, 119–137.
- Schrimpf, W., Müller, K. P., Lienaerts, K., and Rudolph, J., 1995: An optimized method for airborne peroxyacetyl nitrate (PAN) measurements, *J. Atmos. Chem.* **22**, 303–317.
- Schrimpf, W., Lienaerts, K., Müller, K. P., Rudolph, J., Neubert, R., Schüßler, W., and Levin, I., 1996: Dry deposition of peroxyacetyl nitrate (PAN): determination of its deposition velocity at night from measurements of the atmospheric PAN and ^{222}Rn concentration gradient, *Geophys. Res. Lett.* **23**, 3599–3602.
- P. B. Shepson, D. R. Hastie, K. W. So, H. I. Schiff, and P. Wong 1992a: Relationships between PAN, PPN and O_3 at urban and rural sites in Ontario, *Atmos. Environ.* **26A**, 1259–1270.
- Singh H. B. and Hanst, P. L., 1981: Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere: An important reservoir for nitrogen oxides, *Geophys. Res. Lett.* **8**, 941–944.
- E. R. Stephens, 1967: The formation of molecular oxygen by alkaline hydrolysis of peroxyacetyl nitrate, *Atmos. Environ.* **1**, 19.
- Stephens, E. R., 1969: The formation, reactions, and properties of peroxyacetyl nitrates (PANs) in photochemical air pollution, *Adv. Environ. Sci.* **1**, 119–146.
- Talukdar, R. K., Burkholder, J. B., Schmoltner, A.-M., Roberts, J. M., Wilson, R. R., and Ravishankara, A. R., 1995: Investigation of the loss processes for peroxyacetyl nitrate in the atmosphere: UV photolysis and reaction with OH, *J. Geophys. Res.* **100**, 14163–14173.