

Dry deposition of peroxyacetyl nitrate (PAN): Determination of its deposition velocity at night from measurements of the atmospheric PAN and ²²²Rn concentration gradient

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Abstract. During the field campaign POPCORN (Photooxidant Formation by Plant Emitted Compounds and OH-Radicals in North-Eastern Germany) in August 1994 we measured the nighttime deposition velocities of PAN above a corn field. These are the first absolute measurements of PAN deposition velocities in the field. The deposition velocities were derived using a novel method, which uses measurements of the gradients of PAN and ²²²Rn and of the emission rates of ²²²Rn from the soil. A unique data set of about 250 field measurements of the PAN deposition velocity at night was thus obtained. The deposition velocity at night proved to be highly variable with an average of 0.54 cm/s and a standard deviation of 0.94 cm/s. Recent presumptions by Shepson et al. [1992] that the PAN deposition velocity is strongly reduced with increasing relative humidity could not be confirmed by our measurements.

Introduction

PAN, a product of the photochemical oxidation of nonmethane hydrocarbons (NMHC) in the presence of nitrogen oxides (NO_x), is an important player in photochemical smog episodes [Stephens, 1969]. During these episodes PAN is often detected at phytotoxic and eye-irritating concentration levels [Stephens and Price, 1973; Temple and Taylor, 1983; Sun and Huang, 1995]. PAN is formed by photochemical processes only and shows a strongly temperature-dependent thermal decomposition rate [Atkinson et al., 1992]. In the lower troposphere these formation and removal processes dominate the daytime PAN chemistry [Talukdar et al., 1995]. The rates of the photochemical production and the thermal decomposition of PAN are well established, but the impact of dry deposition as a further important removal process is still poorly understood. No direct field measurements have been reported so far. Only laboratory and indirect estimates of the deposition velocity of PAN relative to ozone can be found in the literature. The number of measurements is small [Hill, 1971; Garland and Penkett, 1976; Shepson et al., 1992] and the results show no consistency. The observed values range from about 0.2 cm/s up to 0.8 cm/s. Especially during meteorological situations in which a nocturnal inversion layer is formed [Stull, 1988], removal by dry deposition seems to have a significant

influence on observed PAN mixing ratios [Shepson et al., 1992]. In the presence of a typical nocturnal boundary layer with a mixing height of 100 m the atmospheric lifetime of PAN due to dry deposition calculated from the literature data can vary by a factor of 4 from only 3.5 hours to 14 hours. This compares to atmospheric lifetimes at night due to thermal decomposition of several hours up to a few days in air masses typical for rural areas at Northern mid-latitudes in summer. In this paper the first measurements of the absolute deposition velocity of PAN in the field are presented. The deposition velocities were determined by a novel method, which is based on the comparison of the gradients of PAN and ²²²Rn with the emission rates of ²²²Rn from the soil.

Experimental

The measurements were made as part of the POPCORN campaign which took place from August, 3 until August, 24 in a rural environment in North-Eastern Germany (53.8 °N, 11.7 °E). The measurement site was situated in the center of a 35 ha corn field. PAN was measured with an optimized gas chromatograph (GC) equipped with an electron capture detector (ECD). The separation of PAN was achieved by a two-dimensional separation on two short megabore capillary columns of different polarity. This setup allows a complete separation of PAN within 3 min. Instrument calibration was performed utilizing a diffusion source for generating PAN calibration gas. A constant flow of nitrogen passes over a PAN/n-hexane solution which is kept at -15 °C. The PAN mixing ratio of the calibration gas is determined by hydrolysis and subsequent measurement of the formed nitrite ion concentration [Nicksic et al., 1967; Stephens, 1967]. The instrument performance is characterized by the measurement frequency of one chromatogram every 5 minutes, the detection limit of 10 ppt (3σ), the measurement precision of better 5 %, and the measurement accuracy of better 10 %. The accuracy is mainly determined by the hydrolysis efficiency of our calibration method. This efficiency is higher than 99 %. The stated precision is derived from repeat measurements of the air mixture from our calibration gas source. This already includes several uncertainties which cause short term (within one or two days) variations of the calibration gas source. However, since we cannot differentiate between these variations and instrument sensitivity changes we included these uncertainties in the precision estimate. More details of the instrument and the calibration are published in a previous paper [Schrimpf et al., 1995]. In order to perform the PAN gradient measurements we modified the setup of the inlet

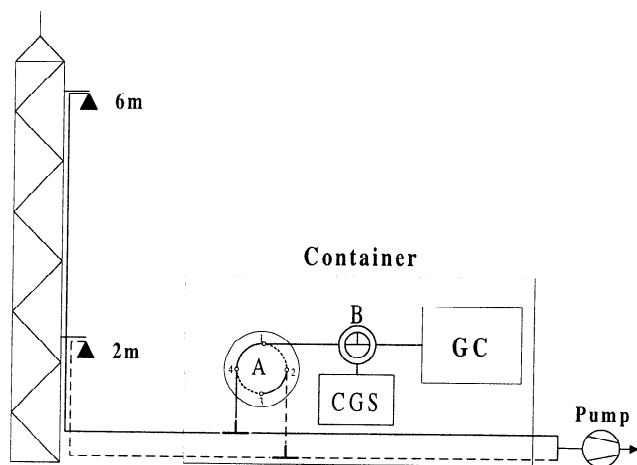


Figure 1. Setup of the inlet system for the PAN measurements during the POPCORN field campaign. A represents the automatic four-way-valve, B the manual three-way-valve, CGS the calibration gas source and GC the gas chromatograph. The three-way-valve (B) is in the position during the "measurement mode".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

system (Figure 1): Two Teflon tube inlet lines of identical diameter and length (6 mm i.d. x 20 m) were fixed at 6 m and 2 m height above ground (≈ 5 m and 1 m above the vegetation surface). They were constantly purged by a pump at a flow rate of 8 m³/h (Figure 1). This way the PAN residence time inside both inlet lines was less than 0.5 sec. A sensitivity of our inlet system due to water vapor concentration changes was not observed. No liquid water was ever found inside the inlet lines. During the "measurement mode" the manual three-way-valve (B) was in the position as depicted in Figure 1. A small flow of about 50 cm³/min was passed permanently through the stainless-steel 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 ambient air from 6 m and 2 m height was injected and analyzed alternately.

In the "calibration mode" the inlet system was operated with the manual three-way-valve (B) in the 90°-turned-clockwise position. This way the calibration gas is passed through the sample loop and thus a defined amount of PAN can be injected.

Simultaneously, the short-lived ²²²Rn daughter activity was monitored in 6 m and 2 m height with an integration time of 30 minutes. Assuming radioactive equilibrium between the ²²²Rn activity and the ²²²Rn daughter activity, the atmospheric ²²²Rn activity has been calculated from the measured short-lived ²²²Rn daughter activity at both heights. About 60 measurements of the ²²²Rn flux from the soil were made throughout the campaign with an inverted-cup method.

Results and Discussion

2500 ambient air samples with PAN mixing ratios ranging from below the detection limit of 10 ppt up to a maximum of 1 ppb were analyzed from 6 m and 2 m height respectively with a time resolution of 10 minutes. About 7 % of all measurements fell below the detection limit and were

discarded from the data set for the calculation of the PAN concentration gradient. By interpolating between two successive measurements we obtained a synchronized 5 minute time grid for the measurements in 6 m and 2 m height. According to Equation (I) the gradient of the PAN mixing ratio $\nabla[\text{PAN}]$ was then calculated from the differences in the mixing ratios at height i $[\text{PAN}]_i$:

$$\nabla[\text{PAN}] = \frac{[\text{PAN}]_{6\text{m}} - [\text{PAN}]_{2\text{m}}}{6\text{ m} - 2\text{ m}} \quad (\text{I})$$

The PAN gradient $\nabla[\text{PAN}]$ showed strong diurnal variations between about -20 ppt/m and +40 ppt/m. The highest values of the PAN concentration gradient were observed at night. The relative gradient of the PAN mixing ratio between 6 m and 2 m height $\Delta[\text{PAN}]_r$ is a useful measure for the degree of PAN removal at the surface. It is defined in Equation (II).

$$\Delta[\text{PAN}]_r = \frac{\nabla[\text{PAN}]}{[\text{PAN}]_{2\text{m}}} \quad (\text{II})$$

Figure 2 depicts the mean diurnal cycle of the relative PAN gradient. It is systematically positive with low values of about 2 %/m during daytime and increasing values up to 10 %/m during the night. During some nights relative PAN gradients of more than 20 %/m were observed. These maxima were mostly found around midnight.

In 80 % of the cases, when large relative PAN gradients were observed, the horizontal wind speeds were below 2 m/s and the temperature difference between 6 m and 2 m below 1 K. During these meteorological conditions typical for summertime at night, the formation of a stable nocturnal inversion layer can be expected at flat rural sites [Stull, 1988]. Hastie *et al.* [1993] observed the formation of a nocturnal inversion layer at sunset and its complete disappearance 3 hours after "detectable" sunrise (solar radiation intensity above the detection limit of a commercial ultraviolet radiometer) at a flat rural site in Canada. During the POPCORN campaign sunset took place between 17:00 and 18:00 UT, "detectable" sunrise between 3:00 and 4:00 UT. The mean diurnal cycle of the relative PAN gradient shows

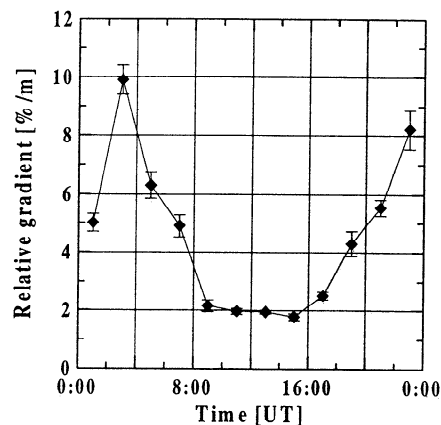


Figure 2. Mean diurnal cycle of the relative PAN gradient between 6 m and 2 m. The PAN mean values are calculated for 2 hour intervals from 300 - 400 measurements for each interval. The error bars show the error of the mean value. The time axis is universal time (UT). Local time (LT) is $\text{LT} = \text{UT} + 2\text{ h}$.

that the time of its increase in the evening and its decrease in the morning coincides respectively with the formation and disappearance of the nocturnal inversion layer as described by *Hastie et al.* [1993].

^{222}Rn is a radioactive noble gas that is emitted from the soil with an emission rate that is nearly constant in time. The measurements of the ^{222}Rn flux from the soil air to the atmosphere Φ_{Rn} , and the ^{222}Rn activity difference $\Delta[\text{Rn}] = [\text{Rn}]_{6\text{m}} - [\text{Rn}]_{2\text{m}}$ enabled us to calculate the mean vertical turbulent diffusion coefficient K , respectively the mean vertical atmospheric transfer resistance between 6 m and 2 m height $R_{6\text{m}-2\text{m}} = 1/K$ (Equation IV). Considering the atmospheric lifetimes of PAN and ^{222}Rn (>30 hours and 5 days) we assume that the observed PAN- and ^{222}Rn -concentration differences between 6 m and 2 m, $\Delta[\text{PAN}]$ and $\Delta[\text{Rn}]$, were caused by vertical transport, deposition of PAN at the ground and emission of ^{222}Rn from the soil. Then the general concept of transfer resistance for the description of diffusive atmospheric transport processes that are caused by a concentration gradient can be applied [*Chamberlain*, 1966]. It leads to a simple mathematical expression for the calculation of the PAN flux to the ground Φ_{PAN} (Equation III), and thus the PAN deposition velocity v_D (Equation V) from the measured quantities:

$$\Phi_{\text{PAN}} = -\frac{1}{R_{6\text{m}-2\text{m}}} \cdot ([\text{PAN}]_{6\text{m}} - [\text{PAN}]_{2\text{m}}) = v_D \cdot [\text{PAN}]_{2\text{m}} \quad (\text{III})$$

$$\Phi_{\text{Rn}} = \frac{1}{R_{6\text{m}-2\text{m}}} \cdot ([\text{Rn}]_{6\text{m}} - [\text{Rn}]_{2\text{m}}) \quad (\text{IV})$$

$$\Rightarrow v_D = \frac{-\Phi_{\text{Rn}} \cdot \Delta[\text{PAN}]}{\Delta[\text{Rn}] \cdot [\text{PAN}]_{2\text{m}}} \quad (\text{V})$$

By averaging the relative PAN gradient between 6 m and 2 m for 30 min intervals we obtained a synchronized time grid for the PAN and ^{222}Rn gradient measurements. Because the relative uncertainty of the ^{222}Rn measurements was about 10 % we calculated the PAN deposition velocity only for ^{222}Rn activity differences larger than the uncertainty of the measurement in 2 m. Such strong gradients occurred only at night so the PAN deposition velocity could be determined only for nighttime. Nevertheless the remaining number of all calculated deposition velocities was still 250. The ^{222}Rn flux showed no systematic fluctuations with time, the relative standard deviation of the ^{222}Rn flux being about 20 %. The

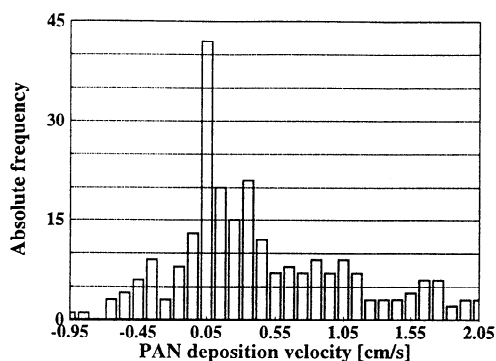


Figure 3. Absolute frequency distribution of the PAN deposition velocity.

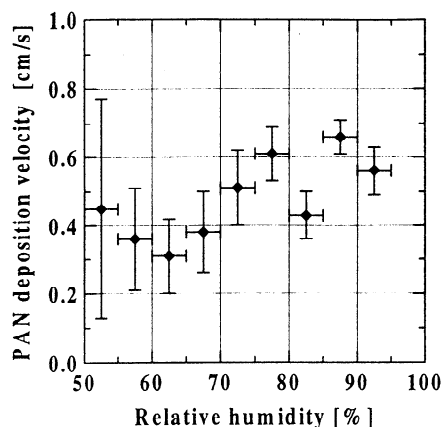


Figure 4. Variation of the mean PAN deposition velocity with the relative humidity at night. The mean values are calculated for 5 % intervals of the relative humidity. The horizontal error bars give the interval size, the vertical error bars show the error of the mean value.

error of the PAN deposition velocity is mainly determined by this uncertainty and the uncertainty of the ^{222}Rn gradient.

Figure 3 shows the absolute frequency distribution of the PAN deposition velocities. They cover a wide range of values from about -1 cm/s up to 2 cm/s. The median of all data is 0.3 cm/s, the 5 %, 16 %, 84 % and 95 % percentiles are -0.47 cm/s, -0.09 cm/s, 1.21 cm/s and 2.12 cm/s respectively. The arithmetic mean value of all data is 0.54 cm/s, the error of the mean 0.06 cm/s and the standard deviation 0.94 cm/s. This mean value is in good agreement with recent estimations of the PAN deposition velocity by *Shepson et al.* [1992]. However, the observed range of values also encompasses the values of the two other studies [*Hill*, 1971; *Garland and Penkett*, 1976].

The key assumption of our method to determine the PAN deposition velocities is the absence of significant loss processes for PAN in the gas phase under the conditions where the deposition measurements were made.

The atmospheric lifetime of PAN in the gas phase depends primarily on the temperature and the ratio of the NO and NO_2 concentrations. During nights with significant NO gradients the mean temperature at the measurements site was about 288 K [*Brauers, T., H. P. Dorn, H. Koch, A. Kraus, and C. Plass-Dülmer*, Meteorological Aspects, Ozone, and Solar Radiation during POPCORN 1994; submitted to *Journal of Atmospheric Chemistry*, 1996]. Measurements of nitrogen oxides at 6 m height during POPCORN [*Rohrer, F., D. Brüning, E. S. Grobler, M. Weber, and D. H. Ehhalt*, Mixing ratios and photostationary state of NO and NO_2 observed during the POPCORN field campaign at a rural site in Germany, submitted to *Journal of Atmospheric Chemistry*, 1996] showed mean NO/ NO_2 ratios of about 0.09 at night. The average nighttime mixing ratio of NO_x in 6 m height was about 530 ppt [*Rohrer, F., D. Brüning, E. S. Grobler, M. Weber, and D. H. Ehhalt*, Mixing ratios and photostationary state of NO and NO_2 observed during the POPCORN field campaign at a rural site in Germany, submitted to *Journal of Atmospheric Chemistry*, 1996]. NO is known to be emitted from the soil especially in a fertilized corn field. During the night the NO flux from the soil at the measurements site resulted in a gradient of about 12 ppt/m between 2 m and 6 m

height and of about 50 ppt/m between the ground and 2 m height [Rohrer, F., D. Brünig, E. S. Grobler, M. Weber, and D. H. Ehhalt, Mixing ratios and photostationary state of NO and NO₂ observed during the POPCORN field campaign at a rural site in Germany, submitted to *Journal of Atmospheric Chemistry*, 1996]. This allows us to calculate the PAN lifetimes for the gas phase. They range from 3.5 hours up to several days, the mean value being about 40 hours. Based on this we can calculate the contribution of PAN gas phase decomposition to the observed total flux. For the shortest atmospheric PAN gas phase lifetime of 3.5 hours only 7 % of the total PAN flux can be caused by gas phase decomposition between 2 m and 6 m height. For the mean gas phase lifetime of PAN the effect is less than 1 %. A similar calculation for the altitude range between the ground and 2 m shows that less than 1.5 % of the flux can be due to gas phase losses of PAN in this altitude range. Therefore our assumption that the vertical PAN gradient is nearly completely due to dry deposition is justified.

A tentative explanation of the variability of the PAN deposition velocity at night was given by Shepson *et al.* [1992]. They argue that the increase of the relative humidity during summer nights under rural inversion layer conditions would result in an increasing coverage of the surfaces with water. Since the PAN deposition velocity to water surfaces is very low [about 0.008 cm/s; Kames *et al.*, 1991], this may cause slower PAN deposition on to the surfaces. The measurements of the relative humidity during POPCORN [Brauers, T., H. P. Dorn, H. Koch, A. Kraus, and C. Plass-Dülmer, Meteorological Aspects, Ozone, and Solar Radiation during POPCORN 1994; submitted to *Journal of Atmospheric Chemistry*, 1996] enabled us to examine this hypothesis. Figure 4 shows the variation of the PAN deposition velocity with increasing relative humidity at the measurement site.

There is no decrease of the PAN deposition velocity with increasing relative humidity. However, it should be noted that our measurements do not include situations where substantial formations of dew occurred.

Conclusions

A novel method for the determination of deposition velocities from field measurements has been successfully applied. Simultaneous measurements of the gradient of the ²²²Rn activity and the ²²²Rn flux from the soil proved to be effective tools to measure the fluxes and the deposition velocity of PAN during the night. This method may be equally useful to investigate fluxes of other trace gases at night provided sufficiently precise measurements of the trace gas gradients are possible.

Dry deposition has a large impact on ground-level PAN mixing ratios at night. Assuming an inversion layer height of 100 m our results predict a mean lifetime of PAN due to dry deposition of about 5 hours. This compares with the average thermal PAN lifetime observed during the night of about 40 hours. Dry deposition is thus the dominant removal process for PAN during summer nights in a rural environment.

The PAN deposition velocity at night was found to be highly variable. The speculation that the relative humidity has

a strong influence on the PAN deposition velocity [Shepson *et al.*, 1992] does not agree with our observations.

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References

- Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, and J. Troc, Evaluated kinetic and photochemical data for atmospheric chemistry, Supplement IV, IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry, *J. Phys. Chem. Ref. Data*, **21**, 1125, 1992.
- Chamberlain, A. C., Transport of gases to and from grass and grass-like surfaces, *Proc. Roy. Soc. A*, **290**, 236, 1966.
- Garland, J. A. and S. A. Penkett, Absorption of PAN and ozone by natural surfaces, *Atmos. Environ.*, **10**, 1127, 1976.
- Hastie, D. R., P. B. Shepson, S. Sharma, and H. I. Schiff, The influence of the nocturnal boundary layer on secondary trace species in the atmosphere at Dorset, Ontario, *Atmos. Environ.*, **27A**, 533, 1993.
- Hill, A. C., Vegetation: A sink for atmospheric pollutants, *J. Air Pollut. Control Ass.*, **21**, 341, 1971.
- Kames, J., S. Schweighöfer, and U. Schurath, Henry's law constant and hydrolysis of peroxyacetyl nitrate (PAN), *J. Atm. Chem.*, **12**, 169, 1991.
- Nicksic, S. W., J. Harkins, and P. K. Mueller, Some analyses for peroxyacetyl nitrate and studies for its structure, *Atmos. Environ.*, **1**, 11-18, 1967.
- Schrumpf, W., K. P. Müller, F. J. Johnen, K. Lienaerts, and J. Rudolph, An optimized method for airborne peroxyacetyl nitrate (PAN) measurements, *J. Atm. Chem.*, **22**, 303 - 317, 1995.
- Shepson, P. B., J. W. Bottenheim, D. R. Hastie, and A. Venkatram, Determination of the relative ozone and PAN deposition velocities at night, *Geophys. Res. Lett.*, **19**, 1121, 1992.
- Stephens, E. R. and M. A. Price, Analysis of an important air pollutant: peroxyacetyl nitrate, *J. Chem. Educ.*, **50**, 351, 1973.
- Stephens, E. R., The formation of molecular oxygen by alkaline hydrolysis of peroxyacetyl nitrate, *Atmos. Environ.*, **1**, 19, 1967.
- Stephens, E. R., The formation, reactions, and properties of peroxyacetyl nitrates (PANs) in photochemical air pollution, *Adv. Environ. Sci.*, **1**, 119, 1969.
- Stull, R. B., *An introduction to boundary layer meteorology*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1988.
- Sun, E. J. and M. H. Huang, Detection of peroxyacetyl nitrate at phytotoxic levels and its effects on vegetation in Taiwan, *Atmos. Environ.*, **29**, 2899, 1995.
- Talukdar, R. K., Burkholder, J. B., Schmoltner, A.-M., Roberts, J. M., Wilson, R. R. and Ravishankara, A. R., Investigation of the loss processes for peroxyacetyl nitrate in the atmosphere: UV photolysis and reaction with OH, *J. Geophys. Res.*, **100**, 14,163, 1995.
- Temple, P. J. and Taylor, O. C., World-wide ambient measurements of peroxyacetyl nitrate (PAN) and implications for plant injury, *Atmos. Environ.*, **17**, 1583, 1983.
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