

# Measurements of Peroxyacetylnitrate in the Marine Boundary Layer over the Atlantic

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**Abstract.** The atmospheric concentration of peroxyacetylnitrate (PAN) was measured during a cruise of the *R.S. Polarstern* from Bremerhaven (Germany) to Rio Grande do Sul (Brazil) in September/October 1988. The measurements were made *in-situ* by a combination of electron capture gaschromatography with a cryogenic preconcentration step. The theoretical lower limit of detection ( $3\sigma$ ) was 0.4 ppt. The mixing ratios of PAN varied by more than three orders of magnitude from 2000 ppt in the English Channel to less than 0.4 ppt south of the Azores (38° N). South of 35° N, PAN levels were below the detection limit, except at 30–31° S off the eastern coast of South America. Here, PAN mixing ratios of 10 to 100 ppt were detected in continentally influenced air masses. Detectable levels of PAN were mostly observed in air masses of continental or high northern origin. Changes in the wind directions were usually associated with substantial changes in the PAN mixing ratios.

**Key words:** Peroxyacetylnitrate, marine boundary layer, Atlantic Ocean.

## 1. Introduction

Peroxyacetylnitrate (PAN) is formed as a product of the photochemical oxidation of nonmethane hydrocarbons in the presence of nitrogen dioxide. The main atmospheric removal process is decomposition into  $\text{NO}_2$  and peroxyacetyl radicals and subsequent removal of the peroxyacetyl radical. In urban photochemical smog, PAN concentrations as high as 2–10 ppb are observed. In nonurban continental Europe, the mixing ratios are significantly lower, seldom exceeding 1 ppb, typically only a fraction of a ppb.

Recent investigations have shown that PAN is also present in the upper troposphere (Rudolph *et al.*, 1987) and the marine troposphere (Singh and Salas, 1986; Goudena *et al.*, 1980; Lovelock and Penkett, 1974). Since one of the main decomposition reactions of the peroxyacetyl radical is the reaction with NO, whereas the reaction with  $\text{NO}_2$  results in the formation of PAN, the formation rate and the effective PAN lifetime will also strongly depend on the atmospheric ratio of NO to  $\text{NO}_2$ . Due to its strongly temperature-dependent thermal decomposition rate, PAN has a variable lifetime ranging from about 30 min at ground level in mid latitudes during summer to several months and longer at high altitudes. Consequently, PAN may be transported over large distances through the cold upper troposphere into

the 'clean' atmosphere (Crutzen, 1979). In this paper, we investigate the distribution of PAN over the remote Atlantic.

## 2. Experimental

The PAN measurements were made during the cruise ANT VII/1 of the German research vessel *Polarstern* in September/October 1988. Figure 1 shows the cruise track from Bremerhaven to Rio Grande. The wind vectors in Figure 1 indicate the wind directions and the wind velocities. More detailed meteorological data are given by Platt *et al.* (1992).

PAN was analyzed by gaschromatographic separation and electron capture detection. By direct injection of  $3 \text{ cm}^3$  of ambient air, the lower limit of detection was roughly 5–10 ppt. This detection limit was improved to 0.4 ppt by implementing a cryogenic preconcentration step. Every 1–1.5 h, a PAN measurement was made by the automatically operating instrument.

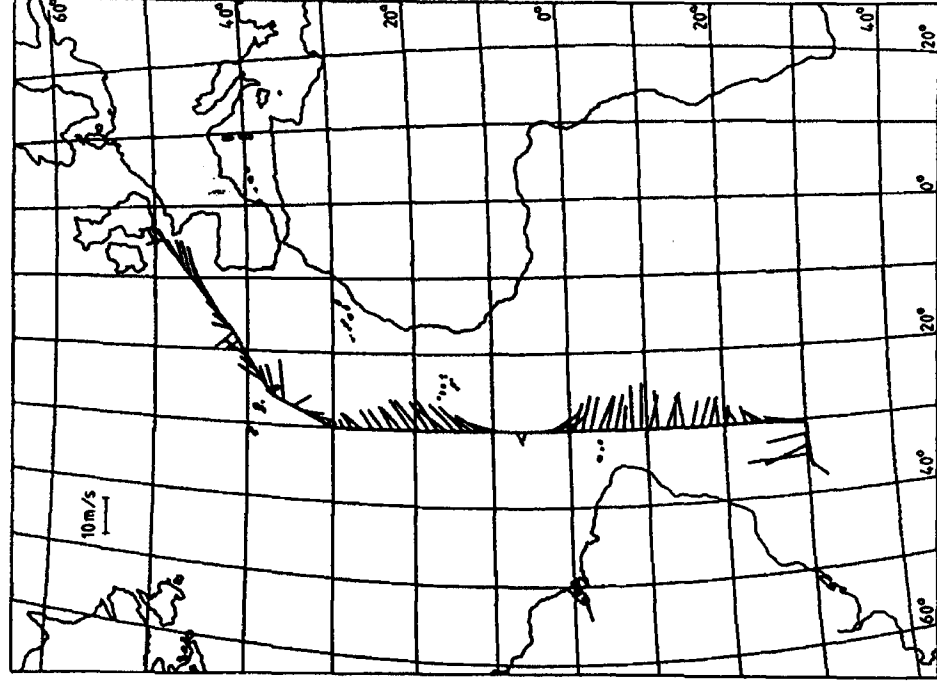


Fig. 1. Cruise track of the RV *Polarstern* from Bremerhaven to Rio Grande do Sul (Brazil) from 15 September to 19 October 1988 (ANT VII/1). The bars indicate wind direction and velocity.

The PAN gas chromatograph was installed in a container on the port side of the navigation deck. The PTFE inlet line extended about 3 m over the structure of the ship. The inlet line was continuously flushed by a pump with a flow rate of about 50 ml/sec.

A schematic drawing of the instrument is shown in Figure 2. In the GC-inlet system, the air is passed through a glass sample loop. A massflow meter controlled the flow rate of the sampled air. During preconcentration, the sample loop is immersed in a cooling liquid at 193 K. At this temperature, PAN is quantitatively adsorbed onto the glass surface of the sample loop. For desorption of PAN, the temperature of the preconcentration loop is raised to about 280 K. Then the sample is injected by means of a 10-way valve. Total sample volume was  $0.5\text{--}1\text{ dm}^3$  at STP.

After injection, the air sample is separated on the GC-precolumn ( $300 \times 2\text{ mm}$ , glass, packed with 5% PEG 400 on Chromosorb WHP 80/100 mesh). In this precolumn, PAN is separated from low-volatile substances and then transferred to the separation column (same as precolumn, but 1000 mm long). The low-volatile constituents on the precolumn are backflushed.

For calibration, a constant gas flow of  $30\text{ cm}^3/\text{min}$  of  $\text{N}_2$  is passed through a permeation device. The permeation device consists of a PTFE tube immersed in a dilute solution of PAN in *n*-heptane. In order to obtain a low and stable permeation rate and to reduce the rate of PAN decomposition in the solution, the permeation

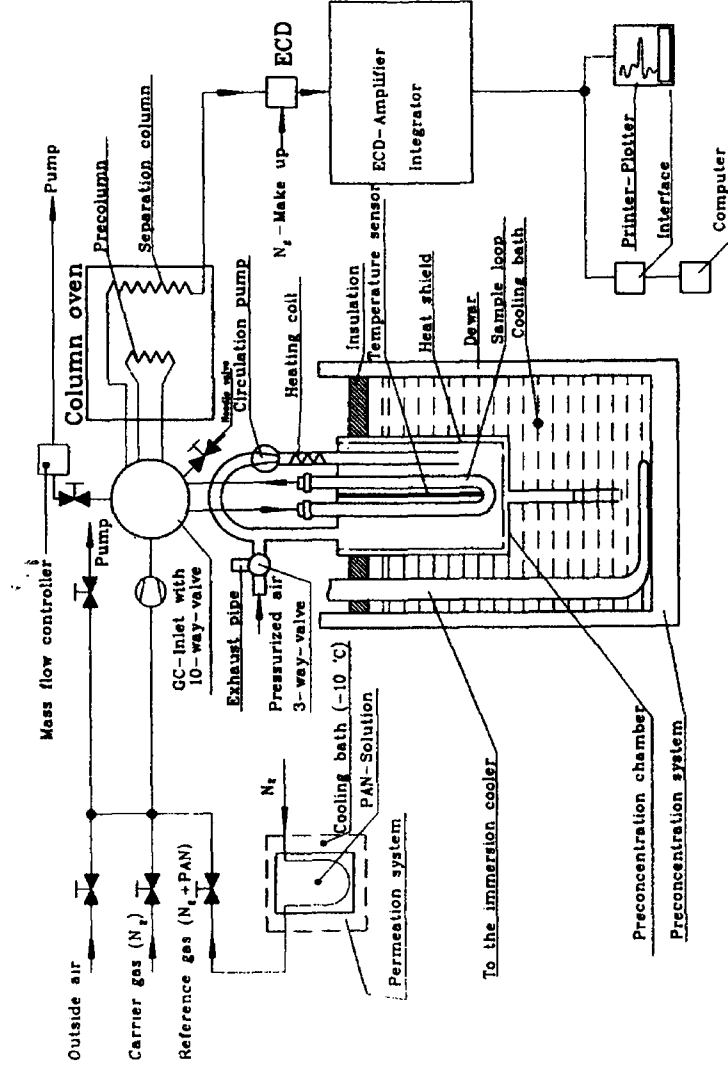


Fig. 2. Schematic drawing of the experimental set up for PAN measurements including calibration and cryogenic preconcentration system.

device is permanently kept in a cryostat at 263 K. This permeation system produced a calibration gas with about 2.5 ppb PAN, which could be diluted to the lower ppt range in a one-step dynamic dilution with PAN free air. The PAN mixing ratio in the gas from the permeation cell is analyzed by passing it through a dilute aqueous sodiumhydroxide solution. In alkaline solution, PAN decays quantitatively to  $\text{NO}_2^-$ , which is subsequently measured by spectrophotometry after derivatization. The change of the PAN concentration in the calibration gas during the ship cruise (about 1 month) is less than 10%. Additionally, the liquid injection of a dilute solution of PAN in *n*-heptane is used for calibration. A comparison between calibration by injection of PAN in the solution and the permeation method showed that both methods agree within an error of 10%. This is within the total error of the measurements. More details of the PAN measurement and calibration technique are given by Müller and Rudolph (1989).

### 3. Results and Discussion

Figure 3 shows the latitudinal profile of PAN. The mixing ratios of PAN varied from about 2000 ppt in the English Channel to less than 0.4 ppt (detection limit) south of the Azores. In tropical latitudes at 30° W between 30° N and 30° S, the mixing ratio was below the detection limit. At 31° S/32–35° W PAN was detected again in continentally influenced air with concentrations between 10 and 100 ppt.

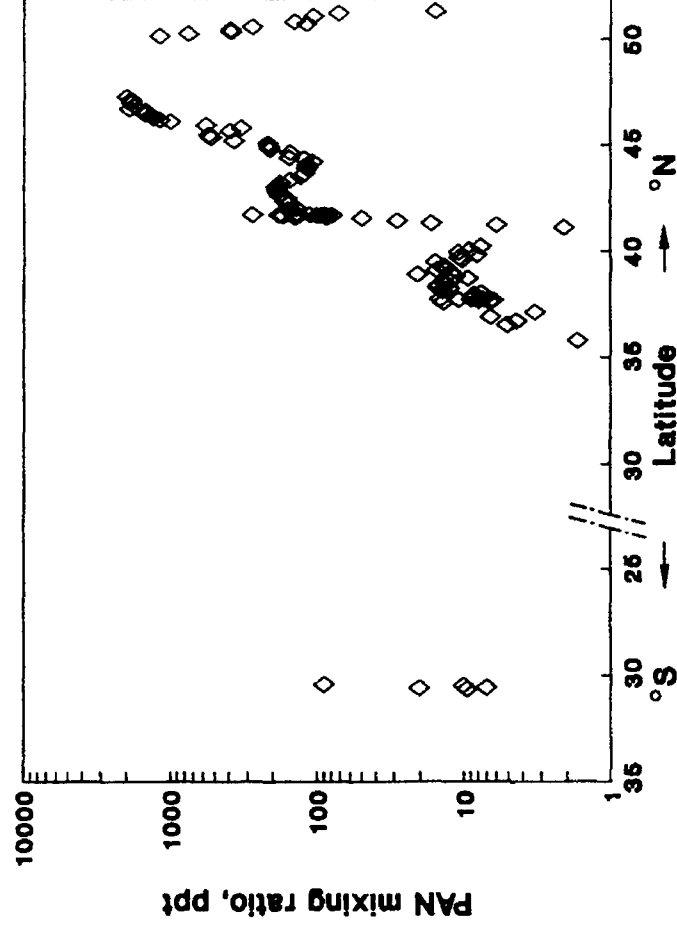


Fig. 3. Latitudinal profile of the PAN mixing ratios in the marine troposphere measured during ANT VII/1, September/October 1989. Between 35° N and 30° S PAN mixing ratios were always below the detection limit of 0.4 ppt.

It is possible to correlate the strong variations in the mixing ratio with the changes in the main wind directions corresponding to different air masses (see Figures 1 and 3).

In the latitude range 30° N–30° S, the air temperatures at sealevel were in general between 22 and 25 °C, sometimes even higher (details are given by Platt *et al.*, 1992). At these temperatures, the thermal lifetime of PAN is half an hour or less. The concentrations of the precursors of PAN (NMHC and NO<sub>x</sub>) were quite low in this latitude range. The ethane mixing ratio was always below 1 ppb, for propane and acetylen below 0.1 ppb, and the mixing ratios of the other NMHC seldom exceeded 50 ppt (Koppmann *et al.*, 1992). The NO<sub>x</sub> mixing ratios were generally less than 50 ppt and only occasionally between 50 and 100 ppt (Rohrer and Brüning, 1992). From these NO and NO<sub>2</sub> data, together with the measured NMHC mixing ratios and OH radical concentrations calculated from a simple box model (cf. Koppmann *et al.*, 1992), an upper limit for the PAN mixing ratios can be derived from in-situ photochemistry. An upper limit for the primary production of peroxyacetyl radicals can be estimated from the NMHC mixing ratios, the OH radical concentration and the corresponding reaction rate constants (cf. Atkinson, 1986; Atkinson *et al.*, 1989), if we neglect the loss reactions of the intermediate radicals, aldehydes, etc., which can be caused by radical-radical reactions, deposition, and adsorption on aerosol particles. We can also estimate a lower limit for the peroxyacetyl radical losses by only considering the reaction with NO which competes with the formation of PAN by the reaction with NO<sub>2</sub>. Considering only the thermal decay of PAN, we can, based on the rate constants recommended by Atkinson *et al.* (1989), estimate an upper limit of 0.2–0.7 ppt for the steady-state concentration of PAN. This estimate is very crude, but the simplifications are such that the calculated PAN mixing ratios are overestimated. Thus, it is justified to conclude that only marginal PAN mixing ratios can be expected from *in-situ* photochemical production. In addition, horizontal transport is not fast enough to maintain substantial PAN mixing ratios over the remote ocean against a decay time of half an hour. Only transport via the middle and upper troposphere might possibly allow long-range transport of PAN at these latitudes. However, only under conditions where the exchange between the free troposphere and the marine boundary layer occurs at timescales of less than a few hours, could this show any effect on the PAN mixing ratios at the sea surface. Consequently, the very low PAN mixing ratios we found over the open Atlantic in tropical and subtropical latitudes are not surprising.

We can compare our results with those from other authors. Goudena *et al.* (1980) measured the latitudinal distribution of PAN during seven ship cruises between Amsterdam or Rotterdam (52° N, Netherlands) and Paramaribo (6° N, Surinam) or Rio de Janeiro (23° S, Brazil). Their experimental technique allowed only measurements of PAN mixing ratios above 50 ppt. Thus, most of their measurements only gave an upper limit. Between 45 and 53° N, they found PAN mixing ratios ranging from less than 50 ppt to several hundred ppt, in the English

Channel, and sometimes even more than 1000 ppt. Towards the lower latitudes, the PAN mixing ratios decreased rapidly, between 33 and 45° N they were only occasionally above the detection limit and they never exceeded 250 ppt. South of 33° N, Goudena *et al.* never found detectable levels of PAN. Lovelock and Penkett (1974) reported considerably higher PAN concentrations for the open Atlantic between 53 and 18° N. During a ship cruise from Hamburg to Santo Domingo in October 1973, they measured PAN mixing ratios with daily averages ranging from 0.1 to 2.5 ppb. But it should be noted that Singh and Viezee (1988) report the formation of PAN artefacts by sampling procedures similar to those used by Lovelock and Penkett.

There are also measurements of the latitudinal distribution of PAN over the Pacific. Singh and Salas (1986) measured PAN concentrations around 50 ppt between 50 and 30° N, decreasing with decreasing latitudes to about 5 ppt at the equator. Their Southern Hemispheric average was around 5 ppt with no systematic latitude dependence. Most of these measurements were made not far from the American west coast and, thus, continental influence on the sampled air masses cannot be excluded. However, no data about wind direction and wind velocity or origin of the air masses are reported.

Our PAN measurements at tropical and subtropical latitudes over the open Atlantic are much lower than these previous measurements and indicate that no significant background levels of PAN exist at sealevel and lower latitudes. This is compatible with the short atmospheric PAN lifetime and the low concentrations of PAN precursors.

## References

- Atkinson, R. A., 1986, Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions, *Chem. Rev.* **85**, 69–201.
- Atkinson, R. A., Baulch, D. L., Cox, R. A., Hampson, R. F., Kerr, J. A., and Troe, J., 1989, Evaluated kinetic and photochemical data for atmospheric chemistry, Supplement III, *J. Phys. Chem. Ref. Data* **18**, No. 2, 881–1095.
- Crutzen, P. J., 1979, The role of NO and NO<sub>2</sub> in the chemistry of the troposphere and stratosphere, *Ann. Rev. Earth Planet. Sci.* **7**, 443–472.
- Goudena, E. J. G., Guicherit, R., and Den Hout, K. D., 1980, Peroxyacetylnitrate, ozone and some halocarbon measurements over the Atlantic, Instituut voor milieuhygiëne en gezondheidsstechniek TNO, Publicatie NO. 725, Postbus 214, 2600 AE Delft, Netherlands.
- Koppmann, R., Bauer, R., Johnen, F. J., Plass, C., and Rudolph, J., 1992, The distribution of light non-methane hydrocarbons over the mid-Atlantic: results of the Polarstern cruise ANT VII/1, *J. Atmos. Chem.* **15**, 215–234 (this issue).

- Lovelock, J. E. and Penkett, S. A., 1974, PAN over the Atlantic and the smell of clean linen, *Nature* **249**, 434.
- Müller, K. P. and Rudolph, J., 1989, An automated technique for the measurement of peroxyacetyl nitrate in ambient air at ppb and ppt levels, *Internat. J. Environ. Anal. Chem.* **37**, 253-262.
- Platt, U., Rudolph, J., Brauers, T., and Harris, G. W., 1992, Atmospheric measurements during *Polarstern* cruise ANT VII/1, 54° N to 32° S: an overview, *J. Atmos. Chem.* **15**, 203-214 (this issue).
- Rohrer, F. and Brüning, D., 1992, Surface NO- and NO<sub>2</sub>-mixing ratios measured between 30° N and 30° S in the Atlantic region, *J. Atmos. Chem.* **15**, 253-267 (this issue).
- Rudolph, J., Vierkorn-Rudolph, B., and Meixner, F. X., 1987, Large-scale distribution of peroxyacetyl nitrate, results from the STRATOS III flights; *J. Geophys. Res.* **92**, 6653-6661.
- Schurath, U., Kortman, U., and Glavas, S., 1984, Properties, formation and detection of peroxyacetyl nitrate, in *Proceedings of the 3rd European Symposium on Physico-Chemical Behavior of Atmospheric Pollutants*, Varese, Italy, pp. 27-37.
- Singh, H. B. and Satas, L. J., 1986, The global distribution of peroxyacetyl nitrate, *Nature* **321**, 588-591.
- Singh, H. B. and Viezee, W., 1988, Enhancement of PAN abundance in the Pacific marine air upon contact with selected surfaces, *Atmos. Environ.* **22**, 419-422.