

Latitudinal distribution of peroxyacetyl nitrate (PAN) over the Atlantic Ocean

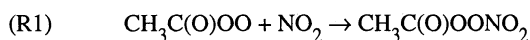
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Abstract. Atmospheric concentrations of peroxyacetyl nitrate (PAN) were measured during a cruise of RV *Polarstern* from Cape Town (South Africa) to Bremerhaven (Germany) in May/June 1998 and at Ny-Ålesund, Svalbard, in March 1998. The continuous in-situ measurements were using electron capture gas chromatography combined with a cryogenic preconcentration technique. The time resolution of the measurements was 10 min with a detection limit of 5 parts per trillion by volume (pptv). The mixing ratios of PAN exhibited a maximum of 1100 pptv in the English Channel and values less than 5 pptv in tropical latitudes between 10°N and 10°S. The latitudinal distribution of PAN showed significantly higher concentrations in the northern hemisphere compared to the southern hemisphere. North of 10°N, daily maximum PAN concentrations normally exceeded 100 pptv. Mean mixing ratios decreased from 244 pptv between 50°N and 54°N to 13 pptv between 20°N and 30°N. Enhanced concentrations were detected in continentally influenced air masses identified by trajectory analysis and simultaneous measurements of black carbon and ozone. Intrusions of air masses from the upper troposphere could not be inferred from trajectory analysis. In temperate northern latitudes, enhanced PAN mixing ratios can be used as an indicator of long-range transport of photochemically active pollutants.

1. Introduction

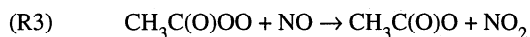
Peroxyacetyl nitrate (PAN) has long been recognized as a minor product of the photochemical oxidation of nonmethane hydrocarbons in the presence of nitrogen oxides [Stephens, 1969]. PAN is formed in the reaction of acetylperoxy radicals with NO₂:



Although the rate coefficient for this reaction ($k_1 = 9.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at 298 K [Bridier *et al.*, 1991]) is large, PAN concentrations are limited owing to the thermal decomposition of PAN:



Thus atmospheric PAN concentrations are strongly dependent on temperature because the rate coefficient for the decomposition reaction (R2) decreases at lower temperatures ($k_2 = 4.6 \times 10^{-4} \text{ s}^{-1}$ at 298 K; $1.1 \times 10^{-6} \text{ s}^{-1}$ at 263 K [Bridier *et al.*, 1991]). In addition, PAN formation is limited by the competing reaction of CH₃C(O)OO with NO:



Reaction (R3) proceeds with a rate constant of $k_3 = 1.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ at 298 K [DeMore *et al.*, 1997] and leads to the final decomposition of the organic peroxy radical.

Therefore the net loss rate of PAN mainly depends on the temperature and the NO/NO₂ ratio. Lower limits of PAN

lifetimes are 30 min at 298 K and 10 days at 263 K which can be calculated from the decay rate of reaction (R2). However, reaction sequence (R1) and (R2) also allows an increase of the effective lifetime of PAN at higher temperatures if reactions of the acetylperoxy radicals with NO (R3) or peroxy radicals RO₂ are suppressed due to high concentrations of NO₂ and/or low concentrations of NO and RO₂. A detailed review of the atmospheric chemistry of organic nitrates given by Roberts [1990] showed that other chemical loss processes like photolysis or reaction with OH radicals become important under conditions with PAN lifetimes larger than 100 days. However, such conditions only exist in the upper troposphere.

Precursors of the acetylperoxy radicals are specific hydrocarbons and aldehydes (e.g., propene, butene, pentene, acetaldehyde). These organic compounds have diffuse background sources as well as large anthropogenic sources confined to relatively small urban areas [Roberts, 1990]. Several experimental and theoretical studies have demonstrated that PAN is transported from polluted continental sites into the upper troposphere and relatively clean marine environments [e.g., Singh *et al.*, 1996; Jaffe *et al.*, 1997] where it can constitute a major component of reactive nitrogen compounds (NO_y). Thus PAN can be used as a specific indicator of anthropogenic photochemical air pollution in remote air masses. Furthermore, PAN can act as a reservoir for odd nitrogen during the transport into remote areas, especially when the transport is directed from colder parts of the troposphere (e.g., upper troposphere and polar regions) to warmer regions. Increasing PAN decomposition at higher temperatures can release NO₂ in remote areas. This can effect the NO_x balance of these regions in the troposphere which are not directly influenced by long-range transport of NO_x from continental sources due to the short chemical lifetime of NO_x of 1-2 days under typical tropospheric conditions [Liu *et al.*, 1987]. In this case, PAN would act as a temporary reservoir for NO_x

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[Singh *et al.*, 1992] influencing not only NO_x concentrations in remote areas but also the chemical production of ozone, which is usually limited by NO_x in the remote troposphere [e.g., Carroll and Thompson, 1995].

This paper reports measurements of PAN performed during two field campaigns in the marine boundary layer (MBL) and at an Arctic site. The latitudinal distribution of PAN is analyzed on the basis of ground-level trajectories. Simultaneous measurements of ozone and black carbon (BC) are also employed in a discussion of PAN mixing ratios in the MBL. The measurements are compared with results of modeling studies of the global distribution of PAN.

2. Methods and Instrumentation

One of the field campaigns was performed aboard the RV *Polarstern* (ANT XV/5). The cruise track started at Cape Town, South Africa (34°S), on May 26, 1998, and ended in Bremerhaven, Germany (54°N), on June 21, 1998. The cruise included an intermediate stay of 2 days in Lisbon, Portugal (June 13–15). The itinerary of the cruise and ground-level 3-day back trajectories are shown in Figure 1.

The gas chromatograph for the detection of PAN and the BC monitor were installed in an air-conditioned laboratory container placed on the compass deck of the ship. The inlet lines were mounted on the compass deck rail approximately 22 m above sea level. The inlet line of the PAN analyzer was 3.7 m of 0.8 cm ID perfluoroalkoxy (PFA) tubing. The outboard end of the line was equipped with a spray deflector to avoid sea spray contamination which was controlled daily by visual inspection. Inside the laboratory container, the line was connected with a manifold and flushed with a flow rate of about 20 L min^{-1} leading to a residence time of the air samples in the inlet line and the manifold of less than 1 s. From the manifold a pump sucked sample air into the analyzer.

Measurements of PAN were also made during spring 1998 at the Koldewey-Station of the Alfred-Wegener-Institute in Ny-Ålesund, Svalbard, at 79°N and 12°E (Figure 2). Ny-Ålesund is a small settlement situated on the southern shore of the Kongsfjord on the west coast of Spitsbergen. The campaign was conducted from March 11–29, 1998. The PAN analyzer was installed inside the chemistry laboratory building located on the east border of the village. The inlet line, mounted approximately 4 m above ground, was the same type as used in the shipborne measurements.

Continuous measurements of meteorological quantities (temperature, pressure, wind speed, wind direction, relative humidity) were routinely performed on board the RV *Polarstern* as well as on Koldewey Station. Shipborne measurements are generally disturbed by possible contamination due to the exhaust of the ship's engines because they are powerful local BC and NO_x sources. O_3 , PAN, and BC concentrations measured during relative wind directions outside a $\pm 80^\circ$ corridor with respect to the ship's heading could be affected by contamination originating from the exhaust plume. In such cases the data were discarded from the original data sets. Only corrected data sets were used for further analysis. Trajectory calculations were used to investigate the effects of large-scale atmospheric flow patterns on the measured concentrations during both field experiments. Trajectories were provided by the German Weather Service (DWD) and were calculated using a global spectral numerical weather prediction model derived from the global model of the European Centre for Medium-Range Weather Forecasts

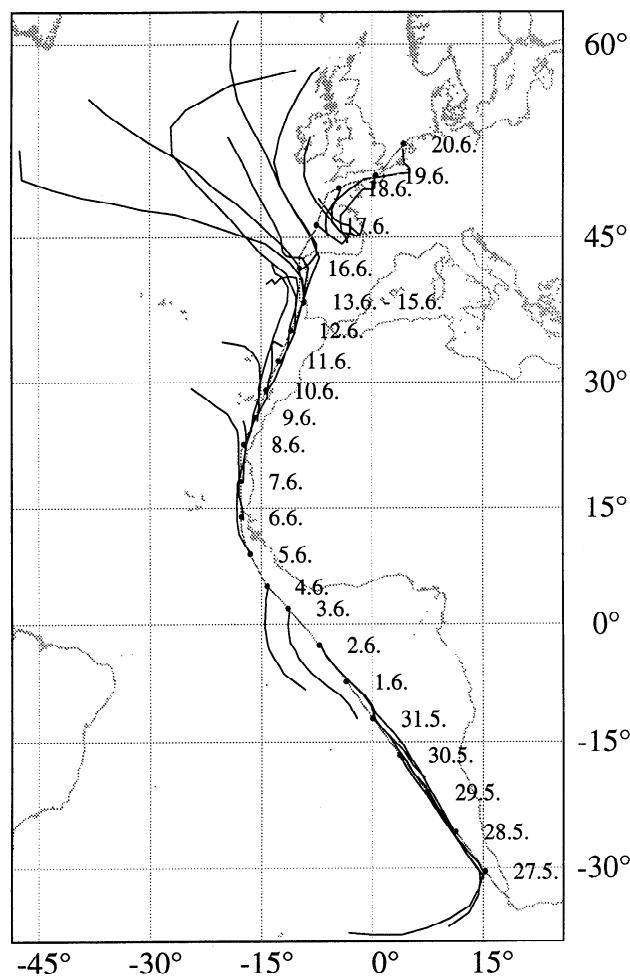


Figure 1. Map of the cruise track of the RV *Polarstern* (ANT XV/5). Also shown are ground-level 3-day back trajectories (arrival time 1200 UTC) provided by the German Weather Service (DWD). Dots indicate the ship's position each day at 1200 UTC.

[Kottmeier and Fay, 1998]. Three-day ground-level back trajectories ending at Ny-Ålesund or at the ship's position at 1200 UTC each day were used to classify the synoptic flow patterns.

2.1. Ozone Analyzer

Measurements of ozone concentrations were routinely performed on board the RV *Polarstern*. Data were obtained by using an electrochemical concentration cell (ECC) based on the iodide-ozone reaction [Winkler, 1988]. The analyzer consisted of a small pump that bubbled ambient air into a cell containing a 2% potassium iodide solution. A flowmeter was installed to control the air volumes which were sampled with a PTFE tube without a filter as the air intake. The current generated by the reaction in the cell is proportional to the ozone concentration in the sample air. Data were continuously recorded and stored together with the meteorological quantities in the database POLDAT. Ten minute averages were extracted and used for further evaluations. On previous cruises, intercomparisons were made with UV photometric analyzers which gave good agreement within a range of ± 1 ppbv [Weller and Schrems, 1996; Weller *et al.*, 1996]. Disturbances due to NO_x and SO_2 seem to be negligible over the ocean [Winkler, 1988].

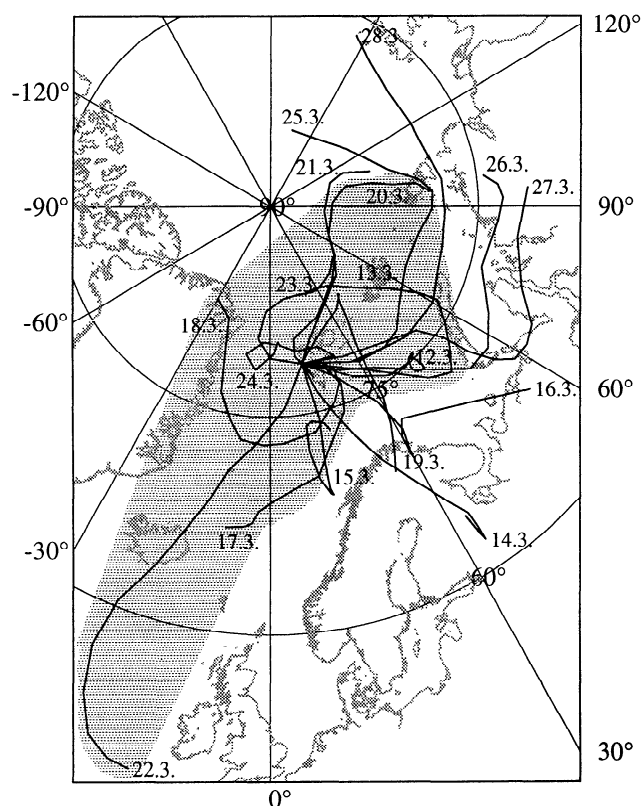


Figure 2. Map of Svalbard with calculated ground-level 3-day back trajectories (arrival time 1200 UTC) provided by the German Weather Service (DWD). A “background” production rate of 1-2 pptv PAN h⁻¹ is assumed for the shaded area (see text).

2.2. PAN Analyzer

A commercial PAN analyzer was used which was based on chromatographic separation with subsequent electron capture detection (Meteorologie Consult GmbH, Glashütten, Germany).

A schematic drawing of the instrument is shown in Figure 3. Ambient air was continuously drawn from the inlet line with a flow rate of about 10 mL min⁻¹. PAN was enriched at 3°C on a cryogenic sampling trap which consisted of a Peltier-cooled column filled with solid absorption material. For the enrichment the sampling trap was flushed with air for 7 min. This period was sufficient to establish an equilibrium between the gas phase concentration of PAN and the amount of absorbed PAN. The calibration procedure showed that absorbed amounts of PAN were constant in mass at constant gas phase concentration and enrichment temperature due to the established equilibrium. Higher gas phase concentrations were linearly correlated with higher amounts of absorbed PAN and vice versa. For desorption the temperature of the preconcentration loop was quickly raised with ballistic electrical heating and switched off when a temperature of 27°C was reached. By means of a 10-way valve the gas mixture was transferred onto the precolumn using nitrogen as a carrier gas. The carrier gas was moistened by a cartridge containing hydrated copper sulfate (Meteorologie Consult GmbH, Glashütten, Germany) that was located in the gas supply in order to ensure constant carrier gas humidity. Both precolumn and main column were wide bore capillary columns [Müller and Rudolph, 1992] which were mounted in a thermostatically controlled oven cooled by Peltier elements. Temperature fluctuations were less than 1°C. The separation was performed isothermally at 17°C on the analytical columns. While the selected fraction of the precolumn eluate was passed onto the main column, the precolumn was back-flushed to prevent column contamination and to decrease analysis running time. The eluates were detected by electron capture detection (ECD) at 60°C. The signal was evaluated by integration of the PAN peak. Chromatograms and calculated areas were recorded and saved for further analysis. PAN measurements were performed in 10 min analytical cycles.

The calibration was based on the photochemical synthesis of PAN from NO premixtures in the presence of a large excess of acetone and synthetic air in a flow reactor which consisted of a glass chamber (~100 mL) equipped with a penray lamp (Meteorologie Consult GmbH, Glashütten, Germany). The UV

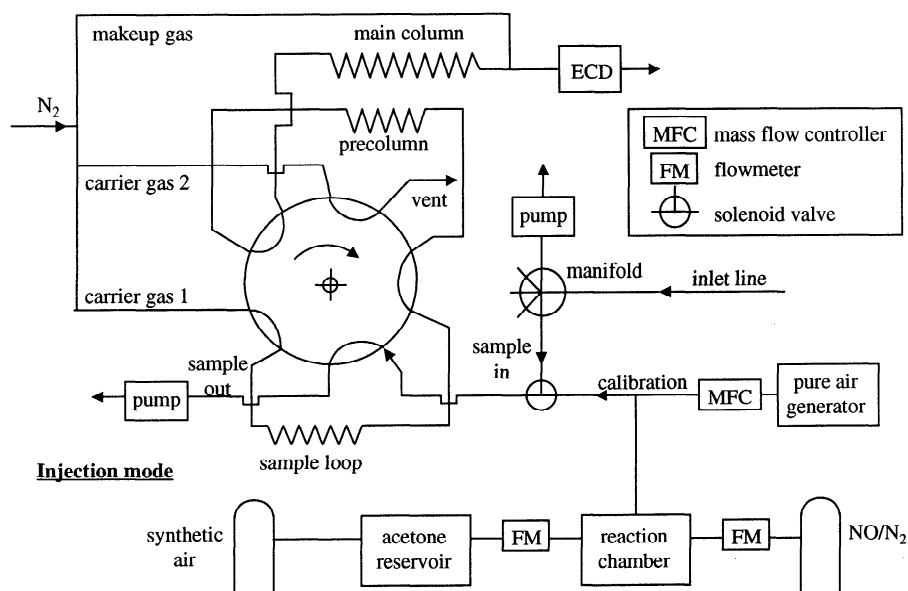


Figure 3. Schematic drawing of the experimental setup of the PAN analyzer.

radiation emitted by the lamp led to the photolytic-induced oxidation of a small amount of acetone. During this oxidation process, acetylperoxy radicals were produced which transformed the employed NO to NO₂ (R3). NO₂ reacted further with excess acetylperoxy radicals leading to the formation of PAN (R1). Within the reaction chamber of the system, reactant flows and photon fluxes were such that complete conversion of NO to PAN is maintained within a wide range of NO and acetone concentrations in the premixtures. A conversion factor of 0.90 ± 0.05 for the employed NO was obtained by using two other analytical techniques for the determination of PAN [Volz-Thomas *et al.*, 1998]. Purified ambient air produced by a clean air generator (PAG 003, Eco Physics GmbH, Munich, Germany) was used for subsequent dynamic dilution to concentrations of 100 parts per trillion by volume (pptv) to 2 ppbv PAN. The procedure required only the determination of the NO calibration gas flow. The calibration of the analyzer was performed on board during the intermediate stay in Lisbon (June 14 and 15). Differences in the operating conditions whether the ship was moving under power or in port were negligible because the complete setup including the power supply was the same during the whole cruise. Moreover, laboratory experiments showed that variations in instrument sensitivity were less than 2% during a period of 3 weeks.

The detection limit of 5 pptv is defined as 3 times the standard deviation calculated from the noise of the output signal of the analyzer when PAN was not present in ambient air samples (June 1-4). The overall error in the PAN measurements was estimated to be less than $\pm 15\%$.

2.3. Black Carbon Analyzer

Black carbon (BC) measurements were based on the optical attenuation method described by Hansen *et al.* [1988] and Hansen and McMurry [1990]. A commercial aethalometer (AE 10, Magee Scientific, Berkeley, California) was used. The aerosol was accumulated on a circular spot with a reduced area of $35 \pm 1 \text{ mm}^2$. This area was obtained by a modification of the sampling

mimic in order to enhance the sensitivity of the instrument. For the calculation of the accumulated BC quantities, an attenuation cross section on the filter material (Pallflex, type T60A20) of $\sigma = 14 \text{ m}^2 \text{ g}^{-1}$ was used.

The detection limit is derived from the noise level of the output signal of the aethalometer in cases where black carbon was absent in ambient air samples (June 11). The detection limit of 50 ng m^{-3} was defined to be 3 times the standard deviation of this noise level. The overall error was estimated to be less than 15%. Owing to problems with the automatic data storage procedure, 10 min means were recorded before June 2 and after June 8.

3. Results

3.1. PAN Concentrations in the MBL

The time series of PAN, ozone, and black carbon measured aboard the RV *Polarstern* during the cruise ANT XV/5 are presented in Figure 4. In the southern hemisphere, PAN mixing ratios above the detection limit of 5 pptv were measured only during 2 days. The highest PAN concentration of about 19 pptv over the South Atlantic was observed at 17°S. In tropical latitudes between 10°N and 10°S, the output of the PAN analyzer showed fluctuations around zero. Apparently, a sufficient amount of measurable PAN was absent in the ambient air during this period. Therefore data obtained between June 1 and 4 were used to calculate a detection limit of 5 pptv.

In the northern hemisphere, PAN was present at higher concentrations. The averages and the range of the mixing ratios calculated for several latitudinal ranges are summarized in Table 1. In the region north of the Cape Verde Islands, PAN concentrations increased strongly. PAN mixing ratios up to about 150 pptv during daytime were found along the west coast of Africa. Close to the European continent, even higher values were observed. The maximum concentration of about 1100 pptv was measured in the English Channel. The high time resolution of the PAN analyzer was very useful in following the strong fluctuations of PAN mixing ratios in the ambient air, but only on

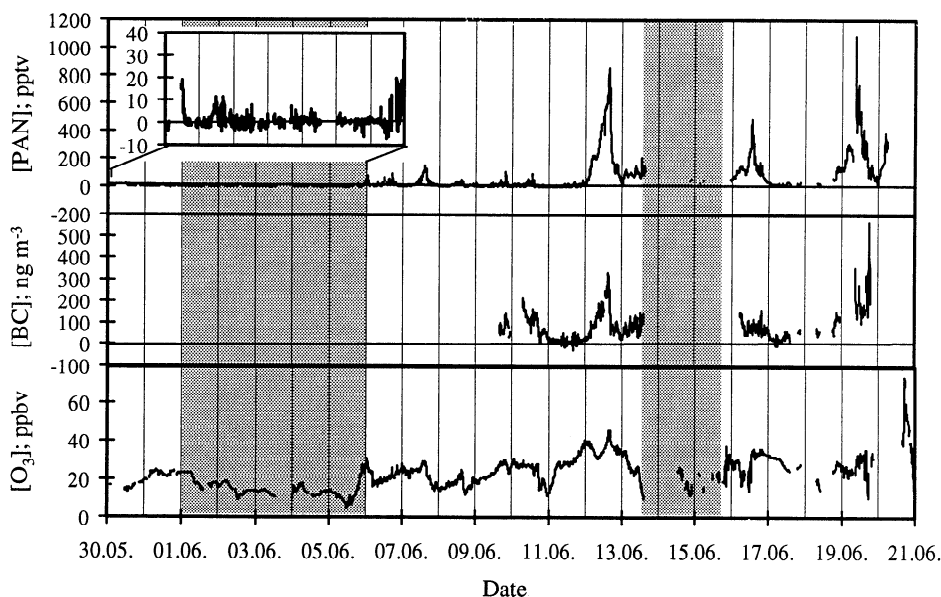


Figure 4. Time series of PAN, black carbon, and ozone concentrations measured on board the RV *Polarstern* (ANT XV/5). The shaded areas represent the latitudinal range between 10°S and 10°N and the intermediate stay in Lisbon, respectively.

Table 1. Measurements of PAN During the RV *Polarstern* Cruise ANT XV/5 From May 29 to June 20, 1998, and a Comparison With Other Studies in the MBL

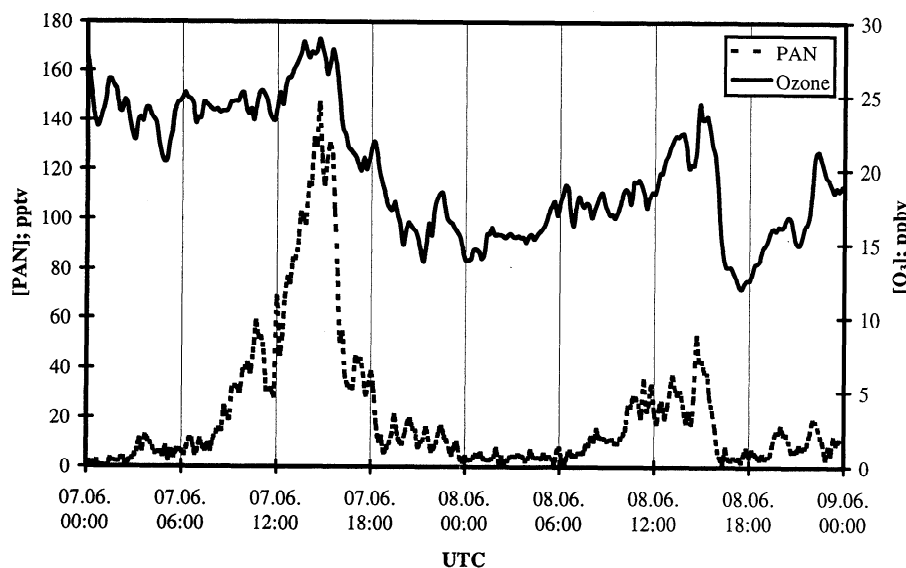
Region	Period	Height	Mean, pptv	Range, pptv	Reference
Pacific cruise 48°N–25°N 25°N–0° 0°–48°S	Nov./Dec. 1984	sea level		30–80 5–40 –5	1
Atlantic cruise 7°N–64°N	Aug./Sept. 1988	sea level		<1–40	2
Atlantic cruise 35°N–54°N 30°S–30°N 31°S	Sept./Oct. 1988	sea level		2–2000 <1 10–100	3
Atlantic flights 34°S–0°	Sept./Oct. 1992	160–320 m	3	1–7	4
Atlantic cruise 24°S–10°S 10°S–0° 0°–10°N 10°N–20°N 20°N–30°N 30°N–40°N 40°N–50°N 50°N–54°N	May/June 1998	sea level	<5 <5 <5 22 13 121 98 244	<5–19 <5–8 <5–12 <5–147 <5–108 <5–850 8–483 23–1088	5

References are 1, Singh *et al.* [1986]; 2, Gallagher *et al.* [1990]; 3, Müller and Rudolph [1992]; 4, Singh *et al.* [1996]; 5, this study.

particular days were distinct diurnal variations of PAN observed (e.g., June 7, 8, and 12). During these days, PAN values increased in the morning, and maximum concentrations were observed in the early afternoon. After the maximum was reached, mixing ratios strongly decreased to low nighttime values (Figure 5).

The meridional distribution of BC measured during the RV *Polarstern* transect differs from the distribution of PAN mixing ratios. Nevertheless, it is possible to identify several episodes with enhanced BC concentrations in the range of 100 to 600 ng m⁻³ coinciding with enhanced PAN concentrations (Figure 4). The ozone concentrations measured on board the RV *Polarstern* were always less than 50 ppbv with mixing ratios below 25 ppbv

in the latitudinal range between 25°S and 10°N (Figure 4). Only when the ship reached the Northern Sea were concentrations up to 75 ppbv observed. The calculated daily means were in the range of 12 to 36 ppbv with lower concentrations in the southern hemisphere. These values are in the same range as the calculated latitudinal distribution of surface ozone over the Atlantic presented by Winkler [1988]. Although diurnal O₃ variations were absent during the main part of the cruise, they could be observed in combination with the diurnal cycles of the PAN mixing ratios. In these cases, the diurnal O₃ cycles were similar to those typical in continental air masses with the lowest mixing ratios occurring before sunrise and maxima occurring in the early afternoon.

**Figure 5.** Time series of PAN and of ozone measured on board the RV *Polarstern* (ANT XV/5) on June 7 and 8.

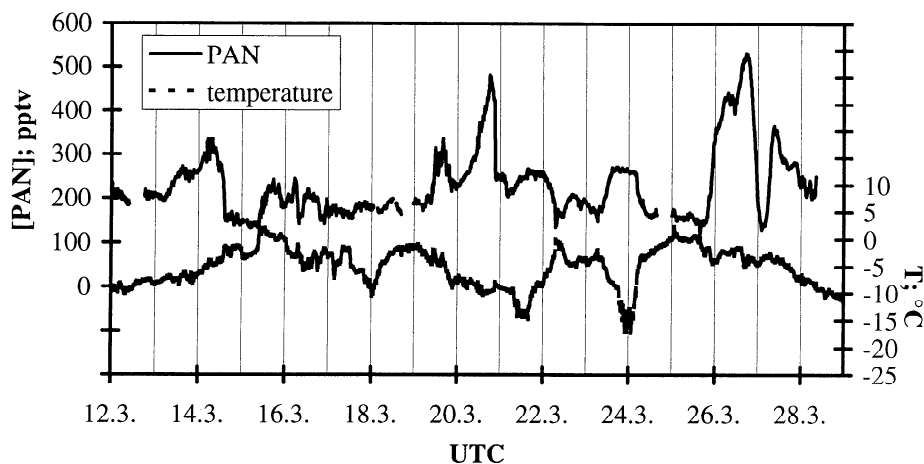


Figure 6. Time series of PAN and temperature measured at Ny-Ålesund, Svalbard (79°N, 12°E).

3.2. PAN Concentrations at Ny-Ålesund

The measured PAN mixing ratios at Ny-Ålesund were in a narrow range from 100 to 420 pptv. A distinct diurnal cycle could not be observed. On the other hand, a temporary relationship between PAN and air temperature was obtained. Figure 6 shows the time series of PAN mixing ratios and temperature during the measuring period. Several short-time episodes can be identified (e.g., March 22 and 24) during which temperature and PAN concentrations were anti-correlated. This anti-correlation may correspond in part to the faster decomposition with increasing temperatures due to reaction (R2). However, the investigation of the relationship between PAN and temperature was inherently hampered by advection of different air masses to the measuring site.

4. Discussion

4.1. PAN Concentrations in the MBL

Since no direct emissions of PAN or PAN precursors occur in the marine or Arctic troposphere, it can only be present in the remote boundary layer if PAN or its precursors are either horizontally or vertically transported from regions with higher concentrations. On a global scale, the continents and the upper troposphere can in general be characterized as regions with enhanced PAN concentrations [Singh and Hanst, 1981; Sandholm *et al.*, 1992; Seinfeld and Pandis, 1998]. This is due either to faster formation rates in the presence of high precursor concentrations or to slower decomposition at low temperatures. Moreover, the continents are the most important source regions of PAN precursors. In order to identify source regions of PAN or its precursors, the data set was interpreted by utilizing the obtained BC and ozone concentrations together with calculated 3-day back trajectories.

BC represents a minor part of carbonaceous aerosol in the troposphere. Carbonaceous aerosol has several sources such as emissions of volatile organic compounds from vegetation, combustion of fossil fuels, and biomass burning [Wolff and Cachier, 1998]. The global budget is dominated by biomass burning in tropical regions and industrial combustion in the temperate latitudes of the northern hemisphere. Owing to its resistance to chemical or physical transformation and its ability to be transported over large distances, BC can be used as tracer for

combustion processes and therefore for continentally influenced air masses. Like PAN, tropospheric ozone is produced from NO_x and reactive hydrocarbons [e.g., Logan, 1985]. It can be demonstrated that in polluted air masses a linear relationship between PAN and O_3 concentrations can be expected regardless of atmospheric dilution rates [Schmidt *et al.*, 1998]. Parrish *et al.* [1993] also showed that ozone can be used as an indicator of continental influence for air transported off North America to the North Atlantic Ocean. In contrast to BC, ozone has an additional strong natural source in the stratosphere. Law and Pyle [1993] calculated a stratospheric ozone flux of 692 Tg y^{-1} compared to a net chemical production of 2074 Tg y^{-1} on a global scale. Therefore enhanced ozone concentrations are not an unequivocal indicator of continentally influenced air masses.

In order to identify the impact of horizontally or vertically transported air masses, the relations between PAN, BC, and ozone were investigated. Figure 7 shows a plot of observed PAN concentrations versus BC concentrations. A linear fit to the data resulted in a regression line with a correlation coefficient of $R^2 = 0.32$. Although higher BC concentrations at lower PAN concentrations occurred, Figure 7 indicates that increased PAN mixing ratios were generally accompanied by enhanced BC concentrations. From these results, it may be concluded that downward vertical transport of PAN from the upper troposphere, which would be accompanied by low BC concentrations, was negligible during the cruise. This is supported by trajectory analysis of the advected air masses, which showed no impact from the upper troposphere or even the stratosphere.

On the other hand, the relation between PAN and ozone was not very pronounced. A linear regression of PAN concentrations versus O_3 concentrations (not shown) resulted in a correlation coefficient of $R^2 = 0.17$. However, the relationship of PAN and O_3 in the MBL is not only dependent on photochemical production or emission but also on the different atmospheric lifetimes of these species. Hov [1984] showed that at elevated temperatures the persistence of PAN over the sea is lower compared to that of ozone due to the thermal decomposition of PAN. Moreover, surface removal affects ozone, but loss of PAN by wet or dry deposition is thought to be negligible in the MBL [Roberts *et al.*, 1996]. While ozone appears to be a good indicator for polluted continental air masses where fossil fuel combustion is a dominant source [Parrish *et al.*, 1993], this correlation is likely to be disturbed by various mixing processes

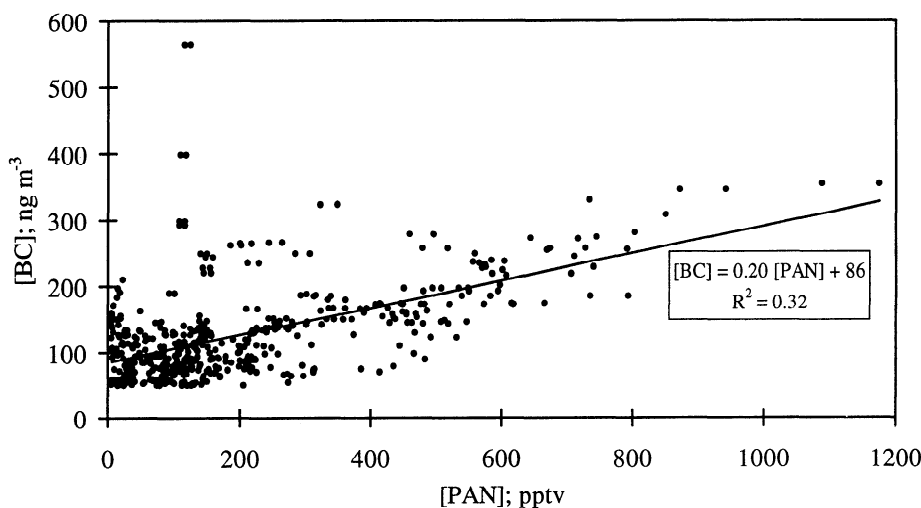


Figure 7. Relation between PAN and BC measured during cruise ANT XV/5. Each dot indicates a 10-min average. Also given is the fit obtained by a linear regression analyses.

and a multiplicity of sources [Singh *et al.*, 1996] which is most probably the case along the African and European coast. These different influences may explain the scatter in the correlation between PAN and O_3 concentrations.

However, several days could be identified with distinct diurnal variations of PAN and O_3 (e.g., June 7, 8, and 12). Both diurnal cycles exhibited an increase of the mixing ratios during daytime with coincident maximum concentrations in the early afternoon (Figure 5). These cycles indicate that photochemical production of ozone and PAN can also occur in the MBL. In this case the precursors of ozone and PAN (hydrocarbons and NO_x) must be transported from their continental source regions into the MBL. The calculated trajectories for these specific days show that the air masses investigated on June 7 and 8 traveled along the coast of West Africa within the last 18 hours, while the air mass sampled on June 12 even crossed Spain and Portugal within the same period. Thus precursors which have tropospheric lifetimes within the range of 1-2 days may have been transported to the cruise track of ANT XV/5. Estimated tropospheric lifetimes of organic compounds which can act as precursors for PAN as well as for O_3 (e.g., acetaldehyde, acetone) are in that range [Seinfeld and Pandis, 1998]. Under typical tropospheric conditions, the estimated chemical lifetime of NO_x is also 1-2 days [Liu *et al.*, 1987]. Therefore it is likely that these pollutants can be transported several hundred kilometers from the West African or European coast into the MBL of the North Atlantic Ocean. In such cases, photochemistry in this marine region is comparable to aged continental air masses leading to the formation of secondary pollutants like PAN and ozone.

In contrast to the northern hemisphere, PAN mixing ratios in the latitude range $10^\circ N$ to $10^\circ S$ were always below the detection limit of 5 pptv. Because in this region air temperatures at sea level were generally around $26^\circ C$, PAN lifetimes were less than half an hour due to thermal decomposition [Bridier *et al.*, 1991]. The lifetime is not only influenced by the temperature but also by the NO/NO_2 ratio. Measurements of NO and NO_2 performed during the cruise ANT XIV/1 of the RV *Polarstern* showed mean ratios of $[NO] / [NO_2] \approx 0.45$ during daytime in the latitudinal range of $10^\circ N$ to $2^\circ S$ [Weller *et al.*, 1999]. This ratio is comparable to results obtained during several airborne campaigns

over the Atlantic and Pacific Ocean [e.g., Carroll *et al.*, 1990; Davis *et al.*, 1993; Kondo *et al.*, 1996]. At NO/NO_2 ratios higher than 0.5, acetylperoxy radicals formed in reaction (R2) will mainly react with NO. Only at much lower NO/NO_2 ratios does the lifetime of PAN significantly increase due to the steady state maintained by reactions (R1) and (R2). Müller and Rudolph [1992] estimated an upper limit of 0.2 to 0.7 pptv for the steady state concentration of PAN at tropical latitudes in the MBL. Under such conditions, PAN cannot serve as an indicator for long-range transport of continentally influenced air masses because any effect on PAN mixing ratios at temperatures higher than $20^\circ C$ can only be observed if the transport occurs at timescales of less than a few hours.

Measurements of PAN concentrations in the remote MBL have previously been performed during two cruises on the Atlantic Ocean (Table 1). Gallagher *et al.* [1990] found the highest PAN concentrations of up to 40 pptv at high latitudes, whereas at lower latitudes PAN was usually below 10 pptv. They described a number of episodes with elevated PAN mixing ratios and attributed these higher PAN levels to air masses with terrestrial influence or to enhanced stability of PAN at cooler temperatures in the sub-Arctic region. They observed discernible diurnal cycles with maximum PAN concentrations at or near local noon, similar to diurnal cycles in continental air masses. Gallagher *et al.* [1990] attributed the noontime maxima to local photochemical processes, contrary to diurnal cycles in continental air masses which are also strongly influenced by nonchemical parameters like surface deposition and nocturnal inversions.

Müller and Rudolph [1992] measured PAN mixing ratios aboard the RV *Polarstern* during cruise ANT VII/1 on the Atlantic Ocean during September/October 1988. They found PAN mixing ratios between 2 and 2000 pptv in the latitude range $54^\circ N$ to $35^\circ N$ with the highest values in the English Channel. South of $35^\circ N$, PAN mixing ratios never exceeded the detection limit of 0.4 pptv. At $31^\circ S$, PAN concentrations between 10 and 100 pptv were detected in continentally influenced air masses.

Measurements of PAN mixing ratios above the Pacific Ocean in November/December 1984 have been reported by Singh *et al.* [1986]. In the northern hemisphere, they found highly variable PAN mixing ratios between <10 pptv and about 80 pptv. The

concentrations sharply decreased toward the equator with mean mixing ratios of 5 pptv. *Singh et al.* [1986] also concluded that high PAN concentrations can be attributed to air masses of continental origin.

The most recent PAN measurements have been performed during the Transport and Atmospheric Chemistry Near the Equator-Atlantic (TRACE-A) campaign [*Singh et al.*, 1996]. This airborne study was conducted in September/October 1992 to investigate the impact of biomass burning on the atmosphere above the southern tropical Atlantic Ocean. Distinct biomass burning plumes were identified at higher altitudes, but the MBL remained relatively clean. In the boundary layer, low PAN concentrations in the range from 1 to 7 pptv were obtained. This is in the same order of magnitude as our observations.

The interhemispheric PAN distribution of these former studies is comparable to our results, especially for the higher northern latitudes. Moreover, in all studies very low PAN mixing ratios have been obtained in the latitudinal region between 10°N and 10°S. However, north of 10°N only during two days did PAN concentrations remain below 100 pptv, whereas the PAN mixing ratios reported by *Gallagher et al.* [1990] and *Müller and Rudolph* [1992] never exceeded this value. *Müller and Rudolph* [1992] found the highest values, up to 2000 pptv, in the English Channel only in air masses influenced by continental emissions. These differences are most likely due to different cruise tracks and seasons. Whereas cruise ANT VII/1 was mainly performed along 30°W [*Müller and Rudolph*, 1992], and *Gallagher et al.* [1990] obtained their results between 20°W and 50°W in late summer, our measurements were performed in late spring in the vicinity of the western coast of Africa and Europe between 20°W and 15°E. North of 10°N, the cruise track had a maximum distance of 500 km from the coast line. The elevated PAN concentrations in this region of the Atlantic Ocean indicate that this part of the MBL is strongly influenced by continental emissions.

4.2. PAN Concentrations in the Arctic (Ny-Ålesund)

Several short- and long-term measurements of PAN at Arctic sites have been performed (Table 2). Peaks in mixing ratios of PAN are usually observed in spring due to wintertime accumulation of oxidant precursors followed by the increase of actinic radiation and temperature [*Beine et al.*, 1997; *Solberg et al.*, 1997]. Mean PAN concentrations during March between 85 pptv at Poker Flat, Alaska [*Beine et al.*, 1997], and around 300 pptv at Alert, Canada [*Bottenheim et al.*, 1993], and Ny-Ålesund, Svalbard [*Solberg et al.*, 1997], have been reported. These values are comparable to the mean PAN mixing ratio of 232 pptv measured in this study. Strong fluctuations in the time series due to short-term episodes have also been observed in former studies. Only *Bottenheim et al.* [1986] found nearly constant PAN concentrations at 210 pptv during a period of 2 weeks at Alert.

Unfortunately, no measurements of other trace compounds like BC and ozone were performed during the field experiment in Ny-Ålesund. Therefore only the calculated 3-day back trajectories (Figure 2) can be used for analysis of the obtained PAN concentrations.

In order to evaluate the influence of continental sources on PAN mixing ratios, the data set was divided into two bins depending on the age of the air masses. Within these two sets, air masses which remained for less than 3 days over the ocean since having passed over any landmass except Greenland were classified as continental air masses. Any other air masses remaining 3 days over the ocean or Greenland were defined as marine. Although the four days with the highest averaged concentrations (March 20, 21, 26, and 27) coincided with trajectories originating from northern Russia; the mean PAN concentration of around 260 pptv in continental air masses was only slightly higher compared to marine air masses with a mean mixing ratio of about 195 pptv. These results are in agreement with the conclusions of *Beine et al.* [1997] and *Solberg et al.* [1997]. However, the standard deviations of 70 and 20 pptv,

Table 2. Measurements of PAN at Arctic Stations

Location	Period	Height	Mean, pptv	Range, pptv	Reference
Alert, Canada 82°N	March 1985	surface	210	180-290	1
Alert, Canada 82°N	April 1986	surface	439	370-590	2
Alert, Canada 82°N	March/April 1988	surface	303	136-505	3
Alert, Canada 82°N	Jan./April 1992	surface		100-900	4
Poker Flat, Alaska 65°N	March/May 1993	501 m	132.1	27-371	5
Ny-Ålesund, Svalbard 79°N	March/May 1994	474 m	255.3	69-729	6
Poker Flat, Alaska 65°N	March/May 1995	470 m	85.4	2-910	7
Ny-Ålesund, Svalbard 79°N	Feb. 1994		156	100-350	
	March 1994		304	150-800	
	April 1994		290	100-700	
	May 1994		164	50-300	
Ny-Ålesund, Svalbard 79°N	March 1998	surface	232	100-420	8

References are 1, *Bottenheim et al.* [1986]; 2, *Barrie et al.* [1989]; 3, *Bottenheim et al.* [1993]; 4, *Muthuramu et al.* [1994]; 5, *Beine et al.* [1996]; 6, *Beine et al.* [1997]; 7, *Solberg et al.* [1997]; 8, this study.

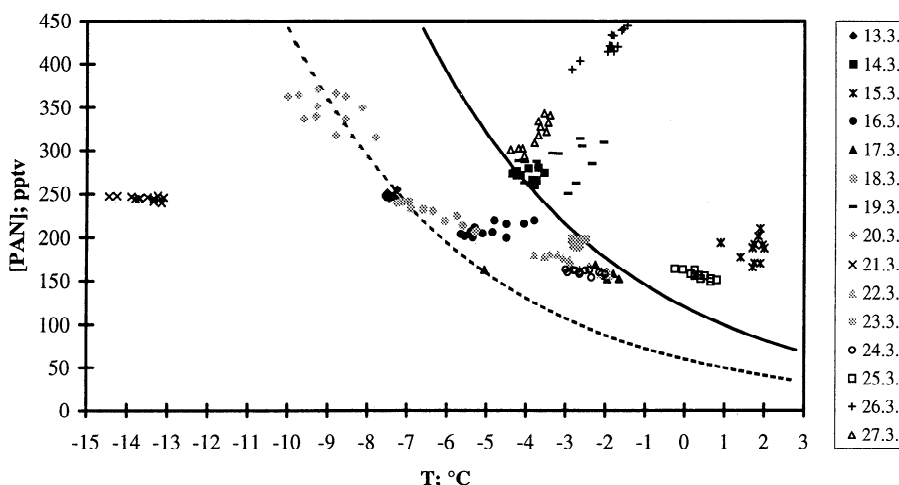


Figure 8. Relationship between PAN and temperature at Ny-Ålesund. Shown are all PAN values measured daily between 1100 and 1300 UTC and calculated PAN concentrations assuming equal rates for thermal loss and photochemical PAN production of 1 pptv h⁻¹ (dashed curve) and 2 pptv h⁻¹ (solid curve).

respectively, show that this difference is not significant and is probably due to the much shorter time series of our study compared to previous field studies. An additional source of uncertainty is the air temperature which leads to different loss rates. These two factors influencing local PAN concentrations in Ny-Ålesund are illustrated in Figure 8. PAN mixing ratios measured daily between 1100 and 1300 UTC are plotted versus air temperature. These data are shown because the calculated trajectories at 1200 UTC allow the identification of the origin of the measured air masses. *Solberg et al.* [1997] showed that a local in situ photochemical production P_{chem} of 1-2 pptv PAN h⁻¹ can occur, which is in the same order of magnitude as the thermal loss rate. PAN concentrations can be calculated assuming equal rates for photochemical production and thermal decomposition described by k_2 .

$$P_{\text{chem}} = k_2 \times [\text{PAN}] \quad (1)$$

This equation neglects the influence of other parameters such as local meteorology, dry deposition, or NO to NO₂ ratios. Figure 8 shows the calculated range of PAN concentrations as a function of temperature using 1 and 2 pptv h⁻¹ for the upper and lower limit of P_{chem} [*Solberg et al.*, 1997]. Because most of the measured concentrations were found in this range, one may conclude that an estimated production rate in the range of 1-2 pptv PAN h⁻¹ is not only valid for Ny-Ålesund but can be regarded as the “background” production rate within large parts of the Arctic region as indicated by the shaded area in Figure 2. The observed PAN mixing ratios in air masses with origins in this region seem to be mainly determined by thermal loss rates and thus by ambient air temperatures.

Nevertheless, considerably higher and lower PAN concentrations compared to the calculated range shown in Figure 8 were also measured. Higher concentrations were probably due to horizontal and vertical long-range transport of air masses with enhanced PAN mixing ratios. However, calculated trajectories indicate no significant vertical intrusions of air masses during the measuring period. The origins of the air masses with elevated PAN mixing ratios can be identified to be Russia (e.g., March 26 and 27) and western Europe (e.g., March 14 and 19). *Beine et al.*

[1997] also reported peak PAN concentrations for periods with trajectories originating from Russia. *Solberg et al.* [1997] defined four different types of air masses: Arctic, Russian, western European, and North Atlantic. Their results indicate that Arctic air masses exhibit substantially enhanced PAN mixing ratios compared to marine air, but the highest average mixing ratios were obtained during airflow from Russia and Europe. *Barrie et al.* [1989] observed correlated concentrations of PAN, sulfate, and potassium. They proposed an anthropogenic origin for all of these compounds. Thus, at Ny-Ålesund, continentally influenced air masses can easily be identified by enhanced PAN mixing ratios at relatively high air temperatures.

Only values measured on March 21 were much lower than the range of PAN concentrations calculated using equation (1). These mixing ratios were due to either lower production rates or additional loss processes. The trajectory indicates that during this day Arctic air masses arrived at Ny-Ålesund which traveled across the Polar Sea. Because PAN deposition in this area was probably not enhanced compared to other Arctic regions, it is most likely that concentrations of PAN precursors in this part of the Arctic were very low.

4.3. Latitudinal Distribution of PAN and Comparison With Modeling Studies

Recent studies with three-dimensional global chemical transport models [*Jaffe et al.*, 1997; *Moxim et al.*, 1996] show different PAN distribution patterns in the northern and southern hemisphere. In the southern hemisphere, higher PAN concentrations have been found above South America and Africa, while PAN remains low in marine regions. Only at higher altitudes does long-range transport of PAN from continental source regions to the oceans occur, especially within biomass burning plumes [*Singh et al.*, 1996]. In the northern hemisphere, PAN is more uniformly distributed. Differences between continental and marine regions are less pronounced and become negligible at higher altitudes during winter and spring. These results are in agreement with our studies showing that PAN is effectively transported to remote areas in temperate northern

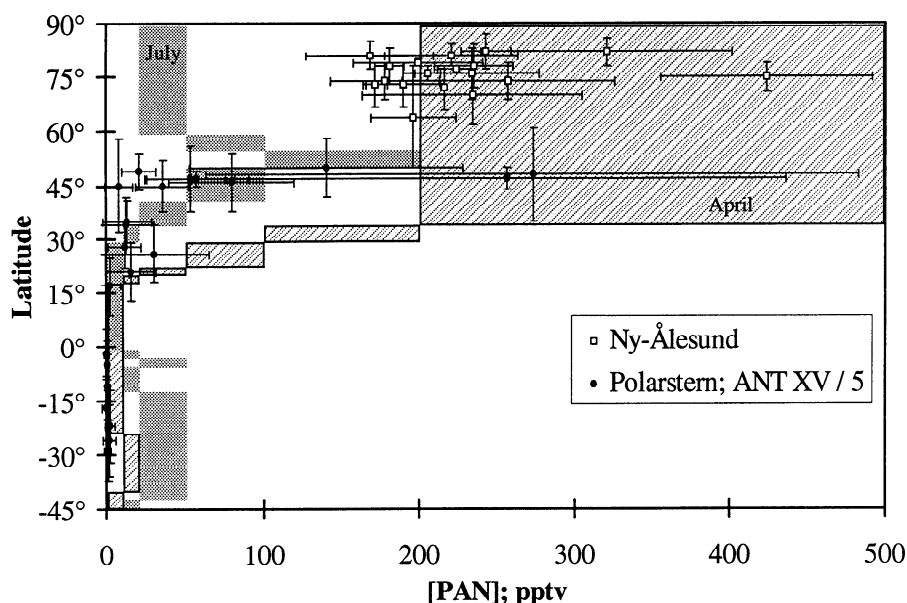


Figure 9. Latitudinal profile of surface PAN concentrations. PAN data obtained from measurements aboard the RV *Polarstern* and at the Koldewey-Station, Ny-Ålesund. Horizontal error bars indicate the standard deviation of daily means of PAN, and vertical error bars indicate the latitude range of the trajectories for the same days. Hatches and shaded boxes represent simulated zonal mean PAN mixing ratios at 990 mbar for April and July, respectively, calculated with a three-dimensional global model [Moxim *et al.*, 1996].

latitudes, whereas PAN mixing ratios in remote marine regions in the southern hemisphere remain low.

The direct comparison of the results of both field experiments of this study is difficult, mainly because the campaigns were performed in different seasons. Particularly in Arctic and sub-Arctic regions, PAN concentrations show a distinct seasonal pattern with the highest mixing ratios in March [Beine *et al.*, 1997, Bottenheim *et al.*, 1994]. This seasonal cycle is less pronounced in temperate northern latitudes and is completely absent in the tropics [Moxim *et al.*, 1996].

Figure 9 shows calculated daily mean PAN mixing ratios as a function of the latitudinal range covered by the ground-level 3-day back trajectories. This latitudinal distribution can only represent a rough estimate because it is calculated from individual measurements in a restricted longitudinal range (9°W–18°E). However, there is evidence that the measured PAN concentrations during both experiments were strongly influenced by long-range transport indicating that different kinds of air masses (e.g., marine, Arctic, continental) were investigated. Because of the different origins of the trajectories, these values may be considered as latitudinal averages. Moreover, Moxim *et al.* [1996] showed that in the northern hemisphere PAN is uniformly distributed. During winter and spring, PAN lifetimes are long enough that PAN is effectively transported from continental source regions to remote areas.

Figure 9 also shows a comparison between the observed data and simulated zonal mean PAN mixing ratios at ground level reported by Moxim *et al.* [1996]. Their study indicates higher PAN concentrations in the northern compared to the southern hemisphere. Highest concentrations are calculated for the northern extratropical troposphere during winter and spring. Concentrations decrease strongly during summer with increasing temperatures. Only in the latitudinal range with the highest NO_x emissions do the PAN concentrations remain high. In the tropics,

the concentrations are always very low, while the southern hemisphere also has maximum PAN mixing ratios during austral winter and spring.

The latitudinal distribution of the observed PAN mixing ratios near the surface exhibits a similar pattern as simulated zonal means. Nevertheless, the calculated values are significantly higher than the measurements and are only comparable to the upper limits of the observed mixing ratios. There are several reasons which can cause discrepancies between surface observations and modeled concentrations. The simulated values are calculated for April or July, whereas the measurements were performed during March and May/June. Other measurements on Arctic sites show that the observed PAN mixing ratios usually peak in April [e.g., Beine *et al.*, 1997]. In northern polar regions, slightly higher PAN concentrations during April compared to March can be expected. Moreover, calculated mean zonal mixing ratios include continental, marine, and remote regions on a global scale, whereas the investigated air masses cover only a restricted geographical region. Calculated PAN mixing ratios are also sensitive to the concentrations of nonmethane hydrocarbons (NMHC) which act as PAN precursors. In their calculations, Moxim *et al.* [1996] increased NMHC concentrations between 30°N and 65°N to reproduce observed PAN levels at three sites in North America. South of 30°N, NMHC concentrations over land have been adjusted to continental NMHC concentrations during summer between 30°N and 65°N. These assumed NMHC concentration levels may lead to an overestimation of PAN concentrations in the model.

5. Conclusions

PAN measurements with a time resolution of 10 min were performed during two field campaigns. Shipborne measurements on the Atlantic and observations at an Arctic site, encompassing

nearly 95° of latitude, were carried out. Observed PAN mixing ratios were enhanced in the northern hemisphere as compared to the southern hemisphere. In the latitudinal range between 10°N and 10°S, PAN concentrations were below the detection limit of 5 pptv. Higher PAN mixing ratios of up to 1100 pptv were found in regions influenced by the advection of continental air masses. These air masses were identified by higher concentrations of other indicators of continental pollution like black carbon and ozone. These results are consistent with previous field experiments and also with the results of modeling studies. However, the latter are only comparable to the upper limit of observed values.

It may be concluded that in temperate northern latitudes, PAN can serve as a useful indicator of photochemical air pollution caused by long-range transport. This has already been confirmed by a former modeling study [Hov, 1984]. However, in tropical and Arctic regions, PAN concentrations are also influenced by air temperature. Simultaneous measurements of PAN and NO_x in the MBL are required to estimate PAN lifetimes and to explore the long-range transport of photochemical pollutants to the South Atlantic Ocean. Such experiments in temperate northern latitudes could also be useful to further investigate the observed diurnal cycles of PAN in the MBL and intrusions from the upper troposphere.

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References

- Barrie, L.A., G. den Hartog, J.W. Bottenheim, and S. Landsberger, Anthropogenic aerosols and gases in the lower troposphere at Alert, Canada in April 1986, *J. Atmos. Chem.*, **9**, 101-127, 1989.
- Beine, H.J., D.A. Jaffe, D.R. Blake, E. Atlas, and J. Harris, Measurements of PAN, alkyl nitrates, ozone, and hydrocarbons during spring in interior Alaska, *J. Geophys. Res.*, **101**, 12,613-12,619, 1996.
- Beine, H.J., D.A. Jaffe, J.A. Herring, J.A. Kelley, T. Krognnes, and F. Stordal, High-latitude springtime photochemistry. I. NO_x, PAN and ozone relationships, *J. Atmos. Chem.*, **27**, 127-153, 1997.
- Bottenheim, J.W., A.G. Gallant, and K.A. Brice, Measurements of NO_y species and O₃ at 82°N latitude, *Geophys. Res. Lett.*, **13**, 113-116, 1986.
- Bottenheim, J.W., L.A. Barrie, and E. Atlas, The partitioning of nitrogen oxides in the lower Arctic troposphere during spring 1988, *J. Atmos. Chem.*, **17**, 15-27, 1993.
- Bottenheim, J.W., A. Sirois, K.A. Brice, and A.J. Gallant, Five years of continuous observations of PAN and ozone at a rural location in eastern Canada, *J. Geophys. Res.*, **99**, 5333-5352, 1994.
- Bridier, I., F. Caralp, H. Loirat, R. Lesclaux, B. Veyret, K.H. Becker, A. Reimer, and F. Zabel, Kinetic and theoretical studies of the reactions CH₃C(O)O₂ + NO₂ + M ↔ CH₃C(O)O₂NO₂ + M between 248 and 393 K and between 30 and 760 torr, *J. Phys. Chem.*, **95**, 3594-3600, 1991.
- Carroll, M.A., and A.M. Thompson, NO_x in the non-urban troposphere, in *Progress and Problems in Atmospheric Chemistry*, edited by J.R. Barker, pp. 198-255, World Sci., River Edge, N.J., 1995.
- Carroll, M.A., et al., Aircraft measurements of NO_x over the eastern Pacific and continental United States and implications for ozone production, *J. Geophys. Res.*, **95**, 10,205-10,233, 1990.
- Davis, D.D., et al., A photostationary state analysis of the NO₂-NO system based on airborne observations from the subtropical/tropical North and South Atlantic, *J. Geophys. Res.*, **98**, 23,501-23,523, 1993.
- DeMore, W.B., S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb, and M.J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, *Eval. 12*, 278 pp., Jet Propul. Lab., Pasadena, Calif., 1997.
- Gallagher, M.S., T.P. Carsey, and M.L. Farmer, Peroxyacetyl nitrate in the North Atlantic marine boundary layer, *Global Biogeochem. Cycles*, **4**, 297-308, 1990.
- Hansen, A.D.A., and P.H. McMurry, An intercomparison of measurements of aerosol elemental carbon during the 1986 carbonaceous species method comparison study, *J. Air Waste Manage. Assoc.*, **40**, 894-895, 1990.
- Hansen, A.D.A., B.A. Bodhaine, E.G. Dutton, and R.C. Schnell, Aerosol black carbon measurements at the South Pole: Initial results, 1986-1987, *Geophys. Res. Lett.*, **15**, 1193-1196, 1988.
- Hov, Ø., Modeling of the long-range transport of peroxyacetyl nitrate to Scandinavia, *J. Atmos. Chem.*, **1**, 187-202, 1984.
- Jaffe, D.A., T.K. Berntsen, and I.S.A. Isaksen, A global three-dimensional chemical transport model, 2, Nitrogen oxides and nonmethane hydrocarbon results, *J. Geophys. Res.*, **102**, 21,281-21,296, 1997.
- Kondo, Y., H. Ziereis, M. Koike, S. Kawakami, G.L. Gregory, G.W. Sachse, H.B. Singh, D.D. Davis, and J.T. Merrill, Reactive nitrogen over the Pacific Ocean during PEM-West A, *J. Geophys. Res.*, **101**, 1809-1828, 1996.
- Kottmeier, C., and B. Fay, Trajectories in the Antarctic lower troposphere, *J. Geophys. Res.*, **103**, 10,947-10,959, 1998.
- Law, K.S., and J.A. Pyle, Modeling trace gas budgets in the troposphere, 1, Ozone and odd nitrogen, *J. Geophys. Res.*, **98**, 18,377-18,400, 1993.
- Liu, S.C., M. Trainer, F.C. Fehsenfeld, D.D. Parish, E.J. Williams, D.W. Fahey, G. Hübler, and P.C. Murphy, Ozone production in the rural troposphere and the implications for regional and global ozone distributions, *J. Geophys. Res.*, **92**, 4191-4207, 1987.
- Logan, J., Tropospheric ozone: Seasonal behavior, trends, and anthropogenic influence, *J. Geophys. Res.*, **90**, 10,403-10,482, 1985.
- Moxim, W.J., H. Levy II, and P.S. Kasibhatla, Simulated global tropospheric PAN: Its transport and impact on NO_x, *J. Geophys. Res.*, **101**, 12,621-12,638, 1996.
- Müller, K.P., and J. Rudolph, Measurements of peroxyacetyl nitrate in the marine boundary layer over the Atlantic, *J. Atmos. Chem.*, **15**, 361-367, 1992.
- Muthuramu, K., P.B. Shepson, J.W. Bottenheim, B.T. Jobson, H. Niki, and K.G. Anlauf, Relationships between organic nitrates and surface ozone destruction during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, **99**, 25,369-25,378, 1994.
- Parrish, D.D., J.S. Holloway, M. Trainer, P.C. Murphy, G.L. Frobes, and F.C. Fehsenfeld, Export of North American ozone pollution to the North Atlantic Ocean, *Science*, **259**, 1436-1439, 1993.
- Roberts, J.M., The atmospheric chemistry of organic nitrates, *Atmos. Environ., Part A*, **24**, 243-287, 1990.
- Roberts, J.M., et al., Episodic removal of NO_y species from the marine boundary layer over the North Atlantic, *J. Geophys. Res.*, **101**, 28,947-28,960, 1996.
- Sandholm, S.T., et al., Summertime tropospheric observations related to N₂O₅ distributions and partitioning over Alaska: Arctic Boundary Layer Expedition 3A, *J. Geophys. Res.*, **97**, 16,481-16,509, 1992.
- Schmidt, R.W.H., F. Slemr, and U. Schurath, Airborne peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) measurements during TRACT 1992, *Atmos. Environ.*, **32**, 1203-1227, 1998.
- Seinfeld, J.H., and S.N. Pandis, *Atmospheric Chemistry and Physics*, 1326 pp., John Wiley, New York, 1998.
- Singh, H.B., and P.L. Hanst, Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere: An important reservoir for nitrogen oxides, *Geophys. Res. Lett.*, **8**, 941-944, 1981.
- Singh, H.B., L.J. Salas, and W. Viezee, Global distribution of peroxyacetyl nitrate, *Nature*, **321**, 588-591, 1986.
- Singh, H.B., D. Herlth, D. O'Hara, K. Zahnle, J.D. Bradshaw, S.T. Sandholm, R. Talbot, P.J. Crutzen, and M. Kanakidou, Relationship of peroxyacetyl nitrate to active and total odd nitrogen at northern high latitudes: Influence of reservoir species on NO_x and O₃, *J. Geophys. Res.*, **97**, 16,523-16,530, 1992.
- Singh, H.B., et al., Impact of biomass burning emissions on the composition of the South Atlantic troposphere: Reactive nitrogen and ozone, *J. Geophys. Res.*, **101**, 24,203-24,219, 1996.
- Solberg, S., T. Krognnes, F. Stordal, Ø. Hov, H.J. Beine, D.A. Jaffe, K.C. Clemmshaw, and S.A. Penkett, Reactive nitrogen compounds at Spitsbergen in the Norwegian Arctic, *J. Atmos. Chem.*, **28**, 209-255, 1997.
- Stephens, E.R., The formation, reactions, and properties of peroxyacetyl

- nitrate (PAN) in photochemical air pollution, *Adv. Environ. Sci. Technol.*, *1*, 119-146, 1969.
- Volz-Thomas, A., N. Houben, A. Lerner, and W. Pätz, Charakterisierung der dynamischen PAN-Kalibriereinheit der Meteorologie Consult GmbH, *Rep. 07 TFS QS 2/4*, 10 pp., Forsch. Jülich, Jülich, Germany, 1998.
- Weller, R., and O. Schrems, Photooxidants in the marine Arctic troposphere in summer, *J. Geophys. Res.*, *101*, 9139-9147, 1996.
- Weller, R., R. Lilischkis, O. Schrems, R. Neuber, and S. Wessel, Vertical ozone distribution in the marine atmosphere over the central Atlantic Ocean (56°S-50°N), *J. Geophys. Res.*, *101*, 1387-1399, 1996.
- Weller, R., O. Schrems, A. Boddenberg, and S. Gäb, Hydroperoxides, formaldehyde and NO/NO₂ measurements in the marine boundary layer of the Atlantic Ocean (48°N-35°S), in *Proceedings of EUROTRAC Symposium '98, Vol. 1*, edited by P.M. Borrell and P. Borrell, pp. 370-374, WIT Press, Southampton, England, U.K., 1999.
- Winkler, P., Surface ozone over the Atlantic Ocean, *J. Atmos. Chem.*, *7*, 73-91, 1988.
- Wolff, E.W., and H. Cachier, Concentrations and seasonal cycle of black carbon in aerosol at a coastal Antarctic station, *J. Geophys. Res.*, *103*, 11,033-11,041, 1998.
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