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Peroxyacetyl nitrate (PAN) distribution over the South Atlantic Ocean

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The atmospheric concentration of peroxyacetyl nitrate (PAN) was measured over the South Atlantic Ocean in the range between 37° and 70 °S in March 1999 in order to investigate its latitudinal distribution and its role in the NO_y chemistry of the remote marine boundary layer (MBL) in the high latitudes of the southern hemisphere. The measurements were performed using an automatic gas chromatographic system aboard RV *Polarstern.* Mean mixing ratios of $62(\pm 21)$ pptv were obtained between 37° and 49 °S. South of 55 °S, PAN concentrations were very low with values of the order of 10–30 pptv. Pronounced diurnal cycles could not be observed. The concentrations over the South Atlantic were considerably lower compared with the North Atlantic where the MBL is influenced by continental air masses.

1 Introduction

Peroxyacetyl nitrate (PAN) is a by-product formed in the course of the atmospheric oxidation of selected non-methane hydrocarbons in the presence of nitrogen dioxide.[1] It constitutes a major contribution to the odd nitrogen budget in the troposphere and acts as a temporary reservoir of nitrogen oxides ($NO_x = NO + NO_2$).[2,3] On the other hand, nitrogen oxides are very important for tropospheric processes such as production and destruction of ozone and regulation of the concentration of hydroxy radicals and can therefore also indirectly affect the climate of the Earth.[4–8]

The only known pathway for the formation of PAN is the reaction of acetylperoxy radicals with NO_2 (R1). Precursors of the acetylperoxy radicals are specific hydrocarbons (*e.g.* acetone, acetaldehyde, methylglyoxal). These organic compounds have diffuse background and large anthropogenic sources confined to relatively small urban areas.[1] The main sink of PAN is thermal decomposition (R2) followed by the destruction of the acetylperoxy radical through reaction with NO (R3) or other peroxy radicals (R4).

$$CH_3C(O)OO + NO_2 \rightarrow CH_3C(O)OONO_2 \qquad (R1)$$

$$CH_3C(O)OONO_2 \rightarrow CH_3C(O)OO + NO_2 \qquad (R2)$$

$$CH_3C(O)OO + NO \rightarrow CH_3C(O)O + NO_2 \qquad (R3)$$

$$CH_3C(O)OO + RO_2 \rightarrow \text{products} \qquad (R4)$$

Thus, PAN mixing ratios are determined by temperature, ambient concentrations of the acetylperoxy radical and the relative rates of the competing reactions of the acetylperoxy radical with NO, NO_2 and RO_2. In the marine boundary layer (MBL) other sinks such as reaction with OH, photolysis or deposition are negligible.[1] Lower limits of tropospheric PAN lifetimes of 30 min at 298 K and 10 d at 263 K can be calculated from the decay rate of reaction (R2).[9] However, lifetimes can further increase due to low NO/NO_2 ratios and low concentrations of RO_2.

While several chemical transport models exist to describe the global distribution of PAN,[10–12] the coverage of observational data is sparse both in space and time.[12,13] However, to validate model simulations of the distribution of reactive nitrogen, reliable PAN measurements are badly needed. Here, we report the first shipborne measurements of PAN mixing ratios over the South Atlantic Ocean. The values are compared with results over the North Atlantic Ocean and a latitudinal distribution in the (MBL) is presented. The importance of NO_x release due to thermal decomposition of PAN in the MBL is investigated.

2. Methods and instrumentation

The field campaign was conducted aboard the German research vessel RV *Polarstern* (ANT XVI/2) in March, 1999. The cruise started at the German Antarctic research station Neumayer (70.6 °S, 8.3 °W) and its final destination was Cape Town, South Africa (33.9 °S, 18.4 °E). The itinerary of the cruise is shown in Fig. 1. Standard meteorological parameters were routinely monitored aboard at the meteorological station and stored in the database POLDAT.

The PAN gas chromatograph was installed in an air-

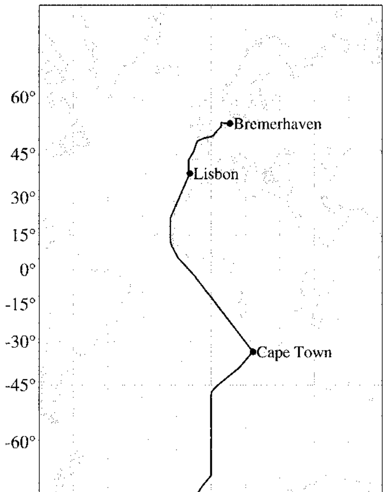

Fig. 1 Map of the cruise tracks ANT XV/5 (Cape Town–Bremerhaven; 25 May–21 June, 1998) and ANT XVI/2 (Neumayer–Cape Town; 1–16 March, 1999) of the RV *Polarstern.*

conditioned laboratory container placed on the compass deck of the ship. The inlet line (10 m of 0.4 cm id PFA tubing) was mounted on the compass deck rail approximately 22 m above sea level. The outboard end of the line was equipped with a spray deflector to avoid sea spray contamination which was controlled each day by visual inspection. Inside the laboratory container, the line was connected with a manifold and flushed with a flow rate of about 10 l min^{-1}, leading to a residence time of the air samples in the inlet lines of less than 1 s. From this manifold a pump sucked sample air into the O_3 and PAN analysers. Surface level O_3 mixing ratios were measured continuously by means of an UV spectrometer ($O_3$41MC, Environnement, Poissy, France).

PAN was measured with a commercial analyser (Meteorologie Consult, Glashütten, Germany) based on the electron capture gas chromatographic technique which has been described earlier.[14] In short, PAN was enriched for 7 min on a Peltier-cooled cryogenic sampling trap. For desorption, the temperature of the preconcentration loop was quickly heated and the gas mixture was transferred onto the pre-column using nitrogen as carrier gas. The separation was performed isothermally at 17 °C on the analytical columns. While the selected fraction of the pre-column eluate was passed onto the main column, the pre-column was backflushed. The eluates were detected by electron capture detection (ECD) at 60 °C. PAN measurements were performed in 10 min analytical cycles. Calibration was based on the photochemical synthesis of PAN from NO-pre-mixtures in the presence of a large excess of acetone and synthetic air in a flow reactor which consisted of a glass chamber chamber (approx. 100 ml) equipped with a penray lamp (Meteorologie Consult). Calibrations were performed on board at the beginning and at the end of the cruise and showed good agreement. A detection limit of 5 pptv is defined as three times the standard deviation calculated from the noise of the output signal of the analyser when only purified air produced by a clean air generator (PAG 003, Eco Physics, Munich, Germany) was investigated. The overall error in the PAN measurements was estimated to be less than $\pm 15\%$.

Shipborne measurements can be disturbed by contamination due to the exhaust gases of the ship's engines. These gases are powerful local sources of numerous reactive compounds.[15,16] PAN concentrations measured during relative wind directions outside a $\pm 90°$ corridor with respect to the ship's heading could be affected by contamination originating from the exhaust plume. However, such cases were identified using the meteorological observations and these data were then discarded from the original data sets. The corrected data sets were used for further analysis.

3. Results

PAN and O_3 were measured within the latitudinal range 37°–71 °S. Within this region the cruise track followed mainly the prime meridian (see Fig. 1). The measured time series of PAN and O_3 are shown together with the air temperature in Fig. 2. From the PAN time series it can be clearly seen that during the cruise no pronounced diurnal variations could be observed. Instead, the values can be divided into three different groups having to some extent rather homogeneous concentrations (see Table 1). Until noon on 8 March, PAN values always remained below 40 pptv, resulting in an average concentration of approximately 18 pptv. On the following days the mixing ratios indicated a clearly rising tendency. Starting at noon on 10 March, PAN concentrations stabilised at a distinct, higher level. Maximum mixing ratios around 140 pptv occurred and the mean value increased to 62 pptv. Obviously, the rise of the PAN concentrations occurred mutually with the increase of the measured air temperature (see Fig. 2). After a first strong increase in the morning of 8 March the temperature was always above 0 °C. The jump of the air temperature indicated the position of an extensive system of cold and warm fronts during the cruise. Therefore, three different regions may be classified as south and north of the front system with PAN values around 18 and 60 pptv, respectively, and between a region, where the PAN mixing ratios constantly increased northward. The different regions may be characterised by different modes in the frequency distribution of the PAN concentration. Since atmospheric dilution of trace gases as well as their chemical degradation follow an exponential evolution with time, frequency distributions of observed mixing ratios often exhibit a log-normal distribution (see *e.g.* ref. 17). Fig. 3 shows the absolute frequency as a function of the natural logarithm of the PAN concentration. Two distinct modes can be identified which correspond to the areas north and south of the polar front. These modes are centred near their mean values of 18 and 62 pptv, whereas the frequency distribution of the transient region is not well defined.

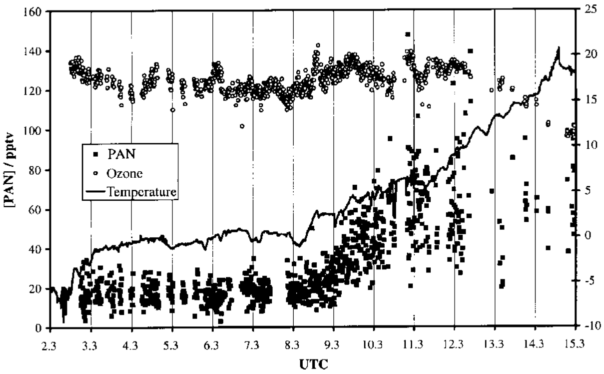

Fig. 2 Time series of PAN and O_3 concentrations measured during ANT XVI/2 on board the RV *Polarstern* in March, 1999. Also included are air temperature measurements.

Table 1 Overview of the measured PAN mixing ratios. Given are the number of PAN measurements per day, daily means, standard deviations (1σ) and the daily position of RV *Polarstern* at 12:00 UTC

Date	Number	Daily mean (pptv)	Standard deviation (pptv)	Ship's position at 12:00 UTC
2/3	36	17.6	7.3	70.1 °S; 7.1 °W
3/3	62	18.2	5.6	66.5 °S; 0 °E
4/3	72	17.6	5.1	63.9 °S; 0 °E
5/3	63	16.6	4.7	61.1 °S; 0 °E
6/3	85	17.5	5.3	59.1 °S; 0.1 °E
7/3	84	17.9	4.9	57.0 °S; 0.1 °E
8/3	137	20.9	7.0	54.4 °S; 0 °E
9/3	139	37.7	11.7	51.1 °S; 0 °E
10/3	78	54.8	19.4	48.1 °S; 0 °E
11/3	78	63.2	17.2	46.5 °S; 0.8 °E
12/3	36	64.4	27.7	43.7 °S; 5.3 °E
13/3	15	52.7	23.0	40.7 °S; 10.1 °E
14/3	14	58.6	13.1	38.2 °S; 14.1 °E

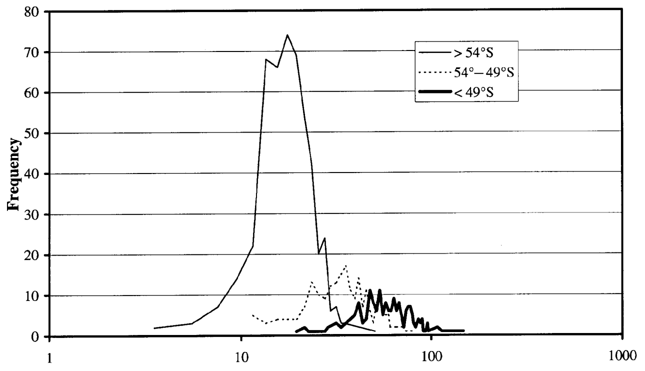

Fig. 3 Frequency distribution of the natural logarithm of the PAN concentrations in pptv measured throughout ANT XVI/2. The given absolute frequency is the number of observations for intervals of log ([PAN]/pptv) with a width of 2.

Comparable sections were not observed for the O_3 mixing ratios. An increase of the O_3 values was ascertainable on 8 and 9 March. However, the concentrations measured in the periods before and after did not differ significantly.

4. Discussion

The results obtained over the South Atlantic can be compared with data measured over the tropical and North Atlantic during another recent campaign performed also on board the RV *Polarstern* (ANT XV/5).[14] Fig. 4 shows calculated mean PAN concentrations from both campaigns averaged in 1°-latitude segments. Obviously, measured mixing ratios were considerably higher in the northern hemisphere. The highest values, about 1500 pptv, were found in the English Channel, while maxima in the southern hemisphere were an order of magnitude lower. In tropical latitudes between 11 °N and 16 °S, the values were generally below the limit of detection of the PAN analyser of 5 pptv. Low values in this latitudinal range are mainly due to the fast thermal decomposition of PAN at high air temperatures.[18]

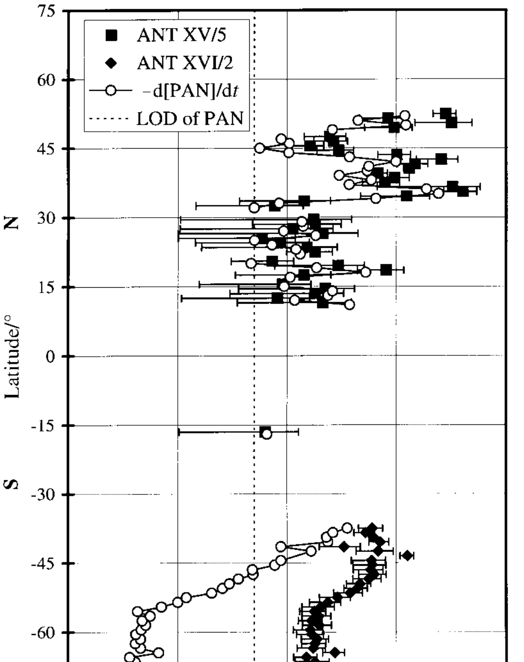

Fig. 4 Latitudinal distribution of PAN concentrations measured on board RV *Polarstern* during cruises ANT XV/5 (25 May–21 June, 1998) (ref. 14) and ANT XVI/2 (1–16 March, 1999). All 10-min means collected during the cruises regardless of time of day are included. The data points indicate the mean and its standard deviation for all averages in a 1°-latitude segment. For the same segments, averaged PAN decay rates solely due to thermal loss are also shown. The dotted line indicates the limit of detection (LOD) of 5 pptv of the PAN analyser.

Higher concentrations in the northern hemisphere can be attributed to various reasons. First, the campaigns were performed during different seasons. While the campaign on the North Atlantic took place at the end of spring 1998 (25 May–21 June), the results of this work were obtained at the end of the austral summer 1999 (1–16 March). In the northern as well as in the southern hemisphere PAN generally increases in remote areas during winter. Maximum values were achieved in early spring with a subsequent decrease until autumn.[1,11] The increase during winter is mainly due to the higher thermal stability of PAN at lower temperatures, whereas the faster thermal decay during summer can be compensated for in part by higher photochemical activity accompanied by higher formation rates of PAN. Therefore, it must be taken into account that the values measured over the South Atlantic at the end of the summer were probably lower compared with the annual mean, while the mixing ratios measured over the North Atlantic may be regarded as annual mean values.

However, more important for the measured differences in the northern and southern hemisphere is the influence of continental air masses. Jacobi *et al.*[14] have shown that the increase of PAN along the coasts of North Africa and Europe can mainly be attributed to horizontal advection of polluted air into the MBL of the North Atlantic. Moreover, several distinct diurnal variations suggest that even in the MBL *in situ* PAN formation can occur.[14] These diurnal variations also explain the much larger standard deviations of the averaged PAN mixing ratios in the latitudinal range of 15° to 50 °N shown in Fig. 4. In contrast to our results, Müller and Rudolph[19] obtained considerably lower PAN concentrations in the remote MBL of the North Atlantic. Along 30 °W, they found PAN mixing ratios around 10 pptv in the latitudinal range of 35° and 41 °N. Consequently, these values are sometimes lower than PAN concentrations over the South Atlantic reported in this work.

A direct influence due to horizontal transport of continental air masses to higher latitudes over the South Atlantic was not identifiable. Moreover, we did not observe diurnal variations in this area. Instead, rather homogeneous PAN concentrations were found, while at higher latitudes the standard deviation of the averaged PAN concentrations further decreases. The homogeneous distribution can probably be attributed to the long atmospheric lifetime of PAN. While the overall chemical lifetime of PAN in the MBL is confined by thermal decay (R2) and the destruction of the acetylperoxy radicals by reactions (R3) and (R4),[1,18] the lower limit is solely given by the thermal decay (R2). Therefore, a minimum lifetime of several days in the region south of 55 °S can be estimated as a consequence of the low air temperatures. A lifetime of this order of magnitude seems to be sufficient to establish homogeneous concentrations due to effective mixing and transport in the MBL.

Such homogeneous PAN distributions are also indicated by results of three-dimensional modelling studies with coupled global transport and chemistry models.[10,11,20] With these models, PAN concentrations in the planetary boundary layer (PBL) south of 60 °S of less than 50 pptv,[11] between 10 and 30 pptv[10] and less than 20 pptv,[20] respectively, have been calculated. The simulated results are partly in good agreement with measured data obtained in this study. However, the increase of PAN mixing ratios north of 55 °S is not reflected by global models. The area with calculated PAN values up to 50 pptv includes the whole South Atlantic and can also extend to

30 °N over the North Atlantic.[10,11,20] The models also show that the MBL close to the continents is influenced by horizontal transport of PAN-rich air masses. This is in good agreement with our results in the northern hemisphere, where we have measured enhanced PAN concentrations while the cruise track crossed regions influenced by polluted continental air masses.[14]

PAN mixing ratios of approximately 60 pptv in the MBL over the South Atlantic in the latitudinal range 40°–50 °S have not been reproduced by recent modelling studies.[10,11,20] A global comparison shows that observed PAN concentrations in the lower layers of the troposphere are frequently underestimated by global models, while calculated values in the upper troposphere are generally too high.[12]

Hauglustaine *et al.*[20] also report higher PAN mixing ratios in the free troposphere of the southern hemisphere. They calculate PAN concentrations for January at 500 mbar in the range of 20–60 pptv over the South Atlantic between 30° and 50 °S. The results of Moxim *et al.*[11] show that the region with PAN up to 50 pptv at 500 mbar extends to 47 °S in April. It may be suggested that strong vertical mixing can lead to enhanced PAN values in the MBL of this region. The synoptical observations made during the cruise showed a cold front around 50 °S accompanied by sleet showers, indicating strong advection which makes effective vertical transport possible. In higher southern latitudes, PAN mixing ratios in the free and upper troposphere are probably too low (<20 pptv), so that advection may not lead to enhanced PAN mixing ratios in the lower troposphere.[11,20]

The possible role of PAN acting as a reservoir species for NO_x has been discussed for many years (see *e.g.* ref. 21). Several field campaigns and modelling studies have shown that the thermal decay of PAN in the remote MBL is sufficient to establish observed NO_x concentrations.[8,22] To investigate the impact of PAN decomposition on ambient NO_x mixing ratios in the MBL over the Atlantic, the decay rates were calculated using observed PAN mixing ratios and air temperatures. The rates averaged in a 1°-latitude segment are shown in Fig. 4. The calculated PAN loss rates in the northern hemisphere can be divided into two different regimes. North of 35 °N, decay rates are between 10 and 100 pptv h^{-1}, while in temperate latitudes between 35° and 15 °N they are around 10 pptv h^{-1}. Mainly due to the very low PAN concentrations in tropical latitudes between 15 °N and 20 °S, decomposition rates are less than 10 pptv h^{-1} and partly even less than 1 pptv h^{-1}. In the southern hemisphere, the rates increase at first until they reach their maximum value of 10 pptv h^{-1} at 40 °S. However, the loss strongly decreases towards higher latitudes. South of 55 °S, the maximum PAN decay is much less than 1 pptv h^{-1} which is mainly due to the high thermal stability at the low ambient air temperatures in that region (see Fig. 2).

The thermal decay of PAN corresponds to the maximum NO_x production because the decomposition of one PAN molecule leads to the release of one NO_2 molecule (R2). However, the overall NO_x formation also depends on other variables such as concentration ratios of NO_2, NO and RO_2. The maximum NO_x formation only occurs if the likewise produced acetylperoxy radical reacts with NO (R3) or RO_2 (R4) and hence will not be available for the back reaction (R1). If NO_2 is high compared with NO and/or RO_2, the back reaction (R1) is strongly favoured, leading to considerably longer PAN lifetimes and corresponding lower NO_x production rates. The ratio of the rate constants of the competing reactions with NO_2 (R1) and NO (R3) accounts for $k_1/k_3 \approx 0.6$ in a temperature range of −20 to +25 °C. If organic peroxy radicals are not taken into account, a concentration ratio of $[NO]/[NO_2] \approx 0.6$ is already sufficient to ensure that half of the produced acetylperoxy radicals react back with NO_2 to form PAN again. Unfortunately, no NO_x measurements were performed during cruise ANT XVI/2. Concentration ratios of $[NO]/[NO_2]$ in the range 0.2–0.7 were derived from recent field campaigns performed in the MBL over the Pacific and Atlantic Ocean in temperate and tropical latitudes, respectively.[23–26] These averaged ratios were obtained during the daytime with solar angles higher than 70°. At noon the ratios are higher due to increased solar radiation, while during night-time NO concentrations are negligible, so that then the reaction (R1) dominates.

In consideration of these approximations it can be suggested that the calculated PAN decomposition rates only reflect the magnitude of the NO_x production during daytime. Modelling studies concerning NO_x and NO_y balances in the MBL of the tropical South Pacific[8] or South Atlantic,[22] respectively, show that NO_x production rates of less than 1 pptv h^{-1} are sufficient to replenish the MBL by 10 pptv of NO_x. Therefore, it can be concluded that even at low temperatures prevailing at high southern latitudes the PAN decay can contribute significantly to NO_x formation in this area, establishing NO_x mixing ratios of the magnitude of a few pptv.

5. Conclusions

The first measurements of PAN in the MBL of the South Atlantic in higher latitudes showed a rather homogeneous distribution. Two regions with different concentration regimes could be identified. South of 55 °S, mean PAN mixing ratios were around 18 pptv, while north of 50 °S, averaged values of 62 pptv were measured. These observations are partly in contrast to results of recent three-dimensional modelling studies which indicate PAN mixing ratios of less than 50 pptv in the MBL both in higher and temperate latitudes over the South Atlantic.[10,11,20]

The homogeneous distribution is probably due to the long lifetimes of PAN at the prevailing low temperatures. The strong differences in the mixing ratios north and south of 50 °S can be influenced by strong vertical mixing with air masses originating from the upper troposphere. A comparison of the concentrations with observations in the northern hemisphere shows that the values over the South Atlantic in the range 37°–50 °S can be higher than mixing ratios obtained in the remote MBL over the North Atlantic.[19] On the other hand, the MBL over the North Atlantic can also be influenced by advection of continental air masses, leading to PAN concentrations more than one order of magnitude higher than over the South Atlantic (see *e.g.* ref. 14).

The role of PAN in NO_x formation in the remote MBL of the South Atlantic due to thermal decomposition was investigated. It was found that even at the prevailing low temperatures and hence slow decomposition, PAN can contribute significantly to the production of NO_x in higher southern latitudes.

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