

Measurement of Gaseous HNO_3 over the Atlantic Ocean

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Abstract. A latitudinal profile (30° W, from 30° N to 30° S) of mixing ratios of nitric acid and particulate nitrate was determined on the Atlantic Ocean during the *Polarstern* cruise ANT VII/1 from Bremerhaven, Germany, to Rio Grande, Brazil. The detection of HNO_3 was performed simultaneously by laser-photolysis fragment-fluorescence (LPFF) and by nylon filter packs. The detection limit was about 30 pptv for a signal accumulation time of 1 h for LPFF and about 5 pptv for the filters at a collection time of 4 h. In general, the mixing ratios of HNO_3 in the Northern Hemisphere were found to be significantly higher than those in the Southern Hemisphere. The Atlantic background concentrations frequently varied between 80 pptv and the detection limit. Larger deviations from this trend were found for the more northern latitudes and for episodes like crossings of exhaust plumes from ships or from continental pollution sources.

Key words: Nitric acid, particulate nitrate, ambient atmospheric concentration, intercomparison, filter, excimer laser.

1. Introduction

Nitric acid is a major oxidation product of NO_x in the atmosphere. In the background troposphere, it is generally the most abundant gaseous odd nitrogen compound, thus playing an important role in the global odd nitrogen cycle. The acid can be in equilibrium with ammonium nitrate and ammonia (Finlayson-Pitts and Pitts, 1986; Stelson and Seinfeld, 1982) provided there is sufficient ammonia present. Its removal from the atmosphere occurs dominantly by wet and dry deposition (Warneck, 1988) and, hence, contributes to the formation of acid rain. Most of the previous detection methods for gaseous HNO_3 , such as filters and denuders, require relatively long collection times, although, most recently, fast and sensitive denuder systems have been developed (LeBel *et al.*, 1990). The samples collected by these methods are usually analyzed with some delay. It has often been difficult to detect diurnal trends or to respond to fast varying events during a campaign at very low ambient concentrations. At Ruhr-Universität, we have developed a laser-photolysis fragment-fluorescence (LPFF) method for the detection of gaseous HNO_3 in ambient air (Papanbrock and Stuhl, 1987). This method was tested so far in polluted and somewhat less polluted areas of continental Europe (Papanbrock

and Stuhl, 1990a, b, 1991). On the occasion of a trip on board of the research vessel *Polarstern*, we investigated the feasibility of this detection method to monitor background concentrations of the unpolluted troposphere in the middle of the Atlantic Ocean. Simultaneously, HNO_3 mixing ratios were determined by filters which were analyzed in the home laboratory at KFA. Both detection methods were operated completely independently (including calibration source, sampling procedure and location on the ship) and, besides a comparison of these two chemically and physically different techniques, mutual confirmation of the low background mixing ratios was obtained.

Fortunately, during this trip, a number of atmospheric trace gases were registered by other scientists using a variety of detection methods (Platt *et al.*, 1992). Therefore, a relatively detailed picture evolves for a number of NO_y compounds.

2. Experimental

The experiment was performed on board of RV *Polarstern* during the cruise ANT VII/1. For the track of the cruise including wind directions and velocities as measured on board, we refer to the report on the PAN measurements of this journey (Müller and Rudolph, 1992) and the overview article by Platt *et al.*, 1991. The LPPF detection of HNO_3 was performed by $\text{OH}(A^2\Sigma^+ \rightarrow X^2\Pi)$ -fluorescence which is generated in the two-photon two-step ArF-laser photolysis (Papenbrock *et al.*, 1984; Kenner *et al.*, 1985, 1986). Reports on the feasibility of the detection of HNO_3 in polluted and moderately polluted air by LPPF including a number of experimental details have been reported recently (Papenbrock and Stuhl, 1987, 1990a). Furthermore, the experimental method, which allows direct on-line monitoring, and measurements on the European continent are described by Papenbrock and Stuhl (1990b, 1991). Therefore, the description of the experimental section will be kept short. Briefly, an ArF excimer laser irradiates a sample of ambient air in a photolysis cell at reduced pressure (8 mbar). The resulting OH fluorescence is observed at right-angles to the laser beam through an interference filter. The signal from the photomultiplier was monitored by a gated integrator and processed by a personal computer. To obtain a useful signal-to-noise ratio, the signals from 3600 laser shots (1 h) were accumulated. The detection limit (3σ of the blank value) thus achieved was about 30 pptv.

The flow of the incoming air sample led directly to the observed photolysis volume. To remove traces of HNO_3 from the cell, the system could be evacuated by a turbomolecular pump. This procedure became repeatedly necessary to obtain a useful 'zero' signal. The calibration of the system was regularly performed during the measurements by permeation of HNO_3 through Teflon. The permeation device was checked regularly (about twice a week) by titration using a NaOH solution (Papenbrock and Stuhl, 1990b, 1991).

The inlet of the sampling system was situated on the port side, 18 m above the water surface, and about 20 m behind the front of the bridge to receive air from the

dominant wind direction before it had contact with the ship. The measurements which were thought to be contaminated by the ship were deleted. The sampling line consisted of three parts: The first part was a 8 m long Teflon tube (16 mm i.d., 1 mm wall thickness) through which air at atmospheric pressure was drawn by a commercial, constantly running vacuum cleaner. The residence time of the air in this tube was ≈ 1 s. This tube ended in a salt separator. This separator was made of Teflon and with a second sampling tube connected such that the flow directions in the first and second tubes resulted in an angle of 135° . The second Teflon tube (4 mm i.d., wall 1 mm thick) sampled air for LPFF and another instrument (Brüning and Rohrer, 1990) through a hole at the separator (1 mm dia.). This line was pumped by a separate pump. After a length of 1.2 m, air was taken from this tube by a third Teflon tube of the same dimensions with a Teflon needle valve at its end. The valve was adjusted by a stepping motor to maintain a constant pressure in the cell. The total dwell time of the sample in all these tubes is estimated to be about 2 s. Because of technical reasons (very large mass flows through the vacuum cleaner, flow rate not accurately known), the calibration was not performed at the inlet of the sampling system, but the calibration mixture was introduced at the needle valve position. In recent tests, it was shown that it didn't matter whether the calibration was performed at the sampling position at the separator or at the adjustable needle valve (Papenbrock and Stuhl, 1990b). This instant and direct calibration was performed twice a day.

The filter sampling system was located on the ships radar tower, 24 m above sea level. The sampling technique is similar to methods described by Forrest *et al.* (1980), Goldan *et al.* (1983), and Huebert (1980). The conditioning of the filters was, however, modified. The nylon filters were thoroughly washed with an aqueous solution of sulfanilamide (0.1%) and dried without any further treatment. Filters conditioned this way gave better than 98% recoveries for HNO_3 . The blank values of these filters were very low and reproducible, allowing the quantitative determination of sampled HNO_3 at levels down to 200 ng per filter. Gaseous HNO_3 was collected on the sulfanilamide-impregnated nylon filters, after removal of particulate nitrate with a Teflon filter (Millipore FGLP, 0.2 μm nominal pore size). A virtual impactor was installed ahead of the filter package to reduce the particle loading on the Teflon filter (Loo *et al.*, 1976). This minimized the risk of losses of HNO_3 due to possible reactions with particles collected on the Teflon filter. The virtual impactor was made of low pressure polyethylene. The distance from the inlet of the line to the filter pack was 8 cm. The flow rate through the impactor was 18 m^3/h , resulting in an average residence time of the air of less than 0.1 s. Laboratory tests at ambient levels (0.3–5 ppbv) with an HNO_3 permeation source showed that between 10 and 30% of the gaseous HNO_3 is lost on a seasalt particle loaded Teflon filter. The use of a virtual impactor reduces the loading of the Teflon filter with seasalt particles by roughly an order of magnitude. The remaining HNO_3 loss on the filter is 2–5% and, thus, below the overall error of the measurements. The sampling rate was about $6 \text{ m}^3 \text{ h}^{-1}$, the sampling period between 2 and 6 h. After

collection, the filters were transferred to small glass vessels and stored at -20°C until the analysis was performed in the home laboratory. Nitrate is extracted from the filters with 20 ml of distilled water and determined by a modified classical, wet chemical photometric method (Saltzman, 1954). The overall detection limit, which is determined by the blank value, is 9 ng ml^{-1} corresponding to 5 pptv of gaseous HNO_3 for a sampling time of 4 h. The reproducibility of this technique is better than 10%.

For the measurement of particulate nitrate, aerosols were collected on a Teflon filter (Millipore FGLP, $0.2\text{ }\mu\text{m}$ nominal pore size). The sampling location was the same as for the classical chemical HNO_3 measurements. The filters were directly exposed to the atmosphere without any inlet line. The flow rate through the filter was $6\text{ m}^3/\text{h}$ and the sampling time typically 4 h. These filters were stored and analyzed by the same procedure which was used for the measurements of gaseous HNO_3 . The lower limit of detection is about 20 ng/m^3 and the reproducibility better than 10%.

In principle, we overestimate the particulate nitrate due to the adsorption of 10–30% of the gaseous HNO_3 on the sampled seasalt particles (see above). However, on average, the amount of particulate nitrate in our measurements exceeds the gaseous HNO_3 by a factor of 5 to 6. Consequently, our measurements of particulate nitrate are between 2 and 5% too high. Since this error is quite small, we decided not to correct our particulate nitrate results for the contribution from gaseous HNO_3 .

3. Results

The HNO_3 data obtained during this cruise are presented in Figure 1. They were taken along the 30°W meridian from 30°N to 30°S . However, the LPFF data measured from 27°S till the end of the journey were discarded because of unfavourable wind directions (from starboard side and behind), possibly causing contamination by the ship. The filter measurements are included as horizontal lines to represent the collection times. With a few exceptions, the agreement between the two different methods is reasonable. Originally, the measurements were not designed as an intercomparison of the two measuring techniques. Therefore, the sampling times and periods are often not identical and a good deal of interpolation is necessary to compare the results. For a comparison, this adds considerable uncertainty to the individual experimental errors. On the other hand, the fact that both experiments were run completely independent allows a most stringent comparison of the two methods. The average ratio of the results from the filter and the LPFF measurements is 1.13 with a standard deviation of 28%. The error of the mean is 7% and the median 0.890. A plot of the classical wet chemical measurements vs. the LPFF data gives a reasonable linear correlation with a correlation coefficient of 0.961 (Figure 2). The interception with the LPFF data axis is at $1.4 \pm 10\text{ pptv}$. Although it is statistically different from zero, this value is well below

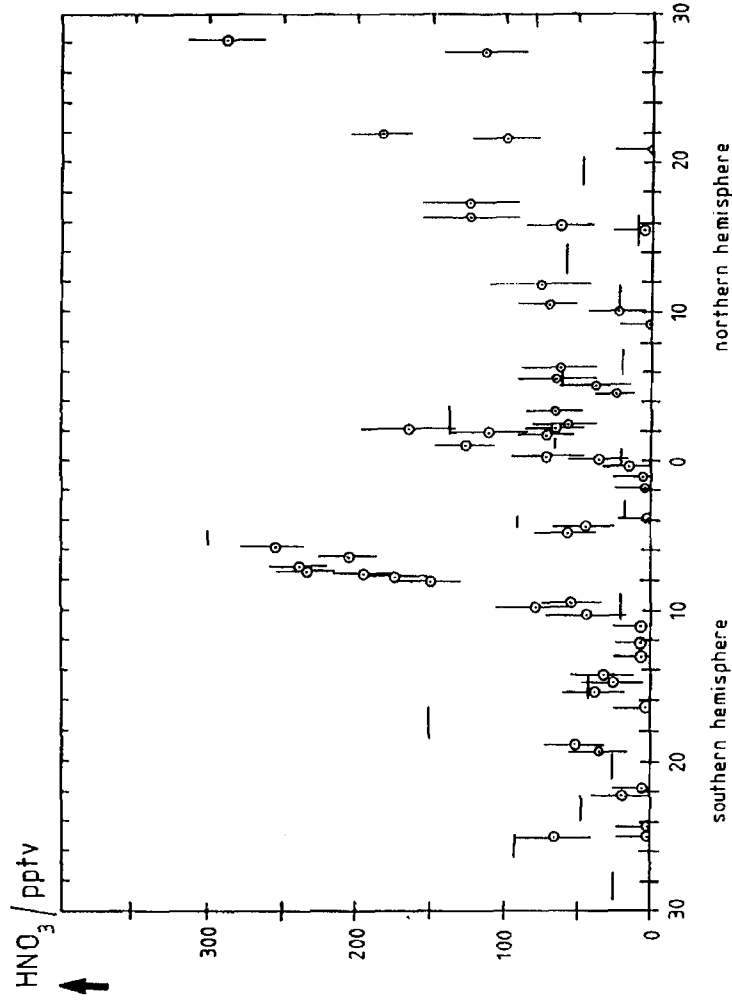


Fig. 1. HNO_3 mixing ratios over the Atlantic Ocean during the cruise ANT VII/1 of RV *Polarstern* from 30°N (24 September 1988) to 30°S (5 October 1988) at 30°W . The circles represent the measurements by LPFF (error bars = 3σ) and the horizontal bars represent measurements by nylon filters. The direction of the journey is from north to south (from right to left).

the detection limit of the present LPFF method and, therefore, of little significance. The slope (filter vs. LPFF) is 1.27 ± 0.1 . This might be indicative for a small error in the absolute calibrations. It should be noted, however, that 10 of the 15 data points, which are available for comparison, are for mixing ratios below 60 pptv but only two above 100 pptv. In an intercomparison of airborne nitric acid, it has been recently concluded that data from different measuring techniques show little correlation for mixing ratios below 150 pptv (Gregory *et al.*, 1990). At variance with that statement, we feel that our two methods did quite well.

Figure 1 shows that there are more data points by the LPFF-method having higher time resolution. Therefore, the discussion mainly refers to the LPFF measurements. The north-south profile was measured during the period from 24 September to 5 October 1988. Some data were taken north of 30°N . They show relatively high mixing ratios of up to 800 pptv (e.g. at the western exit of the English Channel).

The results for particulate nitrate are shown in Table I. The average particulate nitrate concentration for 40°N to 30°S is $0.62 \mu\text{g m}^{-3}$ with a standard deviation of $0.57 \mu\text{g m}^{-3}$. There is no significant difference between the Northern and the Southern Hemispheres. The only values which differ significantly from the average are those at 41.7°N and $9-10^\circ\text{S}$.

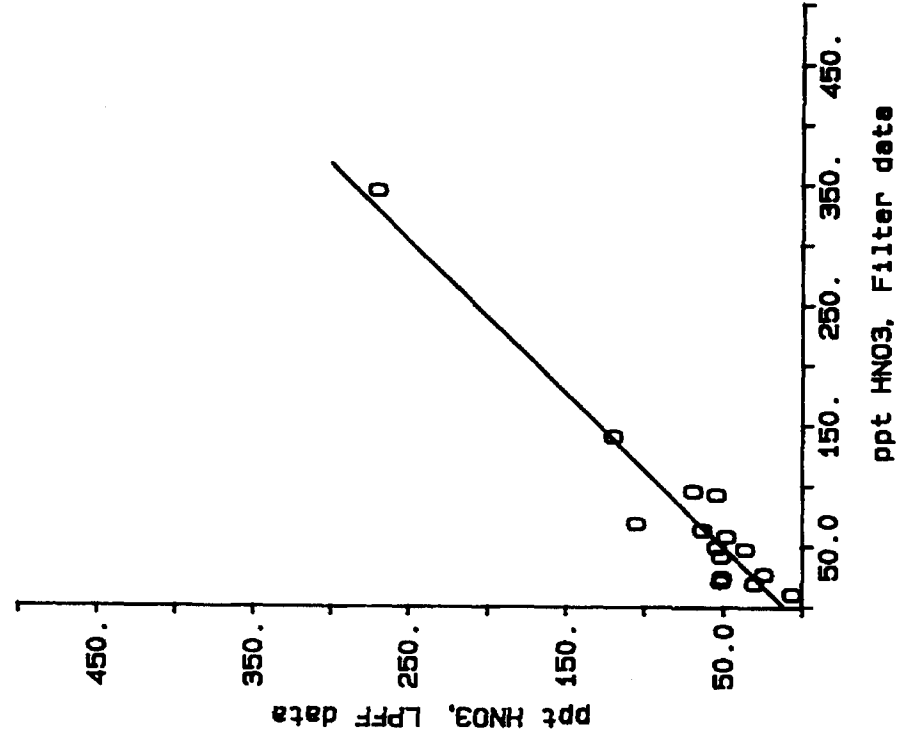


Fig. 2. Plot of the HNO₃ filter data vs. the corresponding LPPF data.

Table I. Measurements of particulate nitrate during the *Polarstern* cruise ANT VII/1 in 1988

Date	Time (UT)	Latitude	Particulate nitrate concentration/ $\mu\text{g m}^{-3}$
9/20	10:23-12:23	41.73° N	5.66
9/22	11:00-20:00	37.73-35.97° N	0.24
9/23	12:00-22:00	34.95-31.26° N	0.71
9/24	12:00-21:15	28.14-26.07° N	0.31
9/25	12:00-21:10	22.66-20.57° N	0.88
9/27	12:00-21:00	11.81-9.91° N	0.46
10/1	11:00-19:00	8.97-10.70° S	2.01
10/2	12:05-20:15	14.43-16.08° S	0.12
10/3	11:00-19:00	19.52-21.32° S	0.42
10/4	11:00-19:00	24.94-26.80° S	0.43

4. Discussion

In general, the mixing ratios measured in clean oceanic air in the Southern Hemisphere (SH) are about two orders of magnitude lower than those observed by LPFF over polluted continental Europe, which were up to about 3.4 ppbv (Papenbrock and Stuhl, 1990a, b). Two episodes of relatively high concentrations were observed at 2° N and about 6° S, which we will disregard for a moment. They will be discussed separately below. In the Northern Hemisphere (NH), the absolute mixing ratios were found to fluctuate between 290 pptv and the detection limit, considerably more than in the SH. These HNO₃ concentrations observed in the NH were considerably higher (average value of the measured data, episodes excluded: 84 pptv) than those in the SH, as seen in Figure 1. Sporadic measurements at latitudes >30° N show even higher values. From the LPFF data of the NH, we find decreasing HNO₃ from 30° N to the Equator with a gradient of about 4.4 pptv/degree. The values obtained in the NH fall into a similar range as that reported previously for the marine boundary layer (Huebert and Lazrus, 1980; LeBel *et al.*, 1990).

In the SH, an average concentration of less than 30 pptv is estimated from the data available. From the fact that the mixing ratio was frequently above the detection limit of the LPFF method, we infer that the average is not expected to be far below 30 pptv. This is supported by the filter data. Apart from one value at 16° N, the lowest HNO₃ mixing ratios were in the range of 20–30 pptv. From these measurements, we conclude (a) that the surface air of the northern Atlantic was contaminated during the time of the cruise, probably by long-range transport of pollution, (b) that clean air (SH) contains less HNO₃ (<30 pptv) than has been estimated before (range for oceanic air ≈ 70–1000 pptv (Graedel *et al.*, 1986)) which is in agreement with previous measurements in the equatorial Pacific region (Huebert, 1980), but somewhat lower than the mean value (70 pptv) previously determined for the marine boundary layer in the SH (Huebert and Lazrus, 1980).

We now compare these data with those for the other nitrogen-containing species (NO, NO₂, NO_y (except HNO₃)) (Brüning and Rohrer, 1990), PAN (Müller and Rudolph, 1992), and nitrate particles determined during this cruise. The mixing ratio of PAN was measured to be very low (<0.4 pptv) between 30° N and 30° S (Müller and Rudolph, 1992). With a few exceptions, the measured values for NO were around 10 pptv or lower (Brüning and Rohrer, 1990). There were two NO₂ detection systems onboard the ship, chemiluminescence (Brüning and Rohrer, 1990) and TDLAS (Harris *et al.*, 1990). Both indicate NO₂ concentrations much lower than those for HNO₃ except in the region from 11° N to 0° and for a few other locations. Also, the NO_y (without HNO₃) values were frequently less than the present HNO₃ values (Brüning and Rohrer, 1990). A notable exception was the NO_y mixing ratios obtained in the ITCZ and south of it where the HNO₃ values were relatively low. Between 40° N and 30° S, the NO₃⁻ concentrations fluctuated from about 0.1 to about 2 μg m⁻³ several times during the trip with a mean of about

$0.6 \mu\text{g m}^{-3}$ which corresponds to about 220 pptv. No obvious trend was noticeable. We conclude that HNO_3 is, most likely, the major gaseous nitrogen-containing constituent in the maritime air encountered during this trip, although much more nitrogen seemed to be stored in the form of nitrate aerosol. In a recent study of equatorial Pacific air (Huebert, 1980), the same trend was reported for surface air, whereas the reverse trend was observed (molar ratio of ≈ 2 for nitric acid/nitrate aerosol) in the remote free troposphere (Galasyn *et al.*, 1987). The boundary layer is certainly more rich in sea-spray aerosol on which gaseous nitric acid can deposit to react with Cl^- -forming nitrate and, additionally, the ocean surface acts as a sink of HNO_3 . These reverse $\text{HNO}_3/\text{NO}_3^-$ ratios for the boundary layer and the free troposphere can, therefore, be understood.

Two episodes of relatively high concentrations were observed at 2°N and about 6°S . These two episodes occurred between 29 September and 2 October and are shown in Figure 3 on the local time scale. The first two increased data points coincide with the crossing of the exhaust plumes of two ships passing within an hour at a distance of about 4 km. Elevated NO concentrations were also registered at the same time by chemiluminescence (Brüning and Rohrer, 1990). Diesel engines are known to emit gaseous HNO_3 (Graedel *et al.*, 1986; Harris *et al.*, 1987) and we believe that ship engines have emitted the measured HNO_3 , because the photochemical conversion $\text{NO} \rightarrow \text{NO}_2 \rightarrow \text{HNO}_3$ appears to be much too inefficient at that time of the day (6.30 and 7.30 h) because of a lack of reactants.

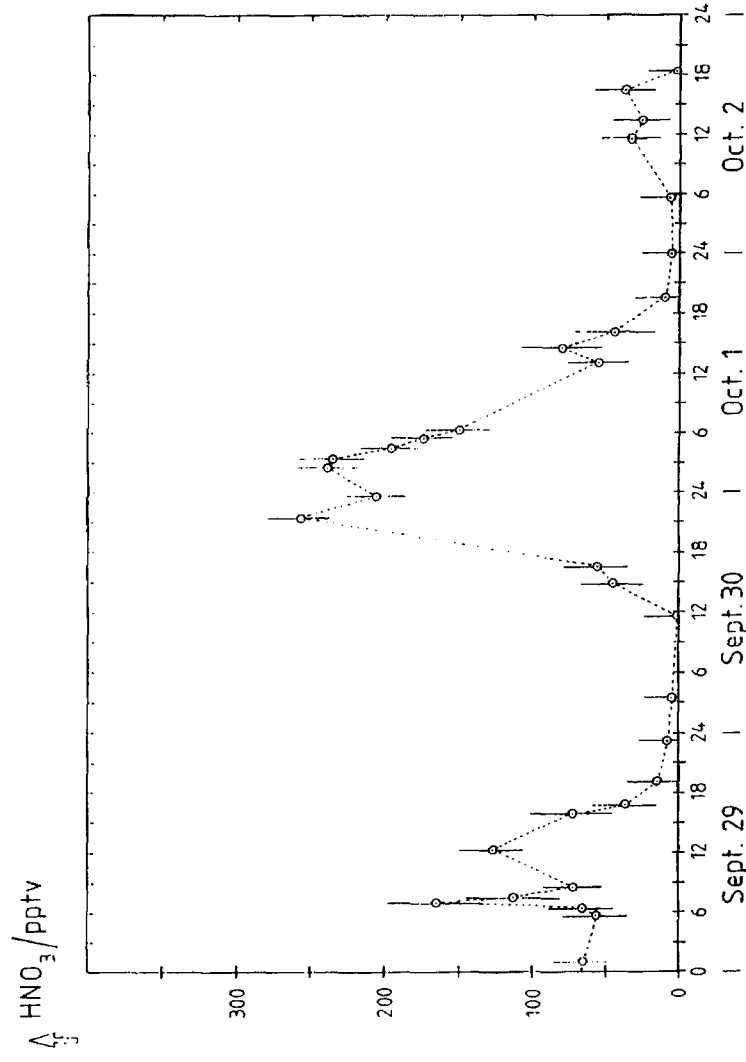


Fig. 3. Diurnal HNO_3 mixing ratios determined by LPFF from 29 September to 2 October placed on the scale of local time.

The second episode with remarkably high concentrations took place during the night from 30 September to 1 October. As will be discussed below, marked maxima at night were uncommon during this trip. Shortly before or during this episode, elevated concentrations of C_2H_2 (Koppmann *et al.*, 1990), K^+ (Bürgermeister, 1989), and CO (Bauer, 1989) were monitored. Further, the concentrations of SO_4^{2-} (Bürgermeister, 1989) and NO_3^- indicated slight maxima. (The data for K^+ and SO_4^{2-} were corrected for seasalt potassium and sulfate, as previously described by Bürgermeister *et al.* (1990).) C_2H_2 , K^+ , and CO are typical tracers of combustion processes (Finlayson-Pitts and Pitts, 1986; Warneck, 1988; Graedel *et al.*, 1986). C_2H_2 and CO have tropospheric lifetimes of about 1 and 2 months, respectively, caused by their gas-phase reactions with OH radicals. The corresponding homogeneous lifetime of HNO_3 also is about 1 month (Warneck, 1988), but wet and dry deposition are usually assumed to be the dominant removal processes resulting in a lifetime of about 2 to 5 days (Warneck, 1988). In spite of this short heterogeneous lifetime, we believe that continental combustion processes, perhaps biomass burning, are the origin of these elevated concentrations of HNO_3 and the other trace gases. The sparse information on wind directions available to us for this region points to long-range transport from Africa and not from South America which is much closer to the measuring site. Previous GAME TAG studies (Huebert and Lazrus, 1980) have deduced an HNO_3 lifetime of approximately 2 months in the free atmosphere and it has been cautioned recently (Huebert, 1980) not to use the 'lifetime' concept thoughtlessly. Most likely, heterogeneous lifetimes can be highly variable with time and location and may certainly depend on the meteorological conditions. It has indeed been recently calculated (Levy and Moxim, 1989) and measured (Huebert, 1980) that soluble nitrogen (principally HNO_3) can be transported very far from North America and Asia to Hawaii during various seasons of the year.

Apart from these pollution episodes, the HNO_3 mixing ratios shown in Figure 3 are generally higher during the afternoon than at night. This trend was observed during this journey on a number of days but the substantial variability of the HNO_3 mixing ratio and the insufficient detection limit prevents giving a clear, statistically significant diurnal cycle. Similar diurnal cycles were also noticed before (Warneck, 1988; Papenbrock and Stuhl, 1990b) for land-based measurements. Because of low NO_2 concentrations, the formation by the reaction $OH + NO_2$ appears to be too slow to explain the increased mixing ratio of HNO_3 during the day. Moreover, the rapid concentration increase is not reflected in a corresponding diurnal decrease of the NO_2 mixing ratio. It is possible that this diurnal trend is caused by the humidity and/or temperature-dependence of the $HNO_3 + NH_3 \leftrightarrow NH_4NO_3$ equilibrium (Stelson and Seinfeld, 1982). It should be noted that the ammonium nitrate data are too coarse to reflect this trend. In the Pacific, Galasyn *et al.* (1987) have observed daytime concentrations at Mauna Loa, Hawaii, which were typically twice those at night. These authors doubt that this diurnal variation reflects that in the free troposphere and have explained it by different efficiencies of dry-surface depo-

sition due to diurnally varying low-level inversion layers.

In conclusion, the LPPF-method was found to be feasible to monitor nitric acid down to levels slightly above the background in the SH boundary layer. For more accurate low-level measurements, it is desirable to improve the detection limit and time resolution. Considering the recent results of an intercomparison of HNO_3 measuring techniques (Gregory *et al.*, 1990), our filter- and LPPF-methods compare reasonably well. The SH boundary layer exhibited a significantly lower mixing ratio than observed in the NH. This is at variance with a previous result from Huebert and Lazrus (1980). The mixing ratio increased in the NH with latitude, an indication of the increasing anthropogenic activity. The results, hence, infer that the air of the North Atlantic boundary layer was polluted by HNO_3 during this cruise. Long-range transport of HNO_3 therefore must have taken place.

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