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Measurements of NH_3/NH_4^+ and HNO_3/NO_3^- by denuder and filter pack

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Data sheet

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Contents

Abstract

A filter pack with a teflon particle filter is validated for the separation of gaseous NH_3/HNO_3 and particulate NH_4^+/NO_3^-. The measurements are compared to denuder measurements of respectively NH_3/NH_4^+ and HNO_3/NO_3^-. A general discussion of the two methods are given. A problem with clogging of the filter pack was observed. In general the total determination of NH_3/NH_4^+ and HNO_3/NO_3^- showed good agreement with the two methods. The filter pack showed a good separation of NH_3 and NH_4^+, but in general the filter pack underestimated the HNO_3 concentration compared to the denuder. The underestimation of HNO_3 is probably due to adsorption on already collected particulate matter on the particle filter, but an overestimation by the denuder due to interferences or particle deposition can not be excluded. Only few observations indicated evaporation of HNO_3 from the particle filter. Denuder determinations of SO_2 and SO_4^{2-} were compared to filter pack measurements. An underestimation of 10-15% both on gaseous SO_2 and particulate SO_4^{2-} on the denuder were found.

1 Introduction

Atmospheric nitrogen input

There is a growing concern about the atmospheric input of nitrogen species to various ecosystems. The nitrogen species can act as plant nutrient as well as acidifying components. The gases ammonia (NH_3) and nitric acid (HNO_3) both have high dry deposition velocities and form a significant amount of deposited nitrogen species. It is therefore important to quantify the concentration and deposition of these pollutants as a part of an assessment of the total nitrogen deposition.

Monitoring with filter pack

During several years filter pack measurements of certain aerosols and gases have been carried out as a part of monitoring programmes on Danish background stations *(Hovmand & Bille-Hansen, 1988; Hovmand, 1990; Hovmand & Grundahl, 1991)*. The filter pack method used here consists of a sandwich of four filters, first a filter to collect particulate matter with subsequent downstream collection of gases by three impregnated filters *(Fuglsang, 1986a)*. Due to interferences and interactions between gases, particles and particle filter the filter pack method provides a total determination of NH_3/NH_4^+ and HNO_3/NO_3^-, but does separate SO_2 and SO_4^{2-}. Since the gases and aerosols have a large difference in dry deposition velocity it is of great importance to know the distribution between the two phases. The filter pack used in the monitoring programmes gives a good separation of SO_2 and SO_4^{2-}, a reasonable separation of NH_3 and NH_4^+ and a poor separation of HNO_3 and NO_3^-. The poor separation of HNO_3 and NO_3^- is caused by adsorption of the gas to the particle filter. The aim of this project is therefore to investigate whether a change of particle filter from cellulose to one of teflon would enable a better separation of the nitrate compounds and still provide a reasonable separation of ammonia and sulphur species. Other workers have had good experiences with particle filters of teflon *(Harrison & Kitto, 1990; Anlauf et al., 1991)*.

Denuder method

In this investigation cylindrical denuders were used for determination of ammonia *(Ferm, 1979)* and nitric acid *(Ferm, 1986a)* and used as a reference to the determinations by the modified filter pack in field intercomparison. The denuder method is based on the difference in diffusion velocity of gases and particles. A laminar air stream is passing a tube coated with a sorbent suitable for the gas in question. The gas diffuses to the tube wall and is absorbed while the particles passes the tube with the laminar air flow.

2 Experimental

Measurements

The experiments were run near Risø, at a location close to arable land, 40 km west of Copenhagen. Different compositions of filter packs were used together with denuders. The experiments were performed in six periods lasting about one week in different seasons. The periods are referred to as "campaigns". Some of the measurements were 24-hour mean values as used in the monitoring programmes. Other measurements were divided in day/night determinations, lasting from 6 to 18 hours. Many of the measurements were made as duplicates. Appendix 1 contains concentration plots with indication of day/night or 24-hour measurements, duplicates and other details concerning the measurements. Description of the methods and campaigns are given below.

2.1 Filter pack measurements

Filter pack

The filter pack method described by *Fuglsang (1986a)* consists of four filters in series: a particle filter followed by three impregnated filters for sampling of gaseous compounds *(Figure 1)*.

Impregnation		**Sampling of:**
$(COOH)_2$	--------	NH_3
KOH	--------	SO_2
NaF	--------	HNO_3 (+SO_2)
inert	--------	particles

⇑
Airflow

Figure 1. The filter pack method consisting of a particle filter followed by three impregnated filters for sampling of gasses.

The filter holder is made of polycarbonate (for 50 mm filters) with PVC inlet (i.d. 40 mm, length 80 mm). The flow is about 40 l min^{-1} (at 0°C) .

Particle filters

The particle filters used in this study are 1) cellulose based (MF-Millipore, 1.2 µm, 50 mm) as in the Danish monitoring programme or 2) teflon filters. In most of the campaigns the type of teflon filter was Gelman TF-1000 (1 µm, 47 mm), but also Fluoropore FA (1 µm, 47 mm) and Gelman Teflo (1 or 2 µm, 47 mm) were used. No differences in the sampling properties of the different types of teflon filters were observed and the results are therefore pooled.

Filter impregnation

The impregnated filters were Whatman 41 (50 mm). Impregnation was done by vacuum drying *(Fuglsang, 1986b)*. All filters were added 350 µl solution for impregnation. The solutions were: 0.7% (w/v) NaF in water, 8% (w/v) KOH in methanol and 2% (w/v) oxalic acid in ethanol.

Extraction and analysis

All filters were extracted in 20 ml deionized water. Analysis of NH_4^+ was done by the indophenol method, while NO_3^- and SO_4^{2-} was determined by ion chromatography *(Hovmand & Grundahl, 1991)*.

PIXE

In the monitoring programmes the cellulose particle filter is analyzed by PIXE (Proton Induced X-ray Emission) for multielement analysis on a routine basis *(Johanson & Cambell, 1989)*. It was investigated whether or not the teflon filters were suitable for this kind of analysis.

2.2 Denuder measurements

Denuder, NH_3/NH_4^+

To determine NH_3 and NH_4^+ the denuder method described by *Ferm (1979)* was used. To determine the gas pyrex glass tubes, 50 cm long and 3 mm i.d., were coated with 1.5% (w/v) oxalic acid in ethanol, leaving a 15 cm uncoated inlet to establish laminar flow. The flow rate was 3 l min^{-1} (at 20°C). To determine ammonium aerosols a filter holder (Millipore, Swinnex) containing an impregnated filter, was connected to the outlet of the tube. The filters, Whatman 40 (25 mm), were vacuum impregnated with 100 µl 3% (w/v) oxalic acid in ethanol. The impregnation method is described by *Fuglsang (1986b)*.

Extraction and detection limit

The tubes were extracted in 3 ml deionized water, avoiding the uncoated inlet. The filters were extracted in 5 ml deionized water. Both extracts were analyzed by the indophenolblue method. The detection limit for a 24 hour samples was about 0.05 µg NH_3-N m^{-3} for gaseous NH_3 and 0.25 µg NH_4^+-N m^{-3} for particulate NH_4^+.

Denuder, HNO_3/NO_3^-

To determine HNO_3 and NO_3^- the denuder method described by *Ferm (1986a)* was used. Of practical reasons some modifications from the described method were done. Soda glass tubes 4 mm i.d. were used. The length was changed from 75 to 50 cm. To maintain the sampling efficiency the flow rate was reduced from 2 l min^{-1} to 1 l min^{-1} (at 20°C). This changes the conditions for the establishment of laminar flow and the uncoated inlet was therefore reduced from 15 to 10 cm. The considerations about the fraction of particles that enters the tube and what fraction might deposit on the tube walls *(Ferm, 1986a)* is only slightly changed by changing the above mentioned conditions. The tubes were coated with 1% (w/v) sodium hydroxide in ethanol, which is expected to be converted to sodium carbonate during drying in the coating procedure *(Ferm, 1986a)*. To determine the particulate NO_3^- an impregnated filter was placed behind the tube as described for NH_4^+. In the first three campaigns the filters, Whatman 40 (25 mm), were vacuum impregnated with 100 µl 0.7% (w/v) sodium fluoride in methanol. In the following two campaigns the filters were impregnated with a few drops of 1% (w/v) sodium hydroxide in ethanol and dried with a HNO_3-free air stream. The last campaign the filters were vacuum impregnated with 70 µl 0.7% (w/v) sodium hydroxide in ethanol.

Extraction and detection limit

The tubes were extracted in 3 ml deionized water, including the inlet of the tube. The inlet is included, because HNO_3 absorbs very efficient to the glass tube itself. The filters were extracted in 5 ml deionized water. Both extracts were analyzed for NO_3^-, NO_2^- and SO_4^{2-} by ionchromatography (IC). In the September 1989 campaign the extracts were not analyzed for NO_2^-. The detection limit for a 24-hour sample varied between 0.01 (analytical detection limit) - 0.04 (based on blank values) µg HNO_3-N m^{-3} for the gas and 0.01 - 0.04 µg NO_3^--N m^{-3} for the particles.

Denuder, SO_2/SO_4^{2-}

The sodium hydroxide coated denuder described to determine HNO_3 and NO_3^- also absorbs SO_2. The results are compared to the results from the filter pack, which in the case of sulphur species is the reference method. In January 1992 it was observed, that the SO_2 was found as SO_3^{2-} and SO_4^{2-} in ionchromatography analysis. Generally only small amounts of SO_3^{2-} was observed, but in one sample 50% of the total sulphur was found as SO_3^{2-}. Excepted January 1992 only SO_4^{2-} analysis was available. This might cause an underestimation of SO_2.

Uncoated denuder, HNO_3/NO_3^-

For determination of HNO_3 and NO_3^- a second denuder type was exposed. This denuder was equal to the one described above for HNO_3/NO_3^- except that the tube not was coated. The soda glass tube itself, washed in an alkaline soap, rinsed in deionized water and dried, was used as an absorbent. The uncoated tube also had an impregnated filter placed behind the tube.

Heating

During exposure all types of denuders were heated a few degrees above ambient temperature to prevent condensation.

2.3 The measuring periods

Measuring periods

Table 1 (next page) contains information about dates for periods, day/night or 24-hour measurements and a qualitative description of meteorological conditions. The measuring periods are referred to as "campaigns".

Table 1. Campaigns: dates, sampling periods and qualitative description of typical meteorological conditions in each campaign.

Campaign (Month, year)	Dates	Sampling periods	Temperature (°C)	Wind-direction	Windspeed (m/s)	Relative humidity (%)	Reference
SEP89	12-14 26-28	24 h	10-14	West		70-100	(1)
JAN91	12-21	24 h, day, night	day>0 night<0	South, East	2-4	75-100	(1)
MAR91	11-18	day, night	3-11	West, South, East	1-6	75-100	(1)
JUL91	23-25 30-31	day, night	7-21, 15-26	East	day 3-7, night 2-3	day 45-60 night ~ 100	(2)
AUG91	14-21	day, night	12-18	South, West	3-8	60-100	(3)
JAN92	20-27	day, night	-5-+2	South-East, West	1-4	80-100	(3)

(1) Kåre Kemp, NERI
(2) Gunner Jensen, Risø
(3) Poul Hummelshøj, Risø

3 Discussion of NH_3/NH_4^+ and HNO_3/NO_3^- sampling with filter pack

Separation priciple

Due to advantages in handling and costs, the filter pack is more used than denuders. The disadvantages of the filter pack is the separation principle. The particles are collected before absorption of the gases in contrast to the denuder, where the gas is absorbed first and secondly the particles are collected. The separation in the filter pack is influenced by gas adsorption and evaporation from the particle filter *(Figure 2).*

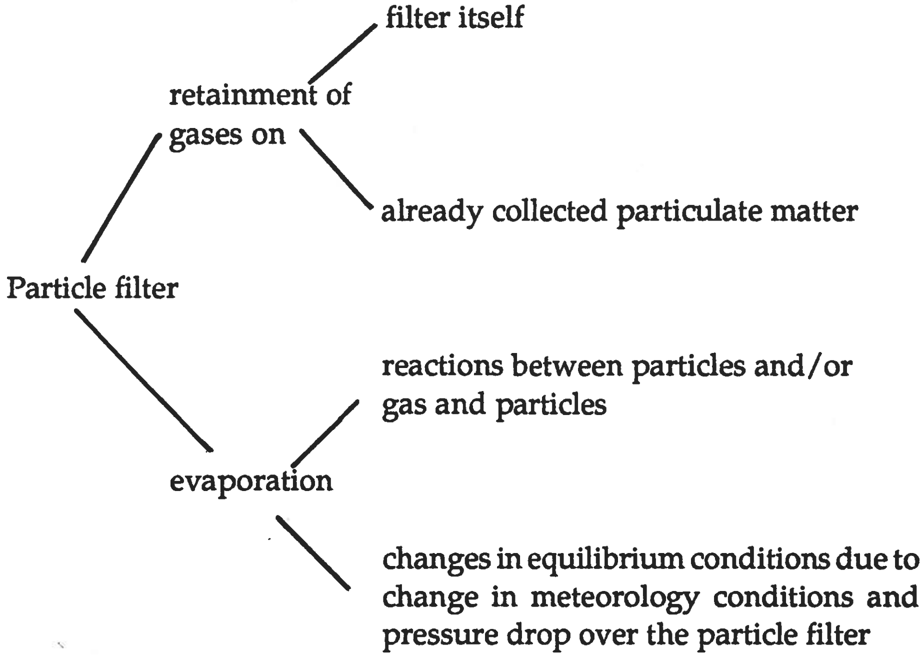

Figure 2. Schematic presentation of problems with separation of gases and particles in filter pack sampling.

3.1 Adsorption of gases on the particle filter/particles

Adsorption to filter material

It is observed that different types of glass fiber filters and cellulose and celluloseester filters to a great extent absorbs HNO_3 *(Spicer & Schumacher, 1977; Appel et al., 1979). Forrest et al. (1980)* found, that HNO_3 also absorbed on quarts filters when the relative humidity was high. Filters of teflon have shown little absorbance of HNO_3 *(Appel et al., 1979; Appel et al., 1981; Dasch et al., 1989; Harrison & Kitto, 1990; Anlauf et al., 1991).* We have not found reports concerning NH_3 adsorption to particle filters. Since NH_3 is a less "sticky" gas than HNO_3 the problem with adsorption to particle filter are assumed to be smaller. We have not found literature concerning NH_3 adsorption to particle filters.

Adsorption to collected particles

It is observed that acid gases can react with the particles on a filter *(Appel et al., 1980; Appel & Tokiwa, 1981). Forrest et al. (1980)* have observed an increasing adsorption of HNO_3 with increasing relative humidity. *Forrest et al. (1982)* suggest that adsorption or retainment of gas is the significant error during longer exposure periods (6 hours), while evaporation (discussed later) seems to be the must important error during short exposure times (15-30 min). Absorption of NH_3 to already sampled acidic particulate matter during sampling have shown to be a problem in the determination of H_2SO_4 aerosols *(Klockow et al., 1979; Koutrakis et al., 1992).*

3.2 Evaporation from particles on the particle filter

Evaporation from collected particles

From theoretical considerations *Brosset (1978)* showed, that NH_3 can evaporate when small acid particles come in contact with the larger alkaline particles on a filter. *Gras (1984)* report measurements from a marine atmosphere consistent with these predictions. Reactions between nitrate salts and acid particles (e.g. $NaNO_3(s) + H_2SO_4(l) = NaHSO_4(s) + HNO_3(g)$; can give evaporation of HNO_3 *(Harker et al., 1977; Appel et al., 1980; Forrest et al., 1980; Appel & Tokiwa, 1981; Koutrakis et al., 1992).* Evaporation of HNO_3 has also been observed from reactions between acid gases and particulate matter *(Appel et al., 1981; Appel & Towika, 1981).*

$NH_4NO_3(s/l) \rightleftharpoons NH_3(g)+HNO_3(g)$

Stelson & Seinfeld (1982a,b) assume that the system $NH_3(g)/HNO_3(g)/NH_4NO_3(s)$ is in equilibrium. From theoretical considerations they find that the product of the gases NH_3 and HNO_3 is dependent of the relative humidity and temperature. This gives a change in equilibrium conditions with changing meteorology conditions during sampling and by that a possibility of evaporation of gases. *Appel et al. (1981)* have observed the largest evaporation from nitrate salts at high temperatures and low relative humidity. *Forrest et al. (1980)* have also observed HNO_3 and NH_3 evaporation at low relative humidity. This is consistent with the predictions of *Stelson and*

Seinfeld (1982a,b). *Cadle (1985)* report from measurements in an urban area that ammonium nitrate evaporation from filters can cause large errors in summertime measurements.

The theoretical predictions and assumptions of equilibrium in the system $NH_3(g)/HNO_3(g)/NH_4NO_3(s)$ *(Stelson et al., 1979; Stelson & Seinfeld, 1982a,b)* have shown good agreement with ambient measurements *(Doyle et al., 1979; Harrison & Pio, 1983a; Hildemann et al., 1984)*. *Allen et al. (1989)* found good agreement between measurements and theory at temperatures above *ca* 5°C and at relative humidities below 80%, but for other conditions higher concentrations were measured in the gas phase than predicted. From theoretical consideration *Wexler & Seinfeld (1990)* conclude, that the time scales for the gas and aerosol phases to equilibrate depend crucially on the ambient conditions and the composition and state of the aerosol. In particular, these characteristic times are too long to justify the equilibrium assumption under cool ambient conditions or when the aerosol particles are large. This hypothesis is supported by data *(Wexler & Seinfeld, 1992)*. *Harrison & Mackenzie (1989)* made a numerical simulation of the atmospheric $NH_3/HNO_3/NH_4NO_3$ system, which demonstrated that kinetic constraints can lead to appreciable deviations of gas phase concentration product from equilibrium predictions.

Tang (1980) has theoretical predictions saying, that the partial pressure of HNO_3 is strongly dependent on the relative humidity and the nitrate-sulphate ratio in the aerosol solution. The partial pressure of NH_3 varies only slightly with humidity, but inversely to the hydrogen ion concentration in the solution.

Jaffe (1988) point out, that the ammonium nitrate equilibrium constants in the atmospheric work involves a large extrapolation to ambient conditions. Given this uncertainty in the equilibrium values, he states that it is not possible to make any conclusive statement with regard to atmospheric equilibria involving NH_4NO_3.

Pressure drop

The filter pack system used in this survey has a high flow (40 l min^{-1}) compared to other workers, who typically use a flow rate of 10-20 l min^{-1}. The higher flow also means a higher pressure drop. Further as particles are collected and clog the filter, the pressure drop might increase. The changed pressure conditions can cause a water evaporation from the particles and by that a change in gas phase equilibrium concentrations above NH_4NO_3/NH_4Cl aerosols and/or evaporation due to raised pH, if the aerosols are neutralized. *Ferm (1986b)* observed increased NH_3 evaporation from particle filters with increasing pressure drop.

4 Discussion of NH_3/NH_4^+ and HNO_3/NO_3^- sampling with denuder

Denuder

The denuder is generally believed to give the best separation of the gases and particles, though some problems might occur.

4.1 Evaporation from particles during sampling

Evaporation from particles during sampling

During denuder sampling, one could expect that the removal of the gas phase would disturb the equilibrium with the particulate phase and course evaporation from the particles. In the denuders used here the residence time is *ca* 0.05 sec. for the NH_3 absorbing tube and *ca* 0.5 sec. for the HNO_3 absorbing tube. *Larson & Taylor (1983)* conclude from experiments with evaporation of NH_4NO_3 from an aerosol (MMD = 0.4 µm) that the observed rates imply negligible sampling errors in denuder tubes. *Appel et al. (1981)* also found negligible sampling errors concerning evaporation of NH_4NO_3, though they will not exclude a possibility of evaporation from coarse particles (> 3 µm). This is rather unlikely, since nitrate containing coarse particle mainly consists of $NaNO_3$ *(Harrison & Pio, 1983b)*, which has a negligible low vapor pressure at ambient conditions. *Harrison et al. (1990)* found evaporation rates of ammonium chloride and nitrate aerosols rather slow and state that the extent of evaporation of the particles in response to removal of the gaseous components should be minimal within the denuder itself during typical air sampling procedures. *Eatough et al. (1985)* verified in field experiments that this artifact is small.

4.2 Particle deposition in the denuder tube

Particle interference

By using a suitable coating the denuder method can be used to determine the diffusion coefficient of the gas in question. One can do this by expose and analyze denuders in series or by analyzing different parts of the coating. If the diffusion coefficient determined in ambient air are lower than the one determined in laboratory tests, the ambient air probably contain other gases and/or particles that interference. *Ferm (1979)* found good agreement between measured diffusion coefficient for ammonia in ambient air and literature value. This indicates, that particle deposition and/or interfering gases are a negligible problem for the ammonia denuder. *Ferm (1987)* made some experiments with diffusion coefficient determinations of SO_2 and HNO_3 in ambient air with the sodium hydroxide coated denuder with an acid coated inlet, which not was extracted. The results are used to investigate interferences and for SO_2 determinations it is seen that a small interference from particle deposition are occurring inside the denuder. The nitrate containing particle are also stated to deposit in the denuder, but it is not possible to distinguish this from a far more dominating gaseous interference. At a rural station in Sweden in August he find an overestimation of HNO_3 of 24%, being about 1% of the ambient NO_2 concentration.

In a denuder similar to the HNO_3/NO_3^- denuder used here *Forrest et al. (1982)* found, that losses of aerosol particles between 0.3 and 0.6 µm were 0.2-2.2% and for particles between 1-2 µm it were 4-5%.

The entrance of the denuder for HNO_3/NO_3^- determination also absorbs HNO_3 and the inlet is therefore extracted. It may occasionally occur that coarse particles are deposit in the inlet and be interpreted as gas phase *(Ferm, 1986a)*. These occasions were experimentally observed to be associated with sea salt particles and high Cl^- indicated the possible error.

The importance of the particle deposition will depend on the gas-particle ratio and the size distribution of the particles.

4.3 Overestimating of HNO_3 due to interfering gases

Interfering gases in HNO_3 determination

In the HNO_3 denuder NO_2 and PAN might be potential interfering gases, but in all tests carried out none or very small interference was observed *(Ferm, 1986a)*. *Koutrakis et al. (1988)* find an artifact formation of NO_3^- and NO_2^-, representing about 5-10% of these species, in a Na_2CO_3 coated annular denuder. For the same type of denuder as used here, *Ferm & Sjödin (1985)* describe the reactions

$$2NO_2 + H_2O \xrightarrow{surface} HNO_2 + HNO_3 \qquad (1)$$

and

$$NO + NO_2 + H_2O \rightarrow 2HNO_2 \qquad (2)$$

as potential interferences in determination of HNO_2. From laboratory experiments they found that NO_2 alone is not an interference of major importance. They also found that the rate of reaction (1) in contact with surfaces is quite slow compared to reaction (2). *Perrino (pers. com., 1992)* describes the reaction

$$SO_3^{2-} + 2NO_2 + 2OH^- \rightarrow SO_4^{2-} + 2NO_2^- + H_2O \qquad (3)$$

as potential interfering with HNO_2 determination, with SO_3^{2-} originating from SO_2. One could expect an error in the HNO_3 determination, if the interfering NO_2^- oxidizes to NO_3^- either in the denuder or in the denuder extract. *Febo et al. (1986)* have observed, that during sampling in photochemical smog episodes NO_2^- might be oxidized to NO_3^-, probably by O_3. *Perrino et al. (1990)* also found evidence for the oxidation of sampled NO_2^-. *Dasch et al. (1989)* have experiences that adding H_2O_2 to the denuder extracts not oxidized NO_2^- to NO_3^-. With sampling by annular denuders *Appel et al. (1990)* found a low percentage retention of NO_2, PAN and other possible pollutants.

5 Results and discussion

Presentation of results

This section presents some general experiences and the results and discussion from the comparison between the determination of NH_3/NH_4^+, HNO_3/NO_3^- and SO_2/SO_4^{2-} by the two measuring methods. The results from each campaign are shown in Appendix 1.

If parallel or triple measurements were run, all the values obtained by the filter pack *(Figures 3, 4 and 5)* respectively the uncoated denuder *(Figure 6)* are plotted against the mean value of the coated denuder determination on the figures.

The sampling volume in the filter pack is the volume at 0°C, while it in the denuders are 20°C. This gives a correction factor of 7%. The data are not corrected for this factor.

5.1 Clogging of the teflon filter

Clogging of teflon filters

During some of the campaigns a problem with clogging of the filter pack with teflon particle filter revealed. It was often observed at the end of an exposure and especially during humid conditions and low temperature. Clogging during cold and foggy conditions were observed after 1 to 2 hours exposure. *Anlauf et al. (1988)* use a filter pack with teflon particle filter of the same size and flow dimensions as the one reported here. They sample from 1 to 6 hours and do not report clogging problems. The clogging problem limit the use of the filter pack with teflon particle filter and 24-hour exposure is not recommended at Danish conditions.

5.2 PIXE analysis of teflon filters

PIXE on teflon filters

It is possible to PIXE analyze the teflon filters, but the filters showed a high background of fluoride, which higher the detection limit considerably for several compounds compared to the cellulose filters.

5.3 Denuder and filter pack measurements of gaseous NH_3 and particulate NH_4^+

Comparison of denuder and filter pack, NH_3/NH_4^+

The NH_3 and NH_4^+ measurements by denuder and filter pack were done in the first three campaigns: September 1989, January 1991 and March 1991. It is seen in *Figures 3 a, b and c* that the denuder and the two filter packs show a good agreement concerning the total amount of NH_3 and NH_4^+, particulate NH_4^+ and gaseous NH_3, although some scatter is seen for gaseous NH_3 *(Figure 3 c)*. The 7% correction for volume definition at different temperatures is not seen. *Wiebe et al. (1990)* also found good agreement between filter pack measurements of NH_3 and other methods. Their particular filter pack had a teflon particle filter and the same size and flow dimensions as the one reported here. *Harrison & Kitto (1990)* also find good agreement between denuder and filter pack measurements, although they report a slightly higher gaseous NH_3 results from the filter pack compared to the denuder, probably related to differences in collection efficiency.

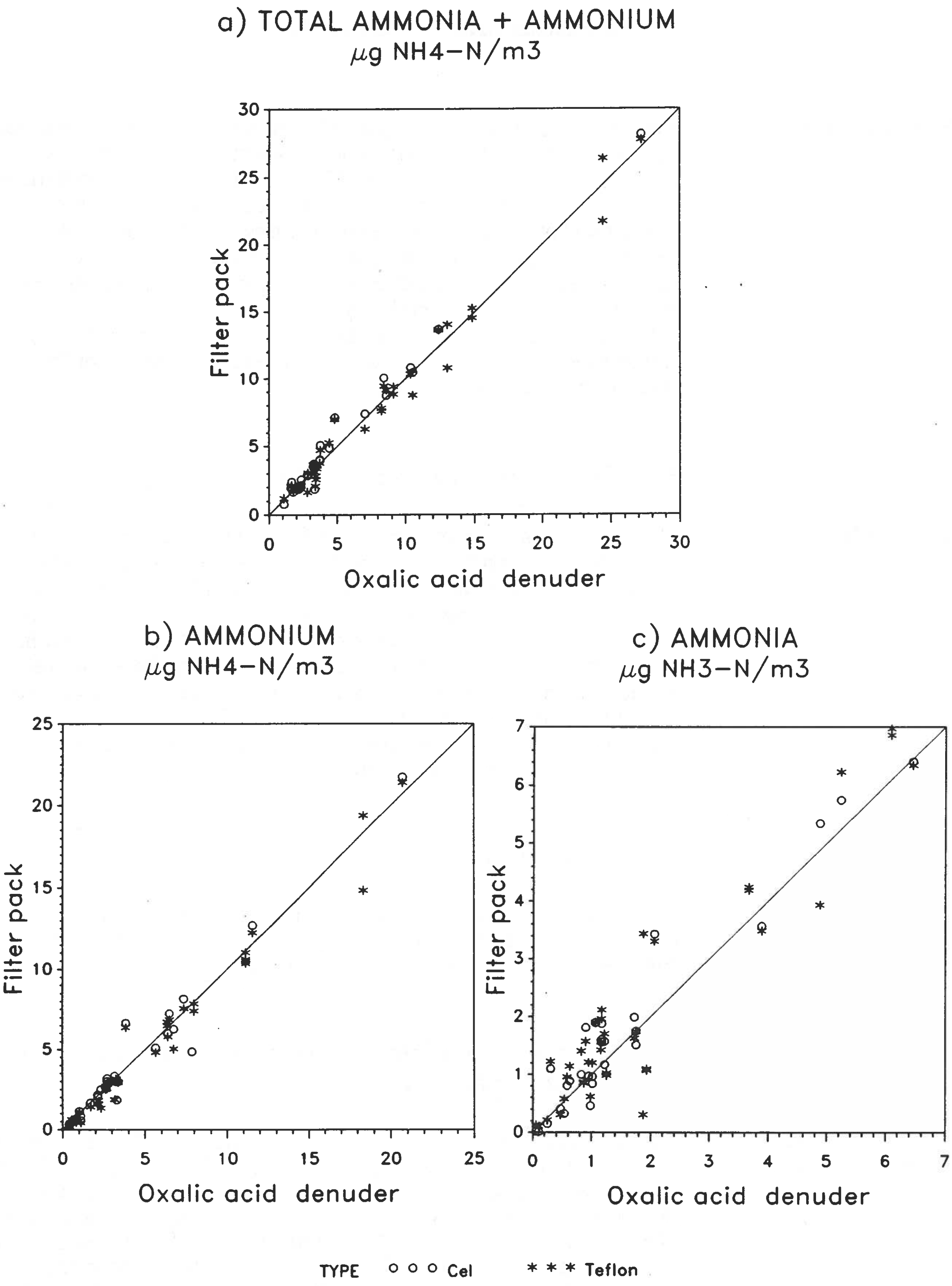

Figure 3. Filter pack with cellulose based particle filter (Cel) and teflon particle filter (Teflon) compared to denuder measurements of a) total amount of NH_3 and NH_4^+, b) the particulate NH_4^+ and c) the gaseous NH_3.

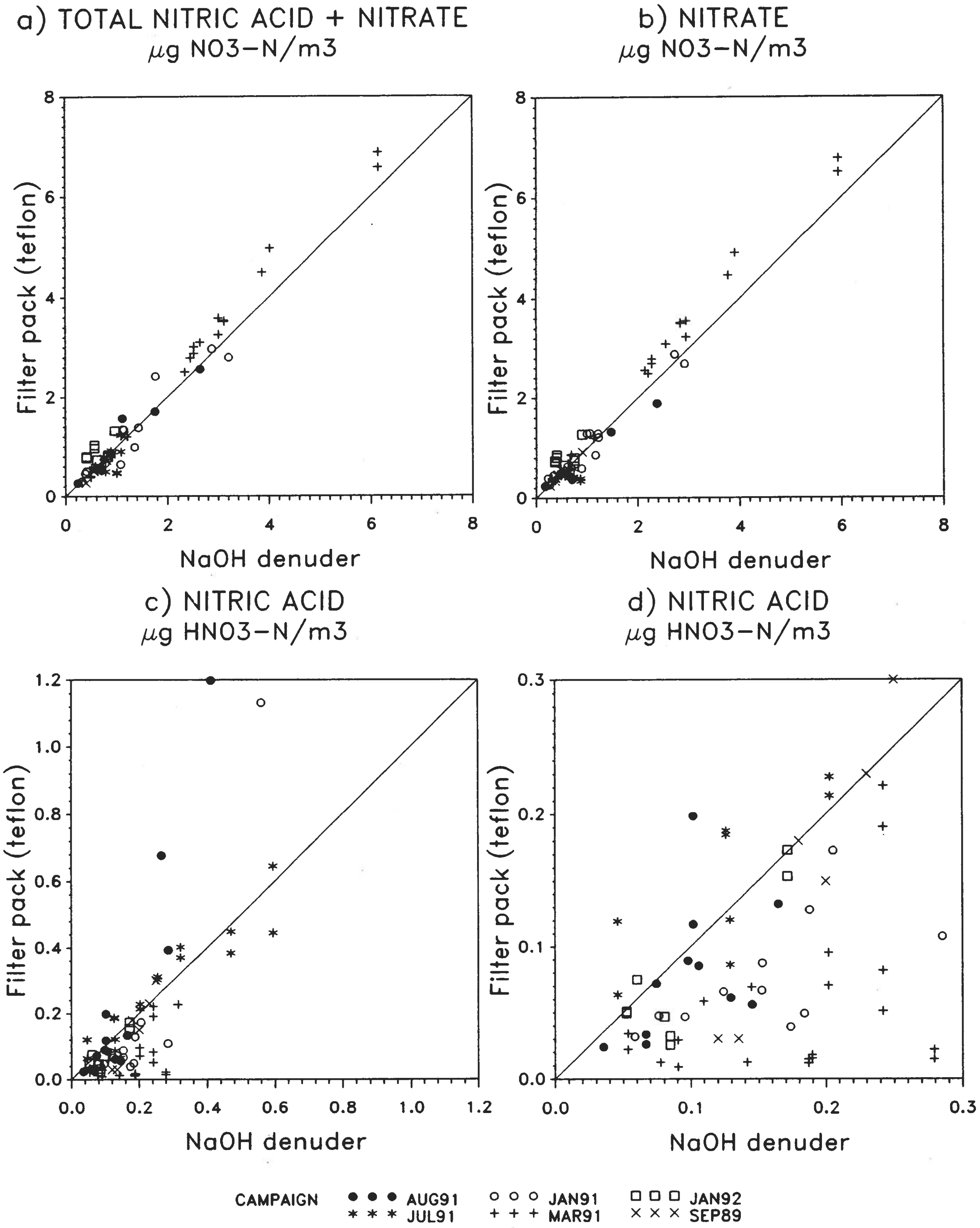

Figure 4. Filter pack with particle filter of teflon compared to denuder measurements of a) total amount of HNO_3 and NO_3^-, b) particulate NO_3^- c) the gaseous HNO_3 and d) the gaseous HNO_3 in the lowest concentrations.

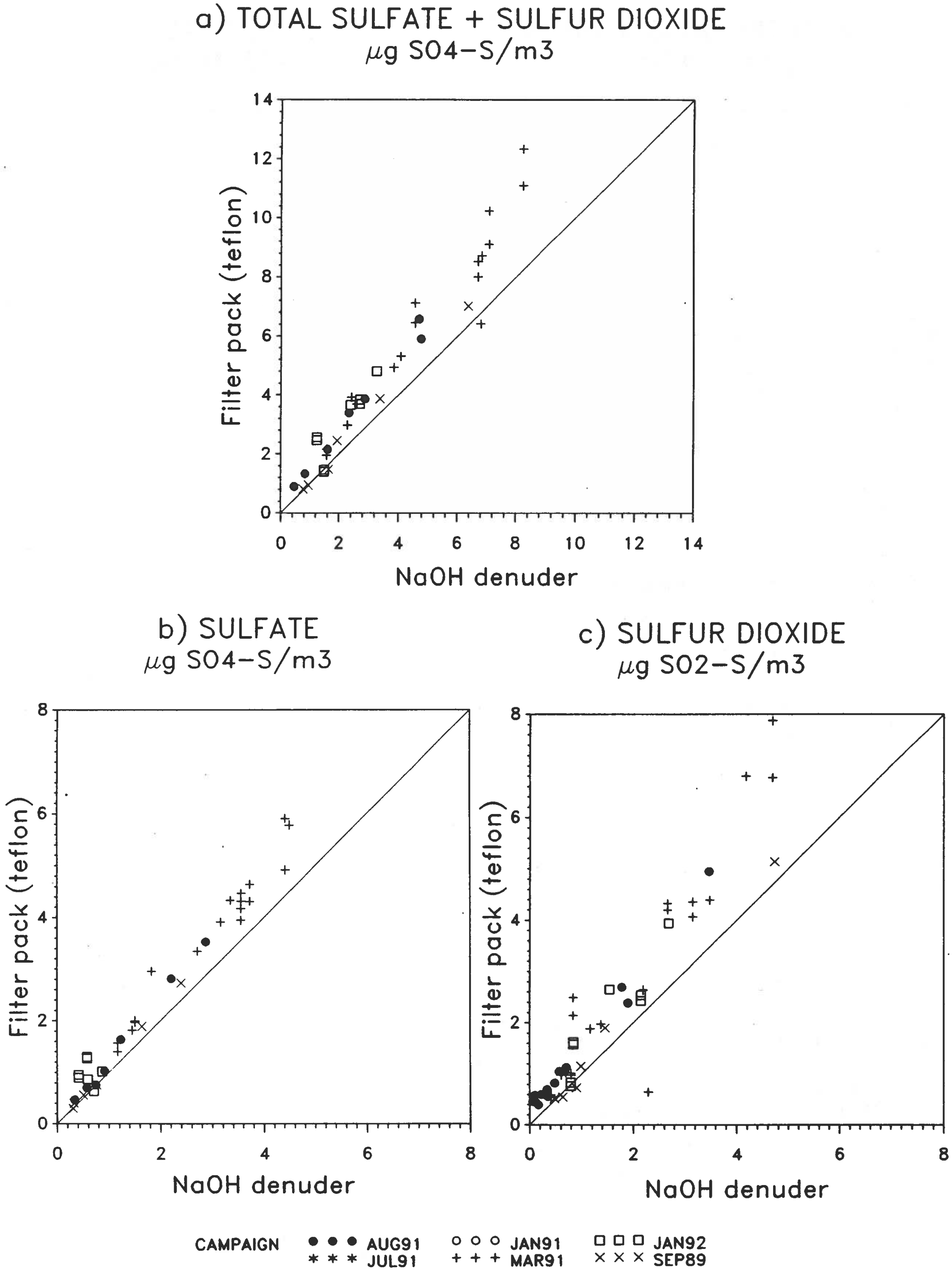

Figure 5. Filter pack with particle filter of teflon compared to denuder measurements of a) total amount of SO_2 and SO_4^{2-}, b) the particulate SO_4^{2-} and c) the gaseous SO_2.

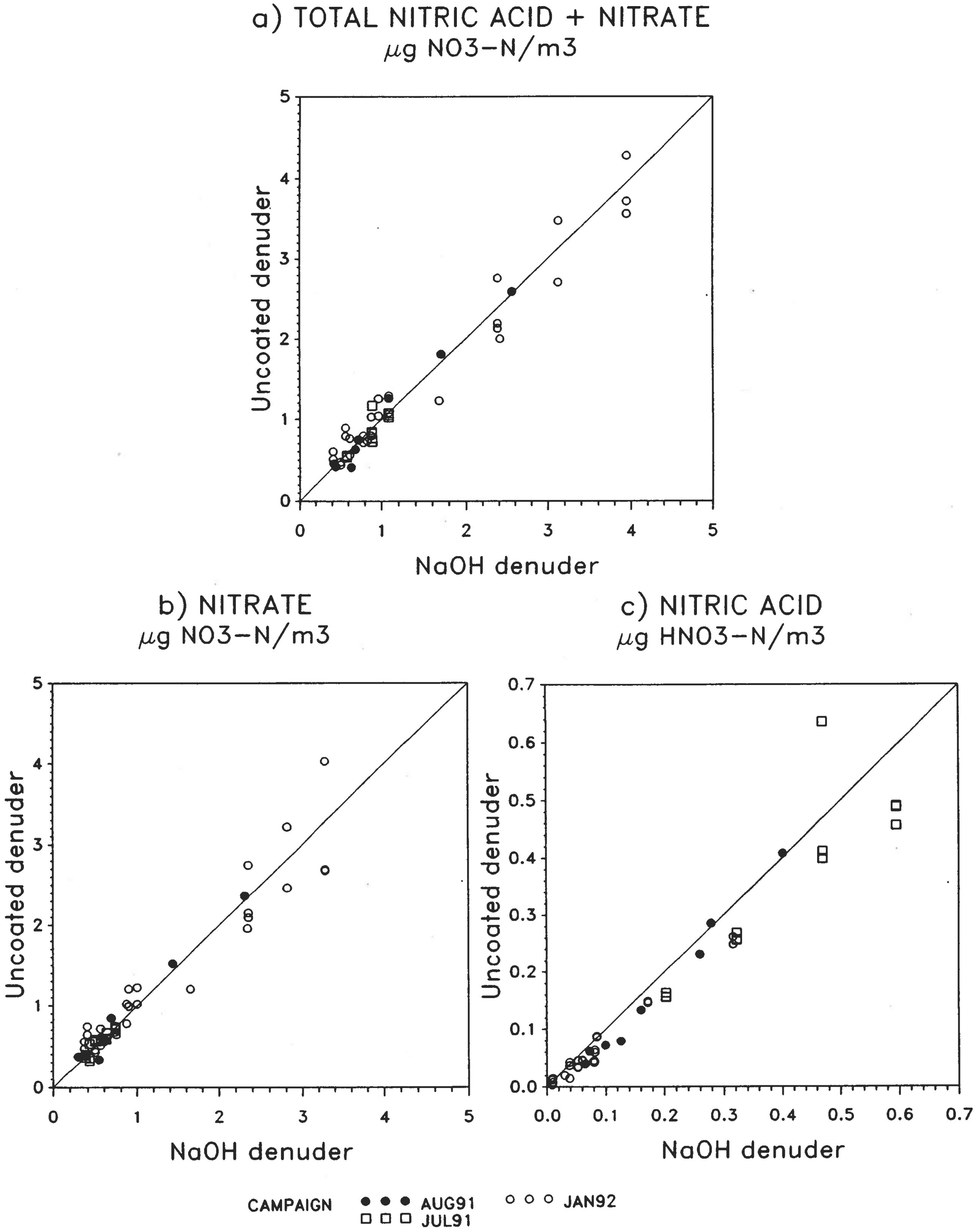

Figure 6. Coated denuder for HNO_3/NO_3^- determination compared to the uncoated denuder for a) total amount of HNO_3 and NO_3^-, b) the particulate NO_3^- and c) the gaseous HNO_3.

5.4 Denuder and filter pack measurements of gaseous HNO_3 and particulate NO_3^-

Comparison of denuder and filter pack, HNO_3/NO_3^-

Figures 4 a, b, c and d show the comparison between measurements of gaseous HNO_3 and particulate NO_3^- done by denuder and the filter pack with teflon particle filter. The data are marked in relation to the different campaigns. For the total amount of gaseous HNO_3 and particulate NO_3^- *(Figure 4 a)* the data obtained from the filter pack are a little higher than the denuder. The difference, also seen on the particulate NO_3^- alone *(Figure 4 b)* probably relate to the volume correction giving 7% higher filter pack results. The difference is more pronounced for the sulfate particles, discussed in section 5.5.

Figure 4 c shows the gaseous HNO_3 determined by the denuder and filter pack methods. In *Figure 4 d* the same data are shown for concentrations smaller than 0.3 µg HNO_3-N m^{-3}. Looking at the specific campaigns, the data from July '91 show a good agreement between the two methods, while the other campaigns show a wide scatter, generally with the filter pack measuring lower values than the denuder. The July '91 campaign with the good agreement for the gaseous HNO_3, is also the campaign with the most equal concentration levels of the gaseous HNO_3 and the particle NO_3^- *(Figure 7)*. In *Figure 4 d* with the low concentrations, it is seen that January '91 and March '91 are most frequent in underestimation HNO_3 by filter pack measurement compared to denuder. The same two campaigns have the highest frequency of high particulate NO_3^- concentrations compared to the rest of the campaigns *(Figure 7)*. The filter pack underestimation of HNO_3 could relate to adsorption of the gas to particles on the filter as observed by *Appel et al. (1980)* and *Appel & Tokiwa (1981)*. Some of the observations in March '91 have a low particle concentration, but these periods had a high relative humidity, which can cause errors with retainment of HNO_3 on the particle filter in the filter pack *(Forrest et al., 1980)*. The difference in the two methods could also relate to overestimation by the denuder either by particle deposition in the denuder and/or interferences from other gases. *Forrest et al. (1982)* found losses up to 5% of particles up to 2 µm. Up to 5% loss of a particle concentration of up to 10 to 20 times the gas concentration (the case in March '91) would give significant errors. Though, if particle deposition in the denuder is a significant problem the concentration pattern for the gas and particles *(Figure 7)* would be expected to be more alike. *Ferm (1987)* report, that some particle deposition occur, but in the case of HNO_3 a much more dominating gaseous interference is occurring. At a rural station in Sweden he state this overestimation to 24% of the measured HNO_3 concentration.

Overestimation of HNO_3 from oxidized NO_2^-

An overestimation of HNO_3 in the denuder could originate from interferences from oxidation of sampled NO_2^- originating from HNO_2, NO, NO_2 or PAN and/or with NO_2 (eq.(1), section 4).

Febo et al. (1986) and *Perrino et al. (1990)* observed artifact NO_3^- from oxidation of sampled NO_2^-. *Figure 8* show that considerably amount of HNO_2 and/or interfering gases producing NO_2^- are present compared to HNO_3, especially in the cold sampling periods. For some of the campaigns NO_2 and NO concentrations were available. It is seen in *Figure 8* for the January 1992 campaign, that the concentration pattern of NO and NO_2^- from HNO_2 and/or interfering gases are alike. It is not possible to say whether this is a relation in ambient air or an indication of interference.

In the discussion of the potential interferences giving HNO_3 overestimation in the sodium hydroxide coated denuder one can compare the measurement for the last three campaigns with the uncoated tube, which do not sample HNO_2 and/or interfering gases producing NO_2^-. It is not possible to exclude or estimate the potential interferences, but by implying some conditions different comments can be given.

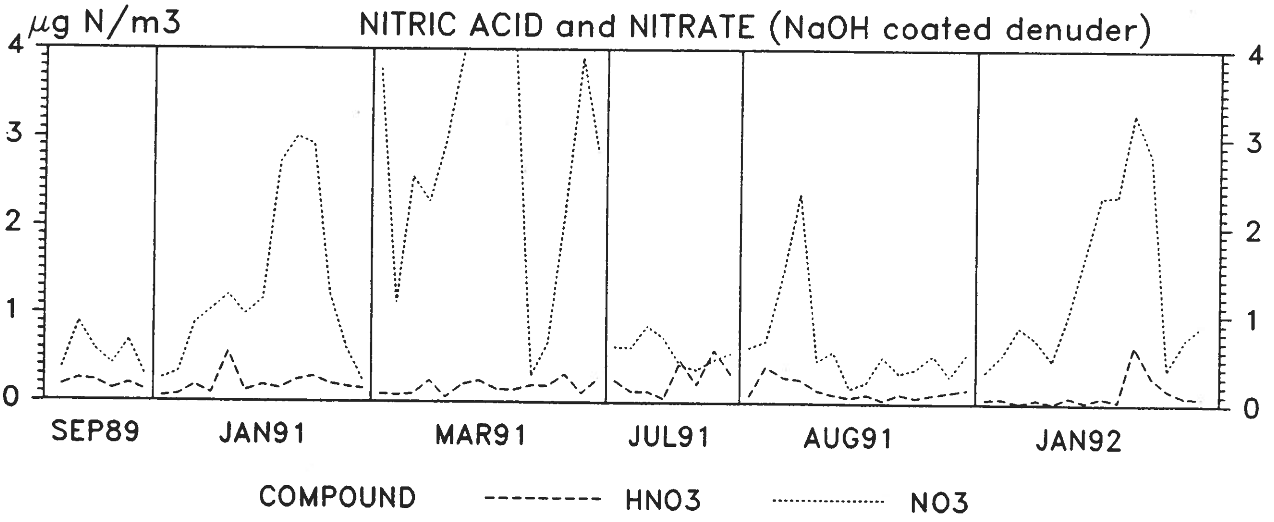

Figure 7. Concentration levels of gaseous HNO_3 and particulate NO_3^- determined by denuder in the different measuring campaigns.

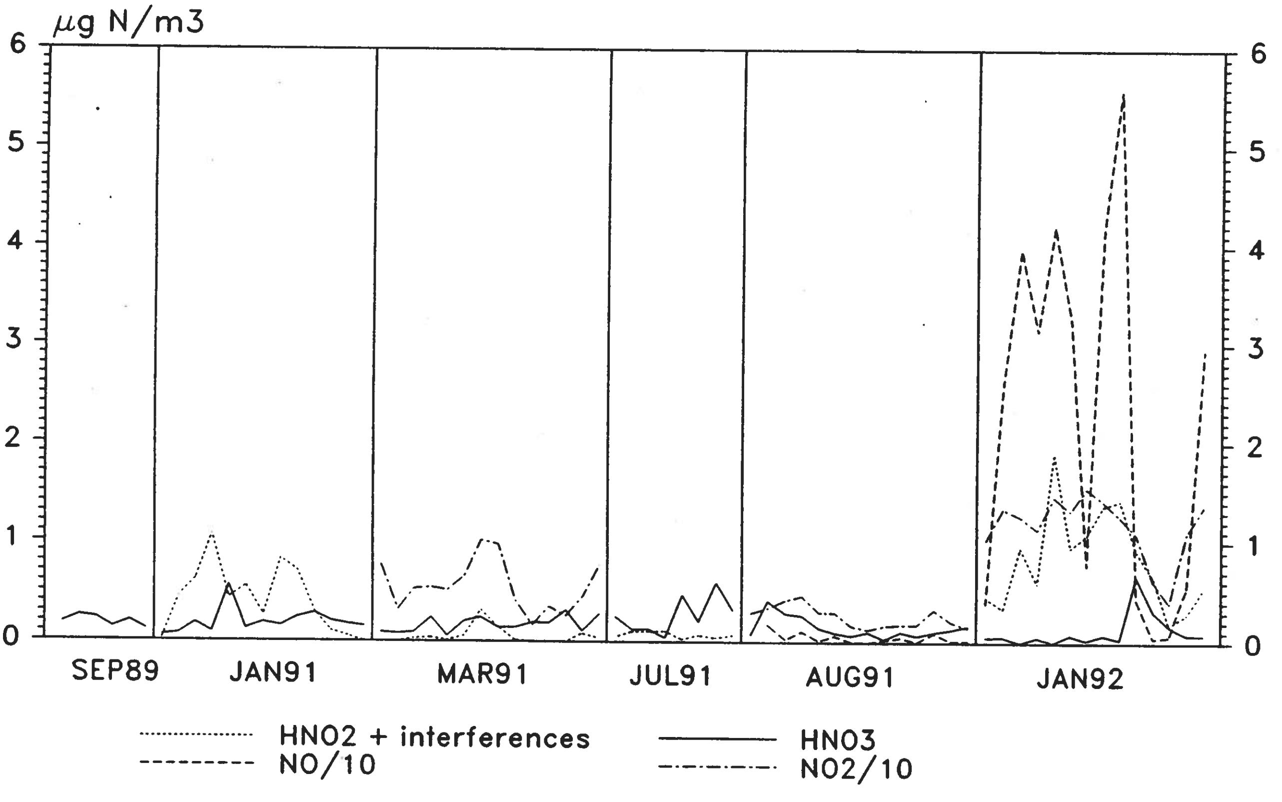

Figure 8. Concentration levels of HNO_3 and HNO_2 and/or interferences determined by NaOH coated denuder and NO/NO_2 determined by chemiluminescence/KI-impregnated filters. NB: Concentrations of NO and NO_2 are divided by 10.

Uncoated and coated HNO_3 denuder

Figure 6 c show the coated and uncoated denuder determination of HNO_3. In general the deviation of the parallel measurements for the uncoated denuder were the same as for the coated (see Appendix 1). A good correlation is seen between the coated and uncoated denuder determinations, with the uncoated being up to 20% lower than the coated. *Figure 6 a* show a good agreement for the total determination. It means, that whatever causes the differences for HNO_3, it is compensated on the impregnated filters behind the denuders. The difference seen on HNO_3 between uncoated and coated denuder indicate that either is the efficiency of the uncoated denuder up to 20% lower than that of the coated and/or some interferences are present in the coated and not in the uncoated. *Ferm (1986a)* found an efficiency about 80% for an uncoated tube of same glass material. In this context two experiments were run with two uncoated tubes in series (March 1992) and the efficiencies were respectively 81% and 87%. Our efficiency test can be questioned, because the efficiency measurements can be affected by interferences of NO_2 eq.(1) or particle deposition. To solve this problem three denuders should have been exposed in series. The fact that the uncoated denuder doesn't sample HNO_2/NO_2^- also excludes the possibility in this denuder, that HNO_3 is overestimated due to NO_2^- oxidation. Assuming that the difference between coated and uncoated tubes is caused by differences in efficiency one can say that an artifact NO_3^- formation in the coated denuder due to oxidized NO_2^-seems to be of minor importance. Concerning overestimation due to oxidation of NO_2^- to NO_3^- in the extracts, *Dasch et al. (1989)* report, that even adding H_2O_2 to the solution, did not oxidize the NO_2^-.

NO_2 interference

An overestimation of HNO_3 from interference with NO_2 (eq.(1)) could occur. This artifact HNO_3 would probably be present in both the coated and uncoated denuder, but not necessarily in the same amounts if the alkaline coating influence the reaction. In the coated denuder the NO_2 interference would also give a NO_2^- determination from the HNO_2 produced, while HNO_2 formed in the uncoated tube will be collected on the following filter. In August 1991 no detectable amounts of NO_2^- were observed in the coated denuder indicating, that interference with NO_2 (eq.(1)) in this campaign is of minor importance. The artifact NO_2^- formation could have been oxidized, giving the little difference seen between the coated and uncoated denuder tube determination of HNO_3, but then one must assume equal efficiencies for the two denuder types. From laboratory experiment *Ferm & Sjödin (1985)* found, that interference from NO_2 alone is of minor importance. *Koutrakis et al. (1988)* find an artifact formation of NO_3^- and NO_2^-, representing about 5-10% of the species in a Na_2CO_3 coated dunuder. *Ferm (1987)* report an overestimation of about 1% of the NO_2 level, giving 24% overestimation on a Swedish rural station.

Overestimation of HNO_3 by filter pack

In *Figure 4 c* three episodes with filter pack overestimation of HNO_3 seen. All of them are day time measurements, two of them occurring in August '91 and one in January '91. The two days in August '91 have a drop in the relative humidity to respectively 40% (filter pack concentration 1.2 µg HNO_3-N m^{-3}) and 60% (filter pack concentration 0.68 µg HNO_3-N m^{-3}). These observations probably relate to evaporation of nitrate salts at low relative humidity as reported by *Appel et al. (1981)* and *Forrest et al. (1980)*. The episode in January '91 show an overestimation in the filter pack measurement, but also a general increase in concentration measured by denuder *(Figure 7)*. In January '92 a similar increase in concentration is observed *(Figure 7)*. The corresponding filter pack measurements are missing due to clogging. Both days, January '91 and January '92, have foggy conditions and NH_3 concentration close to zero *(Figure 8)*. Both campaigns have temperatures about and below the freezing point. The observations here might relate to the predictions of *Tang (1980)*, that the HNO_3 concentration will increase with decreasing pH in the droplet solution as in fog. At the same time HNO_3 might be released from the particle filter in the filter pack due to the acid conditions, resulting in overestimation of HNO_3.

Summarizing results

Summarizing there is good agreement between filter pack and denuder determination of the total amount of gaseous HNO_3 and particulate NO_3^-. Only few observations indicate evaporation of HNO_3 from the particle filter, despite the high flow rate at 40 l min^{-1}. The denuder measured more HNO_3 than the filter pack in most of the observations, especially the low concentrations.

The comparison made here does not clearly reveal whether the filter pack is underestimating the HNO_3 due to adsorption on the particle filter or if the denuder overestimate due to particle deposition and/or other interferences. *Dasch et al. (1989)* report the same observations with denuder measurements being higher than the filter pack and relate this to respectively particle deposition in the denuder and adsorption in the filter pack. This is not consistent with *Harrison & Kitto (1990)*, who find a good agreement between the two methods and with the filter pack giving slightly higher results.

5.5 Denuder and filter pack measurements of gaseous SO_2 and particulate SO_4^{2-}

Comparison of denuder and filter pack, SO_2/SO_4^{2-}

The sodium hydroxide coated denuder and the filter pack with teflon filter were compared for total and separate determination of gaseous SO_2 and particulate SO_4^{2-}. The uncoated denuder tube showed only little absorbance of SO_2 and it is not suitable for this purpose. *Harrison & Kitto (1990)* found good agreement between denuder and filter pack measurements of particulate SO_4^{2-}.

The total amount of gaseous SO_2 and particulate SO_4^{2-} show an underestimation of about 20% by the denuder *(Figure 5 a)*. The particulate SO_4^{2-} alone show good correlation but with an underestimation of about 15% *(Figure 5 b)*. An underestimation of 7% by the denuder is expected from the temperature correction. The SO_2 data from the denuder and filter pack show underestimation and not as good a correlation as the particulate SO_4^{2-} *(Figure 5 c)*. The SO_2 sampled by the denuder might be present as both SO_4^{2-} and SO_3^{2-}. The data in January 1992 the SO_3^{2-} are included. For the other campaigns missing SO_3^{2-} analysis might cause and underestimation of SO_2. This should lead to an underestimation of the total amount of gaseous SO_2 and particulate SO_4^{2-}. This is observed, but is partly due to underestimation of the particulate SO_4^{2-} as well *(Figure 5 b)*. *Ferm (1986a)* report that all SO_2 is found as SO_4^{2-}in the extracts. *Dasch et al. (1989)* report, that SO_3^{2-} seldom is seen during warm weather conditions. The results from the January 1992 campaign showed that during conditions with high SO_2 concentrations up to 50% of the SO_2 sampled was present as SO_3^{2-} in the extracts. A lower efficiency in the denuder for the SO_2 would also lead to underestimation, but this should lead to overestimation of the particulate SO_4^{2-}. A lower efficiency is rather unlikely, since the diffusion coefficient for SO_2 and HNO_3 is very close and sodium hydroxide has high affinity for SO_2. If all the SO_2 is oxidized to SO_4^{2-} or SO_3^{2-} analyzed as in January 1992 campaign, one would expect agreement in the total sulfate determination, even though the efficiency for SO_2 is low. This is not the case.

Former observations

In a intercalibration in Sweden overestimation of SO_2 and SO_4^{2-} by the filter pack compared to the other participants was observed. In order to explain these observations an experiment was carried out, but no overestimation was observed this time *(Grundahl & Kemp, 1992)*. According to the formulas referred by *Ferm (1986a)* the fraction of the ambient concentration of particles that enters the tube can be calculated as a function of particle diameter and wind speed. The higher the wind speed, the more difference is seen in efficiency for collecting particles > 1-2 µm between denuder and filter pack, with the latter having the best efficiency. For the fine particle fraction this is of less importance, but for the coarse particles, including sulfate and nitrate containing sea salt and soil dust particles, this might influence. Though this was not observed for the particulate NO_3^- determination by the two method. There is no obvious explanation for the general underestimation of about 10-15% for both the gaseous and particulate sulfate.

5.6 The measurements in general

Concentration levels and variations

From *Figures 7, 9 and 10* it is seen, that the gaseous and particulate concentrations are variable, both in day/night, day to day and in the different campaigns in the different seasons. *Figures 11 a, b and c* show the concentration levels of the different gases in the different campaigns, marked due to 24-hour, day or night measurement. A pattern with highest daytime measurements is seen for HNO_3. *Figures 12 a, b and c* show the particulate concentration and no clear day/night pattern is seen. *Figures 13 a, b and c* show the NH_4^+ equivalents plotted against respectively the SO_4^{2-}, NO_3^- and total ($SO_4^{2-} + NO_3^-$) equivalents. From the data in the March '91 campaign it is seen, that SO_4^{2-} and NO_3^- raise together to a certain level and above this only NO_3^- increases.

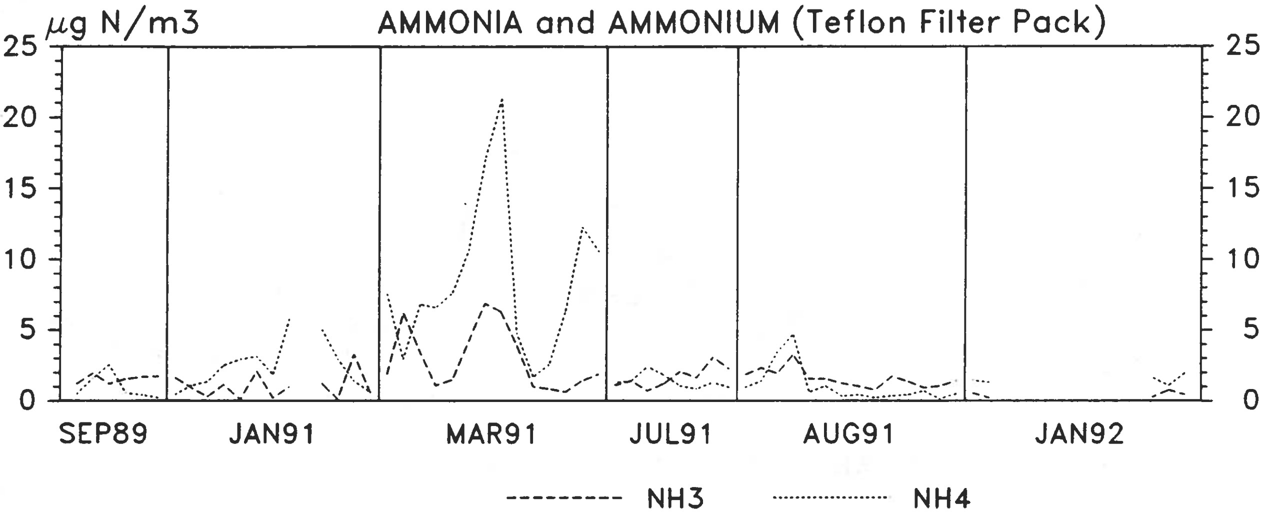

Figure 9. Concentration levels of gaseous NH_3 and particulate NH_4^+ determined by filter pack with teflon particle filter in the different measuring campaigns.

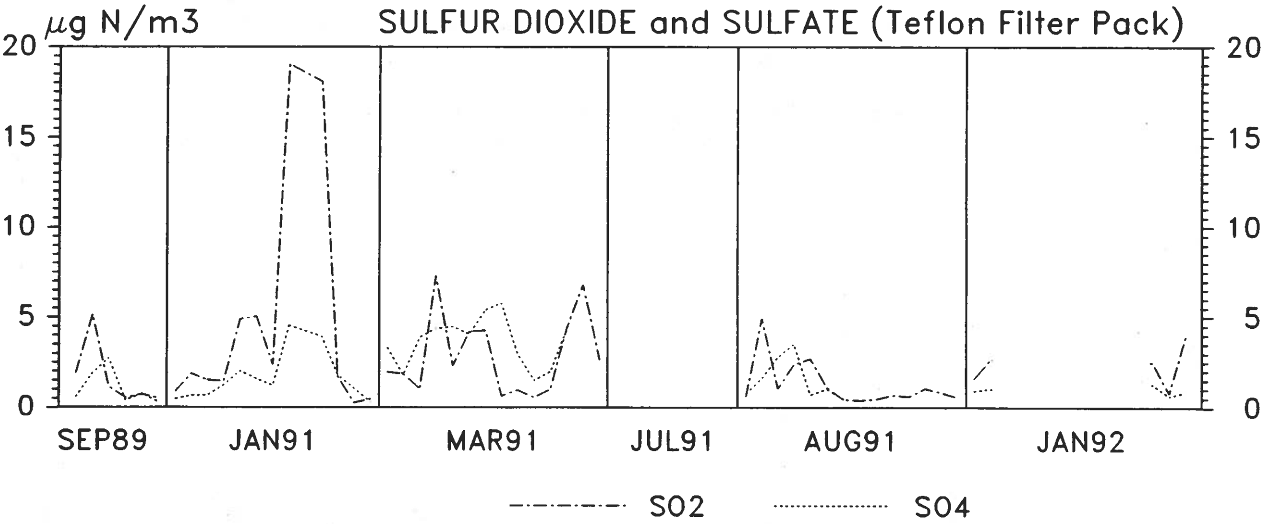

Figure 10. Concentration levels of gaseous SO_2 and particulate SO_4^{2-} determined by filter pack with teflon particle filter in the different measuring campaigns.

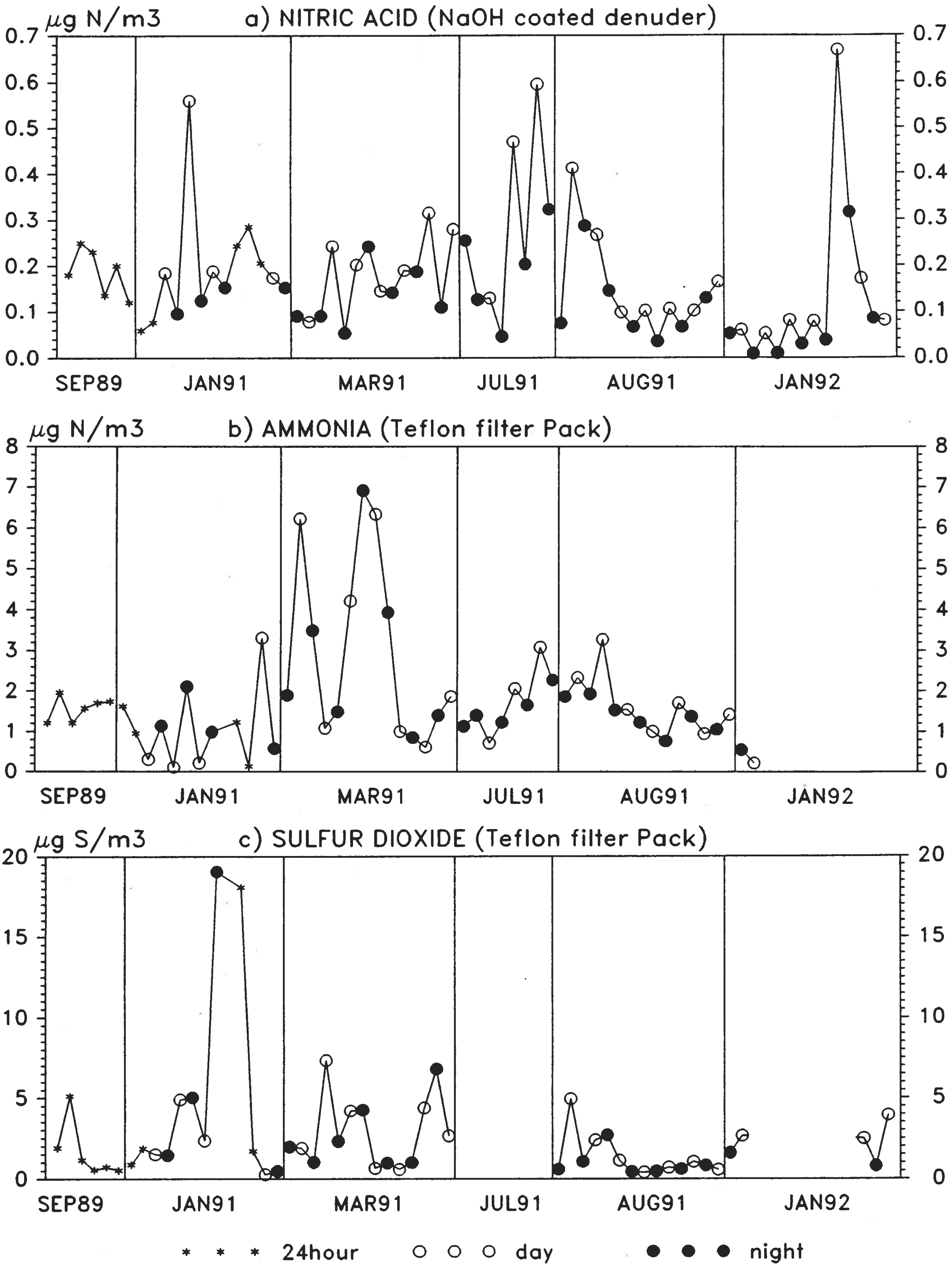

Figure 11. Concentration levels of the different gaseous species divided in 24-hour measurements and day/night measurements for the different campaigns, a) HNO_3 measured by denuder, b) NH_3 measured by filter pack with teflon particle filter and c) SO_2 measured by filter pack with teflon particle filter.

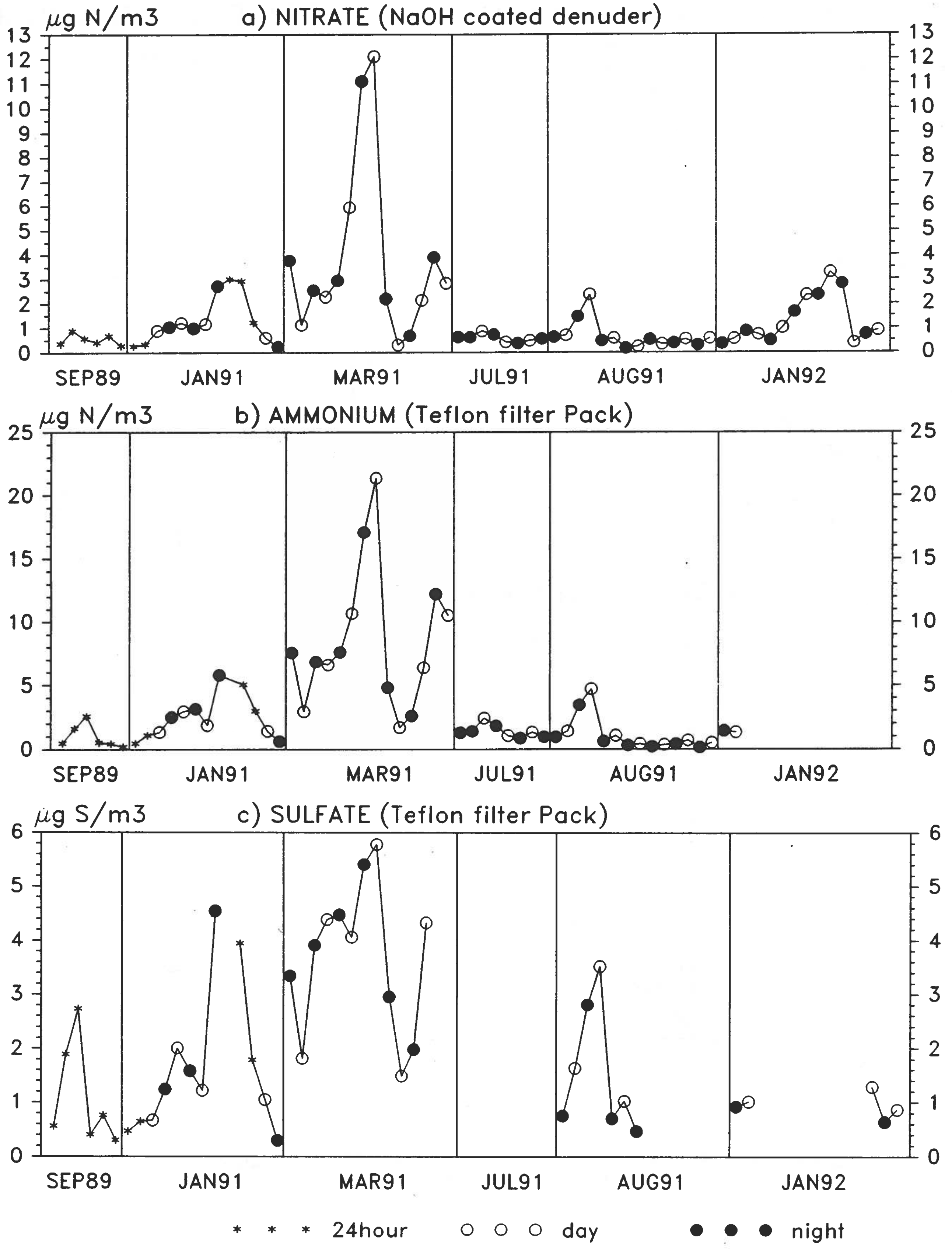

Figure 12. Concentration levels of the different particle species divided in 24-hour measurements and day/night measurements for the different campaigns, a) NO_3^- measured by denuder, b) NH_4^+ measured by filter pack with teflon particle filter and c) SO_4^{2-} measured by filter pack with teflon particle filter.

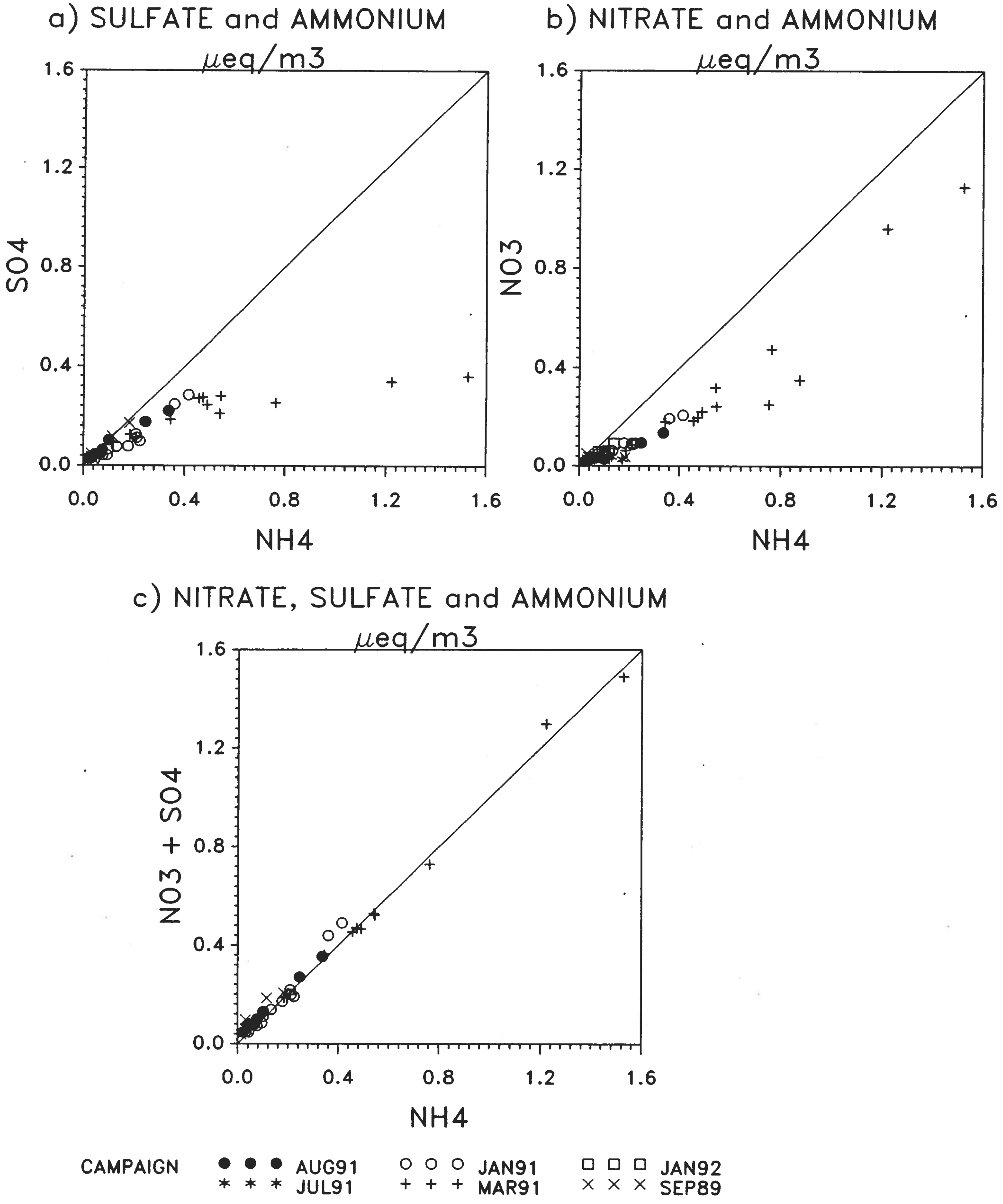

Figure 13. Particulate NH_4^+ concentration in micro equivalents (μmol m^{-3}) compared to a) the particulate SO_4^{2-} concentration in micro equivalents (2 x μmol m^{-3}), b) the particulate NO_3^- concentration in micro equivalents (μmol m^{-3}) and c) the sum of the particulate SO_4^{2-} and NO_3^- concentration in micro equivalents.

6 Summary and conclusion

Summary

A filter pack with a teflon particle filter is validated for separation of gaseous NH_3 and HNO_3 and particulate NH_4^+ and NO_3^-. The results are compared to denuder measurements of respectively NH_3/NH_4^+ and HNO_3/NO_3^-. The denuder for determination of HNO_3/NO_3^- is also validated for SO_2 and SO_4^{2-} determination. A coated and an uncoated denuder for determination of HNO_3/NO_3^- is compared.

Filter pack with teflon filter

The conclusions for the use of a filter pack with a teflon filter are as follows:

- the filter pack have a general problem with clogging, which makes 24-hour exposure unsuitable.
- the teflon filters have a considerably higher detection limit for many of the elements analyzed by PIXE.
- there is good agreement between filter pack and denuder determination of total amount of gaseous HNO_3 and particulate NO_3^-.
- the filter pack generally gives an underestimation of gaseous HNO_3 compared to the denuder at concentrations lower than 0.3 µg HNO_3-N m^{-3}.
- only few observations of evaporation of HNO_3 from the particle filter in the filter pack are observed.
- there is good agreement between filter pack and denuder determination of total amount of gaseous NH_3 and particulate NH_4^+.
- the filter pack shows a good separation of gaseous NH_3 and particulate NH_4^+.
- the filter pack shows 10-15% higher concentrations than the denuder for both gaseous SO_2 and particulate SO_4^{2-}.

Denuder, HNO_3/NO_3^-

The conclusions for the sodium hydroxide coated denuder for HNO_3/NO_3^- determination:

- it seems reasonable that particle deposition in the denuder is a minor problem.
- the denuder tube collect NO_2^- originating from HNO_2 and/or interferences.
- interference from artifact NO_3^- from oxidation of sampled NO_2^- seems to be a minor problem concerning HNO_3 determination.
- interference from NO_2 giving artifact HNO_3 cannot be excluded, although this not was observed in the August 1991 campaign.

Uncoated denuder, HNO_3/NO_3^-

The conclusions for the uncoated denuder for HNO_3/NO_3^- determination:

- the HNO_3/NO_3^- determination show good agreement with the coated denuder, but the efficiency is a little lower for HNO_3 determination.
- the denuder tube does not collect NO_2^- originating from HNO_2 and/or interferences.
- the denuder tube does not collect SO_2 quantitatively.

Denuder, SO_2/SO_4^{2-}

The conclusions for the sodium hydroxide coated denuder for SO_2/SO_4^{2-} determination:

- the denuder underestimate the total amount of SO_2 and SO_4^{2-} about 10-15% compared to the filter pack.
- the correlation between denuder and filter pack determination of SO_4^{2-} is good, although underestimation is observed by the denuder.
- a correlation is seen for the SO_2, but with more scatter than the one for the particulate SO_4^{2-}.
- the extracts in January 1992 campaign were analyzed for SO_3^{2-} and up to 50% of the total SO_4^{2-} originating from SO_2 was present as SO_3^{2-}.
- an underestimation of SO_2 could be due to missing analysis of SO_3^{2-}, although in the January 1992 campaign an underestimation of SO_2 by the denuder tube was still seen even though SO_3^{2-} was analyzed and added to the results.

General observations concerning the comparisons:

Both methods might have artifacts

- the HNO_3/NO_3^- comparison made here does not clearly reveal whether the filter pack is underestimating the HNO_3 due to adsorption on the particle filter or if the denuder overestimate due to particle deposition and/or other interferences.

- the potential interference from NO_2 in the HNO_3 denuders seems to be the same, whether the denuder is coated or not.

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APPENDIX 1

The appendix presents plots of NH_3/NH_4^+, HNO_3/NO_3^- and SO_2/SO_4^{2-} measurements in the individual campaigns. The campaigns were in september 1989, January 1991, March 1991, July 1991, August 1991 and January 1992.

The legends in the plots refer to different types of particle filters in the filter pack and coating/impregnation of denuder tubes and filters.

The different types of particle filters are:

"Cel":	MF-Millipore RA (50 mm, 1.2 µm) (mixed cellulose esther).
"Fluoro":	Fluropore FA (47mm, 1 µm) (teflon).
"TF1000":	Gelman TF-1000 (47 mm, 1 µm) (teflon).
"Teflo1":	Gelman Teflo (47 mm, 1 µm) (teflon).
"Teflo2u":	Gelman Teflo (47 mm, 2 µm) (teflon).

The different types of coating/impregnation are:

"Coated":	NaOH coated tubes and NaOH impregnated filter for HNO_3/NO_3^- and SO_2/SO_4^{2-} determination. Oxalic acid coated tubes and oxalic acid impregnated filters for NH_3/NH_4^+ determination.
"Uncoated":	Uncoated tube (soda glass) followed by NaOH impregnated filter for HNO_3/NO_3^- determination.

TOTAL AMMONIA + AMMONIUM

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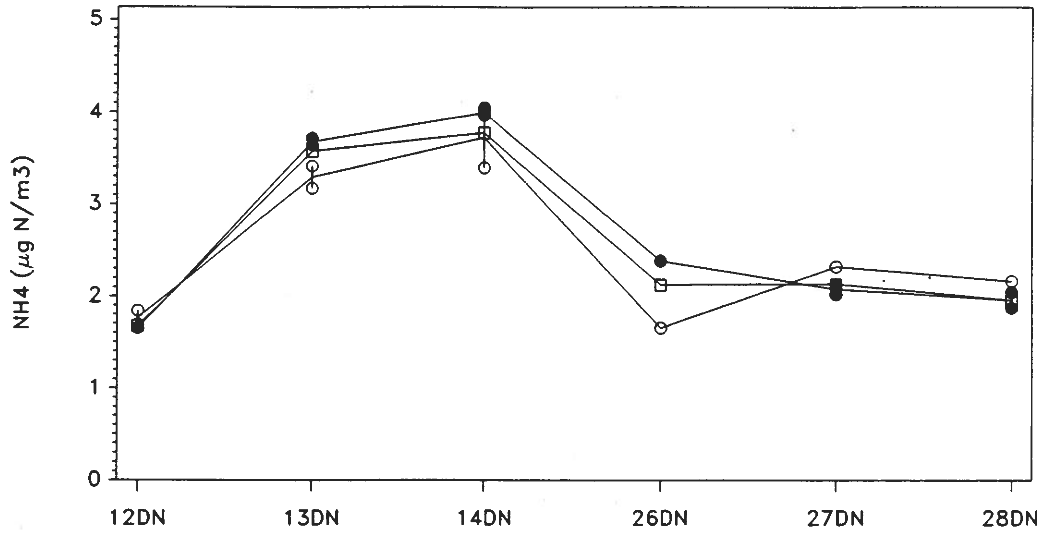

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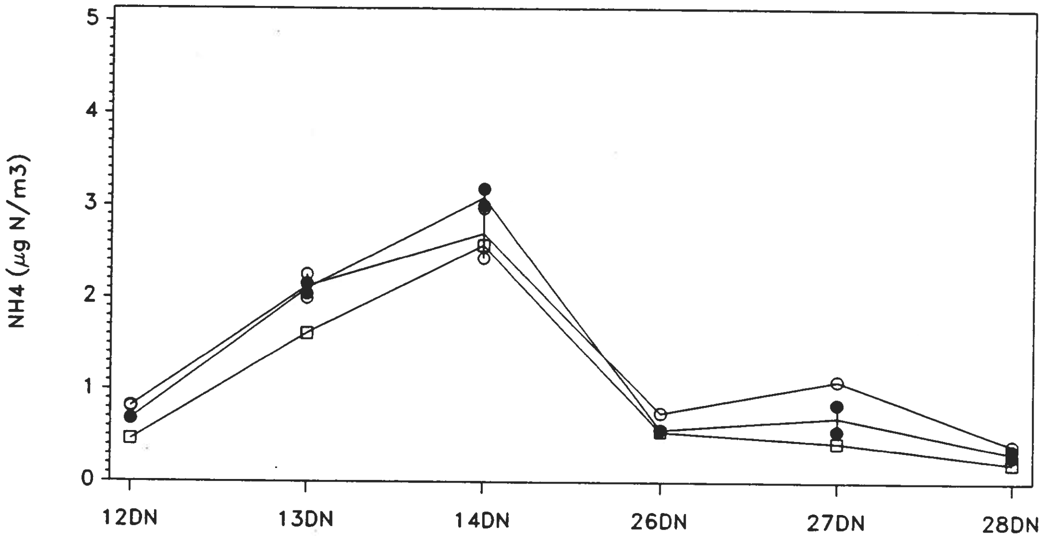

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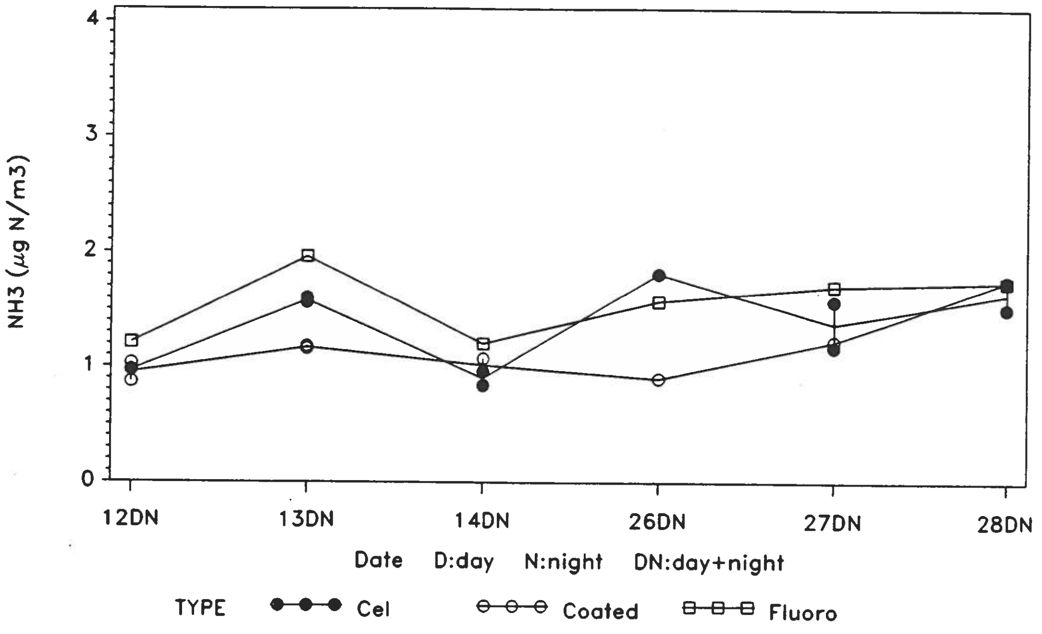

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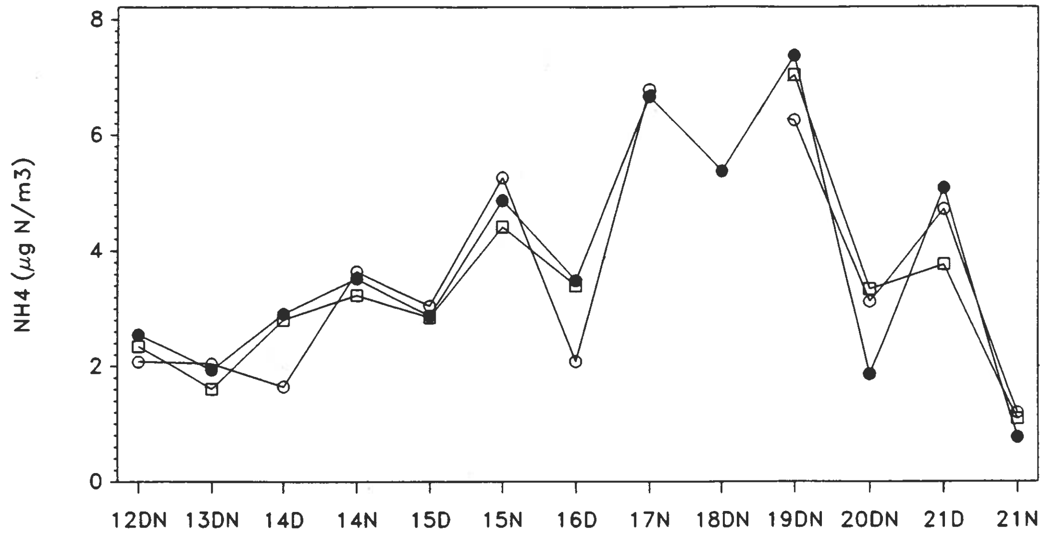

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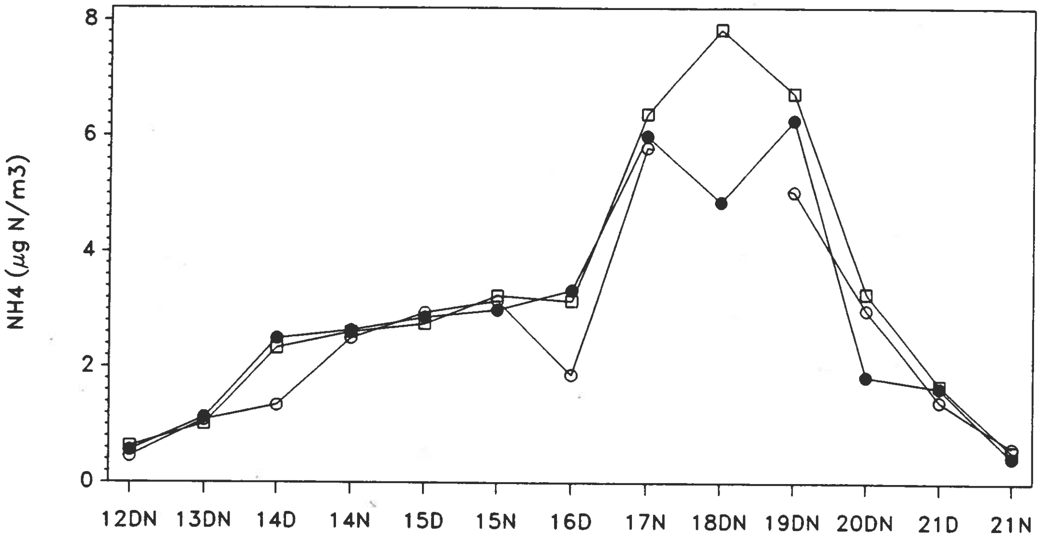

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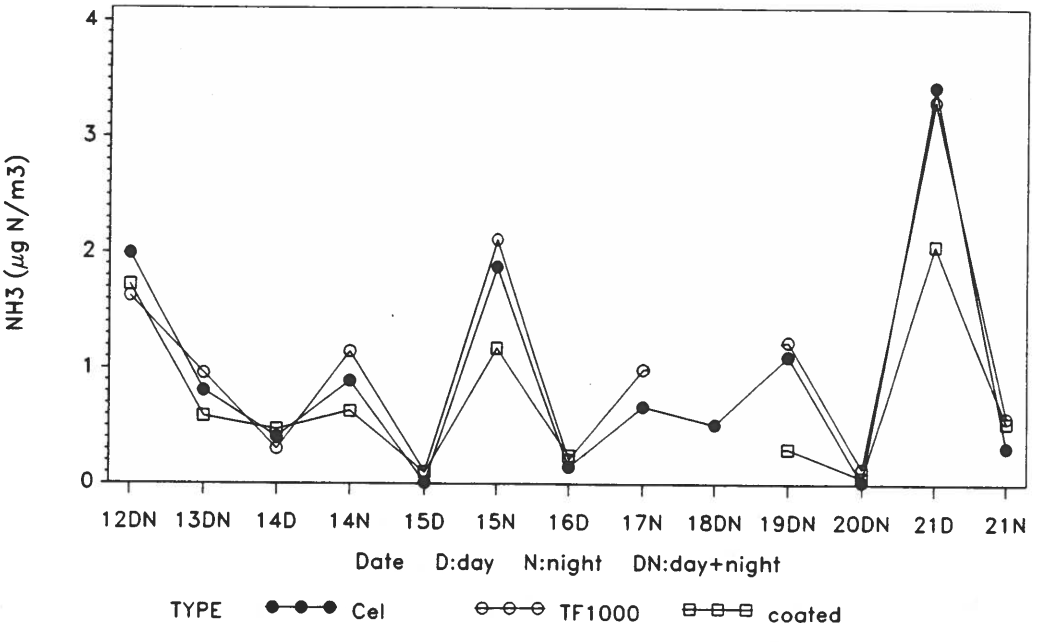

TOTAL AMMONIA + AMMONIUM

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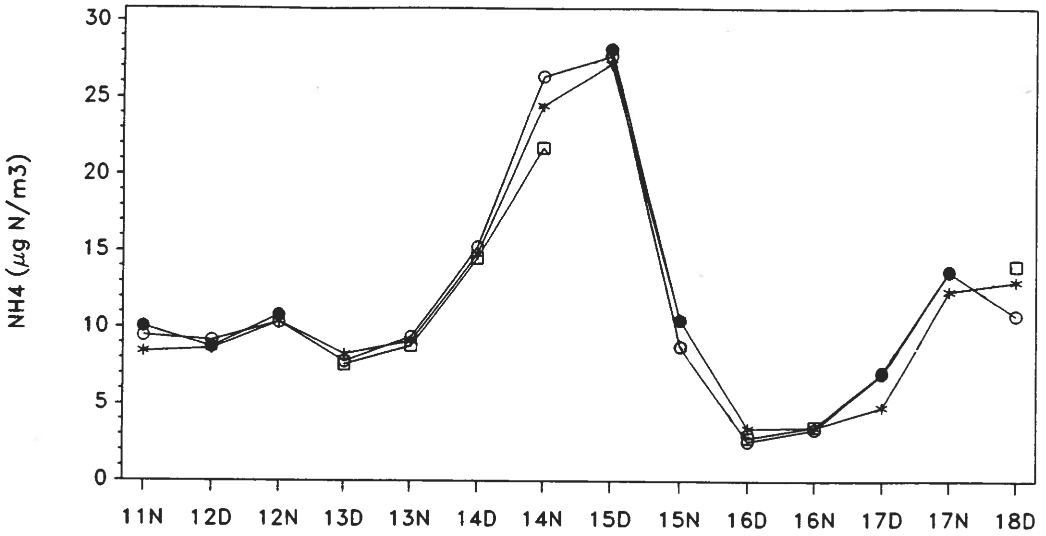

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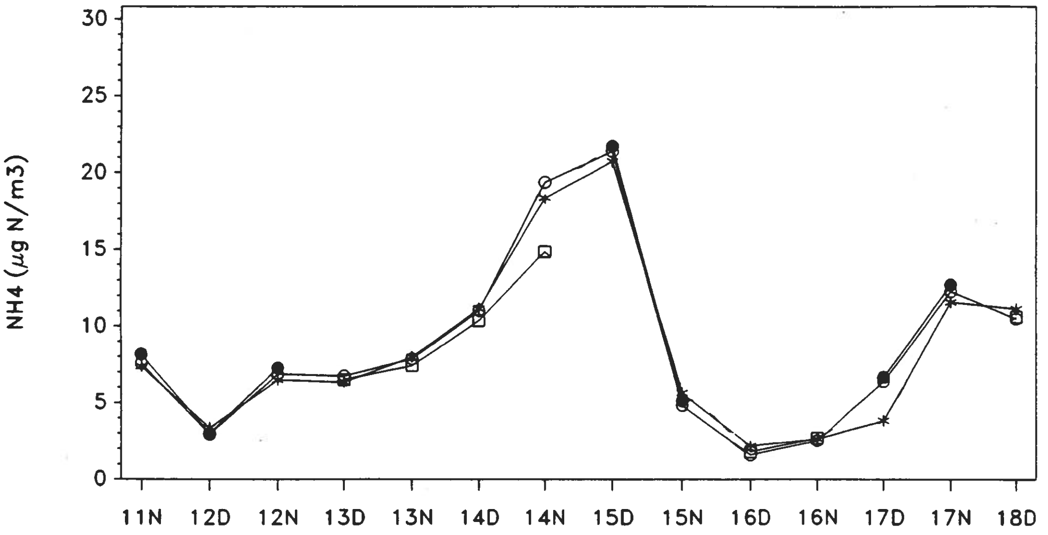

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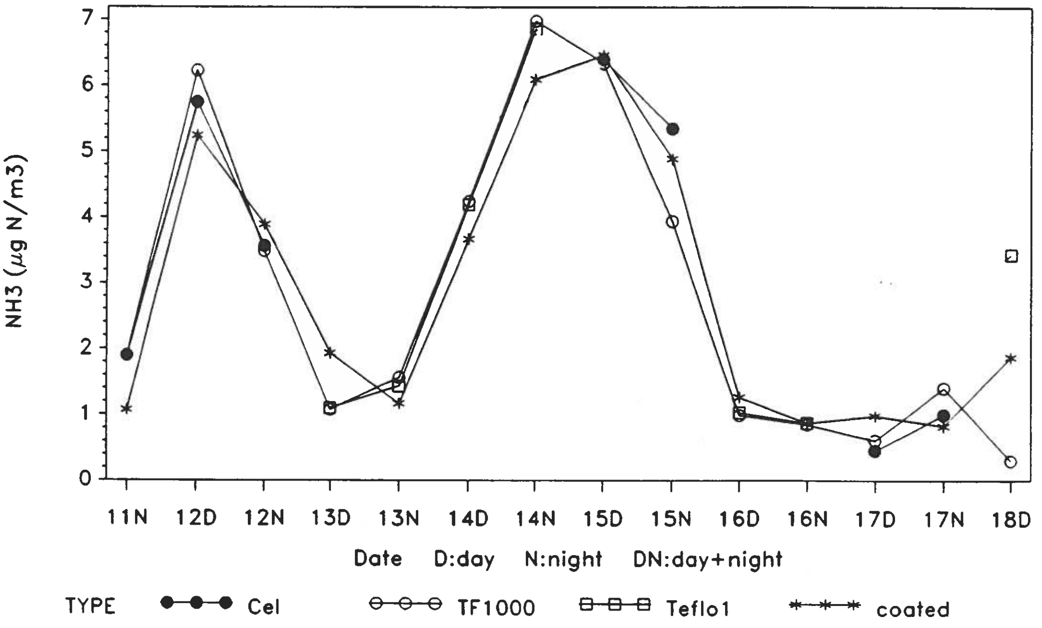

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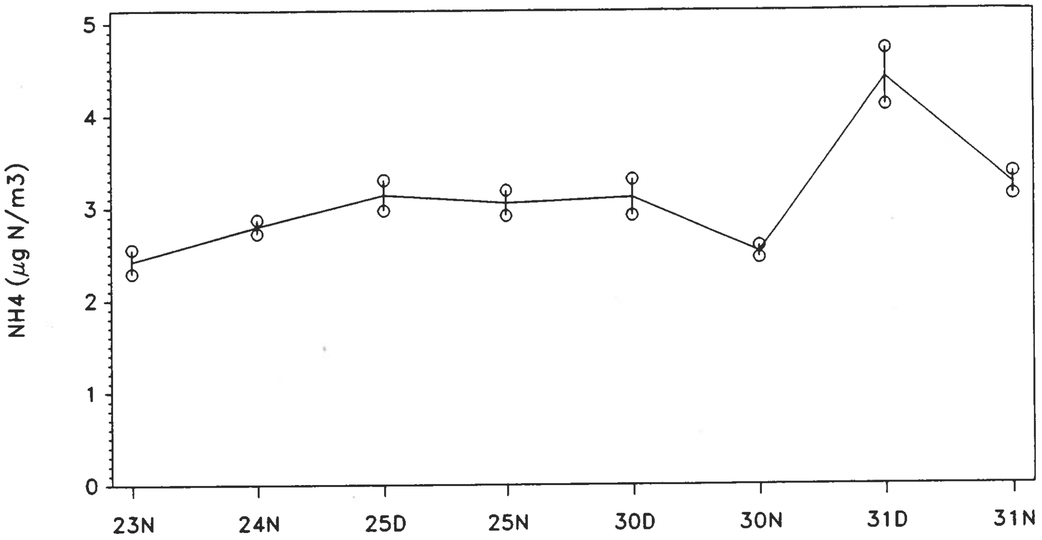

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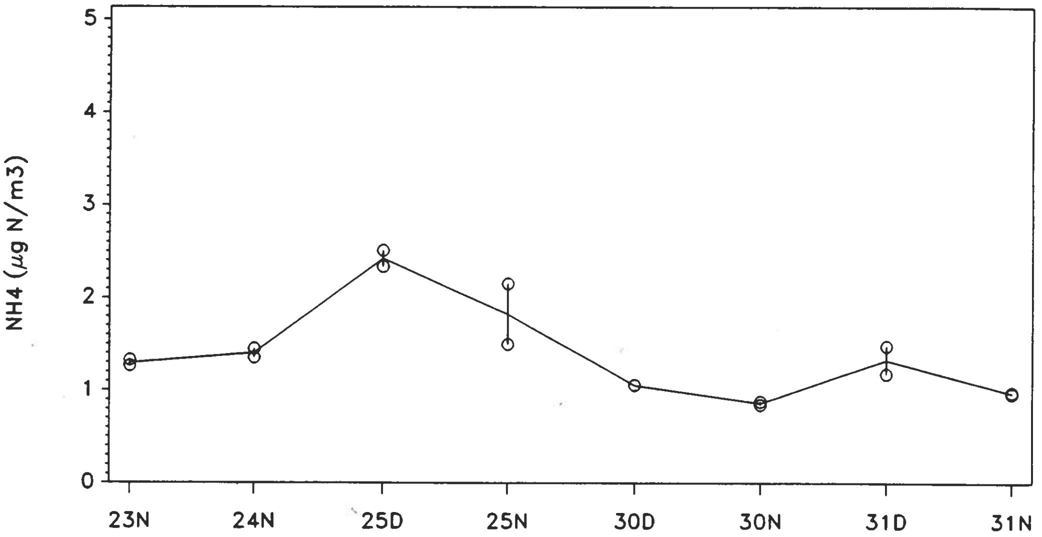

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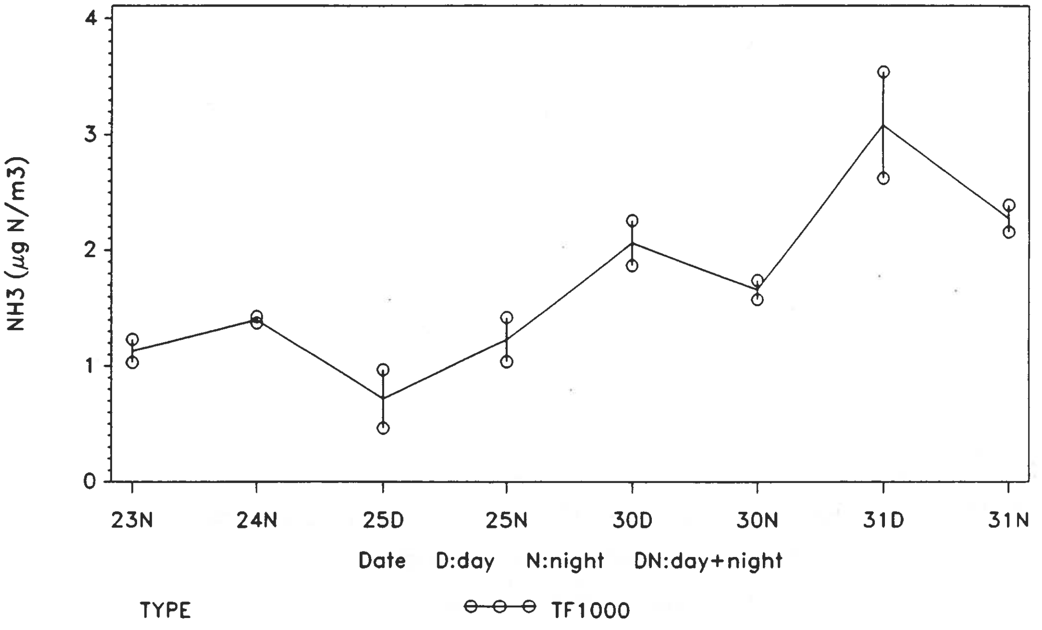

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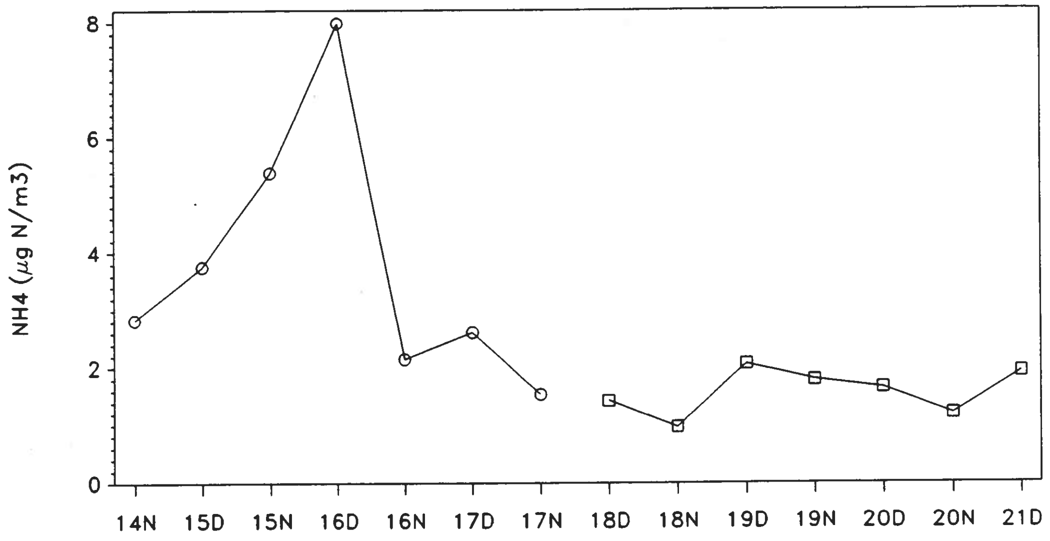

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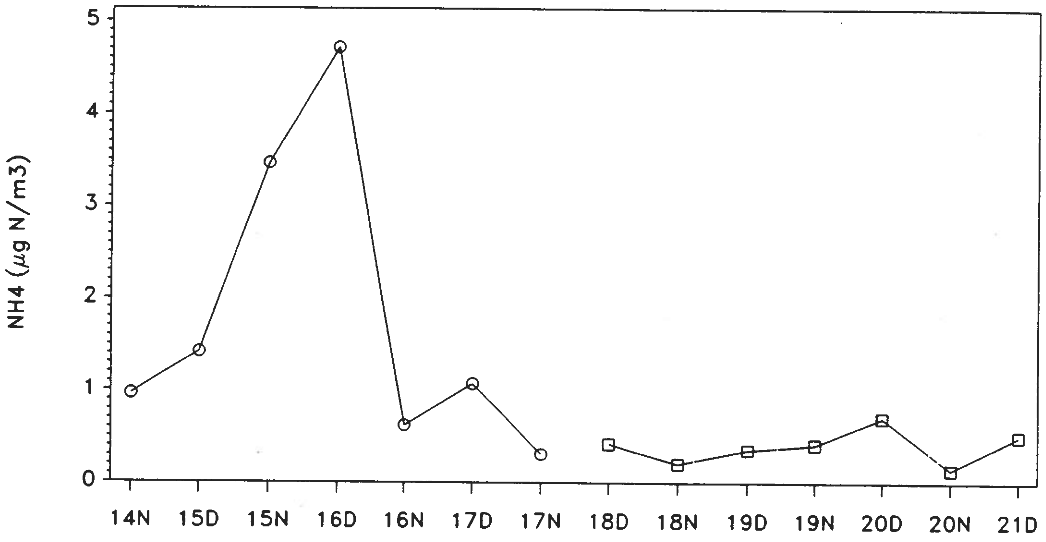

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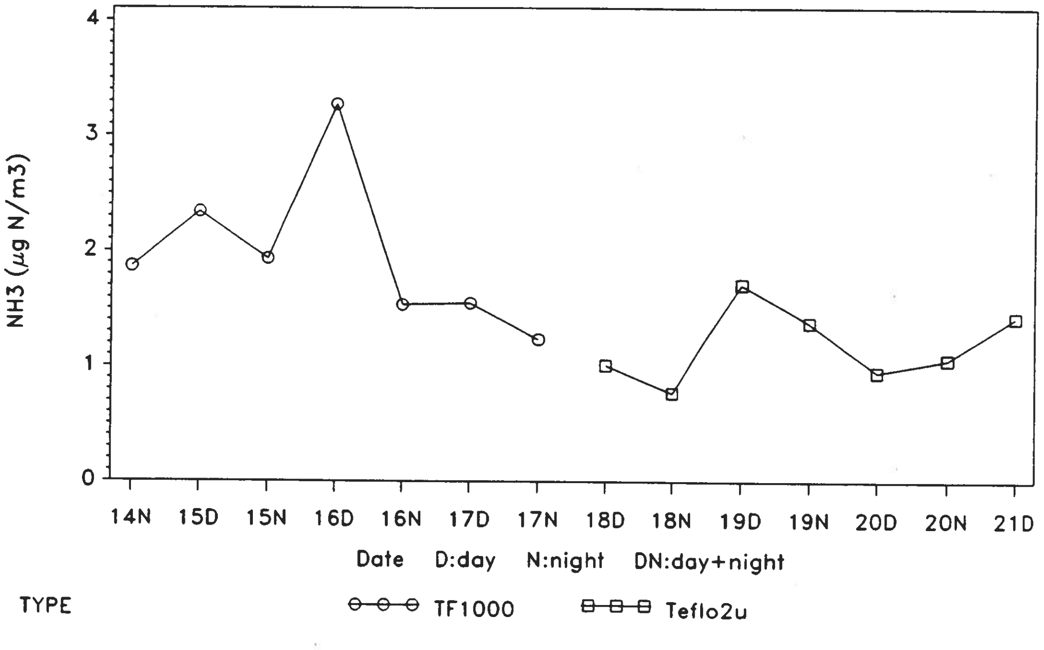

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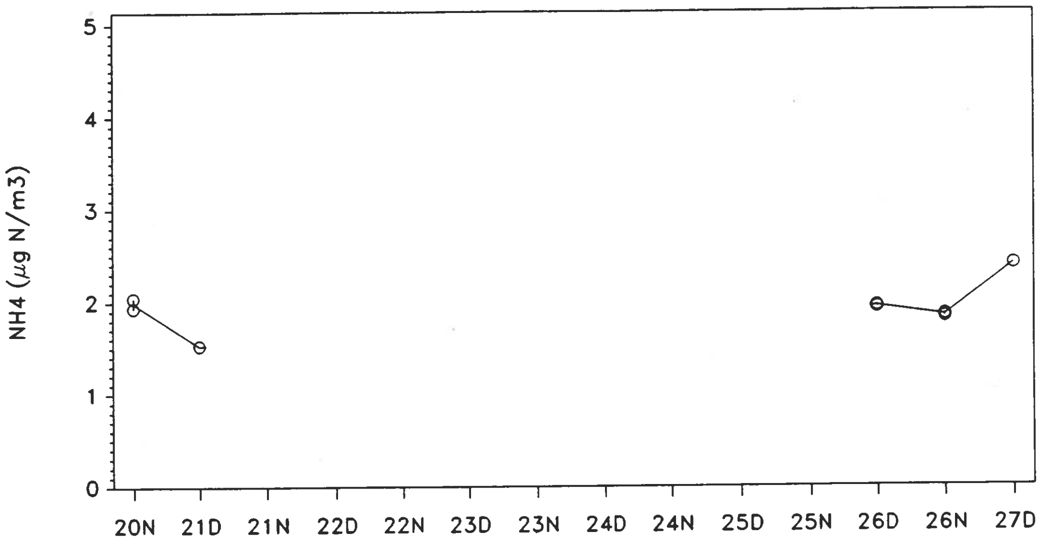

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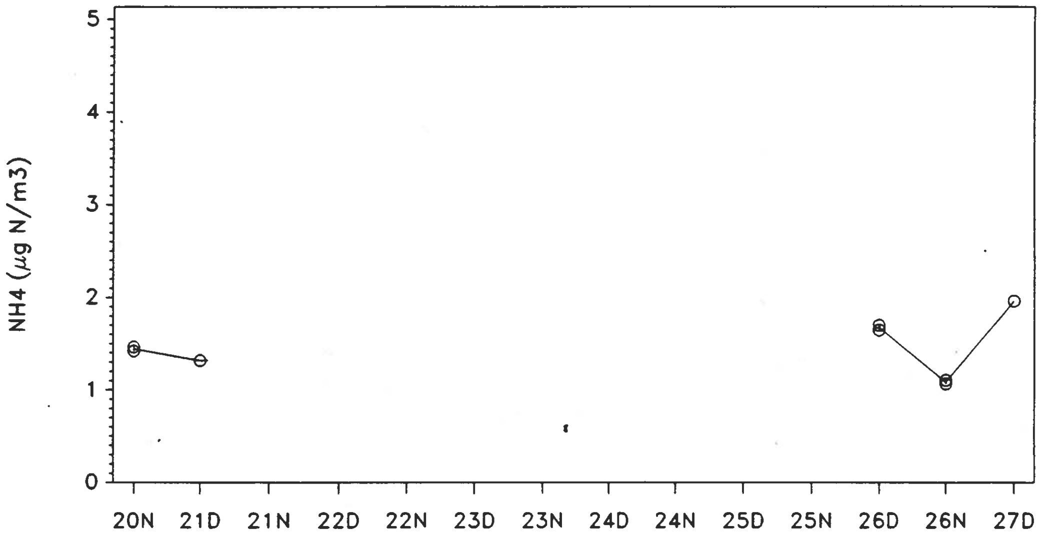

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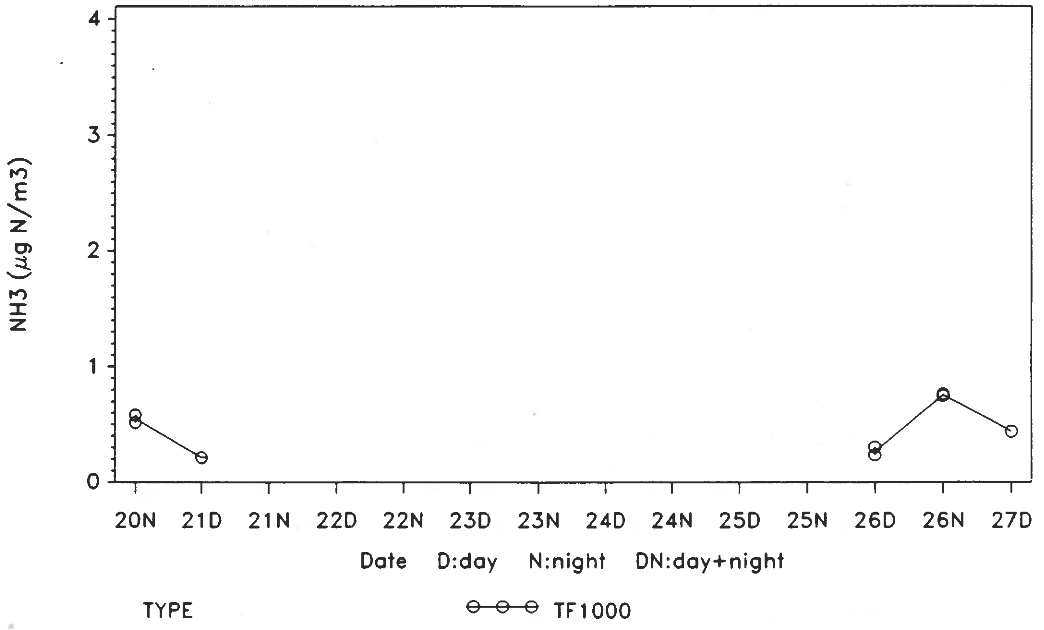

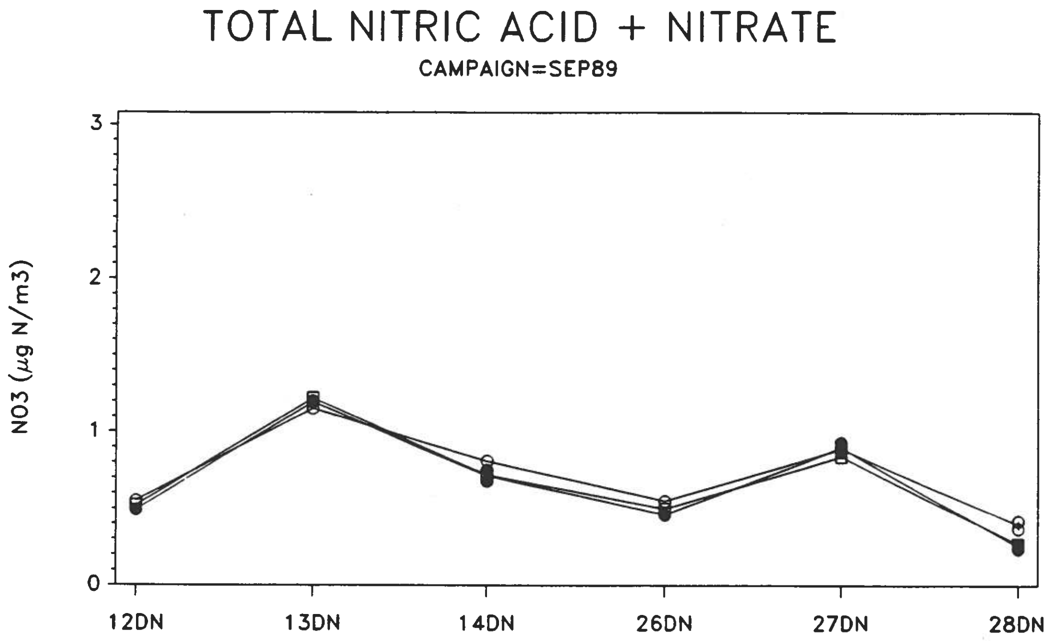
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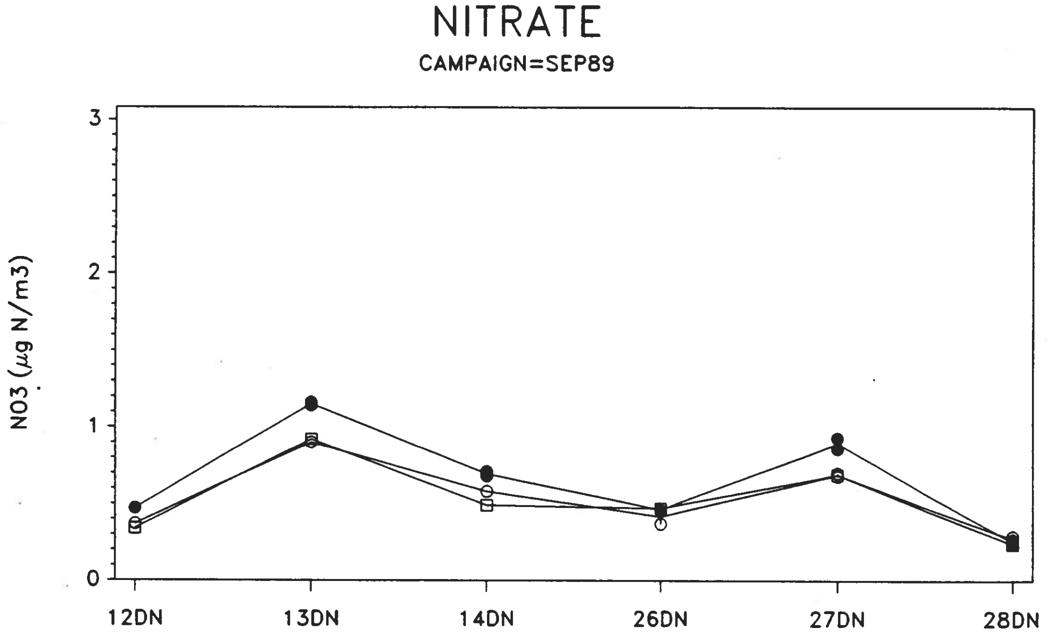
1
2
3
12DN
13DN
14DN
26DN
27DN
28DN


NITRATE
CAMPAIGN=SEP89
NO3 (μg N/m3)
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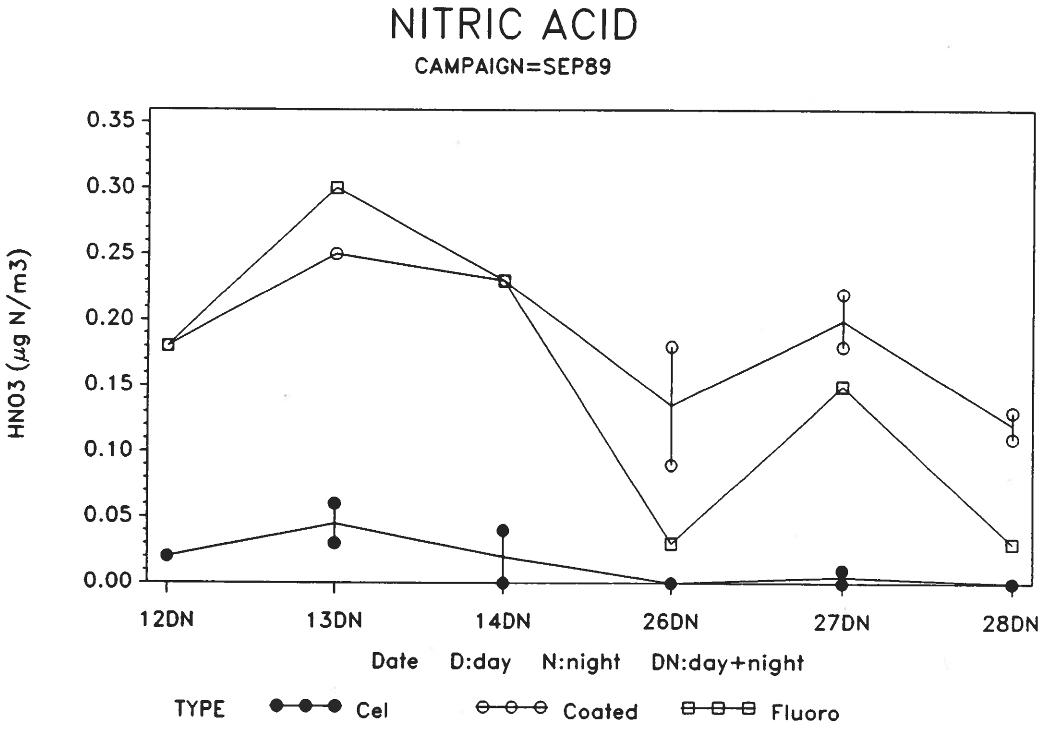
1
2
3
12DN
13DN
14DN
26DN
27DN
28DN


NITRIC ACID
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0.05
0.10
0.15
0.20
0.25
0.30
0.35
12DN
13DN
14DN
26DN
27DN
28DN
Date D:day N:night DN:day+night
TYPE
●–●–● Cel
○–○–○ Coated
□–□–□ Fluoro

TOTAL NITRIC ACID + NITRATE

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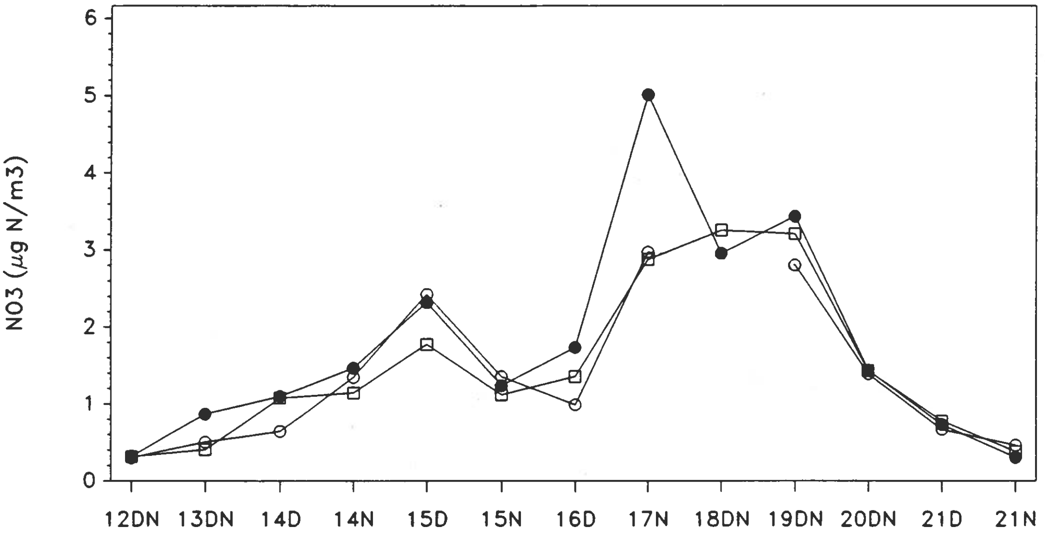

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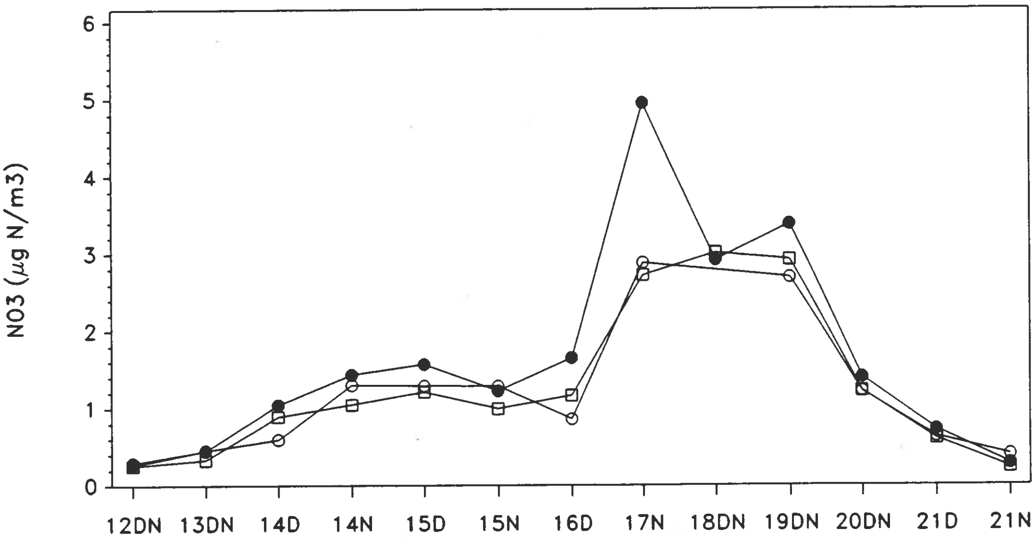

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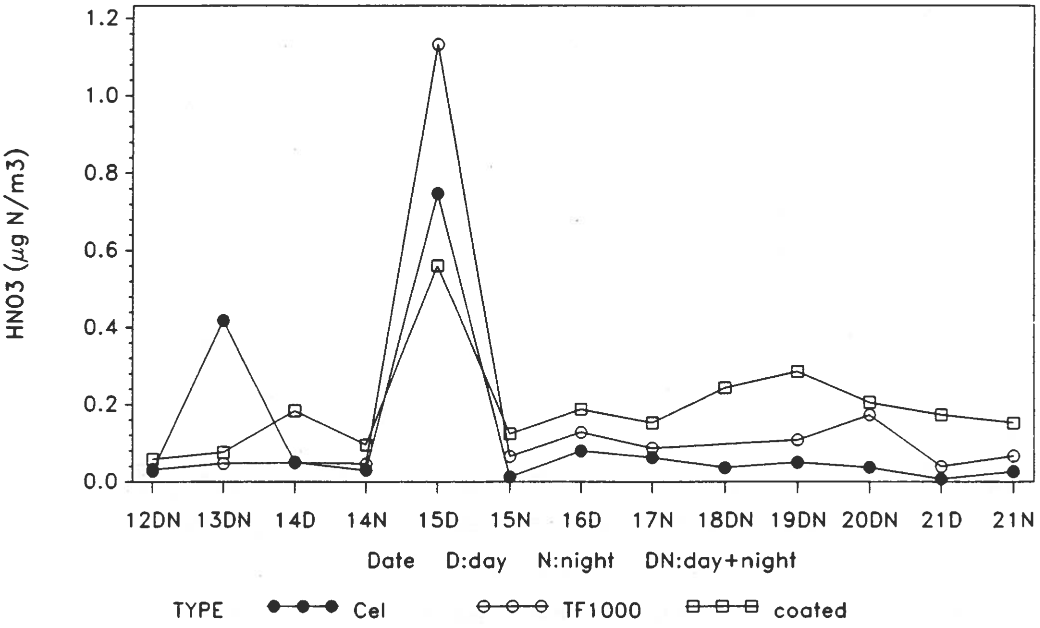

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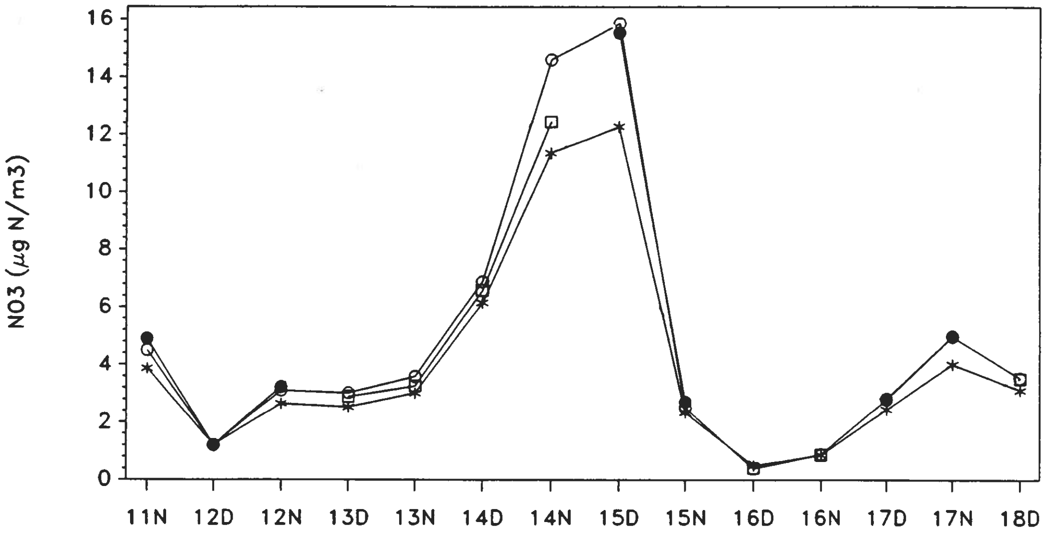

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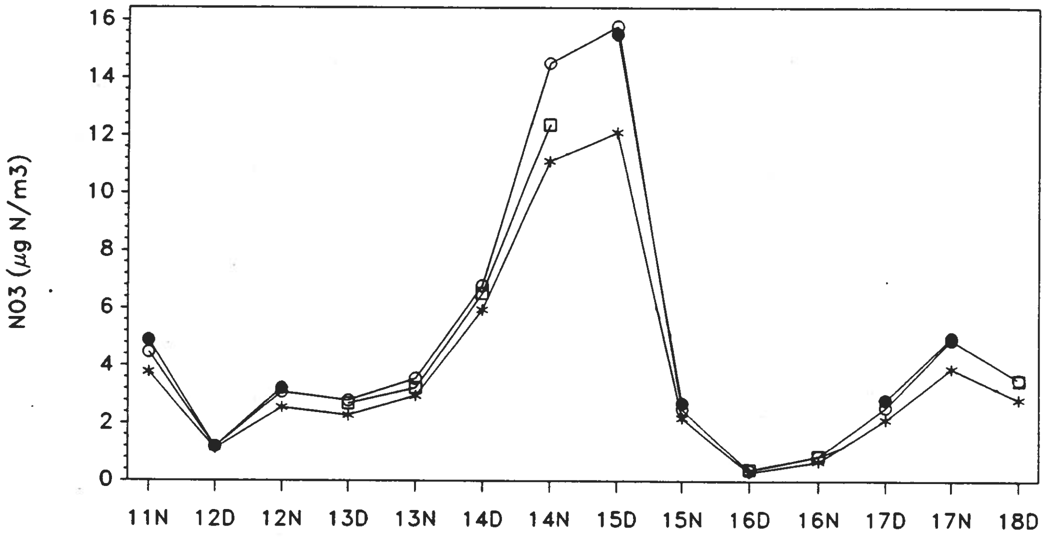

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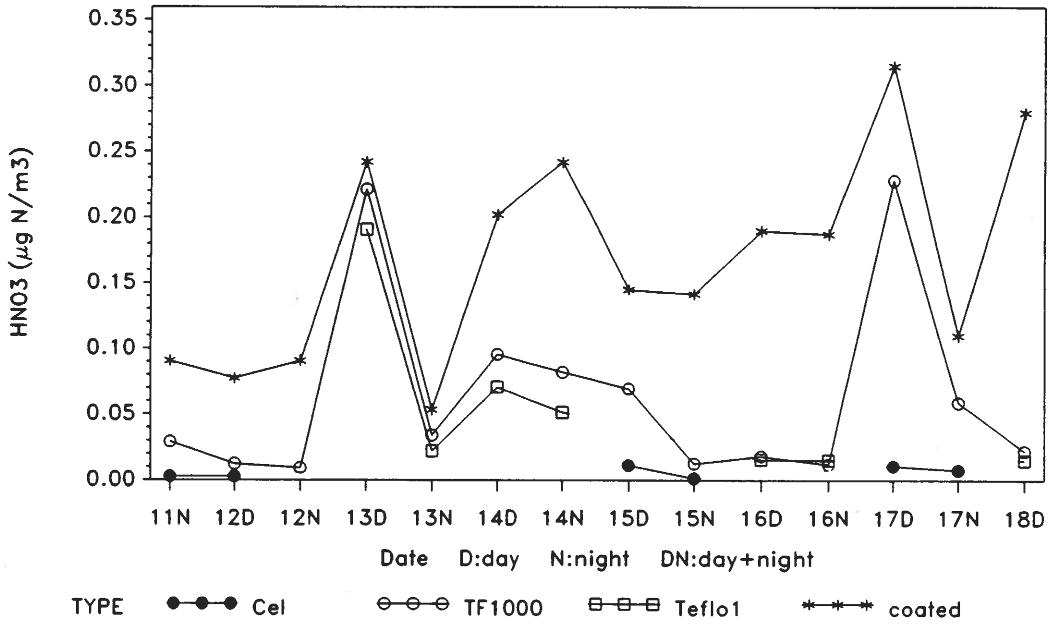

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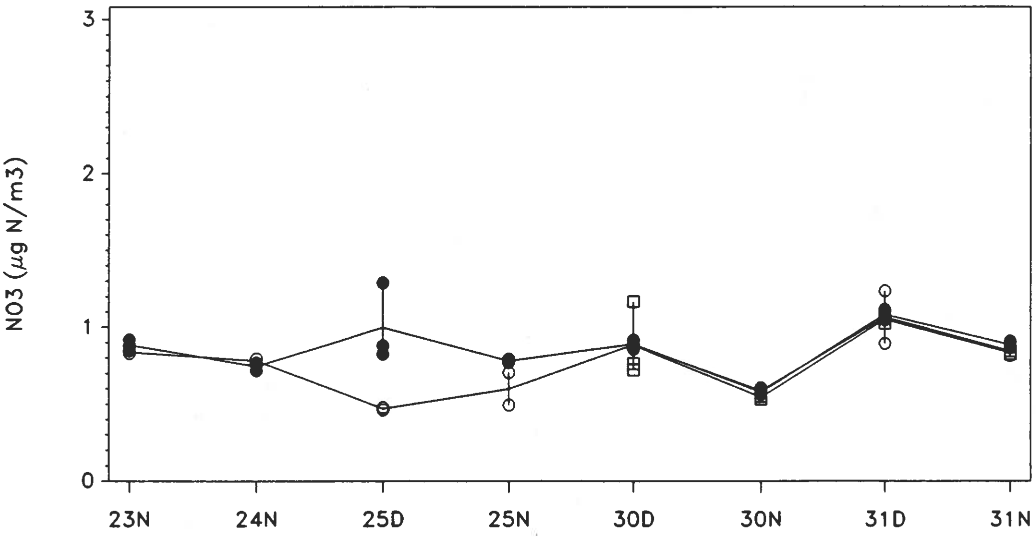

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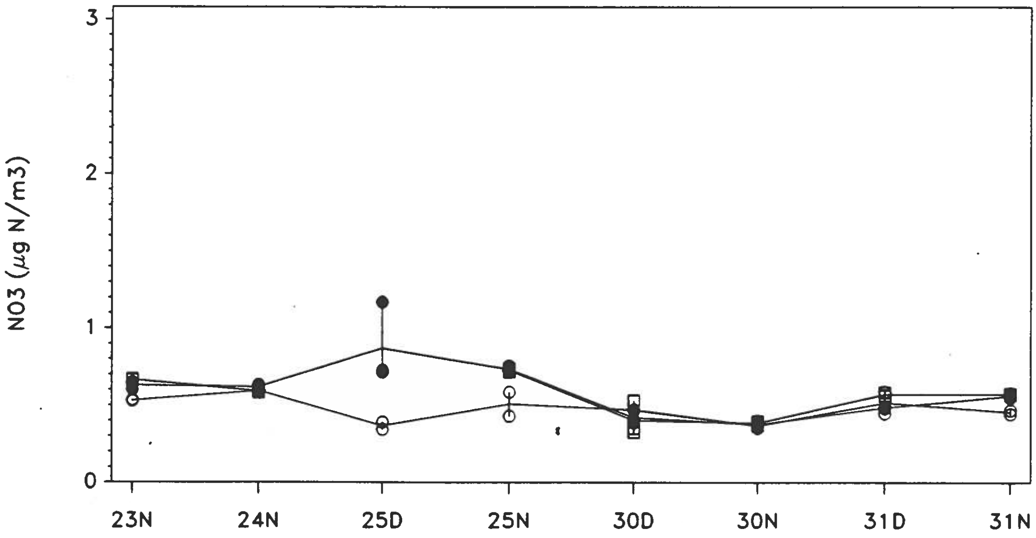

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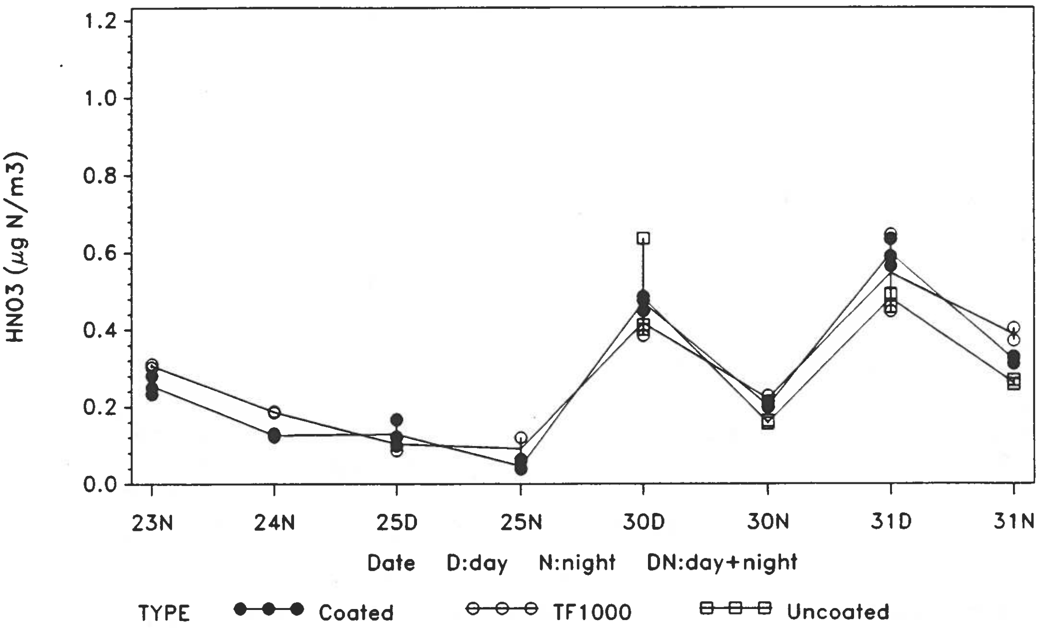

TOTAL NITRIC ACID + NITRATE

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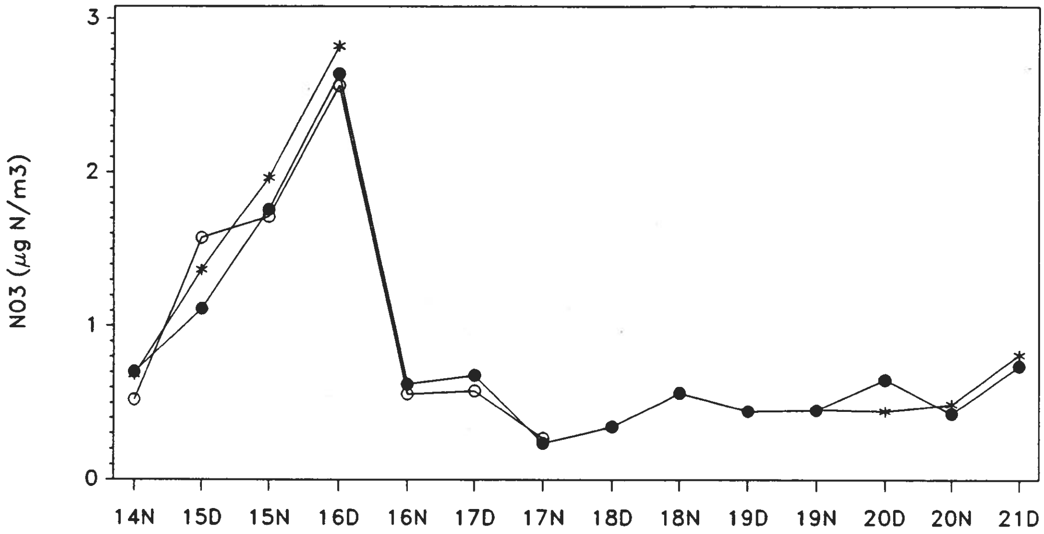

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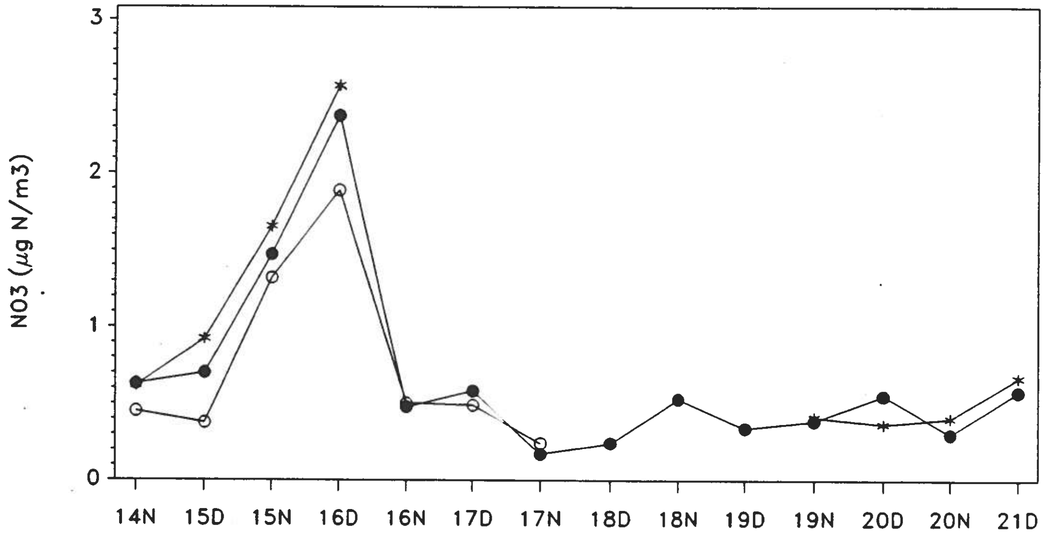

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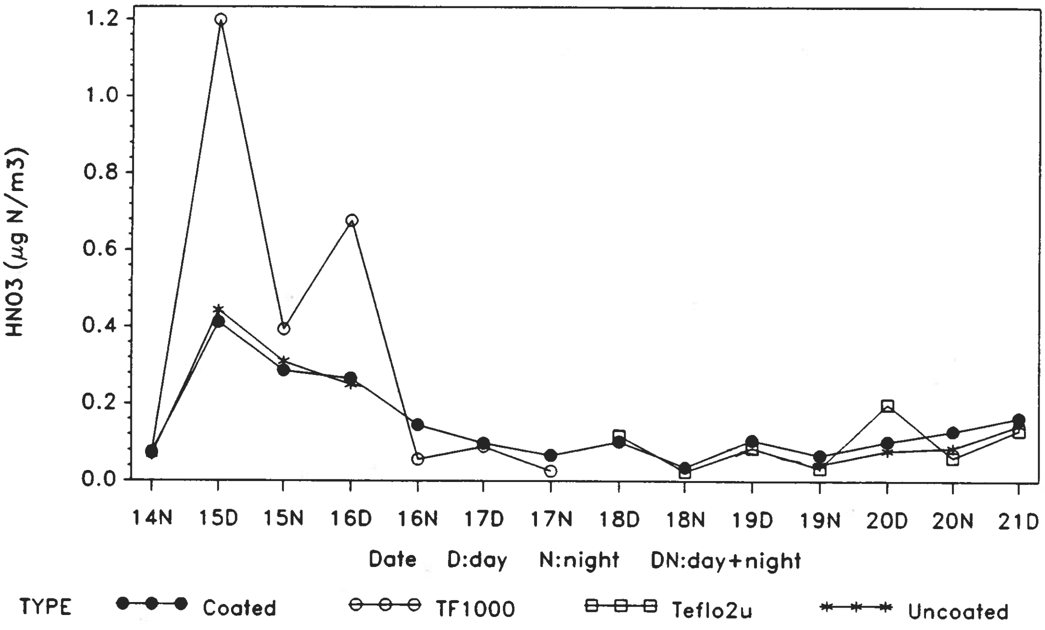

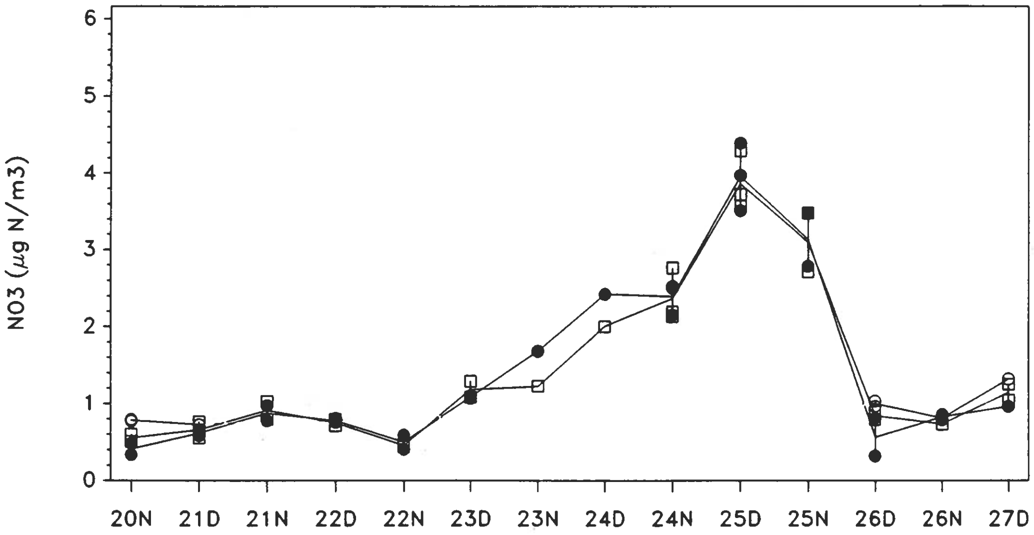

TOTAL NITRIC ACID + NITRATE

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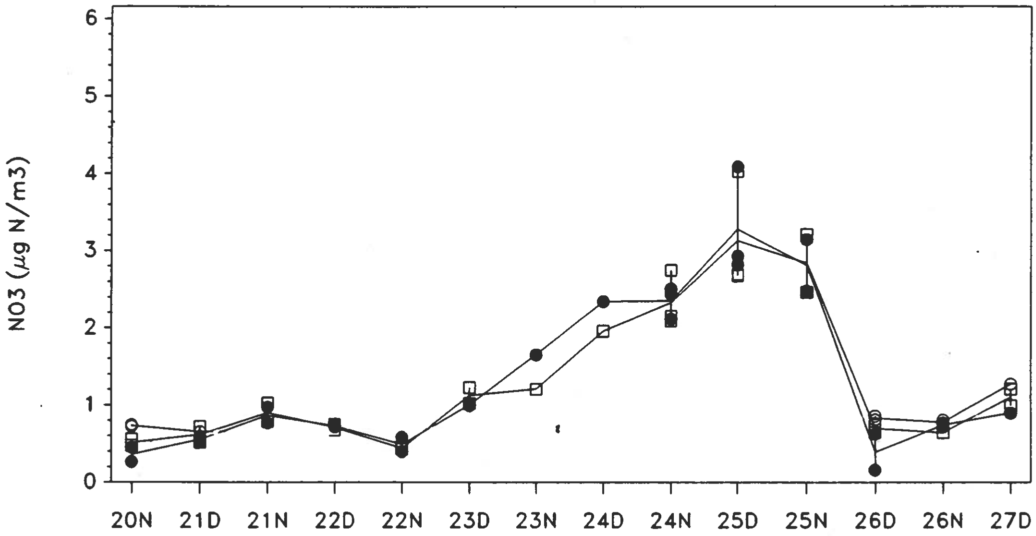

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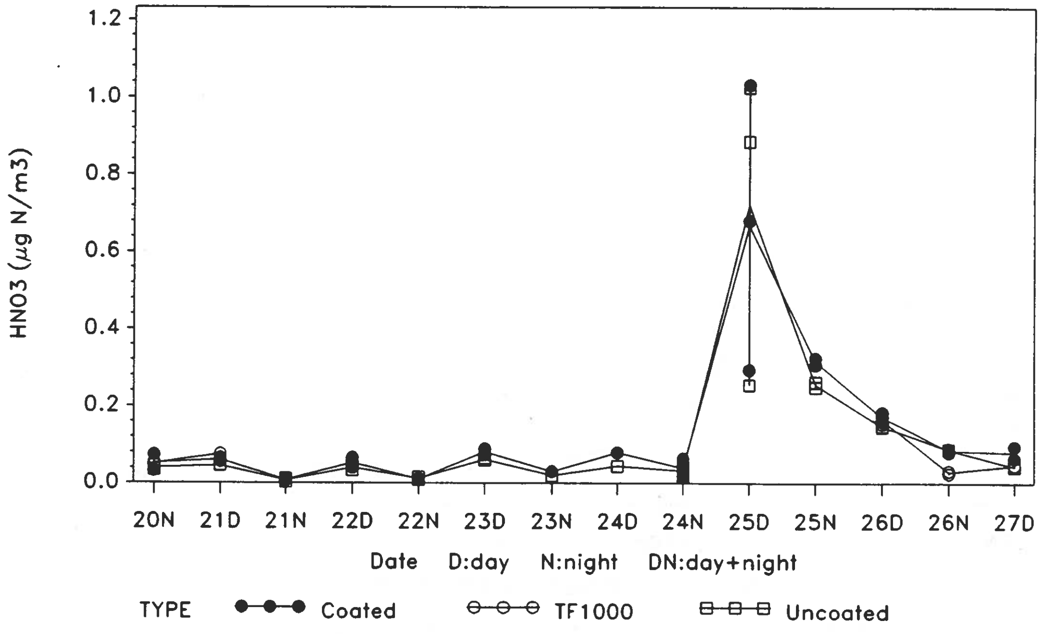
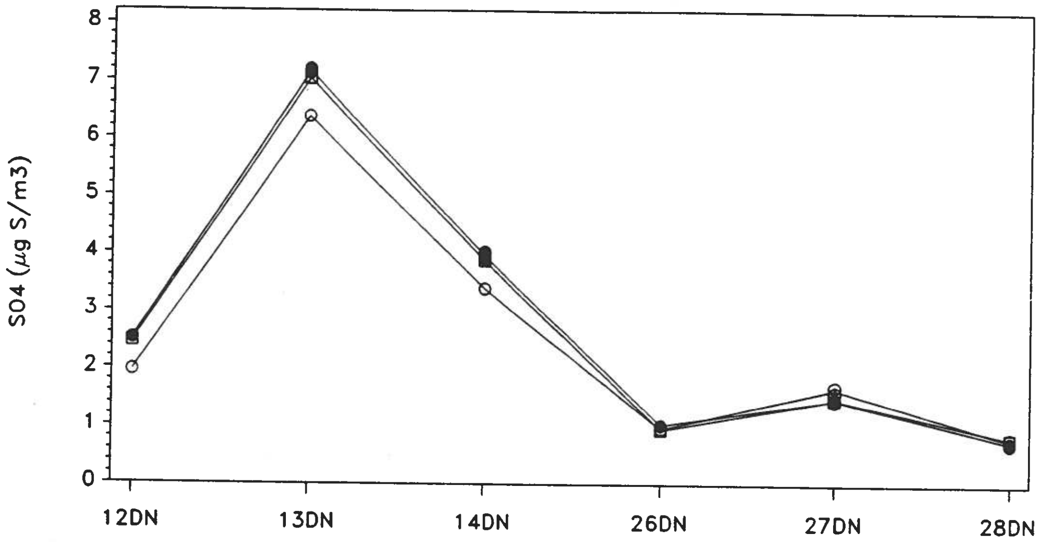


NITRIC ACID

CAMPAIGN=JAN92

TOTAL SULFUR DIOXIDE + SULFATE

CAMPAIGN=SEP89



SULFATE

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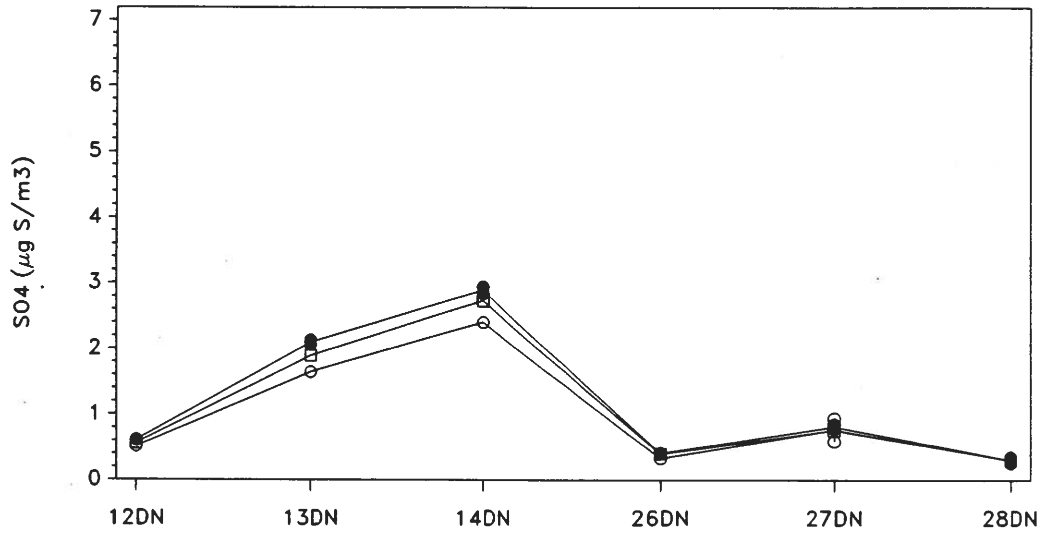

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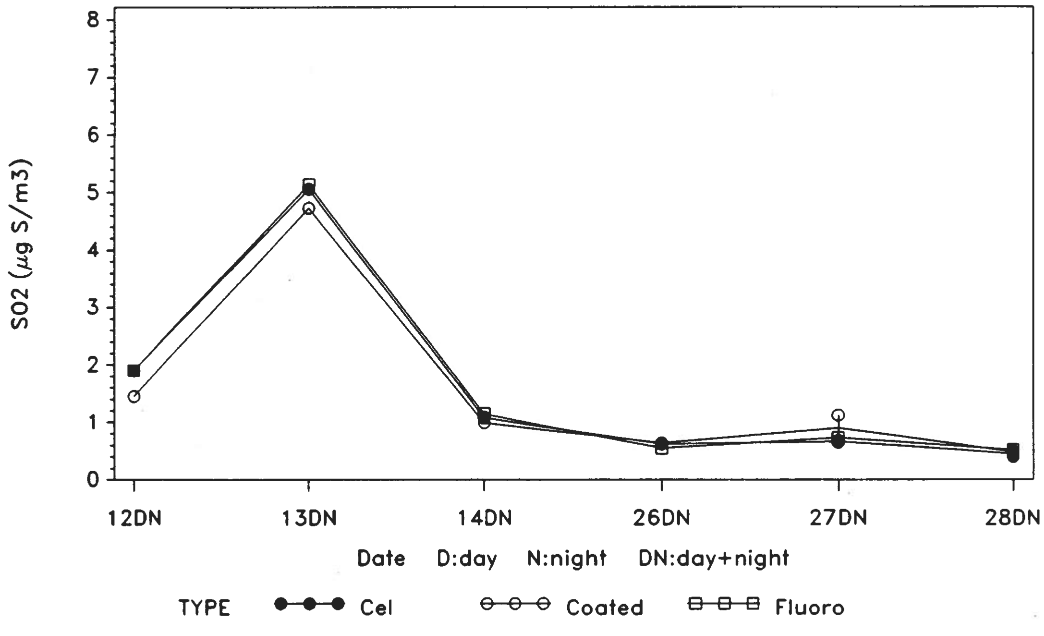

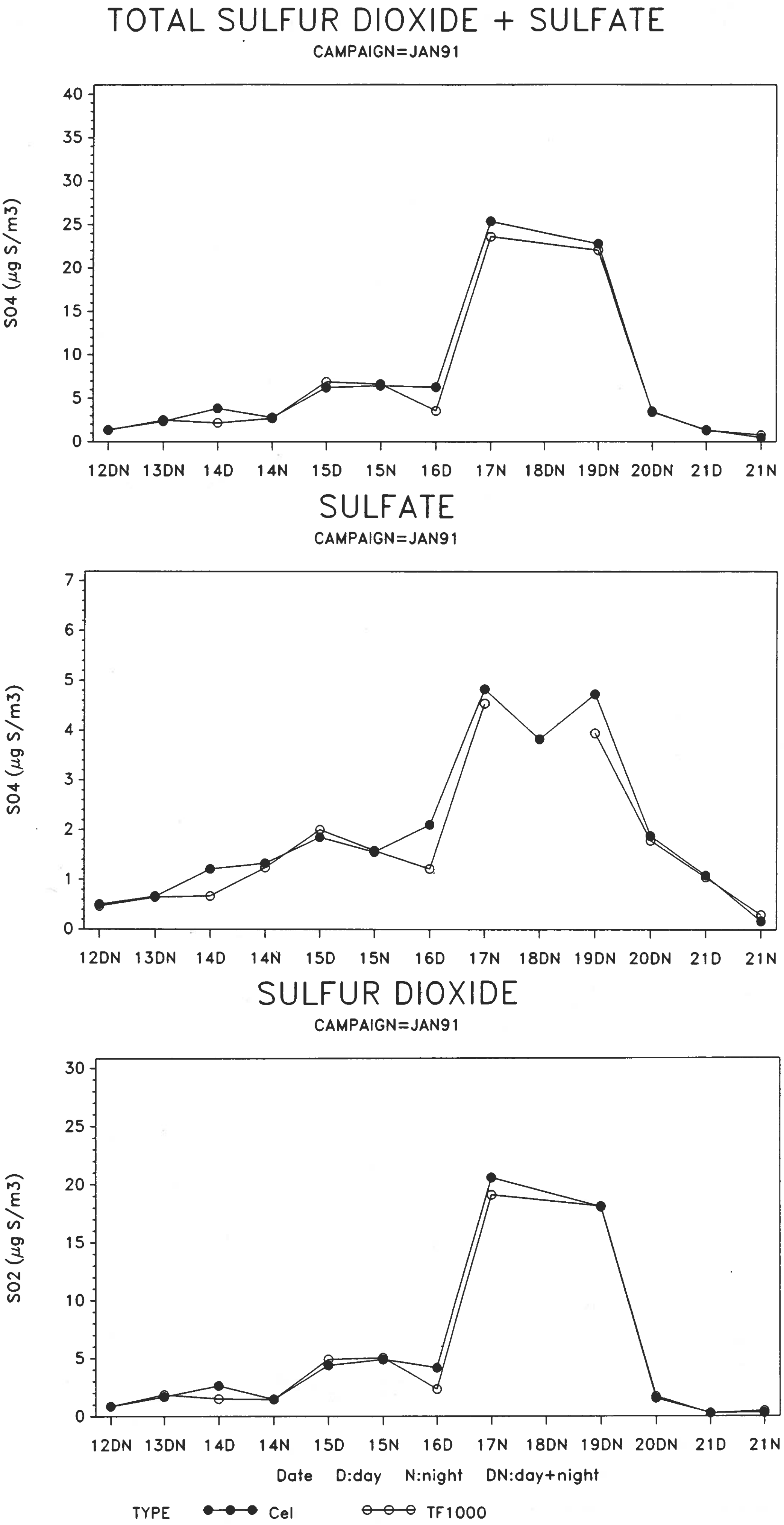

TOTAL SULFUR DIOXIDE + SULFATE

CAMPAIGN=JAN91

SULFATE

CAMPAIGN=JAN91

SULFUR DIOXIDE

CAMPAIGN=JAN91

TOTAL SULFUR DIOXIDE + SULFATE

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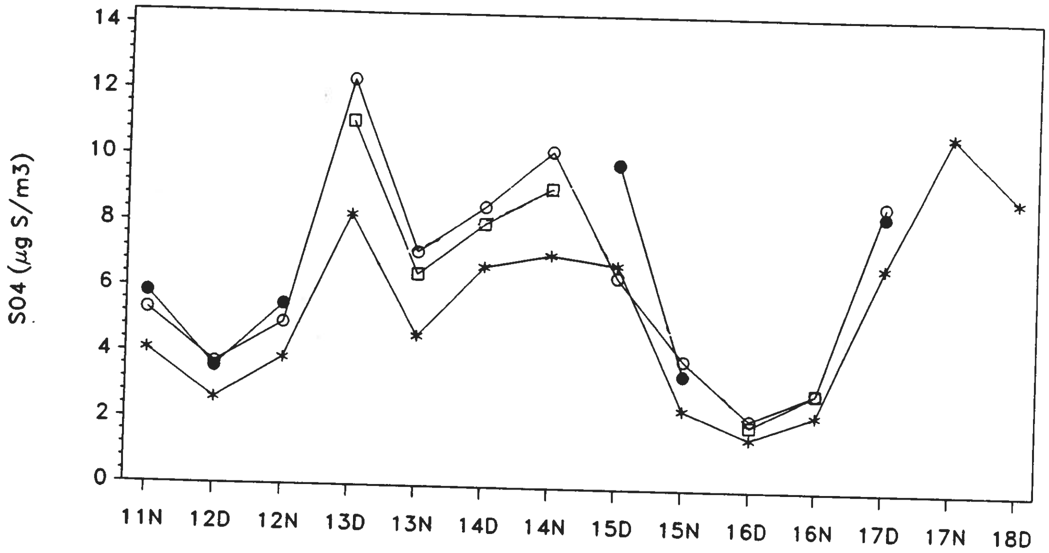

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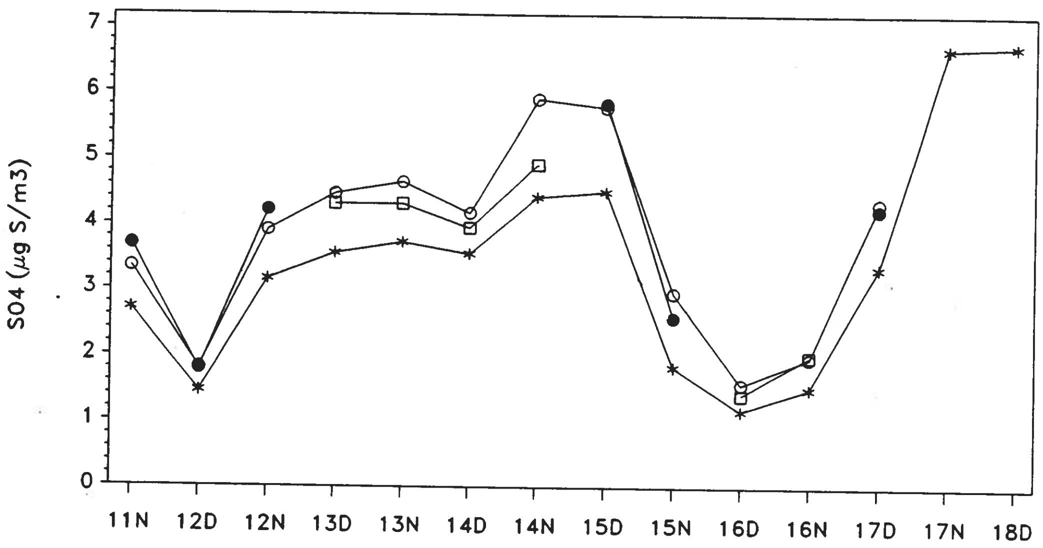

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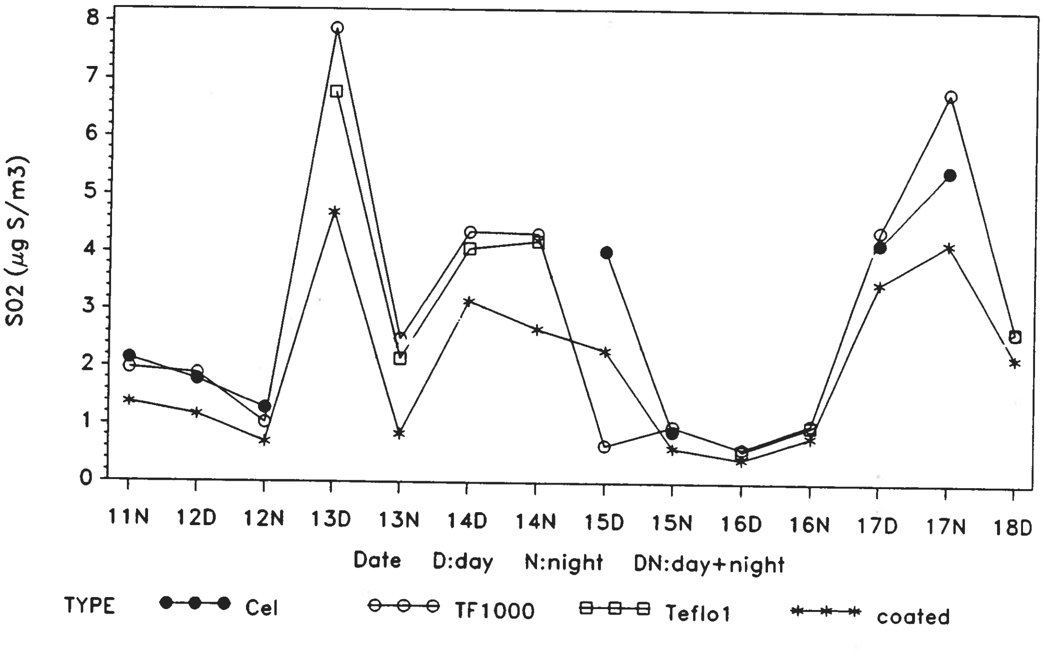

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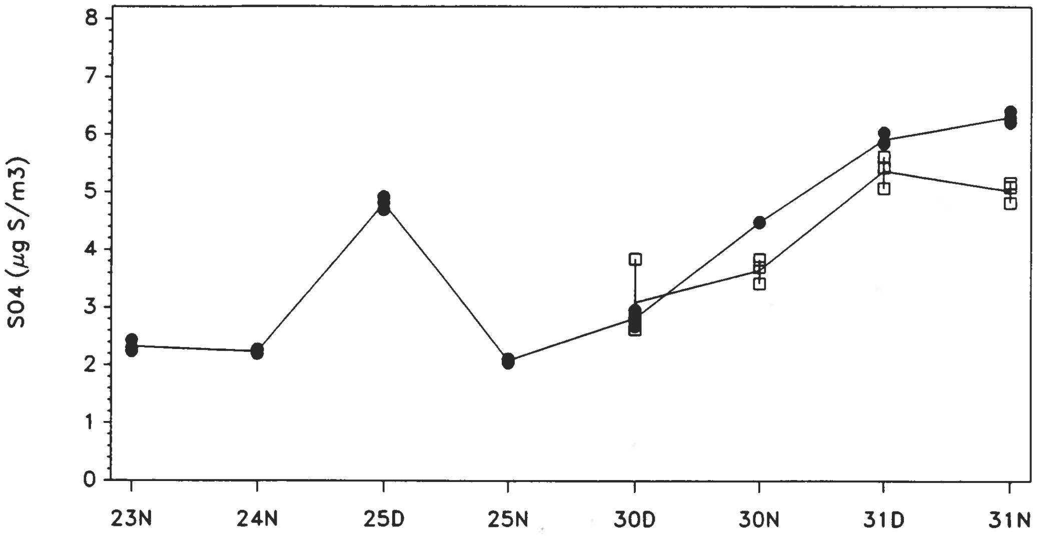

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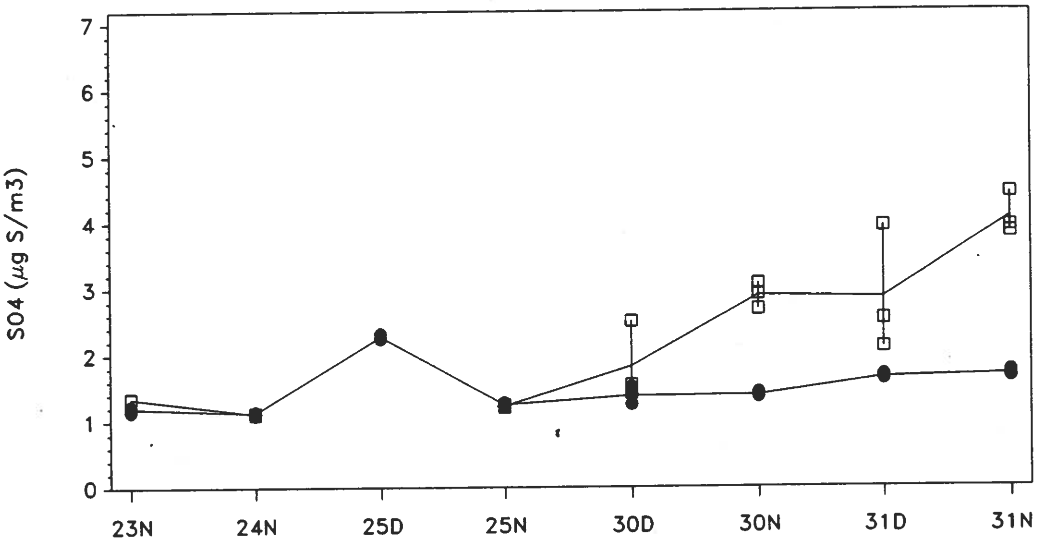

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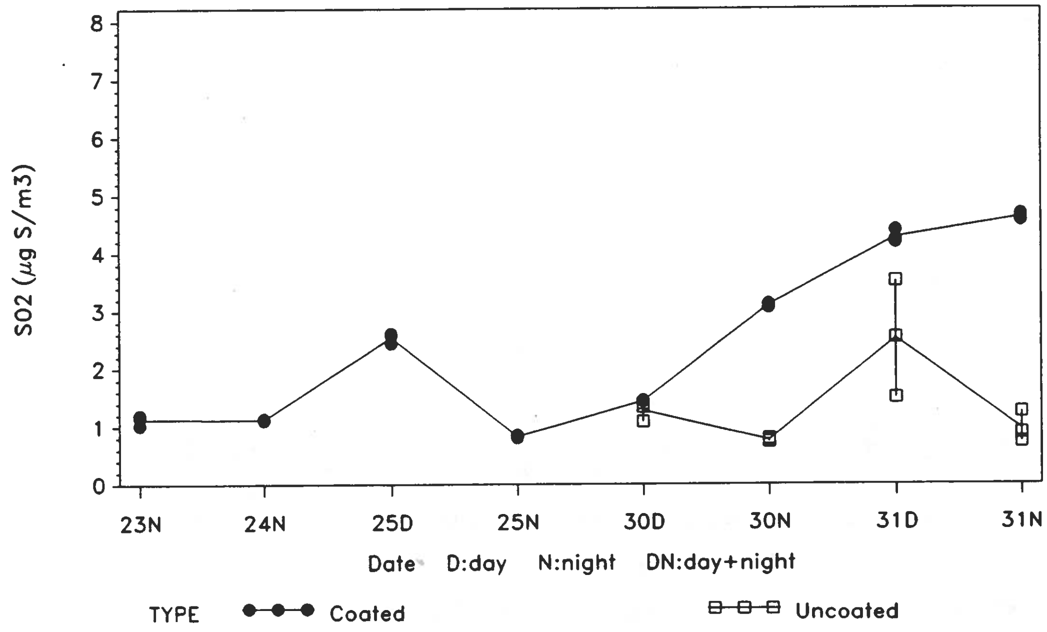

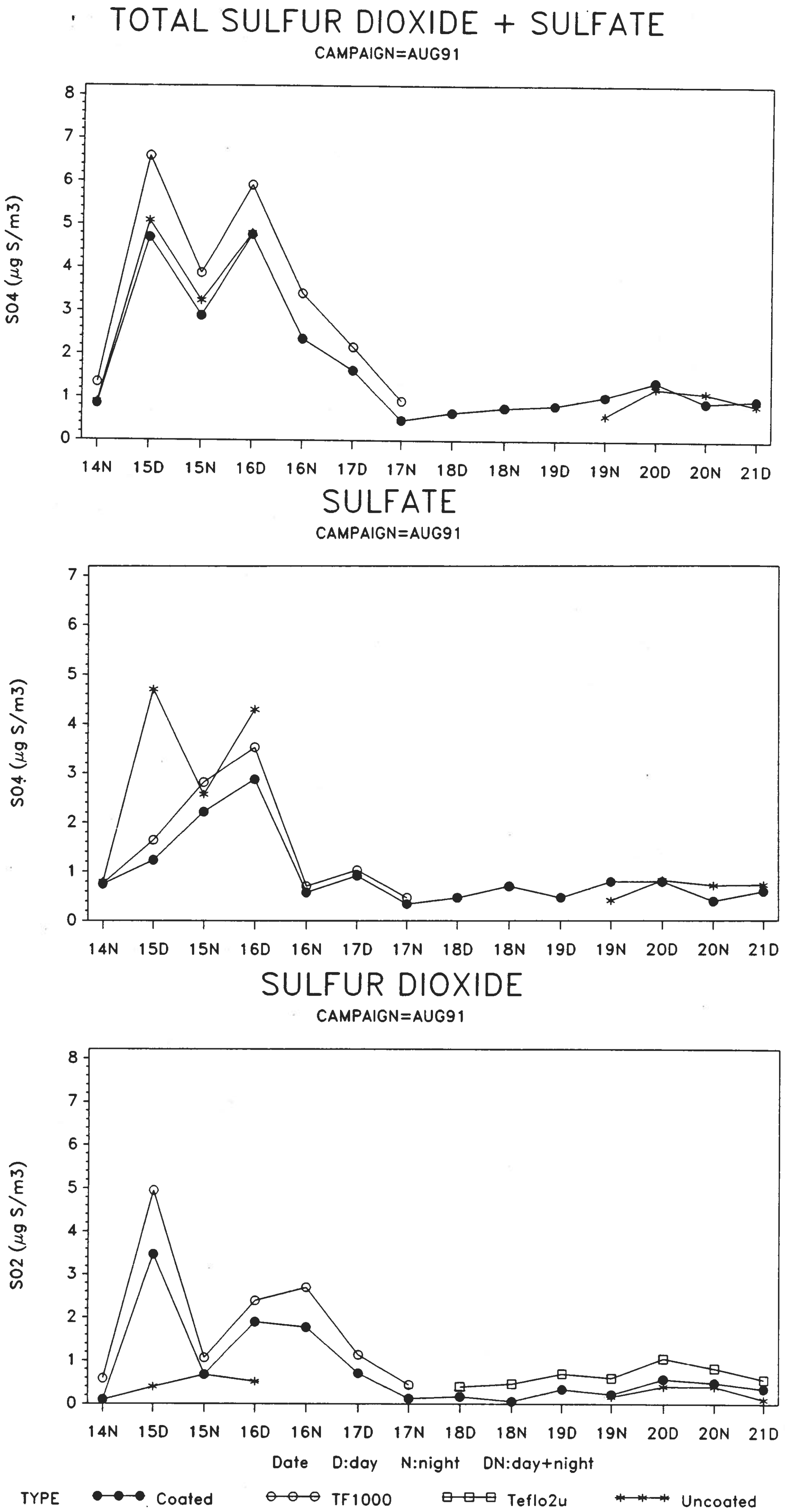
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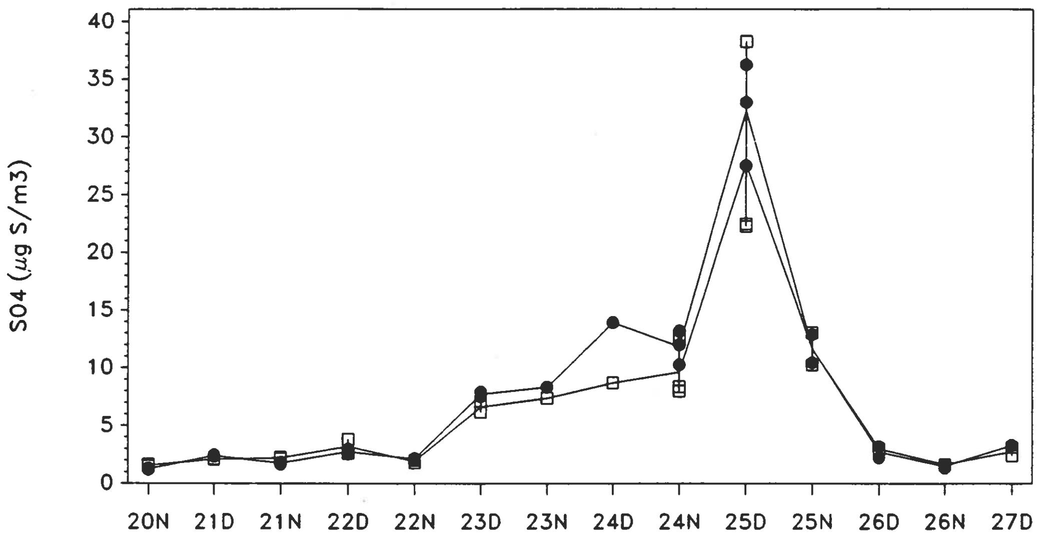
0
1
2
3
4
5
6
7
8
14N
15D
15N
16D
16N
17D
17N
18D
18N
19D
19N
20D
20N
21D
SULFATE
CAMPAIGN=AUG91
SO4 (μg S/m3)
0
1
2
3
4
5
6
7
14N
15D
15N
16D
16N
17D
17N
18D
18N
19D
19N
20D
20N
21D
SULFUR DIOXIDE
CAMPAIGN=AUG91
SO2 (μg S/m3)
0
1
2
3
4
5
6
7
8
14N
15D
15N
16D
16N
17D
17N
18D
18N
19D
19N
20D
20N
21D
Date D:day N:night DN:day+night
TYPE
Coated
TF1000
Teflo2u
Uncoated



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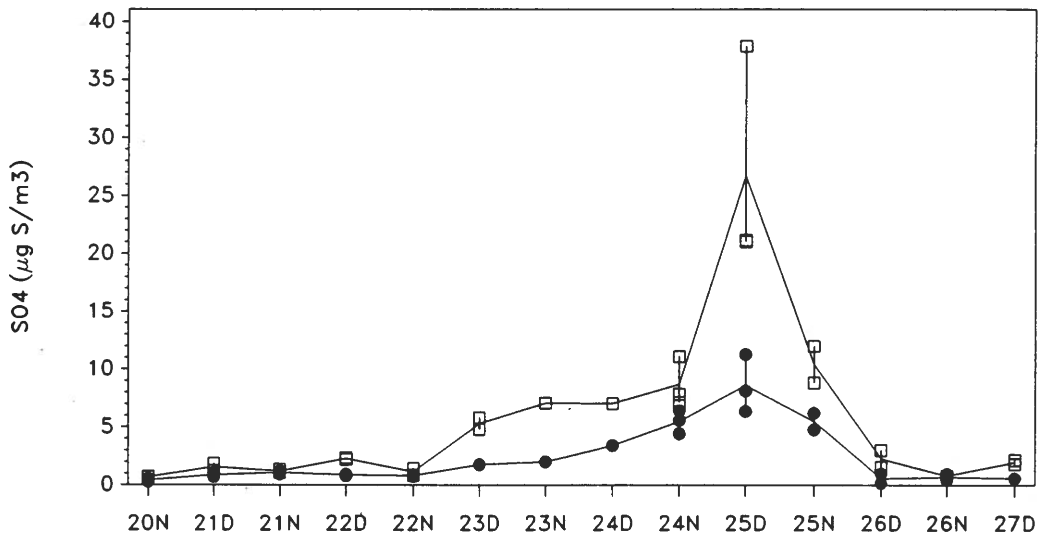

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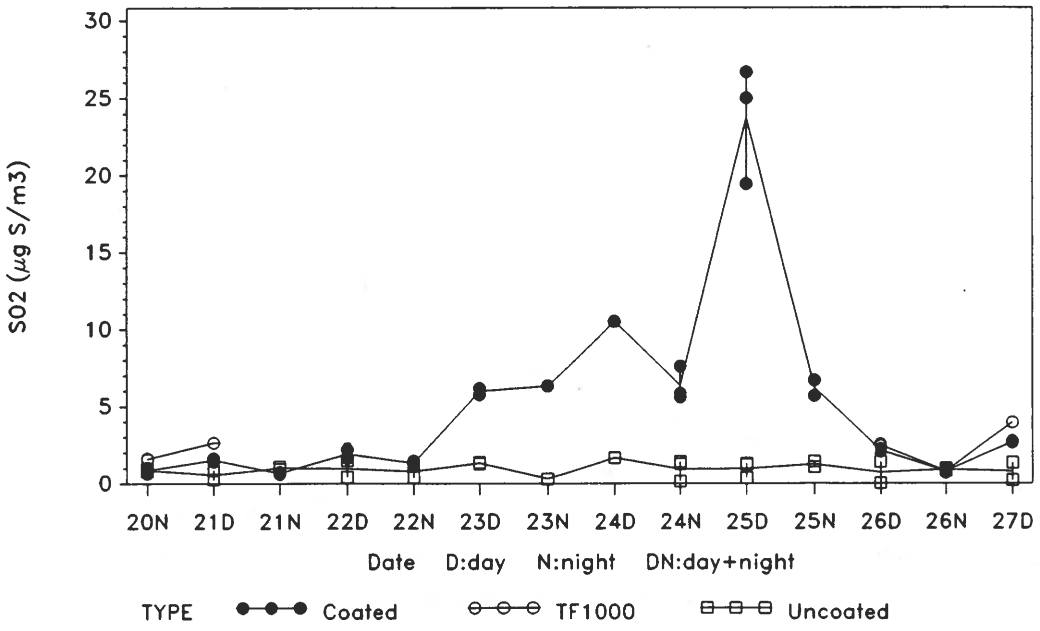

SULFUR DIOXIDE

CAMPAIGN=JAN92

TOTAL NITROUS ACID + NITRITE + interferences

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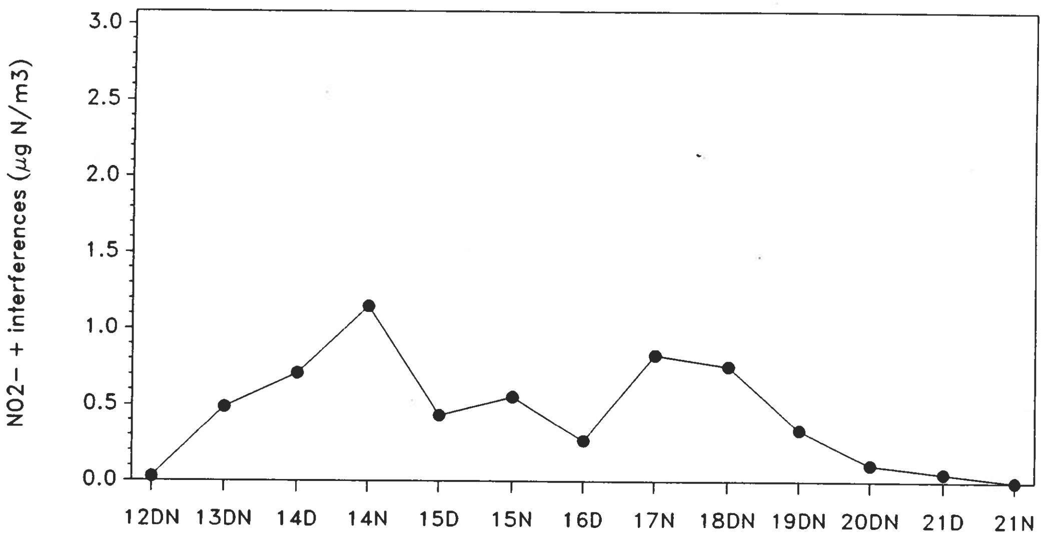

NITRITE + interferences

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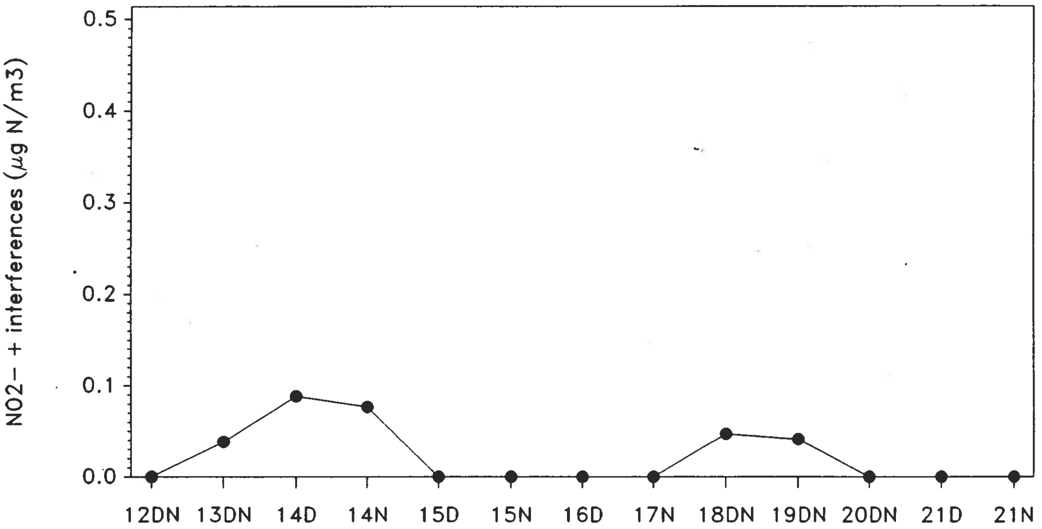

NITROUS ACID + interferences

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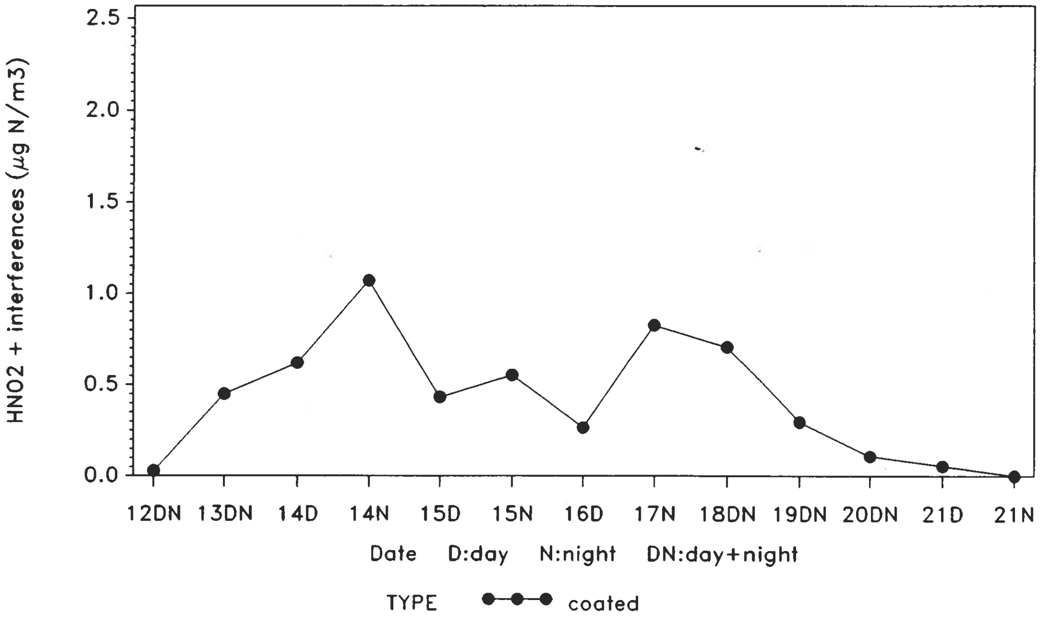

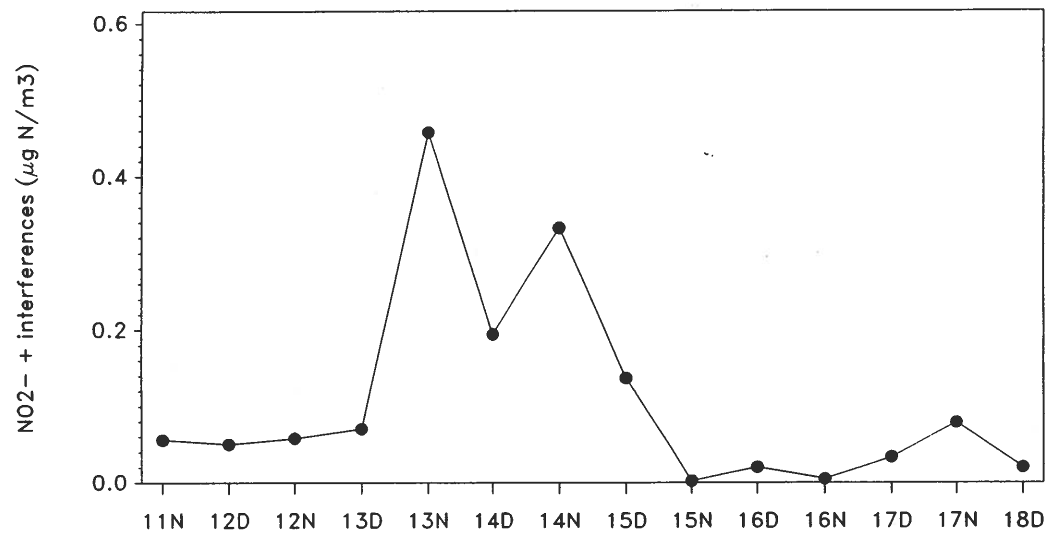

TOTAL NITROUS ACID + NITRITE + interferences

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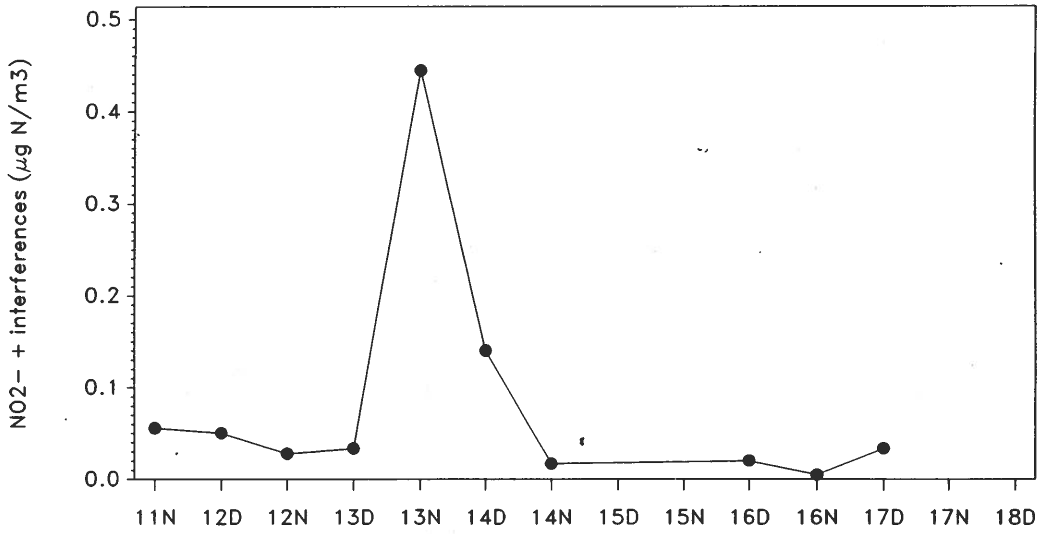

NITRITE + interferences

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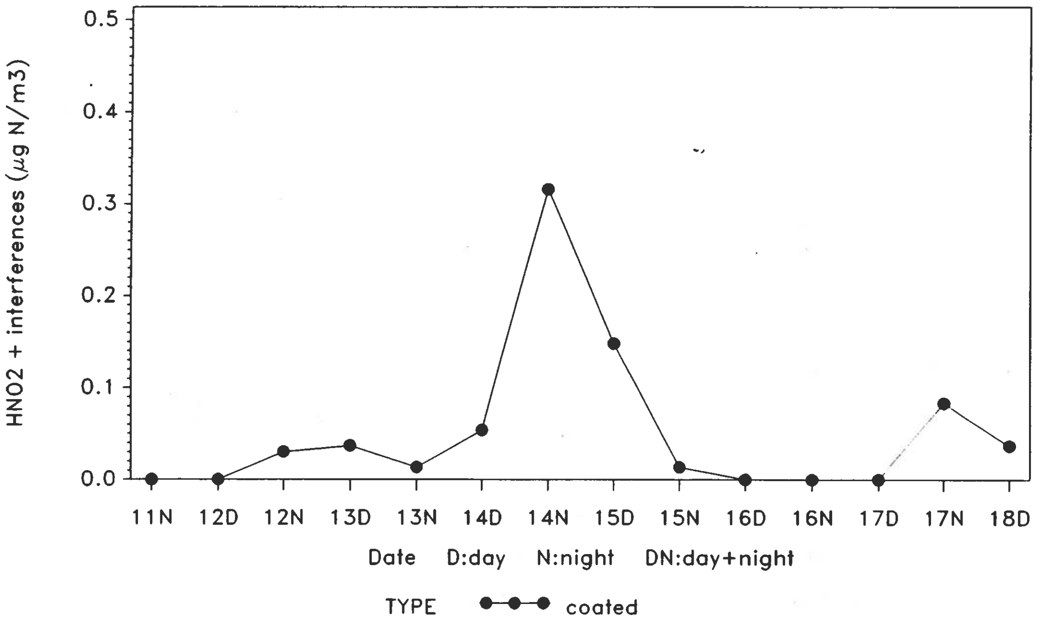
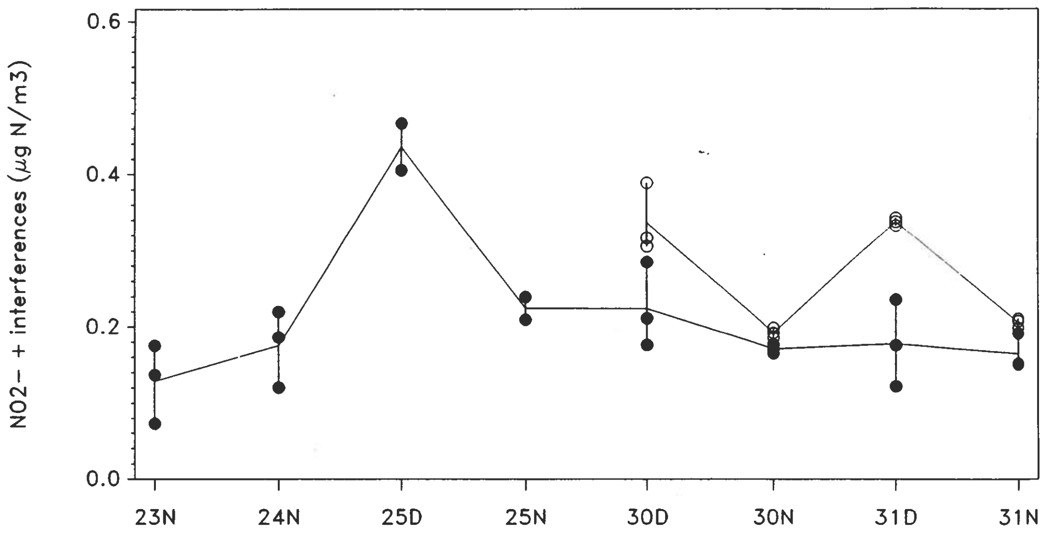


NITROUS ACID + interferences

CAMPAIGN=MAR91

TOTAL NITROUS ACID + NITRITE + interferences

CAMPAIGN=JUL91



NITRITE + interferences

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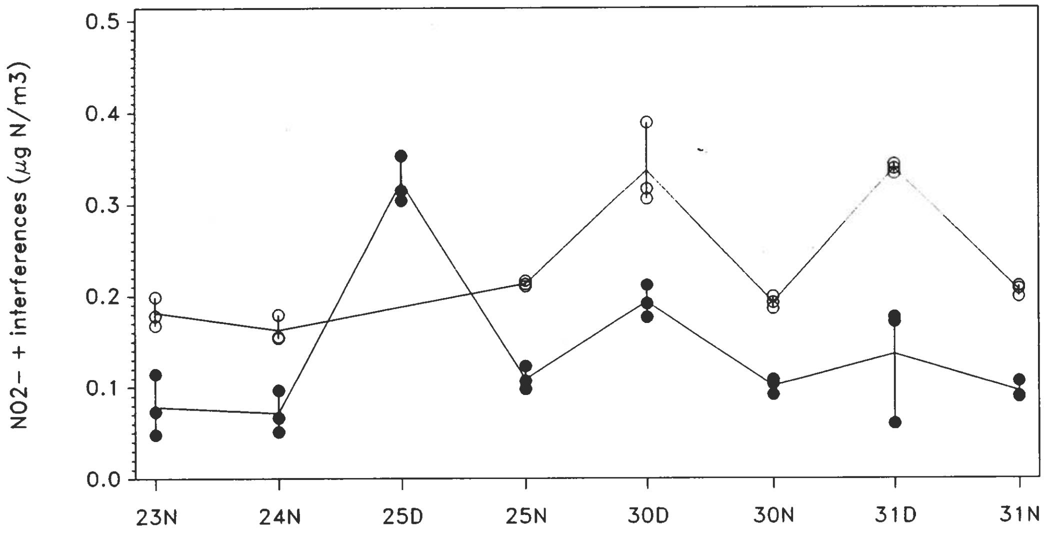

NITROUS ACID + interferences

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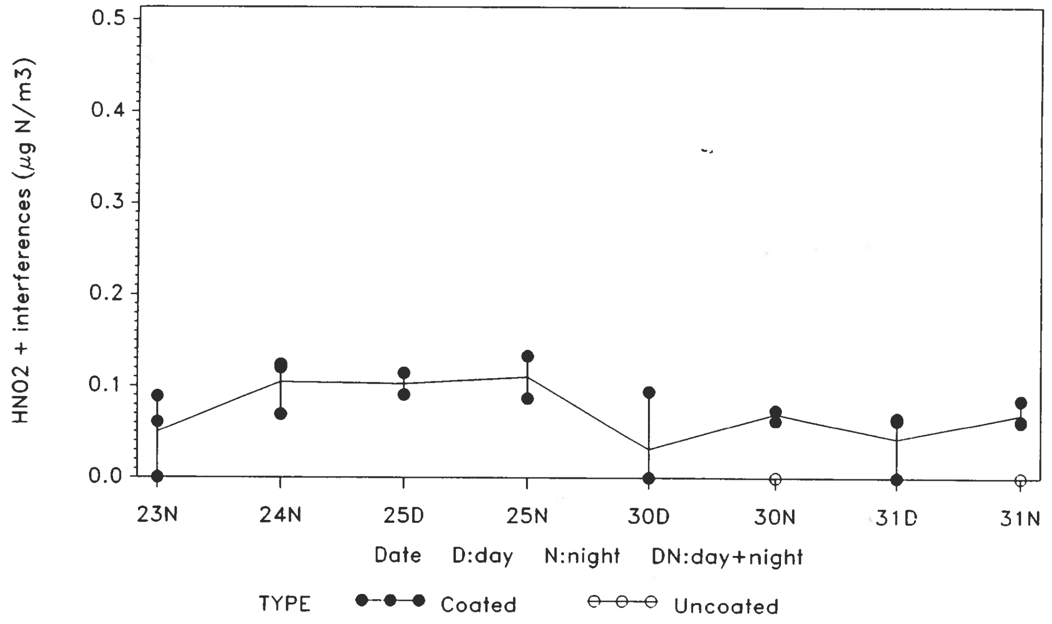

TOTAL NITROUS ACID + NITRITE + interferences

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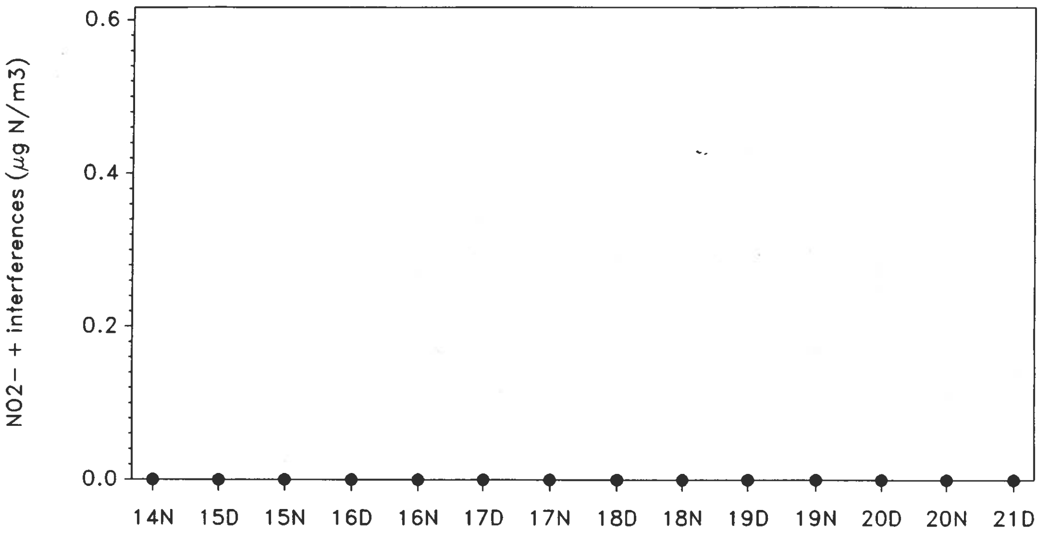

NITRITE + interferences

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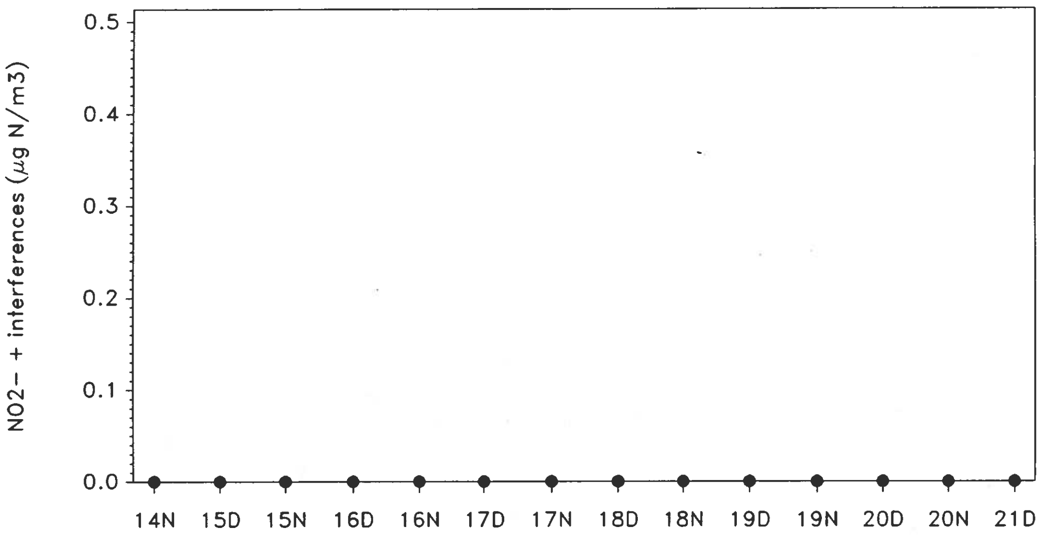

NITROUS ACID + interferences

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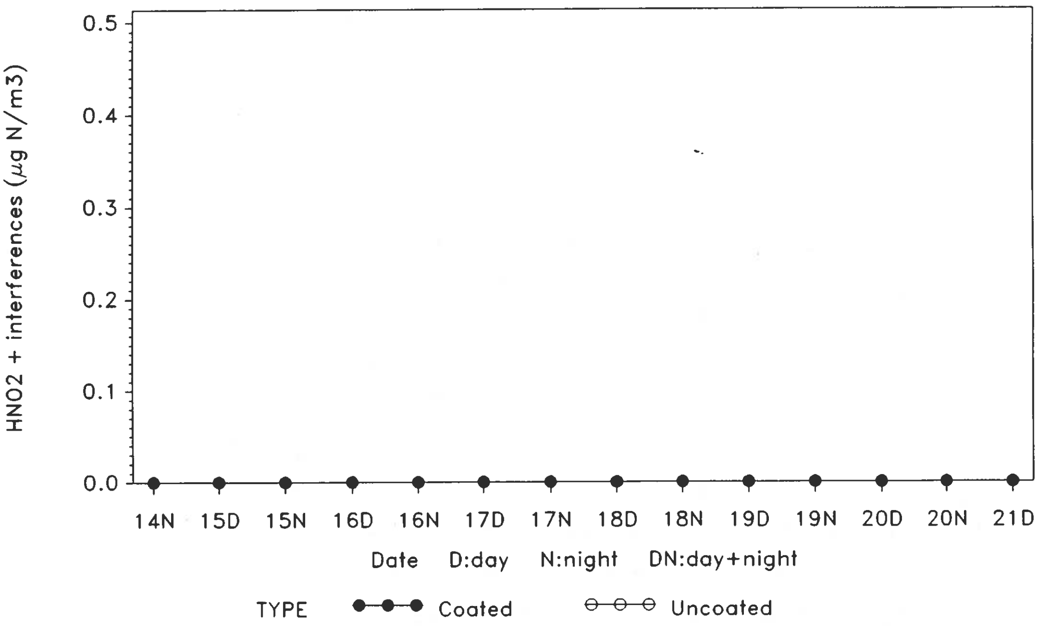

TOTAL NITROUS ACID + NITRITE + interferences

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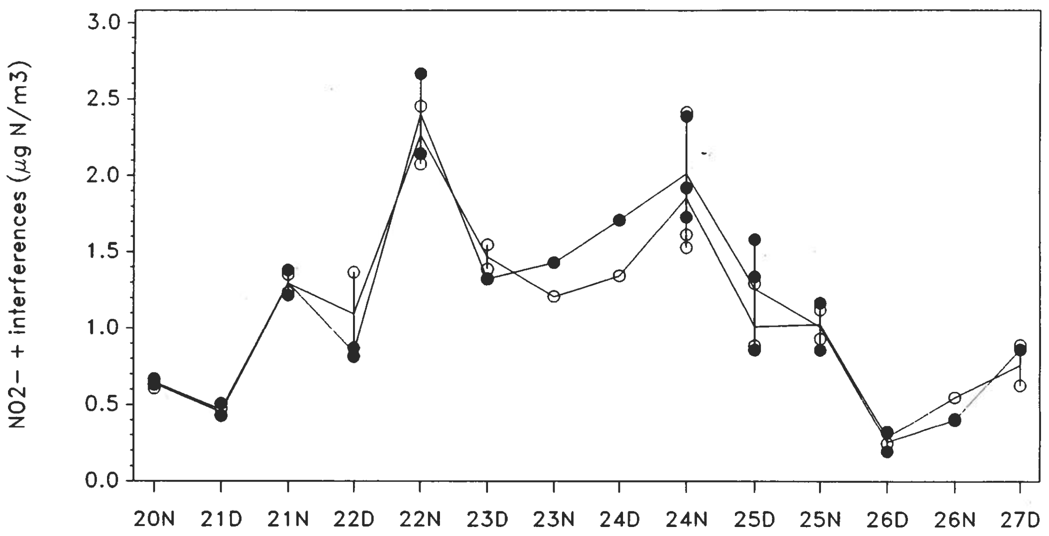

NITRITE + interferences

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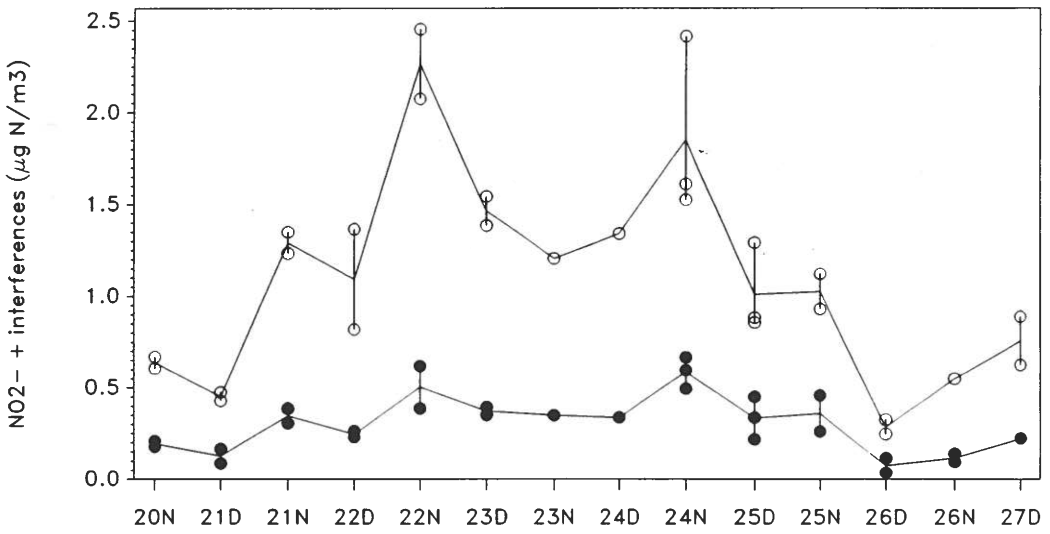

NITROUS ACID + interferences

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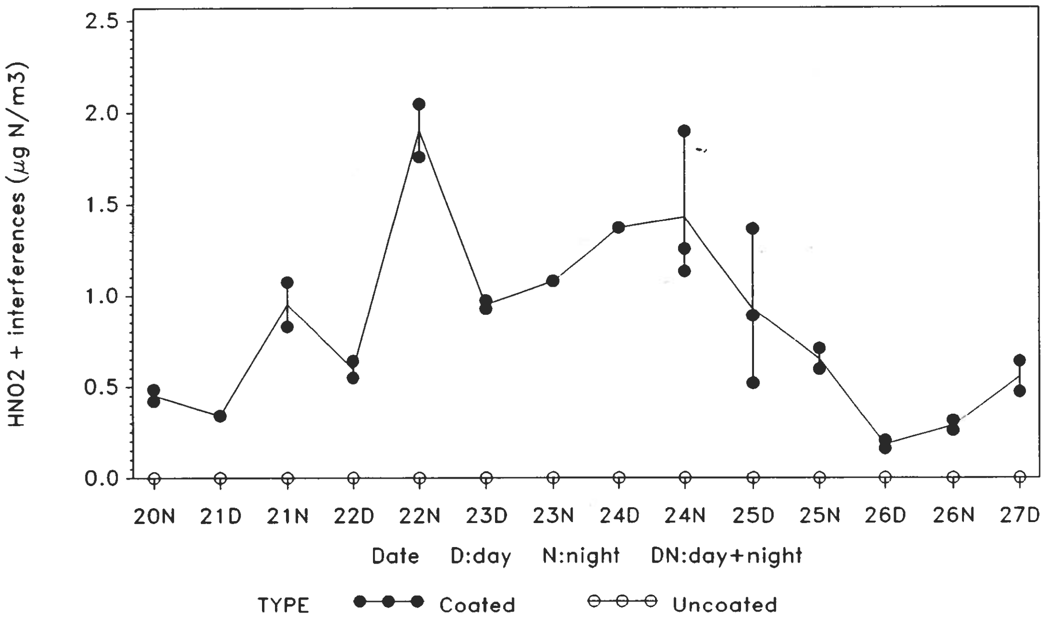

National Environmental Research Institute

The National Environmental Research Institute - NERI - is a research institute of the Ministry of the Environment. Neri's tasks are primarily to do research, collect data and give advice on problems related to the environment and nature.

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Publications:

NERI publishes professional reports, technical instructions, reprints of scientific and professional articles, a magazine of game biology and the Annual Report.

Included in the annual report is a review of the publications from the year in question. The annual reports and an up-to-date review of the year's publications are available on application to NERI.