Levels and pattern of volatile organic nitrates and halocarbons in the air at Neumayer Station (70°S), Antarctic

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Abstract

Levels and patterns of C1–C4/C9 organic nitrates were measured for the first time in Antarctica. The sampling was done by adsorptive enrichment on Tenax TA followed by thermodesorption cold-trap high resolution capillary gas chromatography with electron capture detection. 2–70 l air on-column have been analyzed this way. C1–C9 alkyl mononitrates, C2–C4 alkyl dinitrates, C2–C4 hydroxy alkyl nitrates, and halocarbons could be identified in air samples collected near the German Neumayer Research Station, Antarctica, in February 1999. Volatile biogenic and anthropogenic halocarbons were used to assess the origin of the air parcels analyzed. The average concentration measured for $\sum$C2–C6 alkyl nitrates was in the range of 9.2 ± 1.8 ppt(v), while the sum of the mixing ratios of six C2–C4 hydroxy alkyl nitrates was in the range of 1.1 ± 0.2 ppt(v). Moreover, C2–C4 alkyl dinitrates were found at levels near the detection limit of 0.1–0.5 ppt(v). The concentrations of organic nitrates found in Antarctic air represent ultimate baseline levels due to chemical and physical loss processes during long-range transport in the air. The South Atlantic and the Antarctic Ocean as a general secondary source for organic nitrates in terms of an air/sea exchange equilibrium has to be evaluated yet, but it seems logical. Our results confirm the common assumption that there are no biogenic marine sources of C2–C9 organonitrates. We have found a level of >80 ppt(v) for methyl nitrate. This level if it can be confirmed in a systematic survey requires a strong biogenic source of methyl nitrate in the Antarctic Ocean. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The troposphere has to be considered in general as an oxidative medium with the tendency for species to be converted to a more oxidized state. The results of the light induced photochemistry and oxidation chemistry of hydrocarbons in air depend on the levels of the reaction of starting radicals such as OH, or NO_3, and on the levels of trace gases like odd-nitrogen NO_y, (particularly NO_x ($NO + NO_2$) as main part), ozone, and organosulfur compounds (Atlas et al., 1992a,b; Carroll et al., 1992; Barrie et al., 1994; Kondo et al., 1997; Platt

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and Le Bras, 1997). As a result of combustion emissions, levels of NO_x greatly enhanced over those in the background troposphere can be found in urban and densely inhabited continental areas. NO_x is the key in the organonitrogen chemistry of the urban troposphere. When NO and NO_2 are present in sunlight, ozone formation occurs as a result of photolysis of NO_2 at wavelength $\lambda < 424$ nm.

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad (1)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M^\ddagger \qquad (2)$$

On the other hand, ozone reacts with NO to regenerate NO_2.

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (3)$$

Therefore the steady-state ozone concentration is approximated by Eq. (4)

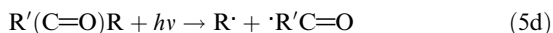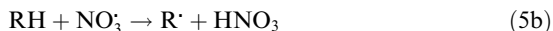$$[O_3] = \frac{J_1[NO_2]}{k_3[NO]} \qquad (4)$$

Expression (4) is named the *photostationary state relation*. The ozone concentration is in a first approximation proportional to the NO_2/NO ratio, which means high NO_2 levels lead to high ozone concentrations. Conversion of NO to NO_2 by HO_2 or peroxyalkyl radicals (7a) will lead to increases in ozone and deviation from Eq. (4).

Members of the NO_y pool are also involved in these processes by increasing or reducing NO_x levels in the air. Alkyl nitrates as parts of the NO_y pool are therefore of potential interest.
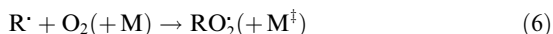
Alkyl nitrates besides being compounds of the atmospheric chemistry are used as propellants, and explosives (Köhler and Meyer, 1995). Together with the alkyl nitrites they are a group of potent pharmaceuticals, e.g. isosorbid dinitrate is a powerful vasodilator (Ahlner et al., 1991). None of the technical and pharmaceutical uses leads however to a general environmental contamination. Local contaminations by explosives may occur.

The source of alkyl nitrates in the troposphere is the conversion of hydrocarbons (Fraser et al., 1997). OH/O_2 (5a) or NO_3/O_2 (5b) attack on an aliphatic carbon–hydrogen or an olefinic C=C bond forms peroxyalkyl radicals RO_2 (6). They are also formed by a thermolysis/O_2 reaction (5c) of long chain alkoxy radicals and by the photolysis (5d) of carbonyl compounds followed by the addition of O_2. The reaction of peroxyalkyl radicals with NO leads to nitrogen dioxide and alkoxy radicals— finally stabilizing as carbonyl compounds (7a) and (7b)—or in a side reaction to alkyl nitrates (reactions (7c)) (Atkinson et al., 1982; Finlayson-Pitts and Pitts, 1986; Atkinson, 1990; Seinfeld and Pandis, 1998).
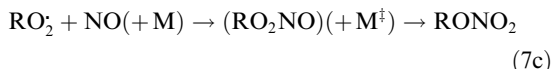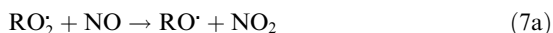
- Formation of alkyl radicals (initial step):

$$RH + OH^\cdot \rightarrow R^\cdot + H_2O \qquad (5a)$$

$$RH + NO_3^\cdot \rightarrow R^\cdot + HNO_3 \qquad (5b)$$

$$R'RHC-O^\cdot + \Delta \rightarrow R^\cdot + R'HC=O \qquad (5c)$$

$$R'(C=O)R + h\nu \rightarrow R^\cdot + {}^\cdot R'C=O \qquad (5d)$$

- Formation of peroxyalkyl radicals:

$$R^\cdot + O_2(+M) \rightarrow RO_2^\cdot(+M^\ddagger) \qquad (6)$$

- Formation of stable products:

$$RO_2^\cdot + NO \rightarrow RO^\cdot + NO_2 \qquad (7a)$$

$$RO^\cdot + O_2 \rightarrow R_1R_2CO + HO_2 \qquad (7b)$$

$$RO_2^\cdot + NO(+M) \rightarrow (RO_2NO)(+M^\ddagger) \rightarrow RONO_2 \qquad (7c)$$

This reaction scheme may repeat itself with alkyl nitrates leading finally to carbonyl alkyl nitrates or to non-vicinal alkyl dinitrates.

The reaction of alkenes with either ·OH during daytime or with NO_3 during nighttime in the presence of NO_x leads to the formation of multifunctional organic nitrates like hydroxy alkyl nitrates or alkyl dinitrates (O'Brien et al., 1995; O'Brien et al., 1997; Kastler and Ballschmiter, 1998; Kastler and Ballschmiter, 1999). Moreover, organic nitrates formed by the reaction of isoprene have recently been reported (Werner et al., 1999). A detailed summary of the reaction schemes leading to alkyl nitrates is given by Roberts (Roberts, 1990).

The yield of alkyl nitrates in the branching of the reaction of a peroxyalkyl radical with NO (7c) increases from <0.014 for ethane to 0.33 for octane. Thus a wide range of homologues and isomeric alkyl nitrates is expected in the atmosphere. The decreasing concentrations of long-chain alkanes are partly offset by the increased yields of alkyl nitrate formation (Atkinson et al., 1982; Schneider et al., 1998a).

While for alkyl mononitrates $\leqslant$ C5 the dominant loss process is photolysis (8) (Clemitshaw et al., 1997), alkyl nitrates with more than five C-atoms and multifunctional alkyl nitrates are mainly degraded by OH radicals (9) (Talukdar et al., 1997).

- Atmospheric chemistry of alkyl nitrates

$$RONO_2 + h\nu \rightarrow RO^\cdot + NO_2^\cdot \qquad (8)$$

$$RONO_2 + OH^\cdot$$
$$\rightarrow \text{multifunctional nitrates, polar products} \qquad (9)$$

In continental air alkyl nitrates contribute 2% to the NO_y budget, increasing up to 15% for marine air (Atlas et al., 1992a,b). They are a sink of the NO_y pool par-

ticularly during polar winters. Thus, in arctic air masses the alkyl nitrates can enrich up to 20% of the total NO_y budget (Bottenheim et al., 1993). Photodegradation of alkyl nitrates results in the formation of NO_x. They can act as an important NO_x source in the polar regions with highest release rates of NO_x during polar sunrise.

Since the first measurements of alkyl nitrates in the marine atmosphere 1988 by Atlas (Atlas, 1988), this class of compounds found increasing interest. Several studies took place in the USA, Canada and Germany. Moreover field campaigns took place in the Pacific air (equatorial and Hawaiian region) and the Atlantic air on board RV "Meteor" (Schneider and Ballschmiter, 1999) and RV "Polarstern" (Fischer et al., 2000). In spite of increasing activities in this field of atmospheric chemistry the number of studies in polar regions is limited.

Concentrations in the low ppt(v) range were found for the North Pacific air by Atlas (Atlas et al., 1992a,b; Atlas et al., 1993). Roberts measured concentrations of 14 ± 8.3 ppt(v) for $\sum$C1–C4 alkyl nitrates at Chebogue Point, Nova Scotia (Roberts et al., 1998). de Kock found mean concentrations of 17.5 ± 8.4 ppt(v) for C3–C5 alkyl nitrates at the South African southeast coast (de Kock and Anderson, 1994). More recently Schneider reported levels of 3–8 ppt(v) for $\sum$C3–C5 alkyl nitrates for the South Atlantic air (Schneider, 1998a,b; Schneider and Ballschmiter, 1999). Fischer reported a mean concentration of 1.7 ppt(v) for $\sum$C4 + C5 alkyl nitrates for the North Atlantic air and 1.3 ppt(v) for $\sum$C4 + C5 for the South Atlantic air (Fischer, 1999; Fischer et al., 2000). Fischer gives a global overview on the levels of short chain alkyl nitrates at different continental and marine sampling sites (Fischer and Ballschmiter, 2001).

O'Brien reported 1995 for the first time the occurrence of four alkyl hydroxy nitrates and one alkyl dinitrate (O'Brien et al., 1995; O'Brien et al., 1997). Recently additional hydroxy alkyl nitrates and 30 alkyl dinitrates were identified in urban air (Kastler and Ballschmiter, 1998; Kastler and Ballschmiter, 1999; Fischer et al., 2000).

We believe to be the first to present in this work levels and patterns of higher organic nitrates in the lower troposphere of the Antarctic. Furthermore we compare the occurrence of alkyl nitrates with the levels of halocarbons as atmospheric markers. A comparison with values obtained in South Atlantic air places the Antarctic data in a greater spatial context.

2. Short hand nomenclature of organic nitrates

Schneider and Ballschmiter recently introduced a shorthand nomenclature of alkyl mononitrates that correlates the structure of a specific alkyl nitrate to the hydrocarbon precursor (Schneider and Ballschmiter, 1996). In our extended shorthand nomenclature the expression organic nitrates represents the whole family of mono- and multifunctional alkyl nitrates (Table 1) keeping the basic settings given by Schneider and Ballschmiter (Fischer et al., 2000).

The longest *unbranched* alkyl chain is taken as the skeleton of the molecule; e.g. C7 means in this case that the longest unbranched carbon chain has seven C-atoms. Furthermore we define for *unbranched* alkyl nitrates that the nitrooxy group possesses the highest priority and is numbered first.

For *branched* alkyl nitrates the alkyl side chains possess now the highest priority above all other groups in the molecule, and therefore the positions of alkyl side chains are numbered first. M is used for methyl, and E is used for ethyl side chains, respectively.

This convention is particularly important and helpful if isomeric hydrocarbon skeletons have to be distinguished. For a better understanding we explain the abbreviations introducing some examples for alkyl mononitrates, alkyl dinitrates, hydroxy alkyl nitrates, keto alkyl nitrates, and alicyclic alkyl nitrates.

Alkyl mononitrates: 2,4M5C7 indicates a heptyl chain with two methyl groups at the 2 and 4 position and the nitrooxy group at the 5 position, specifically a 2,4-dimethyl-5-nitrooxyheptane.

Alkyl dinitrates: 2,3M1,4C5 would be a alkyl dinitrate with a carbon skeleton of five atoms, with two methyl groups at the 2 and 3 position, and two nitrooxy groups at position 1 and 4, specifically a 2,3-dimethyl-1,4-dinitrooxy pentane.

Hydroxy alkyl nitrates: OH is used for the hydroxy group. 3OH1C4 would be 3-hydroxy-1-nitrooxy butane.

Keto alkyl nitrate: The letter O labels the carbonyl group, e.g. 2O1C5 is a 2-keto-1-nitrooxy pentane.

Alicyclic alkyl nitrates: The letters *c* and *t* are used for *cis* and *trans* positions, respectively. Cy indicates an alicyclic skeleton. *c*1,2CyC6 indicates a *cis*-1,2-dinitrooxy cyclohexane.

Aryl alkyl nitrates: Aryl alkyl nitrates are named considering the phenyl- or naphthyl group as a substituent of the alkyl chain (Woidich et al., 1999).

3. Position of the Neumayer Research Station in the Antarctic

The Neumayer Station (70°39′S, 8°15′W) was established in 1992 on the Ekström Shelf Ice as a research observatory for geophysical, meteorological and air chemistry measurements. Fig. 1 shows the geographical position of the research station. The snow-covered station is located on shelf ice that is 200 m thick and almost flat. The shelf ice margin where supply ships (e.g. RV "Polarstern") dock is 10 km away. The isolated location

Table 1
IUPAC and short style nomenclature of the alkyl mononitrates and short-chain alkyl hydroxy- and dinitrates identified in the Antarctic air samples

| No.	IUPAC	Abbreviation	No.	IUPAC	Abbreviation
C_n			C_n		
	Alkyl mononitrates			Alkyl dinitrates	
1	Nitrooxy-methane	C1	2	1,2-Dinitrooxy-ethane	1,2C2
2	Nitrooxy-ethane	C2	3	1,2-Dinitrooxy-propane	1,2C3
3	1-Nitrooxy-propane	1C3		1,3-Dinitrooxy-propane	1,3C3
	2-Nitrooxy-propane	2C3	4	1,3-Dinitrooxy-butane	1,3C4
4	1-Nitrooxy-butane	1C4		2,3-Dinitrooxy-butane	2,3C4
	2-Nitrooxy-butane	2C4		2-Methyl-1,2-dinitrooxy-propane	2M1,2C3
	2-Methyl-1-nitrooxy-butane	2M1C3	5	2,3-Dinitrooxy-pentane	2,3C5
5	1-Nitrooxy-pentane	1C5	6	2-Methyl-3,4-dinitrooxy-pentane	2M3,4C5
	2-Nitrooxy-pentane	2C5		Hydroxy alkyl nitrates	
	3-Nitrooxy-pentane	3C5	3	1-Hydroxy-2-nitrooxy-propane	1OH2C3
	2-Methyl-3-nitrooxy-butane	2M3C4		2-Hydroxy-1-nitrooxy-propane	2OH1C3
6	1-Nitrooxy-hexane	1C6	4	3-Hydroxy-2-nitrooxy-butane	3OH2C4
	2-Nitrooxy-hexane	2C6		4-Hydroxy-2-nitrooxy-butane	4OH2C4
	3-Nitrooxy-hexane	3C6	5	2-Hydroxy-1-nitrooxy-pentane	2OH1C5
7	1-Nitrooxy-heptane	1C7		1-Hydroxy-2-nitrooxy-pentane	1OH2C5
	2-Nitrooxy-heptane	2C7	6	2-Hydroxy-3-nitrooxy-hexane	2OH3C6
	3-Nitrooxy-heptane	3C7		4-Hydroxy-3-nitrooxy-hexane	4OH3C6
	4-Nitrooxy-heptane	4C7		2-Methyl-4-hydroxy-5-nitrooxy-pentane	2M4OH5C5
8	1-Nitrooxy-octane	1C8		2-Methyl-5-hydroxy-4-nitrooxy-pentane	2M5OH4C5
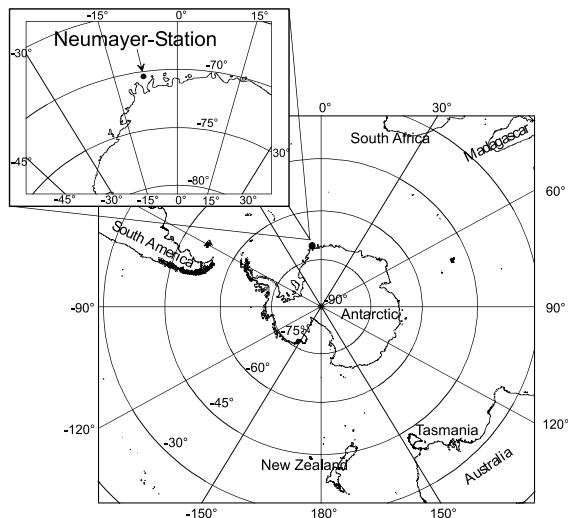
Fig. 1. Geographical position of Neumayer Station; on the Ekström Shelf ice in the Atka Bay, Northeast Weddell Sea (70°39″S, 8°15″W).

of the station makes it a valuable reference site for measurements under conditions of extreme air purity. In addition, the proximity to the ice margin permits the detection of substances released from the ocean to the atmosphere. Table 2 summarizes the meteorological parameters related to the Neumayer Station during the sampling period.

4. Experimental

4.1. Air sampling procedure

The air sampling was done by pulling air through glass tubes (160 mm length, 3 mm, i.d.) filled with 80–100 mg of Tenax TA, 60–80 mesh (Chrompack, Middelburg, Netherlands) at a flow rate of 80–100 ml/min with a sampling pump (SKC model 222-3, Eighty Four, Pennsylvania, United States). Two sampling tubes connected in series have been used to control the sampling efficiency. Volumes of 2–68 l air were sampled. The sampling tubes were flame-sealed in larger glass tubes for transport and were kept refrigerated until analysis.

To detect the whole range of alkyl nitrates parallel sampling of low volumes of 2 l for C2 up to C5 alkyl nitrates and high volumes of 50–70 l as well for alkyl nitrates C > 5 is recommended. In polar regions the breakthrough loss due to sampling temperatures is negligible.

4.2. Analytical procedure: GC separation, detection and quantitation

The high resolution gas chromatography with electron capture detection (HRGC/ECD) chromatographic separation was performed on a Chrompack Model 9001 gas chromatograph equipped with a thermal desorption cold trap (TCT) device (Chrompack, Middelburg,

Table 2
Meteorological parameters related to the Antarctic air samples

Sample	Date	Sample volume (l)	Air temperature (°C)	Wind direction	Wind velocity (m s^{-1})	Humidity (%)
NM 1	13.02.1999	2.0	−7.5	130°SE	4	75
NM 2	22.02.1999	30.2	−5.5	75°ENE	5	73
NM 3	22.02.1999	68.0	−10.0	160°ESE	3	87
NM 4	26.02.1999	10.8	−6.3	90°E	12	96

Netherlands). We used a DB-1701 capillary (58 m × 0.312 mm i.d. × 1.0 μm film thickness, J&W Scientific, Folsom, United States). A detailed description of the analytical conditions is given in (Fischer et al., 2000). Quantitation was done by external calibration with solutions containing known amounts of alkyl nitrates and halocarbons. The limit of detection based on a 30 l air sample was about 0.3 ng/m^3 or 0.05 ppt(v) for alkyl nitrates and 0.2 ng/m^3 or 0.02 ppt(v) for the three halocarbons trichloroethane, tetrachloroethene and bromoform. The overall error for the alkyl nitrates and halocarbons was estimated to be less than ±20% (Fischer, 1999).

5. Results

The measured concentrations of organic nitrates and halocarbons of this work are summarized in Table 3. The results presented in this work are unique for organic nitrates. Table 4 lists all literature data and compares them with the results of this work. Highest in abundance

are the short chain alkyl mononitrates C2, 1C3, 2C3 and 2C4. This observation is consistent with the literature data for Arctic regions (Table 4). The alkyl nitrate levels for the Arctic regions are one order of magnitude higher than the values found in the Antarctic, indicating that the sampling sites in the North are closer to the highly industrialized regions of the North American continent. In terms of the vicinity to non-point sources the Arctic and Antarctic regions have to be considered differently; the effects of a limited photodegradation in the respective polar nights will be similar.

Fig. 2a and b depict TCT–HRGC–ECD chromatograms of air samples collected at Neumayer Station, Antarctica. To our knowledge these are the first chromatograms showing alkyl nitrates in the air of a South Polar region.

The biogenic marker dibromomethane and tribromomethane (bromoform) show relative to alkyl nitrates higher mixing ratios indicating marine emissions sources (the sampling location is only 10 km away from the coastal line). Anthropogenic markers like carbontetrachloride and 1,1,1-trichloroethane with long k_{OH}

Table 3
Mixing ratios for the alkyl mononitrates, hydroxy alkyl nitrates, alkyl dinitrates, and bromo- and chloro-halocarbons in the Antarctic air in ppt(v) ($n = 2$–4)

Mononitrates	Mean (ppt(v))	Hydroxy nitrates	Mean (ppt(v))	Halocarbons	Mean (ppt(v))
C1($n = 1$)	84	2OH1C4	<LOD	Tetrachloromethane	95
C2	4.6	2OH1C3	0.03	1,1,1-Trichloroethane	75
1C3	1.1	RR-3OH2C4[a]	0.3	Trichlorethene	<LOD
2C3	0.7	1OH2C3/RS-3OH2C4[a]	0.8	Tetrachlorethene	0.3
1C4	0.03			Hexachloroethane	0.06
2C4/2M1C3	0.5	1OH2C4	0.02	Dibromomethane	0.8
1C5	0.7	3OH1C4	0.01	Bromodichloromethane	0.05
2C5	<LOD	$\sum$OH	1.1	Dibromochloromethane	0.02
3C5	0.03			Bromoform	0.3
				1,2-Dibromoethane	0.1
		Dinitrates			
1C6	0.5	1,2C3/1,2C2	0.5		
2C6	1.0	2M1,2C3	0.1		
3C6	0.08				
2C7	0.18	$\sum$ C4 + C5	1.3		
4C7	0.02	$\sum$ C3–C6	4.6		

Limit of detection (LOD) = 0.01 ppt(v).
[a] RR/SS-3OH2C4; RS/SR-3OH2C4 co-elution with 1OH2C3.

Table 4
Comparison of mixing ratios of alkyl nitrates in the Antarctic air with Arctic and Alaska reference data in ppt(v)

| | Antarctic (this work) | Alert, Canada | | Arctic, Canada[a] |
		Polar night[b]	Polar day[b]	
1C3	1.11	3.33	3.14	3.96
2C3	0.49	12.44	13.08	12.5
1C4	0.03	1.7	1.18	2.05
2C4/2M1C3	0.48	18.41	13.73	13.98
2M3C4	<LOD	4.84	2.32	2.65
1C5	0.71	1.01	0.53	1.03
2C5	<LOD	5.44	2.47	4.18
3C5	0.03	4.31	2.31	3.02
2C6	0.08	2.46	0.98	1.50
3C6	0.95	4.27	1.65	2.55
2C7	0.18	1.45	0.56	–
3C7	(0.01)	1.86	0.68	–
$\sum$C2–C6	9.2	–	–	34[c]
$\sum$C3–C7	–	–	–	144[d]

Limit of detection (LOD) = 0.01 ppt(v).
[a] Canadian Arctic (69°N–83°N) ''Polar Sunrise Experiment'' April 1992 (Leaitch et al., 1994).
[b] Alert, Northwest Territories of Canada, ''Polar Sunrise Experiment'' January–April 1992, Polar night January–March; day period March–April (Muthuramu et al., 1994).
[c] Poker Flat Research Rang, Alaska (64°N/147°W) winter/spring 1993 (Beine et al., 1996).
[d] Canadian Arctic March–April 1988 (Bottenheim et al., 1993).

lifetimes (τ = month to years) were also found, but markers with short k_{OH} lifetime like trichloroethene (τ = 7 days) are below the limit of detection (<0.01 ppt(v)).

The patterns of the Antarctic air samples are quite similar to the patterns found in the South Atlantic Trade Wind region. Fig. 2c depicts for comparison a chromatogram of this marine region, taken during the ALBATROSS campaign on board of RV ''Polarstern'' (ANT XIV/1) at 10.4°S/25.5°W (Fischer et al., 2000). The Antarctic and the Southern Trades apparently represent baseline levels of clean marine air in terms of organic nitrates.

5.1. Levels of anthropogenic halocarbons in Antarctic air

The mixing ratios for the long-lived halocarbons (Table 3) are in good agreement with earlier measurements. We found 95 ppt(v) for tetrachloromethane (τ = 42a) while Derwent measured 101 ppt(v) in Ireland (Derwent et al., 1998). This indicates a more or less even global distribution in the troposphere. For 1,1,1-trichlorethane we observed 75 ppt(v) (τ = 4.8a); estimations by Derwent for 1999 results in ratios of 70–80 ppt(v) (Derwent et al., 1998). The situation seems to be similar as observed for tetrachloromethane. The mean value for hexachloroethane is in the range of 0.06 ppt(v) and somewhat lower than 0.24 ppt(v) observed by Atlas in 1993 for the Pacific (Atlas et al., 1993). For medium lived C_2^- halocarbons like tetrachlorethene we observed

a mean value of 0.3 ppt(v). During the Albatross–Campaign we found similar mixing ratios in the South Atlantic Ocean and levels by a factor 3 higher for the North Atlantic (Fischer et al., 2000). The good correlation of the measured halocarbon ratios with literature data backs the accuracy of our analytical procedure.

6. Discussion

To interpret the data of the South Polar region in a wider spatial context we enclose the data of the Albatross–Campaign, which also covered the South Atlantic (Fischer et al., 2000).

6.1. Levels of butyl nitrates in marine and Antarctic air

Fig. 3 is a plot of the mixing ratios of the 2C4, the secondary, and the 1C4, the primary butyl nitrate along the Atlantic Ocean (Albatross–Campaign) and at Neumayer Station, Antarctic. The main emission sources are in the industrialized areas of the Northern hemisphere. The accumulation in the Northern hemisphere is enhanced in fall and wintertime by a reduced photodegradation. The concentration for 2-butyl nitrate (2C4) in the coastal region is 3.5–5 ppt(v). An average value of 1 ± 0.2 ppt(v) is observed for 1-butyl nitrate (1C4) in the air of the North Atlantic. A 2C4/1C4 ratio close to 4 indicates a recent continental input or marine local input by islands.
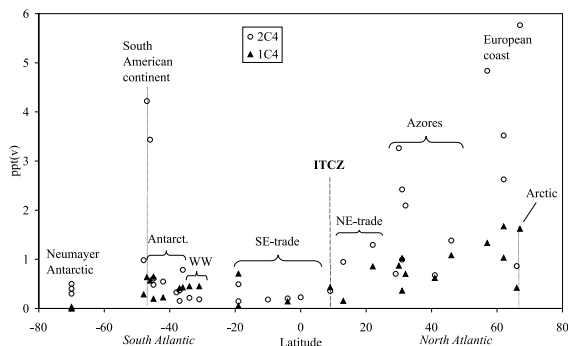
Fig. 2. (a) TCT–HRGC(DB-1701)/ECD chromatogram of an Antarctic air sample, taken at Neumayer Station, sampling and on-column volume (a) 2.0 l (sample NM 1), (b) 68 l (sample NM 3). (c) TCT–HRGC(DB-1701)/ECD chromatogram of a South Atlantic air sample of the trade wind region 10.4°S/25.5°W, sampling and on-column volume 105 l.

Fig. 3. Distribution of butyl nitrates from 67°N to 70°S over the Atlantic Ocean mainly across 30°W longitude (Albatross–Campaign on board RV Polarstern ANT XIV/1, 1996) and at the Neumayer Station, 1999.

In the South Atlantic trade wind region the values for 2C4 decrease to 0.2 ± 0.05 ppt(v) leading to a 2C4/1C4 ratio to about 1 and even below 1. The levels of 2C4 rise again to 0.4 ± 0.08 ppt(v) in the west wind belt of the South Atlantic and remain at 0.4 ± 0.1 ppt(v) for air collected at the Neumayer Station. The levels of 1C4 decrease from 1.0 ± 0.2 ppt(v) in the Northern hemisphere passing the intertropical convergence zone (ITCZ) to the south to levels of 0.4 ± 0.08 ppt(v). A further decrease to levels down to the limit of detection of 0.05 ppt(v) is observed for the air at the Neumayer Station. The 2C4/1C4 ratio covers a span between 0.2 and 7.0 reflecting in one part the dominance of 1C4 in "old" air masses and also a very low level of possible local input in the Antarctic. In the latter case only the dominant 2C4 would be detected.

6.2. Characterization of the age of air masses

An air mass is called "young" if pollution deriving from densely inhabited regions with a corresponding level of traffic and industrial emissions is observed. Several attempts have been made to characterize air mass ages. Atherton used a pure deductive kinetic model (Atherton, 1989). Other models consider differences in photochemical degradation velocities using pairs of molecules or groups of molecules like carbon monoxide and alkyl nitrates (Roberts et al., 1996), PAN and alkyl nitrates (Buhr et al., 1990), hydrocarbons and alkyl nitrates (Roberts et al., 1998), NO_y and NO_x (Trainer et al., 1991), two isomeric alkyl nitrates (Flocke et al., 1998; Schneider and Ballschmiter, 1999) or consider the presence of benzyl nitrate (Schneider et al., 1998a; Schneider and Ballschmiter, 1999). Here we present two different approaches to characterize the "age" of air

masses. It is the 2-butyl-, 2-pentyl nitrate/tetrachloroethene quotient (traffic/industry indicator) and the ratio of isomeric pentyl nitrates (traffic indicator).

6.3. The 2-butyl-, 2-pentyl nitrate/tetrachlorethene ratio as an air mass marker

Here, we present a method based on the differences in the degradation rates of short chain alkyl nitrates and semi-stable halocarbons (e.g. tetrachloroethene). Short chain alkyl nitrates are formed in all regions with traffic that are releasing significant NO and short chain hydrocarbon emissions. Butyl- and pentyl nitrates are degraded by photolysis and OH on their long-range transport finally reaching remote areas like the Antarctic. The anthropogenic halocarbons emerge basically from industrialized continental regions and then undergo photochemistry on their long-range transport. They are degraded mainly by OH radicals and only to a minor extent by photolysis (Class and Ballschmiter, 1986).

The k_{OH} lifetime of tetrachloroethene is in the range of 4 month. Tetrachloroethene shows a three-step decrease in the global mixing ratios in the lower troposphere (Wiedmann et al., 1994). A first decrease is observed when going from continental air to marine air of the Northern hemisphere. This is a mixture of a decrease by degradation and by mixing of the source air with less polluted air of the Northern Hadley cell of the general circulation. The second decrease is observed in the Northern tropics and a third one when passing the ITCZ reaching the air of South East Trades of the Southern hemisphere. This clearly indicates the separation of the air masses of both hemispheres in the lower troposphere by the ITCZ. This has been observed for other anthropogenic volatile chlorocarbons before (Class and Ballschmiter, 1986).

The butyl nitrates do not give this clear difference in atmospheric levels but decrease more or less continuously in going to remote regions. The increased levels around the Azores indicate the importance of quasi-local inputs in the marine atmosphere due to traffic on these islands. Fig. 5a depicts the ratios of the mixing ratios of the secondary alkyl nitrates 2-butyl- and 2-pentyl nitrate relative to tetrachloroethene (C_2Cl_4) in the air of the Atlantic Ocean and in the air of Neumayer Station. Three clusters are formed. Marine air influenced by air masses coming from the South American continent is characterized by a surplus of 2-butyl and 2-pentyl nitrates relative to tetrachloroethene. Unpolluted marine air has low mixing ratios for 2-pentyl nitrate itself and the ratio 2C5/C_2Cl_4 is <1 indicating a strong degradation for 2-pentyl nitrate. The third cluster represents the global baseline level. It is characterized by the fact that both the ratios for 2C4/C_2Cl_4 and 2C5/C_2Cl_4

are well below 1. This third cluster represents the photochemically aged pollution depleted air masses.

6.4. The ratio of isomeric pentyl nitrates as an air mass marker

A further method to decide about the origin or age of an air parcel is to compare the levels of the isomeric pentyl nitrates. In the case of pentyl nitrates significantly increased mixing ratios for primary and secondary pentyl nitrates are found with a surplus of secondary pentyl nitrates (3C5 > 2C5 > 1C5). Very low concentrations of secondary pentyl nitrates, and in contrast noticeably higher concentrations of 1-pentyl nitrates characterize aged air masses (e.g. collected in remote marine or Antarctic regions). The former sequence of the levels in air 3C5 > 2C5 > 1C5 turns now to 1C5 ≫ 3C5 > 2C5. The mixing ratio for 2C5 in the air of the Antarctic Neumayer Station is below the limit of detection (Table 3). The missing of 2C5 and barely detectable traces of 3C5 while 1C5 can be measured confirm that highly degraded air masses were collected.

6.5. Methyl nitrate in Antarctic air

The level found for methyl nitrate found in the Antarctic is unexpectedly high and requires a specific discussion. The branching ratio for the atmospheric reaction Eqs. (7a)–(7c) is normally set close to zero for C1. Degradation of peroxyacetylnitrate (PAN) by the loss of CO_2 or the esterfication of methanol with nitric acid on aerosols (Senum et al., 1986; Orlando et al., 1992; Fan et al., 1994) can result in higher yields of metyl nitrate in polluted continental air.

The reaction of methyl nitrate with OH is the major loss process. The reaction rate constant was first measured by Gaffney et al. (Gaffney et al., 1986). It has recently be redetermined (Kakesu et al., 1997).

Methyl nitrate is very volatile and substantial breakthrough losses will occur if not specific precautions (low sample volume, high amount of adsorbent, low temperature) are set to sample this very volatile alkyl nitrate by adsorption techniques. A correct quantitation of methyl nitrate is therefore difficult and requires optimized sampling conditions. We have found a level of >80 ppt(v) for methyl nitrate in the low volume sample. Co-elution with other compounds in the gas chromatogram of our sample can be excluded by identification of the C1 peak by HRGC/MSD. Recently Jones measured methyl nitrate from 27 to 46 ppt(v) and ethyl nitrate from 5 to 13 ppt(v) sampled at Neumayer Station 1997 (Jones et al., 1999).

Walega et al. found for methyl nitrate 4 ppt(v) at Mauna Loa, Hawaii (Walega et al., 1992) and Flocke

et al. measured 8 ppt(v) in the air over the North Atlantic (Flocke et al., 1998). Atlas supposed a marine emission source for methyl nitrate (Atlas et al., 1997). In the marine boundary layer (MBL) maximum concentrations were found as high as 50 ppt(v) near Christmas Island (1–3°N) and concentrations of 20–35 ppt(v) near Western Samoa (13°S) during ACE 1 (Blake et al., 1999). The authors conclude that methyl nitrate has a significant equatorial marine source. The most logic biogenic source would be the methylation of nitrate ions. We may observe a similar reaction for the nitrate ion leading to methyl nitrate as it is found for the methylation of chloride (Urhahn and Ballschmiter, 1998). Methionine methyl sulfonium chloride (MMSL) e.g. gave an intense release of monohalomethanes when mixed in a buffer with potassium halides.

6.6. Levels of hydroxy alkyl nitrates in marine and Antarctic air

Fig. 4 is a plot of the mixing ratios of hydroxy alkyl nitrates along the Atlantic Ocean (Albatross–Campaign) and at Neumayer Station, Antarctic. All of the observed compounds are vicinal hydroxy alkyl nitrates. Hence, their formation pathway via OH radical addition to olefins is most likely. We observe a NH/SH gradient of about factor 3 with 4.3 ± 0.8 ppt(v) for the sum of 4 hydroxy alkyl nitrates in the air of the Northern hemisphere and 1.6 ± 0.3 ppt(v) in the South Atlantic air. The mixing ratio for hydroxy alkyl nitrates in the air of the Neumayer Station is with 1.2 ± 0.2 ppt(v) somewhat lower than in the South Atlantic air. In accordance with previous discussions the formation of secondary alkyl radicals is preferred to the formation of primary ones (Kastler, 1999). Therefore, if 1-alkenes are degraded by OH radicals, the yield of 1-hydroxy-2-nitrooxy-alkanes must be higher than the yield for 2-hydroxy-1-nitrooxy alkanes. This is consistent with our observations.
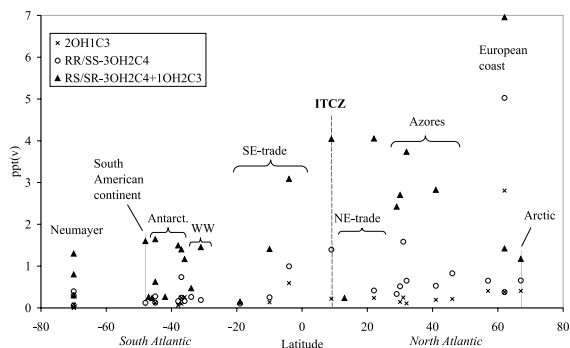

Fig. 4. Distribution of hydroxy propyl- and butyl nitrates from 67°N to 70°S over the Atlantic Ocean and at Neumayer Station.

6.7. Principal compound analysis (PCA) of organic nitrates in marine and Antarctic air

The principal compound analysis is a statistical model to compare the pattern of air samples between different regions. The theoretical feedback of the method is given in (Smith, 1991). The *n*-dimensional expression is reduced to a two dimensional expression. The distance between two points is a measure of the similarity of air samples. Fig. 5b depicts the PCA of all marine and Antarctic air samples. 15 locations and the ratios of 14 alkyl mononitrates are the basis for the PCA given here.

A grouping of air masses is also obtained by plotting two ratios of selected air constituents. This approach has been used to characterize air masses by their complex pattern of polychlorinated biphenyls (PCBs) (Schreitmüller et al., 1994). We have plotted here the ratios of the mixing ratio of 2-butyl nitrate/tetrachloroethene versus 2-pentyl nitrate/tetrachlorethene. The results are given in Fig. 5a. Three clusters of air masses can be differentiated. Cluster I contains all sampling locations representing global baseline levels. Cluster II summarizes marine air samples with slightly polluted air, indi-

cating the influence of islands. The last cluster contains polluted air coming in from the South American continent. The PCA as an independent method confirms the characterization of marine and polar air samples as discussed above.

7. Conclusion

In this paper we presented for the first time a data set of higher organic nitrates in the air of the German South Polar Neumayer Station. We are in a unique position to discuss and compare the levels and patterns of alkyl nitrates and halocarbons in the air of the Atlantic Ocean and in the air of the South Polar region. The organonitrate concentrations in the marine and Antarctic samples reached only 1–10% of the continental samples. The mixing ratio in the South East Trade Wind region and in the air of Neumayer Station are similar and represents the global baseline level for the organonitrates. This is a strong indication for the long-range transport of these molecules. No new alkyl nitrate formation is expected due to the lack of NO_x sources in the marine and the Antarctic atmosphere. Methyl nitrate seems to be the exception from this rule. A biogenic source for this compound appears to be likely as it has been discussed before.

Halocarbons can be used as marker molecules to distinguish between inhabited and biogenic sources. The ratio of tetrachloroethene to secondary alkyl nitrates can be used as a tool to decide about the origin and age of an air parcel analyzed. The ratio of the isomeric pentyl nitrates can also be used to characterize air masses.
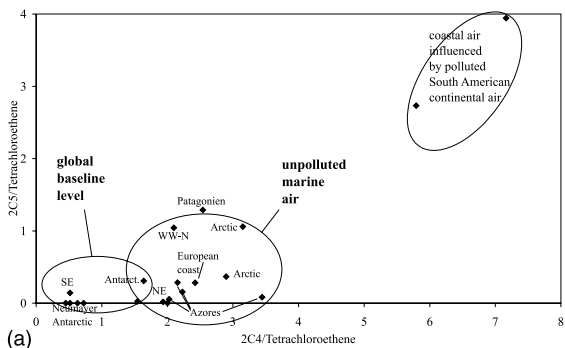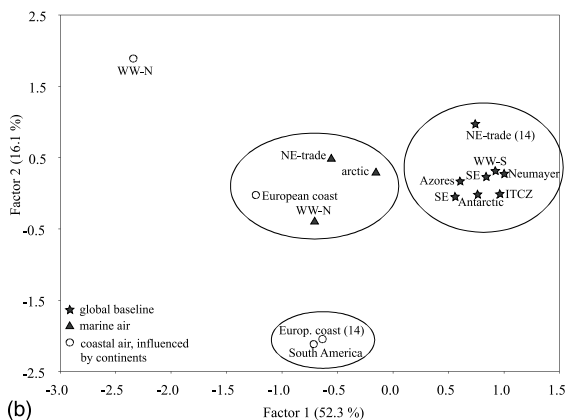
Fig. 5. Grouping of air masses by (a) mixing ratio of 2-butyl nitrate/tetrachloroethene versus 2-pentyl nitrate/tetrachlorethene, (b) PCA of organic nitrates in marine air.

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