Polarforschung 76 (1-2), 39 – 46, 2006 (erschienen 2007)

## The Air Chemistry Observatory at Neumayer Stations (GvN and NM-II) Antarctica

by Rolf Weller<sup>1</sup>, Ingeborg Levin<sup>2</sup>, Dietmar Wagenbach<sup>2</sup> and Andreas Minikin<sup>1,3</sup>

**Abstract:** The air chemistry observatory at the German Antarctic Neumayer Station (NM-II; formerly Georg von Neumayer Station, GvN) is in continuous operation since almost 25 years. It thus provided unique records of atmospheric trace constituents of climatic relevance. The focus of the established observational programme is on characterizing the physical properties and chemical composition of the aerosol, as well as on monitoring the changing trace gas composition of the background atmosphere, especially concerning greenhouse gases. Here a brief outline of the technical concept of the observatory and an excerpt of the most relevant results are presented.

Zusammenfassung: Das Spurenstoff-Observatorium an der deutschen Antarktis-Station Neumayer II (NM-II; vormals Georg-von-Neumayer, GvN) ist mittlerweile seit fast 25 Jahren kontinuierlich in Betrieb und liefert einzigartige Messreihen klimarelevanter atmosphärischer Spurenstoffe. Der Schwerpunkt des Messprogramms liegt in der Charakterisierung der physikalischen Eigenschaften und chemischen Zusammensetzung des Aerosols sowie in der Dokumentation der langfristigen Änderung der Spurengas-Zusammensetzung in der Hintergrund-Atmosphäre, speziell hinsichtlich der wichtigsten Treibhausgase. In diesem Beitrag werden eine kurze Beschreibung der technischen Auslegung des Observatoriums sowie einige der wichtigsten Ergebnisse präsentiert.

## INTRODUCTION

The atmosphere above Antarctica constitutes the cleanest part of the Earth's troposphere which allows here to study the composition and temporal change of the background atmosphere without any direct impact of civilization. Furthermore, with the exception of very few rocky terrains, the Antarctic continent is largely free of aerosol and trace gas sources, so that the main part of atmospheric trace compounds must be advected by long-range transport to Antarctica or has its source region in the surrounding Southern Ocean. Due to this unique position, Antarctica is an outstanding place to document long-term changes of the composition of our atmosphere in the so called "Anthropocene", the era that started with the industrial revolution about 200 years ago. The Neumayer air chemistry observatory is one of the few clean air laboratories operated in Antarctica with an extensive scientific programme, in parts established already in 1982. Since 1997 the air chemistry observatory is part of the GAW (Global Atmosphere Watch; <http://www.empa.ch/gaw/gawsis>) global station network. Another important aspect of studying tropospheric trace constituents in Antarctica is the need to interpret records of particulate or reactive trace compounds ob-served in firn and ice cores. Addressing the coupling between climate and

 Stiftung Alfred-Wegener-Institut für Polar- und Meeresforschung (AWI) in der Helmholtz-Gemeinschaft, Postfach 120161, 27515 Bremerhaven, Germany; <rolf.weller@awi.de>
Institut für Umweltphysik, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120

 <sup>2</sup> Institut für Umweitphysik, Universität Heidelberg, im Neuenneimer reid 229, D-69120 Heidelberg, Germany.
<sup>3</sup> DLR Deutsches Forschungszentrum für Luft- und Raumfahrt, Institut für Physik der

<sup>5</sup> DLR Deutsches Forschungszentrum für Luft- und Raumfahrt, Institut für Physik der Atmosphäre, Postfach 1116, D-82234 Wessling, Germany.

Manuscript received 03 April 2006, accepted 04 May 2006

biogeochemical cycles, polar ice cores provide a unique archive of climate proxies from which information about past changes of temperature and atmospheric aerosol load can be derived even in sub-annual resolution, provided that the controlling mechanisms of the air to firn transfer of relevant species are thoroughly investigated in the present atmosphere. In this context, the realization of deep drilling activities on the Antarctic sheet central ice (EPICA-project; <http://www.awi.de/en/research\_divisions/geosciences/ glaciology/projects/epical>), the need for recent atmospheric observations to interpret ice core records is strongly emphasized.

The purpose of this contribution is to give a brief overview on the technical layout of the observatory and highlight some outstanding scientific results. Concerning the latter, we will focus on conclusions drawn from the established long-term observational programme. For a more comprehensive view, especially concerning particular case studies, which we will not address here, see original publications listed below and in <http://www.awi.de/en/go/air\_chemistry\_observatory>.

# TECHNICAL ASPECTS OF THE AIR CHEMISTRY OBSERVATORY

The first air chemistry observatory at Georg von Neumayer Station (GvN) was initiated and constructed by the Institut für Umweltphysik, University of Heidelberg (UHEI-IUP) in 1982. Following almost thirteen years of operation, the technical equipment and the data acquisition facilities had to be renewed shortly after the old GvN was replaced in March 1992 by the new Neumayer Station II (NM II). The present observatory was designed in collaboration between AWI and UHEI-IUP as a container building placed on a platform some metres above the snow surface (Figs. 1, 2) and was finally set up in January 1995. All experiments installed in the air chemistry observatory are under daily control and daily performance protocols are available. A ventilated stainless steel inlet stack (total height about 8 m above the snow surface) supplies the experiments with ambient air.

Concerning anthropogenic pollutants, the Antarctic atmosphere is "ultra clean". Local pollution by vehicles and the NM-II base itself is, thus, a potential problem for many measurements aimed at representing the background status of the Antarctic troposphere. Consequently, a central aspect of the technical concept concerns the ability of contaminationfree sampling of aerosols and trace gases. This is realized by several means:

(i) The air chemistry observatory is situated in a clean air area



Fig. 1: The present air chemistry observatory at Neumayer II (on the left) together with the first observatory, which was installed in 1983 and finally dismantled in January 1995.

Abb. 1: Das momentan noch betriebene Spurenstoff-Observatorium bei Neumayer II (links) neben dem ersten Observatorium, das 1983 installiert und schließlich 1995 abgebaut wurde (rechts).



**Fig. 2:** A view inside the air chemistry observatory: Aerosol sampling on filters (right hand), integrating nephelometer and condensation particle counters (left hand).

Abb. 2: Blick in das Spurenstoff-Observatorium: Aerosolsammelanlage rechts, integrierendes Nephelometer und Kondensationpartikel-Zähler links.

about 1500 m south of NM-II. Due to the fact that northern wind directions are very rare, contamination from the base can be excluded for most of the time.

(ii) Power supply (20 kW) is provided by a cable from the main station, thus no fuel-driven generator is operated in the very vicinity.

(iii) Contamination-free sampling is controlled by the permanently recorded wind velocity, wind direction and by condensation particle concentration.

Contamination is indicated if one of the following criteria is given: Wind direction within a 330°–30° sector, wind velocity

<2.2 m s<sup>-1</sup> or >17.5 m s<sup>-1</sup>, or condensation particle concentrations >2500 cm<sup>-3</sup> during summer, >800 cm<sup>-3</sup> during spring or autumn and >400 cm<sup>-3</sup> during winter. If one or any definable combination of these criteria are given, high and low volume aerosol and part of the trace gas sampling are interrupted. Interestingly, most of the data loss is provoked by blizzards and drifting snow (wind velocity >17.5 m s<sup>-1</sup>). During such harsh weather conditions aerosol sampling has to be switched off entailing a data loss of roughly 10 % per year. Note, that only about 2 % of data loss is actually caused by potential contamination!

## SELECTED RESULTS

## Overview of the scientific program

Tables 1 and 2 present a summary of the current monitoring and sampling programmes established at the NM-II air chem.istry observatory. Generally, the observatory provides a platform for both, long-term observations and particular studies performed during one or two over-wintering periods or during summer seasons only. The majority of sample analyses have to be conducted in the home laboratories. The long-term observational program can be divided into three categories:

(i) High volume aerosol sampling on precleaned Whatman 541 cellulose filters (diameter 240 mm) at a flow rate of around 120 m<sup>3</sup> h<sup>-1</sup>. Typically about 20000 m<sup>3</sup> and 40000 m<sup>3</sup> of ambient air are sucked through filter pairs for analyses of ionic compounds and radio-isotopes, respectively. The main objective of these investigations is to determine the chemical composition of the aerosol, its seasonality and source apportionment.

(ii) In situ measurements of reactive trace gases like ozone and aerosol physical properties (number concentration, light scat-

category	sampling method	analysed compounds	institution
long lived	compressed air (200 bar)	SF <sub>6</sub> , CH <sub>4</sub> , <sup>13</sup> CH <sub>4</sub> , CH <sub>3</sub> <sup>2</sup> H, <sup>14</sup> CH <sub>4</sub>	UHEI-IUP
trace gases		$^{85}$ Kr, N <sub>2</sub> O, $\delta^{15}$ N-N <sub>2</sub> O*, $\delta^{18}$ O-N <sub>2</sub> O*	UHEI-IUP/IAR
	compressed air (2 bar)	CO <sub>2</sub> , <sup>13</sup> C-CO <sub>2</sub> , <sup>18</sup> O-CO <sub>2</sub>	UHEI-IUP
	(flask sampling)	$N_2O$ , $CH_4$ , $SF_6$ , $CO$ , $H_2$	
	absorption (in NaOH)	<sup>14</sup> CO <sub>2</sub>	UHEI-IUP
water vapour	cryogenic sampling	$H_2O, \delta^2 H- H_2O, \delta^{18}O- H_2O, {}^3H- H_2O$	UHEI-IUP
Reactive trace gases	low volume sampling (teflon/ nylon filter combination)	$SO_4^{2-}$ , $NO_{3-}$ , $Cl^-$ , MSA, $Na^+$ , $NH_4^+$ . $HNO_3$ , $SO_2$	AWI
aerosol	high volume sampling (Whatman541 filter)	$\mathrm{SO}_4^{2^-}$ , $\mathrm{NO}_3^-$ , $\mathrm{Cl}^-$ , MSA, $\mathrm{Na}^+$ , $\mathrm{NH}_4^{+^-}$ .	UHEI-IUP/AWI
		trace elements*	AWI
	high volume sampling	<sup>210</sup> Pb, <sup>7</sup> Be, <sup>10</sup> Be*	UHEI-IUP
fresh snow		SO <sub>4</sub> <sup>2-</sup> , NO <sup>3-</sup> , Cl <sup>-</sup> , MSA, Na <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , <sup>210</sup> Pb, <sup>10</sup> Be,	AWI/UHEI-IUP

**Tab. 1:** Summary of the actual sampling programme. (\*) = measured only during special campaigns; AWI = Alfred Wegener Institute for Polar and Marine Research, Bremerhaven; GSF = National Research Center for Environment and Health, Institute of Hydrology, München-Neuherberg; IAR = Institute for Atmospheric Radioactivity, Freiburg; UHEI-IUP = Institute of Environmental Physics, University of Heidelberg.

**Tab. 1:** Zusammenfassung des aktuellen Messprogramms. (\*) = nur auf speziellen Kampagnen gemessen; AWI = Alfred-Wegener-Institut für Polar- und Meeresforschung, Bremerhaven; GSF = Forschungszentrum für Umwelt und Gesundheit GmbH, Institut für Hydrologie, München-Neuherberg; IAR = Institut für Atmosphärische Radioaktivität, Bundesamt für Strahlenschutz, Freiburg; UHEI-IUP = Institut für Umweltphysik, Universität Heidelberg.

category	property	method	institute
aerosols	particles (>10 nm)	condensation particle counter (CPC)	AWI
physical properties	ultra fine particles (>3 nm)	CPC	AWI
	non volatile particles	thermo-denuder / CPC	DLR/AWI
	aerosol size distribution 0.5-20 $\mu$ m	optical particle counter	AWI
	black carbon, aerosol absorption	Aethalometer and Multi Angle	DLR/AWI
	_	Absorption Photometer (MAAP)	
	aerosol scattering	integrating nephelometer	AWI
trace gases	<sup>222</sup> Rn	$\alpha$ -spectroscopy of <sup>214</sup> Po	UHEI-IUP
	surface O <sub>3</sub>	UV-absorption	AWI
trace gases	column density of O <sub>3</sub> , NO <sub>2</sub> , OClO,	UV spectroscopy (DOAS)	IUPH

**Tab. 2**: Summary of the actual *in situ* measuring programme. AWI = Alfred Wegener Institute for Polar and Marine Research, Bremerhaven; DLR = German Aerospace Center, Institute of Atmospheric Physics, Oberpfaffenhofen; GSF = Research Center for the Environment and Health, Institute of Hydrology, München-Neuherberg; IAR = Institute for Atmospheric Radioactivity, Freiburg; UHEI-IUP = Institute of Environmental Physics, University of Heidelberg.

**Tab. 2**: Zusammenfassung des aktuellen *in situ* Messprogramms. AWI = Alfred Wegener Institut für Polar- und Meeresforschung, Bremerhaven; DLR = Deutsches Zentrum für Luft- und Raumfahrt, Institut für Physik der Atmosphäre, Oberpfaffenhofen; GSF = Forschungszentrum für Umwelt und Gesundheit, Institut für Hydrologie, München-Neuherberg; IAR = Institut für Atmosphärische Radioaktivität, Bundesamt für Strahlenschutz, Freiburg; UHEI-IUP = Institut für Umweltphysik, Universität Heidelberg.

tering, size distribution) for a comprehensive characterization of the aerosol and to assess the photo-oxidation potential of the Antarctic troposphere.

(iii) Whole air samples to determine long-term concentration trends of greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) and their isotopic compositions and anthropogenic tracers (SF<sub>6</sub> and <sup>85</sup>Kr) in the background atmosphere.

Selected results from each category will be presented below. Note that throughout this article atmospheric mixing ratios of trace gases are given in ppm, ppb, and ppt, i.e. molar parts per  $10^6$ ,  $10^9$ , and  $10^{12}$ , respectively.

#### Biogenic sulfur and particle number concentrations

Aerosol formation from biogenic precursor gases such as algae-derived dimethyl sulfide (DMS, CH<sub>3</sub>SCH<sub>3</sub>) plays an important and crucial role in determining the Earths albedo by direct and indirect effects. This is especially true for the Southern Hemisphere, where the emission of man-made aerosol is still much less dominant than in the Northern Hemisphere. Considering the naturally derived aerosol load of the Southern Hemisphere, the atmospheric photo-oxidation of DMS leading to the final reaction products methane sulfonic acid (MSA) and sulfuric acid is believed to be the most important process (YIN et al. 1990). In contrast to sulfate, which comprises a composite signal of marine biogenic, sea salt, terrestrial, and volcanic sources, MSA is known to be virtually exclusively formed by photo-oxidation of DMS (YIN et al. 1990). As for the marine biogenic tracer MSA, long-term aerosol measurements at GvN and NM-II revealed that the main source region is the South Atlantic primarily south of 50 °S with increasing contribution from more local sources south of 60 °S (MINIKIN et al. 1998). The non-sea salt sulfate (nsssulfate) and MSA records from this Neumayer site (Fig. 3) covering now more than 20 years of quasi-continuous observations reveal the strong seasonality of the signal with maximum concentrations in January. In addition the close correlation of nss-sulfate and MSA indicate that most of the sulfate amount in Neumayer aerosol is of marine biogenic origin and thus DMS dominates the overall sulfur budget at this site. The extraordinarily pronounced seasonality of atmospheric MSA and nss-sulfate concentrations is characteristic for coastal Antarctica (MINIKIN et al. 1998) and is linked with the seasonality of the sea ice coverage and insolation. Sea-ice retreat provokes distinct phytoplankton blooms (GÜNTHER & DIECK-MANN 1999) associated with DMS emissions into the atmospheric boundary layer. The impact of volcanic eruptions (El Chichon 1983, Cerro Hudson and Pinatubo 1991) are identifyable in the nss-sulfate signal but secondary compared to the biogenic sulfur source strength (LEGRAND & WAGENBACH 1999). This is in contrast to continental Antarctica, where the imprints of prominent volcanic events clearly exceed the biogenic sulfate signal for 1-2 years after the eruption date (TRAUFETTER et al. 2004).

#### Condensation particle concentrations

Condensation particle (CP) comprise all atmospheric particles which can act as nuclei for condensation of low volatile gaseous compounds like organic species (biogenic or from any combustion process), organic and mineral acids which are both reaction products of atmospheric photo-oxidation processes and most notably water vapour. Generally particles >3 nm in diameter can act as condensation nuclei. Especially particles within the accumulation mode (particle diameter 0.12.5 µm) can act as efficient cloud condensation nuclei and play an important role in cloud formation. The latter fact emphasizes the crucial role of aerosols in determining atmospheric radiation transfer. CP concentrations at Neumayer exhibit a stepwise increase from polar winter (below 100 particles cm<sup>-3</sup>) to a maximum in late austral summer of around 1000 particles cm<sup>-3</sup> (Fig. 4; data can be retrieved from the web as given above). During summer the chemical composition of these particles is mainly MSA and nss-sulfate, thus CN are formed in the marine troposphere by photo-oxidation of DMS emitted by the phytoplankton. During winter and stormy weather conditions, however, sea salt dominates the aerosol mass. Interestingly, the maximum of condensation particle concentration typically appears in late February to early March, i.e. shifted by around 4-6 weeks compared to the MSA and nss-sulfate maxima. Our measurements suggest that during late summer the concentration of very small particles between 3-5 nm diameter (nucleation mode) is significantly enhanced, indicating new particle formation. DMS could act via its photooxidation product sulphuric acid as gaseous precursor for nucleation mode particles, a process known as gas to particle conversion. Due to the relatively short atmospheric lifetime (a few hours) of nucleation mode particles, regional sources should dominate the measured signal. We believe that following the retreat of sea-ice in the nearby Atka Bay during late February, considerable amounts of DMS are released by the now emerging phytoplankton blooms in this area. Note that nucleation mode particles do not contribute much to the total aerosol mass due to their small size, therefore nss-sulfate and MSA concentration maxima do not necessarily coincide with the particle number concentration maximum!

#### Tropospheric ozone

It is generally accepted that the photo-oxidation of trace gases to water soluble compounds, followed by rainout, is the major cleaning procedure of tropospheric air. Photo-oxidation in the troposphere consists of typical radical chain reactions which need to be initiated, mainly by OH radicals. OH in turn is

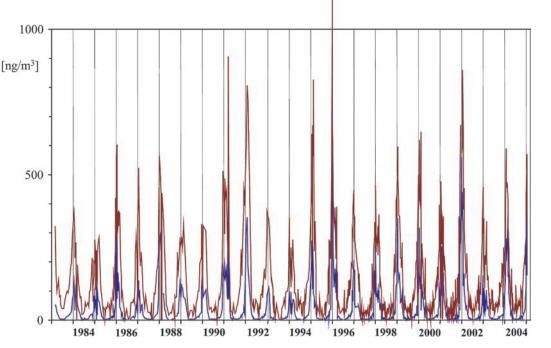


Fig. 3: Atmospheric methane sulfonic acid (MSA, blue line) and non-seasalt sulfate (nsssulfate, red line) concentrations sampled with the high volume sampling system (one week sampling period). Note the distinct seasonality with maximum concentrations in January for both compounds.

Abb. 3: Atmosphärische Konzentrationen von Methansulfonsäure (MSA, blaue Linie) und nicht-Seesalz-Sulfat (nss-Sulfat, rote Linie), beprobt mit der großvolumigen Aerosolsammelanlage (eine Woche Probungsinterval). Beachte die ausgeprägte Saisonalität mit maximalen Konzentrationen der Komponenten im Januar.

42

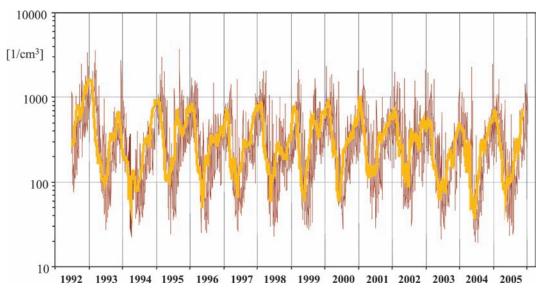


Fig. 4: Daily means of condensation particle (>10 nm) concentrations at Neumayer. The bold yellow line is a low-pass smoothed representation of the data by a 30 points Gaussian filter.

Abb. 4: Tagesmittel der Kondensationspartikel-Konzentration (>10 nm) an Neumayer. Die gelbe Linie zeigt die mit 30-Punkte-Gaußfilter geglätteten Daten.

primarily generated via ozone photolysis and subsequent reaction of the so produced O1D (i.e. electronically excited oxygen) atoms with water vapour. Thus tropospheric ozone is certainly a key trace gas in controlling the chemical composition of the troposphere. Surface ozone is continuously measured since 1982 at the Neumayer site (GvN and NM-II) by electro-chemical concentration cells (ECC, until 1994) and uv-absorption from 1994 ongoing (Fig. 5a). O<sub>3</sub> mixing ratios measured at the former GvN by ECC seem to be significantly lower before 1987, a probably artificial peculiarity which is not yet clarified. Nevertheless from this record, covering now 24 years of observation, no significant trend can be deduced. A more detailed section of this times series is depicted in Figure 5b. Maximum ozone values of about 32 ppbv are generally observed in August while during polar summer (December–January) a distinct minimum of around 13 ppbv is typical. In strong contrast to urban areas where nitrogen oxides  $(NO_x)$  levels are about three orders of magnitude higher, photochemical ozone destruction and not formation occurs in summer leading to surface ozone minima in pristine regions

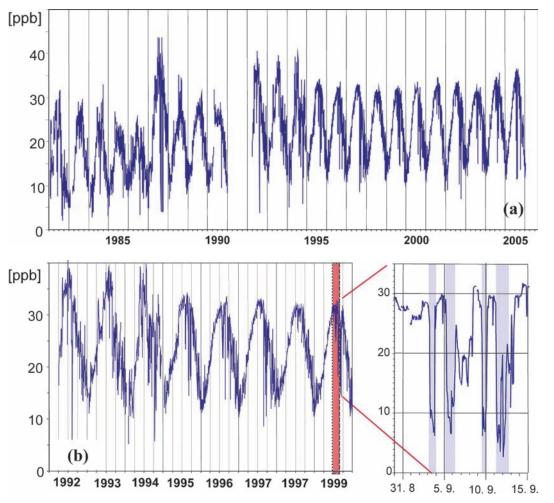


Fig. 5: Surface ozone mixing ratios (daily means) record at Neumayer from 1982 to 2005 (a). The enlarged section on the right hand side of (b) shows typical tropospheric ozone depletion events. Shaded areas show hourly averages in more detail.

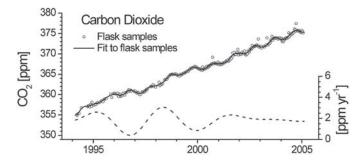
Abb. 5: Tagesmittel der bodennahen Ozonmischungsverhältnisse an Neumayer für den Zeitraum 1982 bis 2005 (a). Der Ausschnitt auf der rechten Seite von (b) zeigt typische troposphärische Ozon-Abbauereignisse (schattiert) in stündlicher Auflösung. like Antarctica. In addition, from August to September extraordinary tropospheric ozone depletion events can frequently be detected (Fig. 5b). Neumayer Station II was the first Antarctic site where this peculiarity was described (WESSEL et al. 1998). Comparable to stratospheric ozone depletion, reactive halogen compounds, here especially BrO, are responsible for this anomaly (FRIESS et al. 2004). However, in contrast to the chemical processes occurring in the stratosphere, tropospheric ozone depletion in polar regions is a natural phenomenon most probably caused by release of reactive bromine compounds eventually derived from sea-salt over sea-ice. There is some recent evidence that frost flowers, which frequently grow on newly-formed sea ice, play an important, if not crucial role as a source for reactive tropospheric halogen compounds (KALESCHKE et al. 2004).

## Greenhouse gases

Neumayer is the only station site in Antarctica where the main greenhouse gases carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O) as well as their isotopic compositions  $\delta^{13}$ C-CO<sub>2</sub>,  $\delta^{18}$ O-CO<sub>2</sub>,  $^{14}$ C-CO<sub>2</sub>,  $\delta^{13}$ C-CH<sub>4</sub>,  $\delta$ D-CH<sub>4</sub>,  $\delta^{18}$ O-N<sub>2</sub>O, and  $\delta^{15}$ N-N<sub>2</sub>O are measured simultaneously. In particular from the isotopic signature information about the corresponding greenhouse gas sources and sinks can be deduced (see LEVIN et al. 1987, HESSHAIMER et al. 1994, LEVIN & HESSHAIMER 2000, POSS 2003, RÖCKMANN & LEVIN 2005). The mixing ratio and isotopic analyses are made on whole air samples collected in high pressure cylinders as well as in 1-litre glass flasks.

## Carbon dioxide

The long-term increase of  $CO_2$ , caused by an ongoing input of  $CO_2$  from fossil fuel burning and land-use change into the atmosphere, was almost linear over the last decade (growth rate 1.8 ppm yr<sup>-1</sup>, Fig. 6), however, large inter-annual variations are obvious. For example in 1997/1998 during a strong El Niño period a positive  $CO_2$  anomaly was observed which is accompanied by a significant decrease of  $\delta^{13}C$ - $CO_2$  (not shown), indicating unusually large continental biogenic  $CO_2$  emissions during this period.

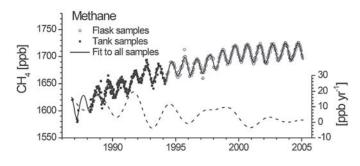


**Fig. 6:** Atmospheric carbon dioxide mixing ratios at Neumayer, measured on flask samples by gas chromatography. The solid lines are smoothed curve fits calculated with a fitting procedure described by NAKAZAWA et al. (1997), the dashed line gives the annual growth rate in ppm yr<sup>1</sup>.

**Abb. 6:** Atmosphärische Kohlendioxid Mischungsverhältnisse an Neumayer aus der gaschromatographischen Analyse der Glaskolbenproben. Die durchgehende Linie ist eine nach dem Algorithmus von NAKAZAWAET al. (1997) an die Daten angepasste geglättete Kurve. Die gestrichelte Linie gibt die jährliche Anstiegsrate in ppm yr<sup>-1</sup> wieder.

#### Methane

At Neumayer stations, methane mixing ratio has been measured on high-volume air samples since 1986 and on flask samples since 1994. Methane increased (globally) by approximately 75 ppb over the last 15 years. Interestingly, the growth rate decreased continuously from about 10-15 ppb yr<sup>-1</sup> in the 1980s to about 5 ppb yr<sup>-1</sup> in the 1990s and finally fluctuates around zero since about the year 2000 (Fig. 7). This trend in the CH<sub>4</sub> growth rate indicates that, in the last years, the sources of this greenhouse gas approach an equilibrium with its sinks (photochemical oxidation). However, with increasing emissions in the future associated with growing population and energy demand, atmospheric CH<sub>4</sub> mixing ratios will possibly increase again in the future. The distinct sinusoid like seasonal cycle of methane in the Southern Hemisphere with minimum mixing ratios during austral summer is caused by the seasonality of the photochemical CH<sub>4</sub> oxidation.



**Fig. 7:** Atmospheric methane mixing ratios at Neumayer, measured on highvolume air samples by gas chromatography. The solid lines are smoothed curve fits calculated with a fitting procedure described by NAKAZAWA et al. (1997), the dashed line gives the annual growth rate in ppb yr<sup>-1</sup>.

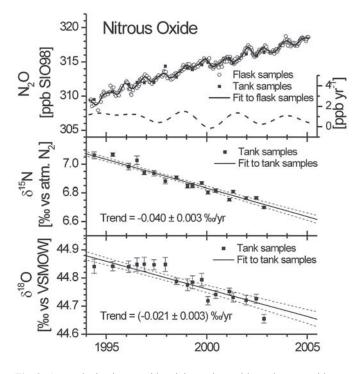
Abb. 7: Atmosphärische Methan Mischungsverhältnisse an Neumayer aus der gaschromatographischen Analyse der großvolumigen Luftproben. Die durchgehende Linie ist eine nach dem Algorithmus von NAKAZAWA et al. (1997) an die Daten angepasste geglättete Kurve. Die gestrichelte Linie gibt die jährliche Anstiegsrate in ppb yr<sup>-1</sup> wieder.

#### Nitrous oxide

During the last decade  $N_2O$  mixing ratio at Neumayer stations increased by 0.83 ppb yr<sup>-1</sup> (Fig. 8). Our isotope observations, the first long-term measurements of this species in the atmosphere, show corresponding trends of  $\delta^{15}N-N_2O$  of -0.040 ‰ yr<sup>-1</sup> and  $\delta^{18}O-N_2O$  of -0.021 ‰ yr<sup>-1</sup> providing observational evidence that mainly isotopically depleted  $N_2O$  from soils must be responsible for a large fraction of the observed  $N_2O$ increase in the global atmosphere (RÖCKMANN & LEVIN 2005). The seasonal variation of the  $N_2O$  mixing ratio with a mean peak-to-peak amplitude of 0.83 ppb is mainly caused by seasonally varying oceanic  $N_2O$  emissions as well as by stratospheretroposphere exchange processes (LEVIN et al. 2002, NEVISON et al. 2005).

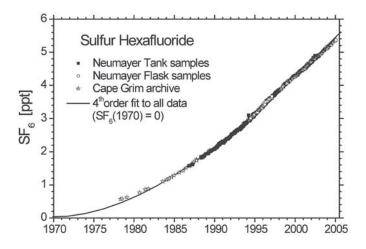
## Sulfur hexafluoride (SF<sub>6</sub>)

Sulfur hexafluoride is almost exclusively emitted into the atmosphere by man and mainly used in electric switch gear and for degassing molten reactive metals. Due to its extremely long atmospheric lifetime of more than 1000 years, almost all SF<sub>6</sub> remains in the atmosphere. Consequently, starting around 1970, mixing ratios persistently increased by several percent per year during the last three decades (Fig. 9). The linear trend observed over the last decade indicates a virtually constant emission rate since 1995. Sulfur hexafluoride is also an excel-



**Fig. 8:** Atmospheric nitrous oxide mixing ratios and isotopic composition at Neumayer, measured on air samples by gas chromatography and isotope ratio mass spectroscopy (IR-MS). The solid lines are smoothed curve fits calculated with a fitting procedure described by NAKAZAWA et al. (1997), the dashed line gives the annual growth rate in ppb yr<sup>-1</sup>.

**Abb. 8:** Atmosphärische Mischungsverhältnisse und isotopische Zusammensetzung von Lachgas an Neumayer aus der gaschromatographischen und IR-MS Analyse der Luftproben. Die durchgehende Linie ist eine nach dem Algorithmus von NAKAZAWA et al. (1997) an die Daten angepasste geglättete Kurve. Die gestrichelte Linie gibt die jährliche Anstiegsrate in ppb yr<sup>1</sup> wider.



**Fig. 9:** Atmospheric sulfur hexafluoride mixing ratios at Neumayer, measured on different air samples (high volume tank, flasks and from archived tank samples) by gas chromatography.

Abb. 9: Atmosphärische Schwefelhexafluorid Mischungsverhältnisse an Neumayer aus der gaschromatographischen Analyse verschiedener Luftproben (großvolumige Proben, Glaskolben und archivierte großvolumigen Proben).

lent tracer to validate atmospheric transport models as the distribution of its sources is well known and mainly restricted to the Northern Hemisphere (LEVIN & HESSHAIMER 1996). From the well established north-south difference of  $SF_6$  mixing ratios, a mean inter-hemispheric exchange time of 1 to 1.5 years can be deduced (MAISS & LEVIN 1994).

#### CONCLUSIONS, PERSPECTIVES AND OUTLOOK

Contamination free air sampling as realized in the air chemistry observatory at Neumayer stations (GvN and NM-II) has proved one's worth and is partly copied in the meanwhile at other stations, e.g., CASlab (Clean Air Sector laboratory) at Halley. After 13 years of permanent operation, the present air chemistry observatory (or "Spuso" as affectionately called by the over-winterers) at NM-II is expected to be replaced in austral summer 2008/2009 concurrently to the planned assembly of Neumayer Station III, the new German Antarctic station. Both containers of the present observatory are now seriously stained (Fig. 10) while part of the equipment is near failure preventing prolonged operation.

Concerning new scientific projects, we intend to install a specially designed Lidar system allowing remote monitoring of tropospheric aerosols. Until now, only very limited information on the vertical aerosol stratification above Antarctica are available. This new experiment will provide us year-round data on vertical aerosol distribution, similar to the set-up already installed at Koldewey Station (Spitsbergen, Arctic). Furthermore, especially regarding ice-core projects like EPICA (European Ice Coring in Antarctica), there is a need to expand our year-round aerosol sampling program to the Antarctic Plateau. Only very few year-round measurements of atmo-



Fig. 10: The Neumayer air chemistry observatory after ten years of continuous operation in January 2005. Note the seriously rusted container casing.

Abb. 10: Das Spurenstoff-Observatorium nach zehn Jahren Betriebszeit im Januar 2005. Man beachte den schweren Rostbefall der Containeraußenhülle.

spheric constituents are available from continental Antarctica and thus e.g., the seasonality of most ionic aerosol compounds is so far unknown for continental Antarctica. Within the EPICA project, an automated aerosol sampler was installed in February 2003 at Kohnen Station, the deep drilling location in Dronning Maud Land (75°S, 0°E, 2892 m.a.s.l.) and will be in operation for the next years. Due to the fact that Kohnen Station is, in contrast to EPICA Dome C, only a summer base and not a wintering station, the installation of an automated aerosol sampler was required. To our knowledge, we succeeded for the first time in running a stand-alone aerosol sampler in Antarctica throughout a year. Nevertheless, automated air chemistry observatories are generally restricted to very few and particular measurements and can definitively not substitute observatories, which are daily attended and whose sophisticated experiments are critically assessed every day by skilled scientific staff.

## **ACKNOWLEDGMENTS**

Parts of the research programme were funded by the Deutsche Forschungsgemeinschaft (DFG). We would like to thank the editor Dieter Fütterer who stimulated the compilation of this contribution. Very special thanks go to the AWI logistic team, the UHEI-IUP workshop and the scientists and technicians of the Neumayer over-wintering crews during the years 1982 to 2006 – you really made a good job of it!

#### References

- Frieß, U., Hollwedel, J., König-Langlo, G., Wagner, T. & Platt, U. (2004): Dynamics and chemistry of tropospheric bromine explosion events in the Antarctic coastal region.- J. Geophys. Res. 109: D06305, doi:10.1029/ 2003JD004133
- Günther, S. & Dieckmann, G.S. (1999): Seasonal development of algal biomass in snow-covered fast ice and the underlying platelet layer in the Weddell Sea, Antarctica.- Antarctic Sci. 11: 305-315
- Hesshaimer, V., Heimann, M. & Levin, I. (1994): Radiocarbon evidence for a smaller oceanic carbon dioxide sink than previously believed.- Nature 370: 201-203.
- Kaleschke L., Richter, A., Burrows, J., Afe, O., Heygster, G., Nothholt, J., Rankin, A.M., Roskoe, H.K., Hollwedel, J., Wagner, T. & Jacobi, H.-W.

 $\oplus$ 

(2004): Frost flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry.- Geophys. Res. Lett. 31: L16114, doi:10.1029/2004GL020655.

- Legrand, M. & Wagenbach, D. (1999): Impact of the Cerro Hudson and Pinatubo volcanic eruptions on the Antarctic air and snow chemistry.- J. Geophys. Res. 104: 1581-1596.
- Levin, I. & Hesshaimer, V. (1996): Refining of atmospheric transport model entries by the globally observed passive tracer distributions of 85Krypton and sulfur hexafluoride (SF6).- J. Geophys. Res. 101: 16745-16755
- Levin, I. & Hesshaimer; V. (2000): Radiocarbon a unique tracer of global carbon cycle dynamics.- Radiocarbon 42: 69-80.
- Levin, I., Kromer, B., Wagenbach, D. & Münnich, K-O. (1987): Carbon isotope measurements of atmospheric CO2 at a coastal station in Antarctica.-Tellus 39B: 89-95
- Maiss, M. & Levin, I. (1994): Global increase of SF6 observed in the atmosphere.- Geophys. Res. Lett. 21: 569-572
- Levin, I., Ciais, P., Langenfelds, R., Schmidt, M., Ramonet, M., Gloor, M., Sidorov, K., Tchebakova, N., Heimann, M., Schulze, E.D., Vygodskaya, N.N., Shibistova O. & Lloyd, J. (2002): Three years of trace gas observations over the EuroSiberian domain derived from aircraft sampling - a concerted action .- Tellus 54B: 696-712.
- Minikin, A., Legrand, M., Hall, J., Wagenbach, D., Kleefeld, C., Wolff, E., Pasteur, E.C. & Ducroz, F. (1998): Sulfur-containing species (sulfate and MSA) in coastal Antarctic aerosol and precipitation.- J. Geophys. Res. 103: 10975-10990.
- Nakazawa, T., Ishizawa, M., Higuchi, K. & Trivett, N.B.A. (1997b): Two curve
- fitting methods applied to CO2 flask data.- Environ. Metrics 8: 197-218. Nevison, C.D., Keeling, R.F., Weiss, R.F., Popp, B.N., Jin, X., Fraser, P.J., Porter, L.W., Hess, P.G. (2005): Southern Ocean ventilation inferred from seasonal cycles of atmospheric N2O and O2/N2 at Cape Grim, Tasmania.- Tellus 57B: 218-229.
- Poβ, C. (2003): Untersuchung der Variabilität des atmosphärischen Methanhaushalts hochpolarer Breiten anhand eines regionalen Trajektorienmodells und der Messung stabiler Isotope.- Diss. Univ. Heidelberg, xx-xx.
- Röckmann, T. and I. Levin (2005): High-precision determination of the changing isotopic composition of atmospheric N2O from 1990 to 2002, J. Geophys. Res., 110, D21304, doi:10.1029/2005JD006066.
- Thoning, K.W., Tans, P.P. & Komhyr, W.D. (1989): Atmospheric carbon dioxide at Mauna Loa Observatory - 2. Analysis of the NOAA GMCC data, 1974-1985.- J. Geophys. Res. 94: 8549-8565.
- Traufetter, F., Oerter, H., Fischer, H., Weller, R. & Miller, H. (2004): Spatiotemporal variability in volcanic sulphate deposition over the past 2 kyr in snow pits and firn cores from Amundsenisen, Antarctica.- J. Glaciol. 50: 137-146.
- Wessel, S., Aoki, S., Winkler, P., Weller, R., Herber, A., Gernandt, H. & Schrems, O. (1998): Tropospheric ozone depletion in polar regions: A comparison of observations in the Arctic and Antarctic.- Tellus 50B: 34-50
- Yin, F., Grosjean, D., Flagan, R.C. & Seinfeld, J.H. (1990): Photooxidation of dimethyl sulfide and dimethyl disulfide: Mechanisms evaluation.- J. Atmos. Chem. 11: 365-399.