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SULFUR HEXAFLUORIDE—A POWERFUL NEW ATMOSPHERIC TRACER

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Abstract—Long-term observations of the atmospheric trace gas sulfur hexafluoride (SF_6) at four background monitoring stations, Neumayer, Antarctica (1986–1994), Cape Grim, Tasmania (1978–1994), Izaña, Canary Islands (1991–1994) and Alert, Canada (1993–1994) are presented. These data sets are supplemented by two meridional profiles collected over the Atlantic Ocean (1990 and 1993) and occasional observations at the regional site Fraserdale, Canada (1994). The analytical system and the method of SF_6 calibration are described. Compared with data from Neumayer and Izaña reported earlier, measurements are updated for all sites until the end of 1994 and the precision has improved by more than a factor of 2. With the Cape Grim archived air samples, the atmospheric SF_6 chronology is extended by 8 more years back to 1978. For the period from January 1978 to December 1994 the data confirm a stable and unbroken quadratic rise in tropospheric SF_6 from 0.50 to 3.11 ppt in the southern hemisphere and for July 1991 to December 1994 from 2.69 to 3.44 ppt in the northern hemisphere. The global mean tropospheric increase rate in late 1994 was 0.225 ppt yr^{-1} (6.9% yr^{-1}). The long term trend and interhemispheric gradients are due to industrial production and emission, rising approximately linearly with time and located predominantly (94%) in the northern hemisphere. The interhemispheric exchange time (1.7 ± 0.2 yr) derived from SF_6 ground level observations when using a two-box model of the atmosphere is considerably larger if compared to the exchange time derived from two- and three-dimensional models (1.1 yr). The chemical and biological inertness of SF_6 up to stratospheric conditions results in an atmospheric lifetime of more than 800 years and makes SF_6 a powerful tool for modelling transport processes in the atmosphere. Moreover, the tropospheric SF_6 chronology is a very valuable input function for mixing studies in linked compartments like the stratosphere, the hydrosphere and the cryosphere.

Key word index: Sulfur hexafluoride, atmospheric trace gas, interhemispheric exchange, GC-ECD.

1. INTRODUCTION

Sulfur hexafluoride is an extremely stable atmospheric trace gas produced entirely anthropogenically. Its unique physico-chemical properties make this gas ideally suited for many specialized industrial applications. Most of the SF_6 produced worldwide (≈ 80%) is used in and released from electrical equipment, predominantly Gas Insulated Switchgear (GIS). This primary use started in the 1960s. Historical release estimates are available for the years 1953–1974 rising from 14 to 1200 Mg SF_6 yr^{-1} (Ko *et al.*, 1993, and references therein). For the beginning of the 1980s a world-wide production rate of 2500–4500 Mg SF_6 yr^{-1} is reported (*Encyclopedia of Chemical Technology*, 1980) rising approximately linearly since 1970 to an estimated value of 5000–8000 Mg SF_6 yr^{-1} around 1990 (SOLVAY, SF_6 producer, personal communication, 1993). These numbers on SF_6 production

are very rough estimates. Beyond this, the amount of SF_6 that is banked inside electrical equipment is highly uncertain. However, observing the global increase of SF_6 in the atmosphere provides a reliable accumulation record from which release rates can be calculated. This approach has been used by Maiss and Levin (1994) to model an atmospheric emission history, namely the history of SF_6 production assuming different residence times associated with its commercial applications. These results agreed reasonably well with the production estimates.

The accumulation of sulfur hexafluoride in the atmosphere is nearly perfectly described by its release rate due to its long atmospheric life-time of probably 3200 yr (Ravishankara *et al.*, 1993). A minimum estimate of 800 yr is given by Morris *et al.* (1995). The oceanic sink to date is negligible due to the low water solubility of SF_6 (Ostwald solubility coefficient ≈ 1%, Wanninkhof *et al.*, 1991) and a relatively slow

oceanic deep-water formation rate. Since the very first atmospheric measurements in 1970 (Lovelock, 1971), the SF_6 concentration has increased by two orders of magnitude from 0.03 ppt (parts per trillion by mole) to a global mean value of 3 ppt at the end of 1993. This dramatic increase recently brought SF_6 into the climatic impact discussion since, on a per molecule basis, the greenhouse effect of SF_6 is likely to be one of the highest of any atmospheric trace gas (Rinsland et al., 1990). In fact, the Global Warming Potential for SF_6 relative to CO_2 on a 100 year time horizon has been estimated to be about 20,000 (Ko et al., 1993; Stordal et al., 1993). Only the present low SF_6 concentrations ($\approx 10^{-8}$ of CO_2; $\approx 10^{-2}$ of CFC) preclude any actual climatic relevance.

Here we describe the Heidelberg low-level SF_6 analysis technique by electron capture gas chromatography including the calibration procedure which was used to achieve the complete SF_6 data set presented here. The main purpose of the paper is to present new world-wide high-precision SF_6 data records now covering the past 18 yr by including samples from the unique air archive from Cape Grim, Tasmania (Fraser et al., 1991). In a similar way, as described by Maiss and Levin (1994) we use a simple two-box model of the atmosphere to explain the interhemispheric difference and to derive a long-term trend function for the tropospheric SF_6 chronology in both hemispheres. The potential to apply SF_6 as a transport tracer in the atmosphere and in linked compartments like the hydrosphere or the cryosphere is also discussed briefly.

2. ANALYTICAL SYSTEM

Analysis of sulfur hexafluoride is performed by gas chromatography using an electron capture detector (Shimadzu GC-8AIE). The system, shown schematically in Fig. 1, is a compact transportable device, primarily designed for on board SF_6 analysis of water samples during a tracer release experiment in Lake Constance, Germany (Maiss et al., 1994a, b). Here we briefly summarize the major features with emphasis on routine air sample analysis for the present work.

The analytical system can be roughly divided into five components: (1) the six-port selection valve V1 to load different types of samples. It allows either the gas content of the stripper reservoir to escape during water sample injection through the vent of V3, or allows one of the two sample loops selected by valve V3 to be flushed with nitrogen (positions D and F of V1) or loaded with standard or a gas sample; (2) the extraction unit for water samples, including the stripper reservoir, the $Mg(ClO_4)_2$ drier, and the ten-port valve V2. During gas sample analysis, this part is used as a through pass and a switch for flushing the content of the in-line sample loop onto the trap; (3) the injection system for gas samples, being loaded through valve V1 and consisting of two sample loops selected by valve V3. Four volume calibrated loops are avail-

able: 0.1040 ± 0.0014, 1.006 ± 0.002, 4.817 ± 0.002 and 15.024 ± 0.002 cm^3. In principle, air samples with sub-ambient pressure can be analyzed as well by connecting a vacuum system at the vent of valve V3; (4) the trapping system, namely the trap, heater/cooler and functions of valves V2 and V4; (5) the chromatographic separation and detection system, including pre- and main-column, valve V4, and the electron capture detector (ECD). Since components are integrated into one unit, most of the valves are involved in more than one function.

Valve switching, heating and cooling of the trap are controlled by a portable PC recording the ECD-signal and providing instantaneous peak integration. In this way, the reproducibility is improved, since only the sample injection remains manual. Standard and blank measurements are automatic. Gas samples take about 10 min analysis time. Ultra-high purity nitrogen further cleaned by an activated charcoal filter is used as carrier gas. This purified nitrogen is tested to be free of SF_6 ($< 10^{-5}$ ppt) and is used also for blank measurements. The four valves V1–V4 (Valco E-2) can be positioned electronically and have very small dead volume stainless steel rotary heads. The content of one or more sample loops is collected in the trap filled with Porapak-Q$^\circledR$ and cooled down to $-77°C$ by a dry-ice/isopropanol bath. The cryogenic preconcentration allows large volume samples and thus high-precision analyses of low mixing ratio samples. Electromechanical repositioning of the isolated trap between two copper blocks held at $+100°C$ completely releases the trapped SF_6. Chromatographic separation starts by the injection of the heated trap content onto the precolumn (30 cm) which is backflushed when SF_6, being the fastest component, has reached the main column (300 cm). This enhances sample throughput. Both columns are made of 2.4 mm ID stainless steel tube, packed with 5 A molecular sieve (80–100 mesh, Alltech), located in the GC oven and kept at 65°C. With a carrier gas flow rate of 20 ml min^{-1}, the SF_6 peak reaches the ECD kept at 330°C 2 min after trap injection.

In the present work, air sample analyses were carried out with the 15.024 cm^3 loop (position 2 at V3), while for standard gas analyses the 1.006 cm^3 loop (position 1 at V3) was always used. All SF_6 measurements are first related to our 93.7 ppt secondary standard. For testing the linearity of the system, different numbers of standard gas aliquots from the 1.006 cm^3 and the 0.104 cm^3 sample loop (at positions 1 and 2 of V3) were collected in the trap and analyzed. The response of the system to SF_6 is linear ($R^2 > 0.9999$) from the minimum detectable level of 0.015 fmol up to 10 fmol with a typical sensitivity of 22 mV s fmol^{-1} (1 fmol $= 10^{-15}$ mol). During routine analysis the sensitivity of the whole analytical system is measured by two standard gas analyses every 8 air samples. The analytical precision of a single sample is dominated by the peak area uncertainty of replicate blank measurements of ± 0.12 mV s leading to an accuracy of
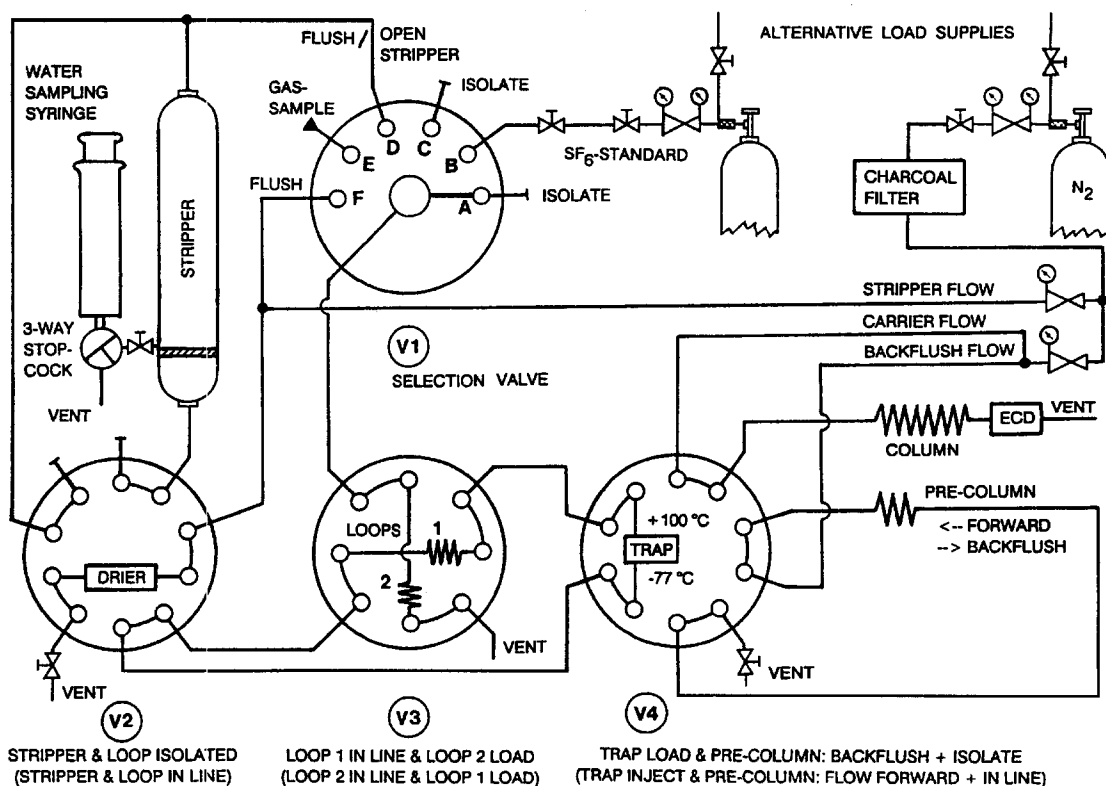
Fig. 1. SF$_6$ analysis system: legends describe the different functions of the valves V1–V4 for the shown position and the reverse position in parentheses.

± 1.3%. Higher precision was achieved when working, in addition, with five air standards at the concentration range of 1.6–3.2 ppt. These background air standards are routinely analyzed together with the samples of unknown concentration. The results for the air standards on an individual day are used in a second evaluation step to adjust the peak area of the blank in an optimum way through least squares fitting. This procedure leads to an improvement of the blank determination on individual days and thereby to an overall analytical precision of about ± 0.5%. A large number of the air samples stored in aluminium or stainless steel tanks over different time periods (up to 6 yr) was analyzed repeatedly over the last 3 yr. No drift in concentration has been observed in these samples.

3. CALIBRATION METHOD

All SF$_6$ measurements are related to our 93.7 ppt SF$_6$ secondary gas standard prepared in the Heidelberg laboratory from a commercially available gravimetric high pressure 0.1 ppm (parts per million) SF$_6$ in N$_2$ primary standard with a certified accuracy of ± 1% (Messer–Griesheim, Germany). A gravimetrically controlled single step static pressure dilution with ultrapure N$_2$ was used, giving an absolute nom-

inal accuracy of our secondary gas standard of ± 1.1%. Even though this method is simple and reliable it is not very common. Therefore we will describe the preparation procedure here in detail.

Firstly, the volume of a normal 2 ℓ aluminium tank (Luxfer) fitted with a stainless steel valve and designated to take the final gas standard, is precisely calibrated by weighing it, repeatedly evacuating, and filling with N$_2$ at ambient pressure and temperature. Gas density and mass difference yield the tank volume V_T. Material and size of the tank were chosen to stay within the usual range of high precision scales (4000 g) even if filled with 200 atm of N$_2$. The scale precision (± 0.01 g) is sufficient to calibrate a volume of about 2000 cm^3 with an accuracy better than 0.5%. We obtained $V_T = 2059 \pm 10$ cm^3. To contain an aliquot of our primary standard (concentration $c_o = 0.1$ ppm (± 1%)) we used a stainless steel cylinder of calibrated volume (Nupro), $V_C = 50$ cm^3 (± 1%), fitted with a stainless steel valve. This cylinder was evacuated, weighed, and filled up to about 6 atm with our primary standard. Due to the lower weight of this cylinder the resulting increase in weight, Δm_C = 0.366 g, is measured with a precision of ± 0.001 g. The filled cylinder was then connected to the evacuated 2 ℓ aluminium tank and its content expanded into the tank. After pressure equilibration, both containers were closed and disconnected. A 50 ℓ tank of

ultrapure, SF_6-free N_2 (200 atm) was then attached to the aluminium tank to bring it close to equilibration pressure (≈ 190 atm). The aluminium tank was weighed and the mass difference relative to the evacuated weight was determined ($\Delta m_T = 379.91 \pm 0.01$ g). Even considering an unprecisely known dead volume of the fittings used for coupling the 50 cm^3 cylinder to the aluminium tank ($V_D \approx 7.5 \pm 1$ cm^3), the final standard concentration $c_s = c_o \cdot \{V_T/(V_T + V_C + V_D)\} \cdot \{\Delta m_C/\Delta m_T\} = 93.7$ ppt is determined with a nominal uncertainty of $\pm 1.1\%$ (Gaussian addition of errors) being mainly due to the $\pm 1\%$ uncertainty of the primary standard. The assumption of ideal gas behavior is used to calculate the tank volume V_T at a pressure of ≈ 1 atm where the non-ideal correction for N_2 ($+ 0.03\%$) can be neglected. Our calibration method needs no accurate measurement of high pressures. Only simple volume and weight determinations are to be made. A dilution factor of $\approx 10^{-5}$ can be achieved by one single step.

There is no internationally accepted gas standard for SF_6 in the ppt range available, and no intercalibration with other laboratories has been undertaken so far. However, a comparison based on atmospheric background concentrations derived recently from oceanic background observations by Law et al. (1994) indicates absolute differences between the two laboratories of less than $\pm 5\%$. Our standard was prepared gravimetrically and is, thus, defined in a mole fraction scale. Consequently, and therewith following conventional practice (R. Weiss, personal communication) all concentrations given in the present paper are mole ratios.

4. SAMPLING SITES

Long-term observations of SF_6 at four background air monitoring stations, Neumayer (Antarctica), Cape Grim (Tasmania), Izaña (Canary Islands), and Alert (Canada) are the basis of the present SF_6 study. In addition to these time series, two shipboard meridional profiles of background air over the Atlantic Ocean were analyzed as well as occasional samples from the regional site Fraserdale (Canada). Except for the Cape Grim baseline station, the samples are high volume air samples originally collected for methane isotope analyses in Heidelberg (Levin et al., 1992). The six sampling sites in the northern and southern hemisphere are characterized as follows:

Neumayer (Antarctica, 71°S, 8°W, 42 m asl). At the German Antarctic Neumayer station, situated on the Ekström ice shelf close to the ice edge, monthly, and in later years up to weekly, spot samples of about 1 m^3 of air were directly compressed into 10 ℓ high pressure tanks using a diving compressor (Bauer, München). Before 1991 stainless steel tanks were used as sampling containers, in the later years, in most cases, we used aluminium tanks. Air sampling is controlled by wind direction to guarantee background conditions. With increasing time resolution, 225 samples from October 1986 till December 1994 have been measured. This data set provides the most comprehensive quasi-continuous time series of SF_6 measurements.

Cape Grim (Tasmania, 41°S, 145°E, 94 m asl). Since 1978 air has been archived at the Cape Grim Baseline Air Pollution Station in pressurized tanks. A detailed description of the sampling technique at this station on the northwestern tip of Tasmania, Australia, is given by Fraser et al. (1991) and Weeks et al. (1992). The Cape Grim air archive has been shown to accurately represent the Cape Grim in situ record for CFC-11 and CFC-12 over the period 1978–1993 (Cunnold et al., 1994). Samples of the Cape Grim air archive were transferred to previously evacuated electropolished stainless steel flasks of 1.6 and 0.9 ℓ volume. Typical pressure in subsamples was 200–500 kPa absolute, mostly achieved by direct transfer, but assisted cryogenically if the parent archive tank had a lower pressure. The integrity of the subsample was assessed by comparing measured values in parent and subsample for a full range of species measured in at CSIRO, including CO_2, CH_4, CO, H_2, N_2O, and several CFCs. Typically, agreement was better than 2% in all cases. In the Heidelberg laboratory, SF_6 analyses were performed on 44 subsamples over the time range of 1978–1994. This time series represents the longest atmospheric SF_6 chronology available to date.

Izaña (Tenerife/Canary Islands, 28°N, 16°W, 2367 m asl). At this high altitude maritime background observatory in the North Atlantic trade wind system operated by the Instituto Nacional de Meteorologica, Madrid, Spain, air is most of the time representative of the free mid-troposphere in this latitudinal belt (Schmitt et al., 1988). Air has been collected continuously over two weeks in high volume bags made of polyethylene coated weldable aluminium foil. These integrated samples of about 1–1.5 m^3 STP were subsequently transferred to 10 ℓ aluminium tanks using a diving compressor (Bauer, München). 85 Izaña air samples have been analyzed for SF_6 since July 1991.

Fraserdale (Canada, 50°N, 82°W, 200 m asl). Weekly integrated samples collected in 1994 have been analyzed from the regional station Fraserdale, run by the Atmospheric Environment Service (AES), Toronto, Canada. The air sampling technique is the same as used at Izaña. The Fraserdale station is located in the Hudson Bay Lowlands far away from anthropogenic sources. Moreover, trajectory analyses show that the station, for most of the time, is influenced by northerly air masses (AES, unpublished results). The station should, therefore, represent continental background conditions in mid-latitudes of the northern hemisphere.

Alert (Canada, 82°N, 63°W, 187 m asl). 36 samples from the High Arctic Research Laboratory, Alert, also operated by the AES, have been analyzed. The station

is located at the northeastern strip of Ellesmere Island and is thus far removed from major industrial regions. This site is well suited to monitor the background air of the high northern latitudinal belt (Trivett and Worthy, 1989). SF_6 measurements on two-week integrated samples collected in a similar way as at Izaña and Fraserdale started in April 1993 and are available until December 1994 except for a six week gap from 2 May to 14 June 1994.

Latitudinal profiles. High volume surface air spot samples were collected during two cruises of the German *RS Polarstern* on the Atlantic Ocean. In November 1990 samples were taken from 30°N to 68°S on a cruise from Germany to Antarctica, and in November 1993 we collected samples from 40°N to 56°S on a cruise from Germany to South Africa.

5. ATMOSPHERIC SF₆ HISTORY

Figure 2 summarizes all SF_6 background observations achieved in this investigation for the northern (NH) and the southern (SH) hemisphere. Compared to the preliminary data from Neumayer and Izaña reported by Maiss and Levin (1994), the measurements presented here have more than double the precision, and are updated until December 1994. Additionally, archived air samples from Neumayer station have been analyzed together with the new samples from Alert, Fraserdale and from Cape Grim archived air. With the latter, the atmospheric chronology of SF_6 is extended by 8 yr back to 1978.

Time-series of sulfur hexafluoride in both hemispheres show very little scatter and a steady long-term increase. The concentration in the NH is persistently higher when compared to the SH due to a relatively strong increase rate resulting from predominantly NH sources, and an interhemispheric exchange time of the order of 1–2 yr. Concentrations observed at Alert normally exceed those observed at Izaña, on average by 0.07 ppt in 1994. Maximum "background" concentrations are observed in mid-northern latitudes, at Fraserdale, exceeding concentrations observed at Izaña, on average by 0.14 ppt in 1994. These maximum concentrations can be explained by the fact that the main sources of SF_6 are located in northern mid-latitudes. For comparable sampling periods in the Southern Hemisphere (SH), the Cape Grim and Neumayer data are identical within their inherent variations. This impressively shows that, with respect to SF_6, mid-to-high latitudes of the SH seem to be well mixed. Also before 1986, the Cape Grim data reflect a nearly perfect back-extrapolation of the long-term trend established by the Neumayer data. This means a stable and unbroken trend in the rise of atmospheric SF_6 since 1978. For the period from May 1991 to February 1992, the Neumayer record shows a concentration bump in combination with data variations larger than in the remaining part of the SH record. An error during sample analysis can be ex-

cluded. However, since the period exactly coincides with the use of new tanks (Spectra-Seal, BOC), we are still investigating if this concentration bump comes from a small contamination in the sample containers. These debatable data are shown in Fig. 2 but have been excluded in the long-term trend fitting given below.

Both shipboard latitudinal profiles, shown by the inset of Fig. 2, are consistent with the time series. An identical concentration scale for the inset allows for direct comparison of the latitudinal distribution with the time series data. Southern hemispheric means for the troposphere of 2.34 ± 0.03 ppt for November 1990 and 2.91 ± 0.02 ppt for November 1993 are calculated by weighting the cruise data by the area of the equivalent latitude band. For the NH, means of 2.57 ppt (1990) and 3.15 ppt (1993) were derived with the same method. These NH means are likely to be minimum values since missing cruise data for mid-to-high latitudes result in underestimated NH means. Therefore, based on the cruise data for the latitude of Izaña, we have used the above mentioned mean concentration shifts for the sites Fraserdale (+ 0.14 ppt) and Alert (+ 0.07 ppt) to create two supplementary "data points" at 50° and 82°N. These values are shown as well in the inset of Fig. 2. With these additional estimates for 50° and 82°N we have calculated NH means again and obtain 2.67 ppt (1990) and 3.21 ppt (1993) as probably the more realistic values.

Maiss and Levin (1994) have already shown that, based on Neumayer observations, an extrapolation of the global increase of SF_6 back to 1970 matches other historical measurements in the 1970s and early 1980s reasonably well. Further, using a simple two-hemispheric box model, the long-term trend of SF_6 observed in the troposphere is best fitted by a quadratic increase. Linear or exponential trend curves would conflict with earlier observations and are not able to describe the onset of marked SF_6 emissions in the 1960s when the predominant industrial application in GIS systems started. Interpretation of the SF_6 concentrations obtained in both this study and earlier work, requires a model for atmospheric mixing as well as for the global source distribution of SF_6. For the latter we will make the following estimates:

The dominant use of SF_6 (80%) is in heavy electrical equipment, such as gas insulated switchgear (GIS) and substations (Niemeyer and Chu, 1992). The remaining 20% is mainly used in metal industries for blanketing or degassing the molten reactive metals aluminium and magnesium (Stordal *et al.*, 1993). In the case of GIS, the occasional release of SF_6 into the atmosphere, either through small leakage from equipment or discharge during equipment repair or maintenance, should be distributed down to a country scale and directly correlated with electric power production. In 1987, the NH produced 94%, 88% and 100% of total electric power, aluminium and
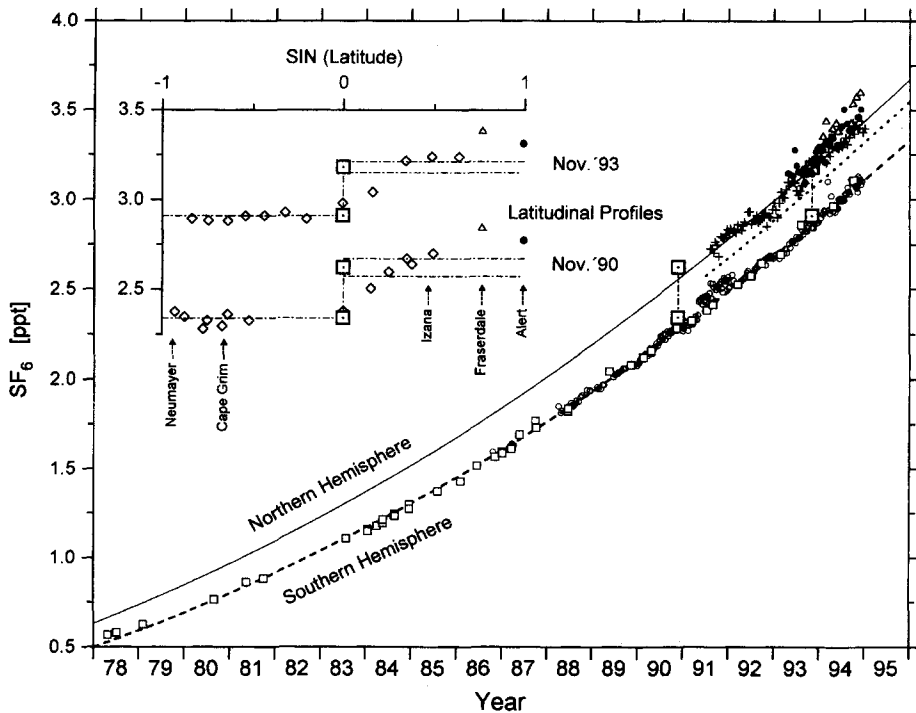
Fig. 2. SF_6 observations in the atmosphere: southern hemispheric records for Neumayer station (O) and Cape Grim (□) are based on spot samples. northern hemispheric time series for Izaña (+) Alert (•) and Fraserdale (△) are obtained from one- and two-week integrated samples. Not shown are three outliers from Fraserdale and one outlier from Izaña being probably contaminated by polluted air mass plumes. The analytical uncertainty of individual data points is always below symbol size. Assuming 94% of SF_6 emissions occurring in the northern hemisphere, results of a quadratic trend model fitting are given as dashed curve for the southern hemisphere and as solid and dotted curve for the northern hemisphere, using an interhemisphere exchange time of 1.7 and 1.1 yr, respectively. Inset: (◇) Latitudinal profiles of SF_6 ground level concentrations over the Atlantic Ocean. Hemisphere means are indicated by dashed-dotted lines. A second higher mean in the northern hemisphere is obtained if indicated estimates for Alert (•) and Fraserdale (△) are considered additionally. Open squares joined by a dashed-dotted line allow to link the latitudinal profiles information to the time-series of the main figure.

magnesium production, respectively. For a variety of smaller, more sophisticated SF_6 uses, a 100% NH contribution seems realistic. If the 80% heavy electrical use of SF_6 is associated with 94% of the total power production in the NH, and the remaining 20% of SF_6 uses are associated with the 88–100% use in the NH, between 93% and 95% of the total SF_6 emissions occur in the NH. Prather et al. (1987) estimated a figure of 95% for the NH power production in 1978, and we assume that a similar percentage of northern hemispheric SF_6 emissions (94 ± 1%) is applicable for the period back to that time.

For a simple analytical long-term representation of our tropospheric data, a two-box mass balance model can be formulated assuming an atmospheric lifetime of SF_6 much longer than its atmospheric occurrence, and an emission rate $E(t)$ of SF_6 (10^{-12} mol yr^{-1}) increasing linearly with time:

$$dc_{NH}(t)/dt = \gamma \cdot E(t) \cdot 2/n_{eff} - \Delta c_{NS}(t) \tau_{ex} \quad (1)$$

$$dc_{SH}(t)/dt = (1 - \gamma) \cdot E(t) \cdot 2/n_{eff} + \Delta c_{NS}(t)/\tau_{ex} \quad (2)$$

where $c_{NH}(t)$ and $c_{SH}(t)$ are the mean surface concentrations in both hemispheres; $\Delta c_{NS} = c_{NH}(t) - c_{SH}(t)$ is the mean interhemispheric difference; n_{eff} is the mass of the effective atmospheric reservoir in moles (to get the global inventory from surface concentrations); τ_{ex} is the interhemispheric exchange time and γ (94%) is the ratio of NH emissions to total emissions. With time t in years AD (e.g. $t = 1992.0 \Leftrightarrow 1$ January 1992) and with $c_{NH}(t_o) = c_{SH}(t_o) = 0$ the solution of equations (1) and (2) can be approximated for $t > (t_o + 2 \text{ yr})$ by the following quadratic time dependency for the SH:

$$c_{SH}(t) = u \cdot (t - t_o)^2 \quad [\text{ppt}]. \quad (3)$$

The values of u and t_o were derived by fitting equation (3) to the Neumayer and Cape Grim data, and found to be 0.003865 and 1966.635, respectively. Figure 2 displays this result by a dashed curve providing an excellent representation of the observed SF_6 record in the SH. Further, in terms of the revised parameters u and t_o if compared to the earlier estimate of Maiss and Levin (1994), the model solution for the emission rate and the interhemispheric concentration difference

is given by:

$$E(t) = 2u\,n_{\text{eff}}\{t - t_o + \tau_{\text{ex}}\cdot(\gamma - 0.5)\}$$

$$[10^{-12}\,\text{mol yr}^{-1}] \tag{4}$$

$$\Delta c_{\text{NS}}(t) = 2u\tau_{\text{ex}}\{(2\gamma - 1)(t - t_o + \tau_{\text{ex}}\cdot(\gamma - 1))\}$$

$$[\text{ppt}]. \tag{5}$$

A value for n_{eff} is only needed for emission calculations through (4). From own unpublished vertical SF_6 profiles we estimated that during the last 15 years n_{eff} is at least 95% of the total atmospheric dry mass ($n_{\text{atm}} = 1.77 \times 10^{20}$ mol). Neglecting this slight difference of $< 5\%$ ($n_{\text{eff}} \approx n_{\text{atm}}$) and using derived values for u, γ, t_o and $\tau_{\text{ex}} = 1.7$ yr, equation (4) can be simplified to a emission rate estimate in Gg yr^{-1} as follows: $E(t) = 0.2\cdot\{t - 1966\}$. For example 5.7 Gg yr^{-1} are obtained for 1994 fitting well into emission scenarios based on earlier data (Maiss and Levin, 1994, and references therein).

Using SH fit values for u and t_o and adding (5) to (3) gives the model solution $c_{\text{NH}}(t)$ for the NH. The only unknown τ_{ex} is obtained by least squares fitting of $c_{\text{NH}}(t)$ to the Izaña data set. An interhemispheric exchange time $\tau_{\text{ex}} = 1.7 \pm 0.2$ yr yields the best fit for $\gamma = 94\%$ and is shown in Fig. 2 by a solid curve. A variation of γ by 1% alters the value for τ_{ex} only by ± 0.04 yr.

With equation (5) solved for τ_{ex}, interhemispheric exchange times can be calculated from the north–south concentration difference, Δc_{NS}, derived from hemispheric means of measured latitudinal profiles as well. Depending on which of the two different estimates for the Northern Hemiseperic mean (Fig. 2) the computation of Δc_{NS} is based on, a range for τ_{ex} from 1.4 to 2.0 yr and from 1.3 to 1.6 yr is obtained for November 1990 and 1993, respectively. The minimum values for τ_{ex} are obtained if only measurements up to 40°N are considered. Within the obtained uncertainty ranges, the results are consistent with the long-term mean $\tau_{\text{ex}} = 1.7 \pm 0.2$ yr derived from the continuous data. On the other hand, the wide ranges also show how sensitive estimates of τ_{ex} are on the way the NH means have been determined.

6. DISCUSSION

Agreement between the interhemispheric exchange time as derived from long-term observations and those calculated from November 1990 and November 1993 cruise results is not compelling as each measured latitudinal distribution is affected by the actual position of the Inner Tropical Convergence Zone (ITCZ) showing seasonal and interannual variations. Interhemispheric exchange times of 1.3–2.0 yr with a best long-term mean of 1.7 yr obtained in the present work are significantly larger than the value of 1.1 yr derived from continuous SF_6 observations by Maiss and Levin (1994) in a previous study. This has two reasons: introducing the emission ratio $\gamma = 94\%$,

thereby dropping our former assumption that SF_6 is exclusively emitted in the NH, is responsible for one half of the apparent increase of τ_{ex}. The second half is due to a revision of the fitting parameters u and t_0 to the considerably extended SH database. Further, the time overlap of the SH and the NH records is now four years, which ensures 1.7 ± 0.2 yr being a more representative determination of τ_{ex}.

We implied as first order approximation that observations from Izaña and Neumayer (or Cape Grim) are representative means for the NH and the SH surface concentrations, respectively. Hemispheric means calculated from our latitudinal profiles justify this first order approximation. Further, two-dimensional model estimates for SF_6 by Levin and Hesshaimer (1995) confirm that the concentration difference between Izaña and Neumayer (or Cape Grim) nearly exactly represents the mean concentration difference between the two hemispheres at ground level.

Weiss *et al.* (1983) and Jacob *et al.* (1987) have estimated comparative τ_{ex} values of 1.7 and 1.6 yr, respectively, using hemispheric surface means of ^{85}Kr in a two-box model. With a 3D general circulation model, Jacob *et al.* (1987) have computed from same ^{85}Kr database a distinctly lower mean τ_{ex} of 1.1 yr. They pointed out that the obvious difference in τ_{ex} (1.1 yr vs 1.6 yr) is due to the overestimation of the real hemispheric difference when using ground level observations in a simple two-box model of the atmosphere.

The difference between hemispheric surface means is obviously well described in a two-box model by an interhemispheric exchange time of 1.7 ± 0.2 yr for both transport tracers, ^{85}Kr and SF_6. This is verified also by the time-lag ($\approx \tau_{\text{ex}}$) between representative records for surface means in each hemisphere. As shown in Fig. 2 by a dotted curve, a value $\tau_{\text{ex}} = 1.1$ yr does not fit the SF_6 surface difference between both hemispheres. This is an important finding, since, in the past, many workers (e.g. Butler *et al.*, 1992; Elkins *et al.*, 1993) have used the apparently "better" 3D-model result for τ_{ex} (1.1 yr) from Jacob *et al.* (1987) being inappropriate for a simple two-box model if working with surface data.

7. CONCLUDING REMARKS

All atmospheric SF_6 data presented in this study confirm a stable and unbroken long-term increase of this anthropogenic trace gas which is described reasonably well by a quadratic trend model fitting the past 14 yr of observations. This smooth and steadily increasing atmospheric SF_6 concentration curve, unaffected by chemical and biological processes, and distinct for both hemispheres is a powerful tool for model investigations of transport processes in the atmosphere. With a global mean increase rate of 0.225 ppt yr^{-1} (6.9% yr^{-1}) in late 1994, SF_6 shows a persistently increasing trend, in contrast to CFC-11

and CFC-12 now rising comparatively slowly as a result of production restrictions (Elkins et al., 1993). Compared to the established transport tracer [85]Kr, SF_6 is a promising alternative since it is easier to measure and both, temporally and geographically more regular in emissions. The high analytical precision now achieved in combination with an extended continuous observational network, including vertical profiles extending far up into the stratosphere, will allow the study of longitudinal, meridional and seasonal transport patterns within each hemisphere. These signals require a general three-dimensional transport model of the atmosphere for interpretation.

Beyond the promising application of SF_6 as a calibration tracer to validate the transport part of complex atmospheric circulation models, the long-term observations provide an extremely valuable input function for mixing studies in linked compartments like the stratosphere, the hydrosphere and the cryosphere. Such potential applications using tropospheric background levels of SF_6 are, for example, (1) troposphere/stratosphere mixing studies comparable to those performed by Schmidt and Khedim (1991) using CO_2; (2) groundwater investigations (Dalmolin, 1993); (3) oceanic mixing studies from surface water to the deep ocean as proposed by Law et al. (1994); and (4) investigations of the air ventilation rate in firn (see Schwander et al. (1993) for the principal approach). A common feature in all these applications is the possibility of air sample dating with the clear tropospheric SF_6 chronology applicable for the time span of the last 20 yr. Data of the present work are available on request under the E-mail address of Ingeborg Levin: LV@uphys1.uphys.uni-heidelberg.de.

REFERENCES

Butler J. H., Elkins J. W., Hall B. D., Cummings S. O. and Montzka S. A. (1992) A decrease in the growth rate of atmospheric halogen concentrations. *Nature* **359**, 403–405.

Cunnold D., Fraser P., Weiss R., Prinn R., Simmonds P., Miller B., Alyea F. and Crawford A. (1994) Global trends and annual releases of CFC-11 and CFC-12 estimated from ALE/GAGE and other measurements from July 1978 to June 1991. *J. geophys. Res.* **99**, 1107–1126.

Dalmolin J. (1993) Sulfur hexafluoride (SF_6) as tracer for groundwater transport processes. M.A. thesis in German language, Institut für Umweltphysik, University of Heidelberg, INF 366, 69120 Heidelberg.

Elkins J. W., Thompson T. M., Swanson T. H., Butler J. H., Hall B. D., Cummings S. O., Fisher D. A. and Raffo A. G.
(1993) Decrease in the growth rates of atmospheric chlorofluorocarbons 11 and 12. *Nature* **364**, 780–783.

Encyclopedia of Chemical Technology (1980) Vol. 10, 3rd ed. Wiley, New York.

Fraser P. J., Langenfelds R., Derek N. and Porter L. W. (1991) Studies in air archiving techniques. Part 1: Long term stability of atmospheric trace gases in dry, natural air stored in high-pressure, surface treated aluminium cylinders. In: *Baseline Atmospheric Program (Australia) 1989.* (edited by WilsonS, R. and Gras J. L.), pp. 16–29. Department of the Arts, Sport, the Environment, Tourism and Territories and CSIRO.

Jacob D. J., Prather M. J., Wofsy S. C. and McElroy M. B. (1987) Atmospheric distribution of [85]Kr simulated with a general circulation model. *J. geophys. Res.* **92**, 6614–6626.

Ko M. K. W., Sze N. D., Wang W.-C., Shia G., Goldman A., Murcray F. J., Murcray D. G. and Rinsland C. P. (1993) Atmospheric sulfur hexafluoride: sources, sinks and greenhouse warming. *J. geophys. Res.* **98**, 10,499–10,507.

Law C. S., Watson A. J. and Liddicoat M. I. (1994) Automated vacuum analysis of sulphur hexafluoride in seawater: derivation of the atmospheric trend (1970–1993) and potential as a transient tracer. *Marine Chemistry* **48**(1), 57–69.

Levin I. and Hesshaimer V. (1995) Refining of atmospheric transport model entries by the globally observed passive tracer distribution of [85]Krypton and sulfur hexafluoride (SF_6) *J. geophys. Res.* (submitted).

Levin I., Bösinger R., Bonani G., Francey R. J., Kromer B., Münnich K. O., Suter M., Trivett N. B. A. and Wölfli W. (1992) Radiocarbon in atmospheric carbon dioxide and methane: Global distribution and trends. In *Radiocarbon After Four Decades—An Inter-disciplinary Perspective* (edited by Taylor R. E., Long A. and Kra R. S.), pp. 503–517. Springer, New York.

Lovelock J. E. (1971) Atmospheric fluorine compounds as indicators of air movements. *Nature* **230**, 379.

Maiss M. and Levin I. (1994) Global increase of SF_6 observed in the atmosphere. *Geophys. Res. Lett.* **21**, 569–572.

Maiss M., Ilmberger J. and Münnich K. O. (1994a) Vertical mixing in Überlingersee (Lake Constance) traced by SF_6 and heat. *Aquatic Sci.* **56/4**, 329–347.

Maiss M., Ilmberger J., Zenger A. and Münnich K. O. (1994b) A SF_6 tracer study of horizontal mixing in Lake Constance. *Aquatic Sci.* **56/4**, 307–328.

Morris R. A., Miller T. M., Viggiano A. A., Paulson J. F., Solomon S. and Reid G. (1995) Effects of electron and ion reactions on atmospheric lifetimes of fully fluorinated compounds. *J. geophys. Res.* **100**, 1287–1294.

Niemeyer L. and Chu F. Y. (1992) SF_6 and the atmosphere. *IEEE Trans. Electrical Insulation* **27**, 184–187.

Prather M., McElroy M., Wofsy S., Russell G. and Rind D. (1987) Chemistry of the global troposphere: fluorocarbons as tracers of air motion. *J. geophys. Res.* **92**, 6579–6613.

Ravishankara A. R., Solomon S., Turnipseed A. A. and Warren R. F. (1993) Atmospheric lifetimes of long-lived halogenated species. *Science* **259**, 194–199.

Rinsland C. P., Brown L. R. and Farmer C. B. (1990) Infrared spectroscopic detection of sulfur hexafluoride (SF_6) in the lower stratosphere and upper troposphere. *J. geophys. Res.* **95**, 5577–5585.

Schmidt U. and Khedim A. (1991) In situ measurements of carbon dioxide in the winter arctic vortex and at midlatitudes: An indicator of the 'age' of stratospheric air. *Geophys. Res. Lett.* **18**, 763–766.

Schmitt R., Schreiber B. and Levin I. (1988) Effects of long-range transport on atmospheric trace constituents at the baseline station Tenerife (Canary Islands). *J. atmos. Chem.* **7**, 335–351.

Schwander J., Barnola J.-M., Andrié C., Leuenberger M., Ludin A., Raynaud D. and Stauffer B. (1993) The age of

the air in the firn and ice at Summit, Greenland. *J. geophys. Res.* **98**, 2831–2838.

Stordal F., Innset B., Grossmann A. S. and Myhre G. (1993) SF$_6$ as a greenhouse gas: an assessment of Norwegian and global sources and the global warming potential. *NILU-Report* **15/93**, Norwegian Institute for Air Research., P.O. Box 64, 2001 Lillestrøm, Norway.

Trivett N. B. A. and Worthy D. E. J. (1989) Analysis and interpretation of trace gas measurements at Alert, NWT, with emphasis on CO_2 and CH_4. In: Proc. 3rd Int. Conf. on analysis and evaluation of atmospheric CO_2 data, present and past. *WMO Report* **59**.

Wanninkhof R., Ledwell J. R. and Watson A. J. (1991) Analysis of sulfur hexafluoride in seawater. *J. geophys. Res.* **96**, 8733–8740.

Weeks I., Francey R., Beardsmore D. and Steele L. P. (1992) Studies in air archiving. Part 2: Filling high pressure cylinders with baseline air. Baseline Atmospheric Program (Australia) 1990 (edited by Wilson S. R. and Gras J. L.), pp. 16–23. Department of Administrative Services and CSIRO.

Weiss W., Sittkus A., Stockburger H. and Sartorius H. (1983) Large-scale atmospheric mixing derived from meridional profiles of Krypton 85. *J. geophys. Res.* **88**, 8574–8578.