Global increase of SF$_6$ observed in the atmosphere

Manfred Maiss and Ingeborg Levin

Institut für Umweltphysik, University of Heidelberg, Germany

Abstract. High precision long-term observations of the trace gas sulphur hexafluoride (SF$_6$) in background air at Neumayer station, Antarctica (1986-1991), and at Izaña observatory, Tenerife (1991-1992), are presented. Since the very first measurements in 1970 (0.03 pptv), the purely anthropogenic greenhouse gas SF$_6$ has increased by two orders of magnitude to a global mean value of 2.8 pptv in 1992. The observations can best be fitted by a quadratic curve with a recent increase rate of 8.3 % yr^{-1}. A significant north-south gradient of 0.29 pptv is observed. From this gradient an interhemispheric exchange time of 1.4 years is derived. A modeled atmospheric budget history agrees reasonably well with estimates of global SF$_6$ production rates and leads to an extrapolated SF$_6$ concentration of about 20 pptv for the year 2030.

Introduction

SF$_6$ is a very stable atmospheric trace gas believed to be produced entirely by man. Its unique physico-chemical properties make this gas ideally suited for many applications, predominantly in electrical insulation and switching. Due to a growing industrial production of SF$_6$ combined with an atmospheric lifetime of probably 3200 years [*Ravishankara et al.*, 1993] the atmospheric SF$_6$ concentration has increased by two orders of magnitude since 1970 (0.03 pptv, parts per trillion by volume) [*Lovelock*, 1971]. As the greenhouse effect of SF$_6$, on a per molecule basis, is likely to be one of the highest of any atmospheric trace gas [*Rinsland et al.*, 1990], the nearly irreversible accumulation of SF$_6$ in the atmosphere may not be ignored. Our observed mean hemispheric SF$_6$ concentration trends allow for an estimate of the SF$_6$ emission history from 1970 onwards. This input function will be extremely valuable in modelling investigations of the atmosphere and the hydrosphere when using SF$_6$ as transport tracer.

Experimental

Three sets of air samples, originally collected for methane isotope and [85]Krypton analyses [*Levin et al.*, 1992; *Weiss et al.*, 1992], form the basis of the present SF$_6$ study. The most extensive continuous series of compressed air samples was collected at Neumayer station (GvN), Antarctica (71°S, 8°W, 16 m asl) from 1986-1991. From the WMO background air pollution monitoring station Izaña, Tenerife (28°N, 16°W, 2376m asl), samples have been available since July 1991. At this maritime high-altitude site, most of the time the air is representative for the free mid-troposphere in this latitudinal belt [*Schmitt et al.*, 1988]. At Izaña, 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 or stainless steel tanks using a diving compressor. At GvN, monthly spot samples of about 1 m^3 of air were directly compressed into 10 L tanks. In addition to these time series, a meridional profile of high volume surface air spot samples was collected during a ship cruise of *FS Polarstern* on the Atlantic Ocean from 30°N to 68°S in northern winter 1990/1991.

SF$_6$ has been analyzed by electron capture gas chromatography. The analytical system is a new compact transportable device, primarily designed for on-board SF$_6$ measurements in water samples [*Maiss*, 1992]. Basic elements of the system are identical to a similar device described in detail by *Wanninkhof et al.* [1991]. Analyses of air samples were carried out on a volume of 4.8 mL with a reproducibility of ±2 % for modern SF$_6$ background concentrations. There is no internationally accepted gas standard avaible for this SF$_6$ concentration range. All measurements are related therefore to a 94 pptv SF$_6$ gas standard prepared from a commercially available 0.1 ppmv standard with a certified accuracy of ±1 % (Messer Griesheim, FRG) by a gravimetrically controlled single-step static pressure dilution with ultrapure N$_2$. This procedure nominally leads to an absolute accuracy of our gas standard of ±1.5 % [*Maiss*, 1992].

Results and Discussions

Figure 1 summarizes the SF$_6$ background concentrations derived in this investigation for the northern (NH) and the southern (SH) hemisphere. Both time series, at GvN and at Izaña, show very little scatter and a steady increase. The concentration in the NH is persistently higher if compared to the SH due to the predominate release of SF$_6$ in the NH, and an interhemispheric exchange time of air in the order of 1 year. The meridional profile for the end of 1990 is in good agreement with the two time series. Mean hemispheric concentrations of 2.67±0.08 pptv for the NH and 2.38±0.07 pptv for the SH are calculated by weighting the cruise data by the area of the equivalent latitude (horizontal hemispheric lines in inset of Figure 1).

In order to obtain long term trends of SF$_6$ in the atmosphere linear, quadratic, and exponential fitting models have been applied on the Antarctic data base. The quadratic fit is shown in all figures as a solid curve. The linear and exponential fits are only shown in Figures 2 and 3 by a dashed line and a dashed-dotted curve, respectively. The slight differences in the least-squares-sum of the three SH fits for the period of our measurements, e.g. 1986-1992, are not appropriate to prefer one of them. This can, however, be done in the historical context with earlier observations and additional information on emission rates.

The interpretation of SF$_6$ concentrations obtained in both, this study and earlier work, requires a model for atmospheric mixing as well as for the emission history of SF$_6$. For the latter only estimates are available. About 80 % of the world-wide production of SF$_6$ are used in heavy electrical equipment and
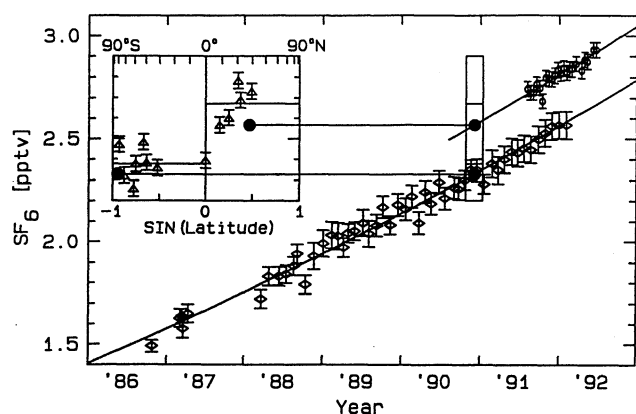
Figure 1. Long-term atmospheric SF$_6$ concentration records at GvN, 71°S ($\Diamond$) and at Izaña, Tenerife, 28°N ($\bigcirc$). Error bars reflect the analytical uncertainty of individual data points. Continuous fitting curves correspond to a quadratic trend model presented in Figure 2. Inset: latitudinal profile of SF$_6$ ground level concentrations over the Atlantic Ocean ($\triangle$).

have risen approximately linearly since 1970 (*SOLVAY, European SF$_6$ producer, personal communication*, 1993). This predominant application has started in the sixties. In order to establish an analytical model solution as simple as possible, this sparse information is, however, sufficient to exclude the linear or exponential trend model fits shown in Figure 2. Both are not able to describe an onset of SF$_6$ emissions in the sixties and are far away from earlier observations. So the best fit to the Antarctic GvN data in a historical context and by means of a simple complete and analytical solution is the quadratic model which is further mathematically consistent with a linearly increasing emission of SF$_6$ starting in the year 1968.

The following two-box model can be formulated by assuming an atmospheric lifetime of SF$_6$ much longer than its actual history, a release rate S(t) of SF$_6$ increasing linearly with time and occuring solely in the NH

$$dc_{SH}(t)/dt = (c_{NH}(t) - c_{SH}(t)) / \tau_{ex} \qquad (1)$$

$$dc_{NH}(t)/dt = S(t) - (c_{NH}(t) - c_{SH}(t)) / \tau_{ex} \qquad (2)$$

where $c_{NH}(t)$ and $c_{SH}(t)$ are the mean hemispheric SF$_6$ concentrations, and τ_{ex} is the interhemispheric exchange time. With $c_{NH}(t_o) = c_{SH}(t_o) = 0$ the solutions of equations (1) and (2) are

$$c_{SH}(t) = u \cdot (t - t_o)^2 \qquad (3)$$

$$c_{NH}(t) = 2 \cdot u \cdot \tau_{ex} \cdot (t - t_o) + c_{SH}(t) \qquad (4)$$

$$S(t) = 4 \cdot u \cdot (t - t_o + \tau_{ex}/2) \qquad (5)$$

with u and t_o being unknown constants to be derived from fitting (3) to the GvN data (time t in years AD, e.g. t = 1992.0 = January 1, 1992):

$$c_{SH}(t) = 0.004763 \cdot (t - 1968.82)^2 \quad [pptv] \qquad (6)$$

Using t_o and u from (6) we can calculate $c_{NH}(t)$ from (4). The unknown τ_{ex} is obtained by minimizing the least-squares-sum of the Izaña data set to $c_{NH}(t)$ through variation of τ_{ex}.

An interhemispheric exchange time $\tau_{ex} = 1.1$ years yields the best fit. This $c_{NH}(t)$ - curve is shown in Figure 2 by a dotted line. With $c_{NH}(t) - c_{SH}(t) = 0.29$ pptv derived from the observed meridional profile in Figure 1, equation (4) leads to a τ_{ex} of about 1.4 years. Both results are in very good agreement with calculations of τ_{ex} derived from corresponding [85]Krypton data: the differences in hemispheric mean surface concentrations yield a τ_{ex} between 1 and 1.7 years [*Weiss et al.*, 1983], global hemispheric mean concentrations yield a τ_{ex} of 1.1 years [*Jacob et al.*, 1987].

Figure 2 also summarizes available earlier measurements of tropospheric SF$_6$ concentrations in background air derived by electron-capture gas chromatography (values (a)-(j)). Except for the present study the only reported values after 1984 are infrared spectroscopic detections of SF$_6$ [*Rinsland et al.*, 1990, 1993; *Zander et al.*, 1991;]. With more than 3 pptv for the late eighties the absolute calibration for this new technique seems to be incorrect and results are only used for the trend discussion below. The very first atmospheric SF$_6$ observation (a) was reported by *Lovelock* [1971] with a value of 0.03 pptv for August 1970. As a whole, the values (a)-(j) describe an increasing SF$_6$ burden, although there is considerable scatter in the data. This scatter could be attributed to different observation sites, but probably mainly to problems with the comparability of results from the different laboratories. Using the SF$_6$ history in the seventies as reference, we find that our quadratic model solutions for $c_{NH}(t)$ and $c_{SH}(t)$ are in reasonable agreement with earlier data. We will, thus, use the quadratic fit for calculating the SF$_6$ emission history and to derive future scenarios.
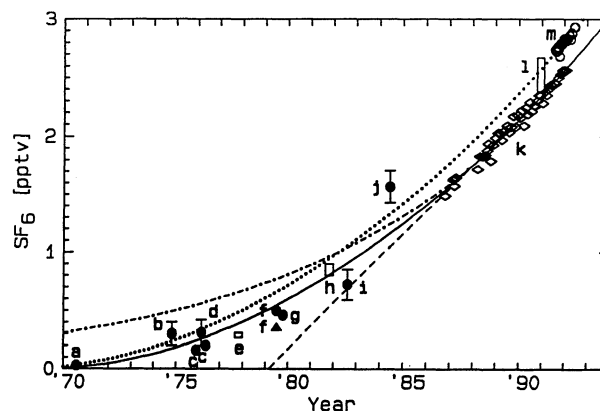

Figure 2. Long-term trends in the atmospheric SF$_6$ concentration including the measurements from this study at GvN (k), at Tenerife (m) and from the meridional profile over the Atlantic Ocean (l) as in Figure 1. Also shown are concentration ranges of latitudinal profiles (open bars) and tropospheric background concentrations in the northern ($\bullet$) and the southern hemisphere ($\blacktriangle$) obtained by the following authors: (a) [*Lovelock*, 1971]; (b) [*Elias et al.*, 1976]; (c) [*Singh et al.*, 1977]; (d) [*De Bortoli et al.*, 1976]; (e) [*Singh et al.*, 1979]; (f) [*Rasmussen and Khalil*, 1983]; (g) [*Leifer et al.*, 1982]; (h) [*Singh et al.*, 1983]; (i) [*Hirota and Muramatsu*, 1986] (j) [*Watson and Liddicoat*, 1985]. The curves represent a linear [— — — — — — — $c_{SH}(t) = (0.197795 * t) - 391.466$], a quadratic [———— $c_{SH}(t) = 0.004763*(t - 1968.82)^2$], and an exponential [—··—··—·· $c_{SH}(t) = \exp ((0.096676 * t) - 191.631)$] trend model fitting to the Antarctic data (k) where $c_{SH}(t)$ is in [pptv] and t in [years AD]. The dotted fitting curve is an optimization of a global quadratic trend model to the Tenerife data (m).
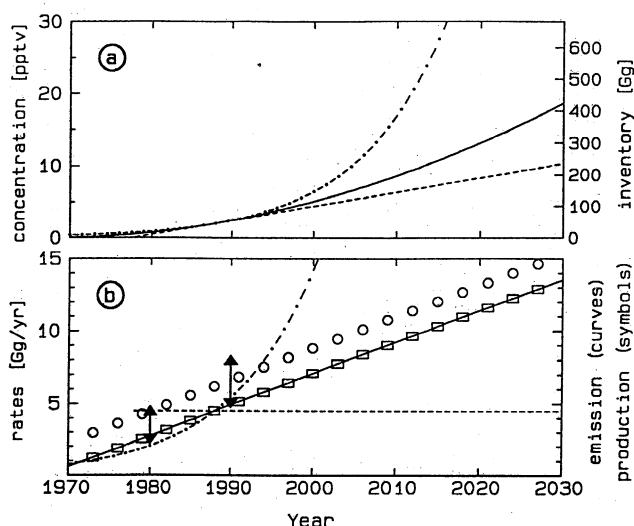
Figure 3. Trend scenarios for mean tropospheric concentrations, global inventories, emission and production rates of SF_6 based on fitting curves in Figure 2 : exponential (—·—·—), quadratic (————) and linear (– – – –) increase of concentration and inventory in Figure 3a correspond to exponential, linear and zero increase in emission rates in Figure 3b; (◄——►) estimated ranges of the total world production rate of SF_6 [Enzyclopedia of Chemical Technology, 1980; SOLVAY, SF_6 producer, personal communication, 1993]; modelled production rates for the case of full release (□) and for a banking over 10 years of 80% of the production (O).

Global Trend Scenarios

From the quadratic model, the global average SF_6 increase rate for 1992 is estimated to be 8.3±0.3 % yr⁻¹. Trends computed for earlier years are in agreement with SF_6 increase rates obtained and summarized by Zander et al. [1991]. Based on the different fitting models presented in Figure 2 actual and future tropospheric SF_6 concentrations, the global atmospheric SF_6 burden, and emission rates could be calculated (see Figure 3). In this scenario exponential and linear concentration increases are shown as limiting curves for the probably most realistic quadratic growth, corresponding to a continuing linear increase of SF_6 emissions. The global atmospheric SF_6 inventory in $Gg = 10^9$ g is obtained by multiplying the global mean background surface concentrations $c(t)$ in pptv by a factor of 22.69. This conversion of surface concentrations to global burden bases on a effective reservoir with a mean mass of $4.5*10^{21}$ g equal to 88 % of the total mass of the atmosphere ($5.137*10^{21}$ g; [Trenberth, 1981]). The emission rates in Figure 3b are directly obtained by differentiating the global inventory curves of Figure 3a.

The world-wide production rate of SF_6 was estimated to be 2.5-4.5 Gg yr⁻¹ around 1980 [Enzyclopedia of Chemical Technology, 1980]. It has risen approximately linearly since 1970 to an estimated 5-8 Gg yr⁻¹ around 1990 (Figure 3b) [SOLVAY, SF_6 producer, personal communication, 1993]. Regarding the lower ranges even the case of full production release did not disagree with calculated emission rates. For the 80% of the annual production going into capsuled electrical applications a mean banking time of 10 years could be assumed. Based on the calculated linearly increasing emission rate such a banking

model assumption leads to production rates shown by open circles in Figure 3b which conform to the upper ranges of production estimates. So both models, the full release model and the banking model are compatible with the mentioned range of estimates of the world-wide SF_6 production.

Conclusions

Notwithstanding its present low atmospheric concentration ($\approx 10^{-2}$ of CFC), the greenhouse effect of SF_6 on a per molecule basis is likely to be one of the highest of any atmospheric trace gas [Rinsland et al., 1990]. In combination with atmospheric lifetime estimates of 3200 years [Ravishankara et al., 1993] the long-term accumulation in the atmosphere should, therefore, be kept as low as possible by recycling techniques. It is impossible to rule out such a long lifetime by a global budget analysis over a history of only 30 years [Chang and Penner, 1978]. Using the concentration increase derived in the present work as source function we will narrow the uncertainty in the lifetime of SF_6 by measurements of vertical profiles in the stratosphere up to 70 km height. The monitoring in both hemispheres will be continued. Besides the actually not so relevant climatic impact discussion [Ko et al., 1993], the relatively strong increase rate, the distinct north-south gradient, and the negligible atmospheric sink make SF_6 a well suited and easy to measure tracer for global atmospheric, oceanographic, and hydrological mixing models.

References

Chang, J.S., and J.E. Penner, Analysis of global budgets of halocarbons, Atmos. Environ., 12, 1867-1873, 1978.

De Bortoli, M., and E. Pecchio, Measurements of some halogenated compounds in air over Europe, Atmos. Environ., 10, 921-923, 1976.

Elias, L., M. McCooeye, and G. Gardner, On-site measurement of atmospheric tracer gases, Geophys. Res. Lett., 3, 17-20, 1976.

Encyclopedia of Chemical Technology, Vol. 10, 3rd. ed., John Wiley & Sons, New York, 1980.

Hirota, M., and H. Muramatsu, Gas-chromatographic measurements of atmospheric sulfur hexafluoride, Bull. Chem. Soc. Jpn., 59, 329-331, 1986.

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

Ko, M.K.W., N.D. Sze, W.-C. Wang, G. Shia, A. Goldman, F.J. Murcray, D.G. Murcray, and C.P. Rinsland, Atmospheric sulfur hexafluoride: sources, sinks and greenhouse warming, J. geophys. Res., 98, 10499-19507, 1993.

Leifer, R., R. Larsen, and L. Toonkel, Trends in stratospheric concentrations of trace gases in the northern hemisphere during the years 1974-1979, Geophys. Res. Lett., 9, 755-758, 1982.

Levin, I., R. Bösinger, G. Bonani, R.J. Francey, B. Kromer, K.O. Münnich, M. Suter, N.B.A. Trivett, and W. Wölfli, Radiocarbon in atmospheric carbon dioxide and methane: Global distribution and trends, in Radiocarbon after four decades - An inter-disciplinary perspective, edited by R.E.

Taylor, A. Long, and R.S. Kra, pp. 503-517, Springer, New York, 1992.

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

Maiss, M., Schwefelhexafluorid (SF$_6$) als Tracer für Mischungs-prozesse im westlichen Bodensee, Ph.D. thesis, 219 pp., University of Heidelberg, December 1992.

Rasmussen, R.A., and M.A.K. Khalil, Rare trace gases at the south pole, Antarctic J. U.S., 18, 250-252, 1983.

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

Rinsland, C.P., L.R. Brown, and C.B. Farmer, Infrared spectroscopic detection of sulfur hexafluoride (SF$_6$) in the lower stratosphere and upper troposphere, J. geophys. Res., 95, 5577-5585, 1990.

Rinsland, C.P., M.R. Gunson, M.C. Abrams, L.L. Lowes, R. Zander, and E. Mahieu, ATMOS/ATLAS 1 measurements of sulfur hexafluoride (SF$_6$) in the lower stratosphere and upper troposhere. J. geophys. Res., 98, 20491-20494, 1993.

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

Singh, H.B., L.J. Salas, H. Shigeishi, and A. Crawford, Urban-nonurban relationsships of halocarbons, SF$_6$, N$_2$O, and other atmospheric trace constituents, Atmos. Environ., 11, 819-828, 1977.

Singh, H.B., L.J. Salas, H. Shigeishi, and E. Scribner, Atmospheric halocarbons, hydrocarbons, and sulfur hexafluoride: Global distributions, sources, and sinks, Science, 203, 899-903, 1979.

Singh, H.B., L.J. Salas, and R.E. Stiles, Selected man-made halogenated chemicals in the air and oceanic environment, J. geophys. Res., 88, 3675-3683, 1983.

Trenberth, K.E., Seasonal variations in global sea level pressure and the total mass of the atmosphere, J. geophys. Res., 86, 5238-5246, 1981.

Wanninkhof, R., J.R. Ledwell, and A.J. Watson, Analysis of sulphur hexafluoride in seawater, J. geophys. Res., 96, 8733-8740, 1991.

Watson, A.J., and M.I. Liddicoat, Recent history of atmospheric trace gas concentrations deduced from measurements in the deep sea: application to sulphur hexafluoride and carbon tetrachloride. Atmos. Environ., 19, 1477-1484, 1985.

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

Weiss, W., H. Sartorius, and H. Stockburger, Global distribution of atmospheric [85]Kr - A database for the verification of transport and mixing models, IAEA proceedings: Isotopes of noble gases as tracers in environmental studies, 29-39, Vienna, 1992.

Zander, R., C.P. Rinsland, and P. Demoulin, Infrared spectroscopic measurements of the vertical column abundance of sulfur hexafluoride, SF$_6$, from the ground, J. geophys. Res., 96, 15447-15454, 1991.

M. Maiss and I. Levin, Institut für Umweltphysik, University of Heidelberg, Im Neuenheimer Feld 366, D-69120 Heidelberg, Germany (e-mail: MAI@uphys1.uphysn. uni-heidelberg.de).