

Tropospheric SF₆: Observed latitudinal distribution and trends, derived emissions and interhemispheric exchange time

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Abstract. Sulfur hexafluoride (SF₆), an anthropogenically produced compound that is a potent greenhouse gas, has been measured in a number of NOAA CMDL air sampling programs. These include high resolution latitudinal profiles over the Atlantic and Pacific oceans, weekly flask samples from seven remote, globally distributed sites, hourly in situ measurements in rural North Carolina, and a series of archived air samples from Niwot Ridge, Colorado. The observed increase in atmospheric mixing ratio is consistent with an overall quadratic growth rate, at $6.9 \pm 0.2\%$ yr⁻¹ (0.24 ± 0.01 ppt yr⁻¹) for early 1996. From these data we derive an early 1996 emission rate of 5.9 ± 0.2 Gg SF₆ yr⁻¹ and an interhemispheric exchange time of 1.3 ± 0.1 years.

Introduction

SF₆ is an extremely stable gas that has received considerable attention lately. It is rapidly accumulating in our atmosphere because of its long lifetime of ~3200 years [Ravishankara *et al.*, 1993]. It is used predominantly for insulating high voltage electrical equipment, such as transformers and circuit breakers, from which it escapes to the atmosphere through leaks and intentional release [Ko *et al.*, 1993]. SF₆ is generally thought to be a solely anthropogenic compound, however, natural radiogenic production has been recently suggested [Harnisch *et al.*, 1996]. Per molecule, SF₆ is one of the strongest greenhouse gases known, but with an ambient mixing ratio of less than 4 parts per trillion (ppt, 10⁻¹² moles per mole in dry air), it does not currently cause any significant climatic forcing [Albritton *et al.*, 1995; Ko *et al.*, 1993]. Its great stability and high sensitivity to analysis make SF₆ a valuable tracer of atmospheric and hydrologic dynamics.

The United Nation's Framework Convention on Climate Change does encourage the assessment and regulation of SF₆ emissions, but so far only a few countries have made any attempt to do so [Cook, 1995]. Thus at this point, atmospheric measurements provide one of the only ways to estimate global SF₆ emissions.

Here we report global measurements of SF₆ based on a new NOAA CMDL gravimetric calibration scale. The data include high resolution latitudinal profiles over both the Pacific and

Atlantic oceans obtained on two cruises in 1994, flask samples obtained in 1995-1996 from seven remote sampling stations, hourly in situ measurements from a rural North Carolina tower site in 1994-1996, and archived air from Niwot Ridge, Colorado, dating back to 1987 (Table 1). From these data we characterize the global distribution of SF₆, calculate its long term growth rate, and, using vertical profile data from the NASA ER-2 aircraft [Elkins *et al.*, 1996], derive emissions estimates and an interhemispheric exchange time.

Experimental

SF₆ is analyzed by gas chromatography with electron capture detection (GC/ECD). SF₆ is separated, along with N₂O, on a 2 m precolumn and a 3 m main column, both of 4.8 mm i.d. stainless steel, packed with 80/100 mesh Porapak Q (Waters Associates; Millford, Massachusetts). The columns are kept isothermal at 80°C. The carrier gas (95% argon/5% methane, purified with 350° zirconium or a molecular sieve-13X trap) is maintained at a flow of 40 mL min⁻¹, with a 60 mL min⁻¹ backflush flow to remove more retentive compounds from the pre-column. In this configuration, SF₆ elutes at ~7 min, well separated from N₂O, which elutes at 6 min. Typically, the ECD (Shimadzu; Tokyo, Japan) is held at 360°C [Geller, 1996].

The ECD is highly sensitive to SF₆. Consequently, no sample pre-concentration is required and a 10 mL air sample is injected directly onto the column. During the research cruises, some of our laboratory's earliest SF₆ measurements, a typical signal-to-noise ratio (S:N, defined as peak height to 2σ of the baseline

Table 1. Summary of the Data Sets Used in This Study

Data Set	Sampling Frequency	Time Span	Comments
E. Pacific cruise	Hourly	Jan. 26- Feb. 18, 1994	a, b
Atlantic cruise	Hourly	Oct. 18 - Nov. 21, 1994	a, b
Tall tower site, North Carolina	Hourly	Nov. 1994 - Aug. 1996	a, c
Archive samples, Niwot Ridge	Periodic	1987-1996	d
Flask samples (seven sites, see text)	Weekly	July 1995 - May 1996	c, d
UOH archive samples, Cape Grim	Periodic	1978-1994	e

a - In situ measurements

b - Hemispheric means used for calculations

c - Monthly background means used for calculations

d - Analyzed at Boulder laboratory

e - See Maiss *et al.*, [1996] for details

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noise) for SF₆ was 15:1. The minimum detection limit, defined as S:N of 3:1, was estimated at 0.6 ppt, and the instrumental precision ranged from ± 2.5 to $\pm 4.0\%$ (1 σ). Now, however, precision of around $\pm 1.0\%$ is routinely obtained using a Valco ECD (Valco Instruments Inc.; Houston, Texas) which is more sensitive to SF₆ (S:N~35:1) [Elkins *et al.*, 1996; Hurst *et al.*, 1997].

Shipboard data. SF₆ was measured during two research cruises as part of the NOAA CMDL Bromine Latitudinal Air-Sea Transect 1994 (BLAST 94) project. The first cruise was a 13,600 km latitudinal transect in the E. Pacific Ocean. The second cruise was a 15,900 km latitudinal transect of the Atlantic Ocean. More than 1500 air measurements were obtained during the two cruises, providing the only high resolution latitudinal profiles of SF₆ to date.

On both cruises, ambient air was pumped continuously at 4–6 L min⁻¹ from the most forward point of the bow through 9.5 mm o.d. Dekabon tubing, by means of a pump installed in the ship's laboratory. From this air stream, samples were drawn at about 60 mL min⁻¹ through a Nafion dryer and a 10 mL sample loop. The analytical system used was a custom-built, three-channel gas chromatograph [Lobert *et al.*, 1996].

Flask data. As a part of an ongoing flask sampling program, weekly samples are collected in pairs of electropolished stainless steel flasks at seven remote sampling locations covering a wide latitudinal range: Alert, NorthWest Territories, Canada (82.5°N, 62.3°W, 21 m asl [above sea level]), Pt. Barrow, Alaska, (71.3°N, 156.6°W, 11 m asl), Niwot Ridge, Colorado, 40.1°N, 105.5°W, 3475 m asl), Mauna Loa, Hawaii, (19.5°N, 155.6°W, 3397 m asl), Cape Matatula, American Samoa (143°S, 170.6°W, 42 m asl), Cape Grim, Tasmania, Australia (40.7°S, 144.8°E, 94 m asl) and South Pole, Antarctica (90°S, 2810 m asl). All of these samples are collected with a KNF Neuberger diaphragm pump (Model UN05SV1; Trenton, New Jersey). Flasks are analyzed on a Hewlett Packard-5890 GC/ECD system. The average precision for replicate analyses of SF₆ is about $\pm 1.3\%$ (0.05 ppt).

Archive data. SF₆ was also measured in a set of high pressure archived air cylinders collected at the Niwot Ridge site between 1987 and 1996. The cylinders were filled with a RIX Industries, Model SA3, oilless air compressor into Aculife-treated, aluminum and steel cylinders (6 and 29 L cylinders; Scott Specialty Gases; Plumsteadville, Pennsylvania) and electropolished, 33-L stainless steel containers (Scientific Instrument Specialists Inc.; Moscow, Idaho). The archived samples were analyzed with a custom-built GC/ECD system similar to the one used during the cruises.

In situ station data. Ambient SF₆ is monitored at a sampling site at Grifton, North Carolina (35°N, 77°W, 9 m asl), with an automated, custom built, four channel GC. At this site, air from three heights (51 m, 123 m, 496 m above ground) on a 610 m-high television transmission tower is analyzed hourly; only the highest elevation (496 m) measurements are reported here. This site is sometimes influenced by polluted air masses from population centers located 100–250 km away; accordingly, only the data between the 5th and 25th percentiles of the mixing ratios measured each month are considered representative of regional background values, and are used for calculating monthly means [Hurst *et al.*, 1997].

Calibration. Ambient air measurements are bracketed by measurements of whole-air working standards which, in turn, were calibrated with gravimetric standards prepared at NOAA

CMDL. Primary standards were prepared by quantitatively transferring a weighed amount of pure SF₆ to an Aculife-treated, aluminum cylinder, which was then pressurized with a known mass of purified air. Portions of this primary standard were diluted gravimetrically to create secondary standards with mixing ratios ranging from 3 ppt to 108 ppt. Over the range of these standards, the ECD response is linear for SF₆ (to within 1%, $r^2 = 0.9998$), and no blank signals were detected when SF₆-free air was analyzed. A calibration curve is shown in Geller [1996].

The CMDL SF₆ calibration scale was recently compared to that of the University of Heidelberg (UOH), which uses GC/ECD with sample pre-concentration for SF₆ analysis [Maiss *et al.*, 1996]. For a cylinder of Niwot Ridge air (ALM-9289), our laboratory assigned a mixing ratio of 3.68 ± 0.08 ppt (1 σ), whereas the UOH laboratory assigned a mixing ratio of 3.714 ± 0.013 ppt. In addition, CMDL measurements were compared indirectly with those of the Atmospheric Trace Molecule Spectroscopy (ATMOS) Fourier transform infrared spectrometer (FTIR), used on the NASA space shuttle during the November 1994 mission. Within the limits of the FTIR precision (5–10%), the ATMOS SF₆ data agreed with those obtained concurrently by the NOAA CMDL Airborne Chromatograph for Atmospheric Trace Species (ACATS-IV) instrument [Chang *et al.*, 1996].

Results

In all of the latitudinal profiles collected (two cruise profiles and eight monthly mean profiles compiled from flask and in situ station data), SF₆ decreases from high latitudes toward the equator in the northern hemisphere (NH) but appears relatively well mixed throughout the southern hemisphere (SH) (Figure 1). These features would be expected for a gas of anthropogenic origin and high emission rate. An interesting feature in the Atlantic cruise profile is the elevated SF₆ mixing ratios at ~43°N. Back-trajectory analysis shows that this feature was caused by an air mass transported from Western Europe. This pollution event was excluded in the calculation of hemispheric means.

Hemispheric and global means were calculated for each profile by binning the data into latitudinal bands which were then weighted by the cosine of the mean latitude within each band. The hemispheres were split at the observed Interhemispheric Tropical Convergence Zone (ITCZ) for the cruise data and at the equator for the station data. For the SH, a constant mixing ratio was assigned to latitudes between the end of the cruises and the South Pole. However, in the NH, mixing ratios increase with latitude; from the flask data, we find that the high latitude sites at Barrow (72°N) and Alert (82°N) are, on average, 0.07 ppt higher than the midlatitude site at Niwot Ridge (40°N). Thus, to extrapolate cruise data to the North Pole, a 50–90°N latitude bin was assigned a mixing ratio 0.07 ppt higher than the mixing ratio at the highest latitude measured. These data are available via the internet at <ftp://ftp.cmdl.noaa.gov/noah>.

The latitudinal distribution of most long-lived, atmospheric compounds fluctuates over time, reflecting seasonal and interannual changes in interhemispheric transport, vertical mixing, and sources and sinks. However, the SF₆ interhemispheric difference (IHD) obtained from the eight monthly mean latitudinal profiles, 0.27 ± 0.02 ppt, is relatively constant. The cruise profiles show a larger range of IHDs (0.35 for the E. Pacific cruise, and 0.24 for the Atlantic cruise); since they reflect more instantaneous pictures of SF₆ mixing ratios, cruise profiles can be significantly influenced by local transport phenomena.

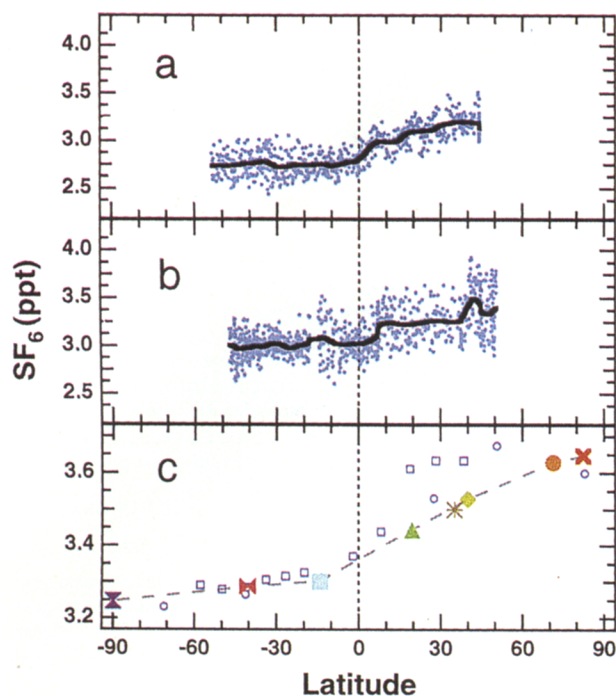


Figure 1. Latitudinal profiles of atmospheric SF₆ as mixing ratios (ppt) in dry air. For (a) the E. Pacific cruise profile and (b) the Atlantic cruise profile, the solid line is a running mean of the raw data (35 point filter). (c) shows mean mixing ratios for the last quarter of 1995 obtained from station sampling. For all NOAA CMDL stations, the standard error of the mean of the weekly flask pair mixing ratios was about ± 0.02 ppt. Symbols are defined in Figure 2. Also shown, for comparison, are data from UOH, both annual means from their sampling stations (○) and Atlantic cruise data (□) [Levin and Hesshaimer, 1996]. The UOH data, which were collected in 1993, have been extrapolated to late 1995 values with the SF₆ growth rate given in this paper, and adjusted to the NOAA CMDL calibration scale.

Using the CMDL archived samples from Niwot Ridge, and the recent cruise and station data described above, we examined the growth rate of SF₆ over the past decade (Figure 2). Since we do not have long term CMDL measurements from the SH, UOH data from Cape Grim [Maiss *et al.*, 1996] were included in the trend analysis. It should be noted that UOH has long term SF₆ records from several other stations as well; we chose to use their Cape Grim data since CMDL also samples at this site. The hemispheric and global trends of the combined data set are described by:

$$x = 3.5768 (\pm 0.0112) + 0.2379 (\pm 0.0111) t + 0.0048 (\pm 0.0015) t^2 \text{ (NH)} \quad (1)$$

$$x = 3.2954 (\pm 0.0067) + 0.2374 (\pm 0.0039) t + 0.0051 (\pm 0.0004) t^2 \text{ (SH)} \quad (2)$$

where x is the mean SF₆ mixing ratio and $t = \text{year} - 1996.0$. These are averaged to give:

$$x = 3.4361 (\pm 0.0089) + 0.2376 (\pm 0.0075) t + 0.0049 (\pm 0.0009) t^2 \text{ (global)} \quad (3)$$

Over the period 1987–1996, SF₆ shows a quadratic growth trend. For the beginning of 1996, the global growth rate is $6.9 \pm 0.2\%$ yr⁻¹ (0.24 ± 0.01 ppt yr⁻¹).

Discussion

Because of the virtual absence of sinks for SF₆, both at the earth's surface and in the lower 50 km of the atmosphere, the budget of this compound can be well described with a simple two-box model, based on the following equations [Elkins *et al.*, 1993]:

$$\frac{dX_n}{dt} = \frac{2\alpha f}{n_a} E - \frac{X_n}{\tau_a} + \frac{\Delta X_{ns}}{\tau_{ex}} \quad (4)$$

$$\frac{dX_s}{dt} = \frac{2(1-\alpha)f}{n_a} E - \frac{X_s}{\tau_a} + \frac{\Delta X_{ns}}{\tau_{ex}} \quad (5)$$

X_n and X_s are the mean tropospheric mixing ratios in each hemisphere; ΔX_{ns} is the interhemispheric difference; α is the ratio of NH emissions to total emissions, estimated to be 0.94 ± 0.01 , based on global electricity use [Maiss *et al.*, 1996]; τ_a is the atmospheric lifetime of SF₆, 3200 years [Ravishankara *et al.*, 1993]; τ_{ex} is the interhemispheric exchange time; n_a is the total number of moles in the atmosphere (1.771×10^{20}); and f is the fraction of total atmospheric SF₆ in the troposphere divided by the fraction of the total atmospheric mass in the troposphere [Butler *et al.*, 1992]. Our best estimate for f is 1.04 ± 0.01 , derived from concurrent measurements of SF₆ in the stratosphere during the ER-2 missions [Elkins *et al.*, 1996] and in the troposphere during the 1994 Atlantic cruise.

Using the hemispheric mixing ratios calculated from our eight monthly mean profiles and the hemispheric growth rates from equations (1) and (2), equations (4) and (5) were solved algebraically for E , the emission rate, and for τ_{ex} . Calculated emission rates increased linearly over the period of our data, which is consistent with a quadratic atmospheric growth rate. The calculated emission rate for the beginning of 1996 is 5.9 ± 0.2 Gg SF₆ yr⁻¹.

Of more general scientific interest is the calculation of the interhemispheric exchange time. The average τ_{ex} determined

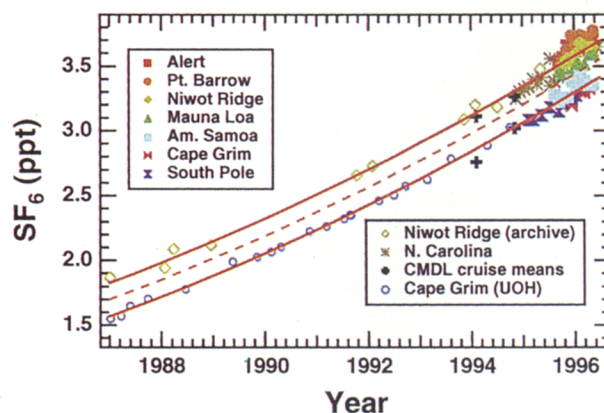


Figure 2. History of atmospheric SF₆ as mixing ratios (ppt) in dry air. Shown are monthly means from the NOAA CMDL sampling stations, hemispheric means from the cruises, and the archived data from Niwot Ridge. The UOH data, from Maiss *et al.*, [1996], have been adjusted to the NOAA CMDL calibration scale. Curve fits are described in the text. January 1 begins at the center tic mark above the year label.

from the eight monthly latitudinal profiles is 1.3 ± 0.1 years. Similar box models done by Maiss *et al.*, [1996] and Levin and Hesshaimer [1996], with UOH SF₆ data, yielded somewhat higher τ_{ex} values (1.7 years and 1.5 years, respectively). The discrepancy between these and the CMDL results is related to how one chooses representative data for the northern midlatitudes, where the longitudinal and vertical variations of anthropogenic compounds like SF₆ can lead to problems of sampling bias. As seen in Figure 1c, the UOH N. midlatitude data from Fraserdale, Canada (50°N, 82°W, 200 m asl), Izana, Tenerife (28°N, 16°W, 2367 m asl), and an Atlantic cruise, all show significantly higher mixing ratios than those observed at the CMDL N. midlatitude sites. The CMDL mixing ratios are lower because Niwot Ridge and Mauna Loa are high altitude sites that sample mostly free tropospheric air, and the North Carolina data are stringently filtered to remove local, continental influences.

The SF₆ latitudinal profile generated by the 2-D model of Levin and Hesshaimer [1996] does agree well with their own UOH data, but this model was tuned to fit Atlantic cruise profiles of ⁸⁵Kr mixing ratios. As was illustrated in Jacob *et al.* [1987], the northern Atlantic can frequently be influenced by polluted air masses from Europe and the United States and is not necessarily representative of zonal mean mixing ratios.

Jacob *et al.* [1987] also pointed out that, due to vertical concentration gradients over the NH, τ_{ex} values calculated from vertically integrated data will be smaller than τ_{ex} values calculated from surface data. Indeed, the Levin and Hesshaimer [1996] study calculated a τ_{ex} of 1.1 years when using vertically integrated data (over both the troposphere and stratosphere), as opposed to the τ_{ex} value of 1.5 years calculated from surface data. It is not surprising then, that the CMDL data set, which is largely representative of the free troposphere, yields a τ_{ex} value (1.3 years) that is intermediate between these two. Considering the likely zonal asymmetries of atmospheric SF₆ mixing ratios, it seems that 3-D modeling studies would be most useful in confirming a 'best estimate' of τ_{ex} .

Conclusion

Atmospheric SF₆ continues to be monitored by NOAA CMDL. In addition to the sampling programs described above, SF₆ is now being measured in flask samples from a subset of sites in the NOAA CMDL Cooperative Air Sampling Network. Shortly we will initiate flask measurements of SF₆ from all 45 network sites, as well as in situ measurements at baseline monitoring stations. All together, these data will yield extensive global coverage of atmospheric SF₆, providing an excellent means of verifying the accuracy of transport models and aiding our ability to study atmospheric mixing on large spatial scales.

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