NOAA SF_6 Measurements from 1987 to 2009

Brad Hall[1], Geoff Dutton[2], Debbie Mondeel[2], Ed Dlugokencky[1], David Nance[2], Pat Lang[1], Gabrielle Petron[2], James Butler[1], James Elkins[1]

[1]National Oceanic and Atmospheric Administration, Earth System Research Laboratory
[2]University of Colorado, Cooperative Institute for Research in Environmental Science

Introduction

We have worked to improve our SF_6 measurements from flasks and *in situ* instruments. A new calibration scale was developed in 2006 and all measurements were updated to the 2006 scale. Here we present:

1) Conversion to the 2006 SF_6 calibration scale
2) SF_6 results from the Halocarbons (HATS) flask program
3) Comparisons among NOAA SF_6 measurement programs
4) Implications for estimating SF_6 emissions

Improved SF_6 Precision

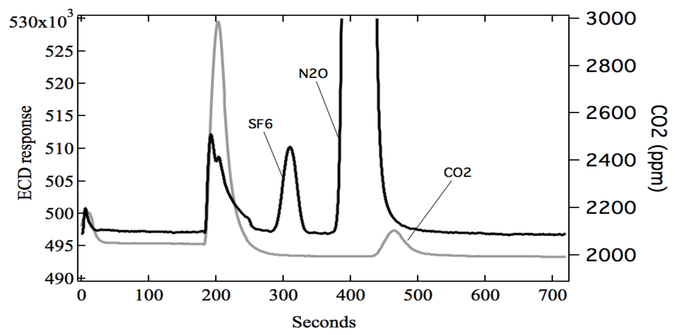
SF_6 calibration precision was improved in 2006 with the addition of a molecular sieve 5A post-column (185 deg C). By forcing SF_6 to elute prior to N_2O, we increased the SF_6 peak height without increasing baseline noise. SF_6 precision improved from ~1% to ~0.3%. This has improved our ability to link different SF_6 measurement programs to a common scale.

Updating to the 2006 SF_6 Calibration Scale

With better precision, we detected a small difference between the 2006 and 2000 SF_6 calibration scales. A number of air standards were analyzed on the SF_6 "calibration" instrument in order to convert data analyzed on the 2000 scale to the new 2006 scale. Results from a prior instrument (2000-2004) were adjusted to provide a consistent record of calibrations on the 2006 scale from 2000 to present.

Conversion: $Y = 4.8546E\text{-}3 * X^2 + 9.3479E\text{-}1 * X + 0.2166$
(where Y = 2006 scale, X = 2000 scale).

2000 scale	2006 scale	Difference (ppt)
1.0	1.156	0.156
2.0	2.106	0.106
3.0	3.065	0.065
4.0	4.033	0.033
5.0	5.012	0.012
6.0	6.000	0.000



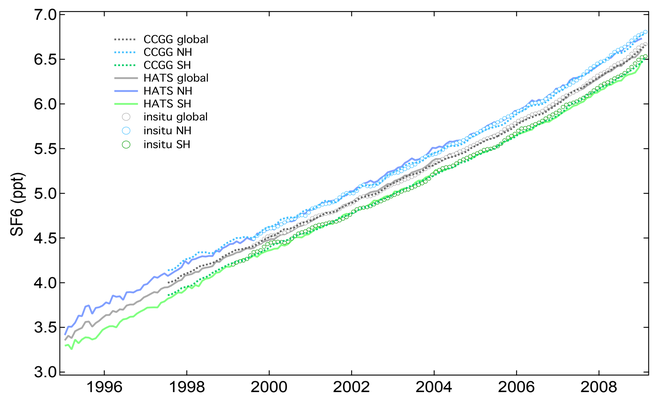
NOAA Baseline SF_6 Measurements

Halocarbon (HATS) Flasks: Collected weekly from 11 sites
- Analyzed on a single instrument
- All results subject to similar calibration uncertainties and instrument performance

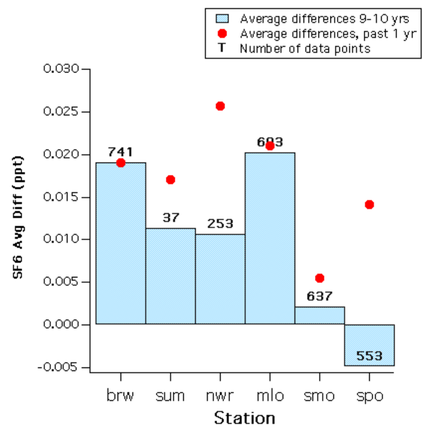
Carbon Cycle (CCGG) Flasks: Collected weekly from over 50 sites
- Analyzed on a single instrument
- All results subject to similar calibration uncertainties and instrument performance

In situ (HATS): hourly measurements at 6 sites
- Multiple instruments
- Calibration uncertainties tend to be smoothed out
- Instrument performance varies among sites

SF_6 Measurements from 3 NOAA Networks

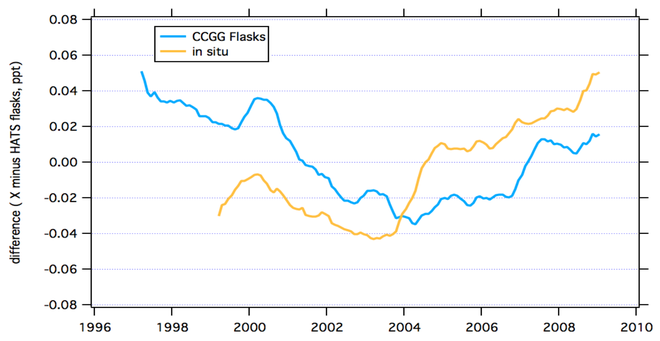


Comparisons Between Programs



CCGG Flasks vs *in situ*

Global Mean SF_6 from Three Programs
(CCGG flask and in situ minus HATS flask)



Differences in global mean SF_6 among programs could be caused by:

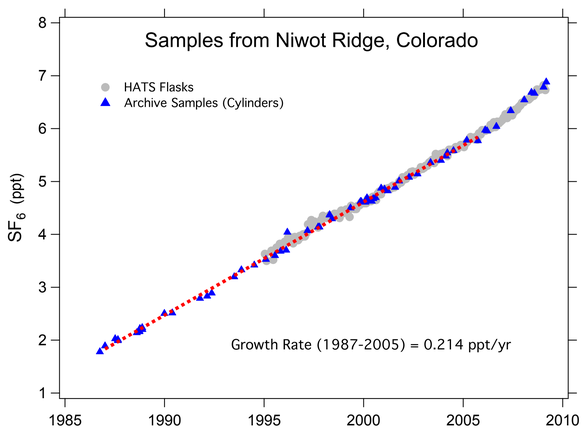
Flasks:
1) calibration offsets
2) instrumental issues (ie. non-linear response)
3) sampling issues (not likely)

In situ:
1) calibration offsets (less likely)
2) instrument issues (particularly at tropical stations)

All: differences in how global mean mixing ratios are calculated

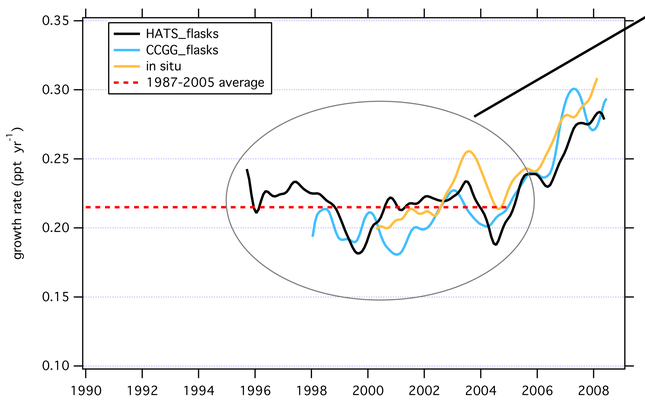
Long-Term Trends

A 20 year record of SF_6 was constructed from the analysis of air collected at Niwot Ridge, Colorado in gas cylinders and stored as a pseudo air archive. We have analyzed archive-quality samples dating to 1987. The trend in northern hemispheric SF_6 inferred from this air archive reveals a nearly linear growth rate of 0.214 ppt yr^{-1}.

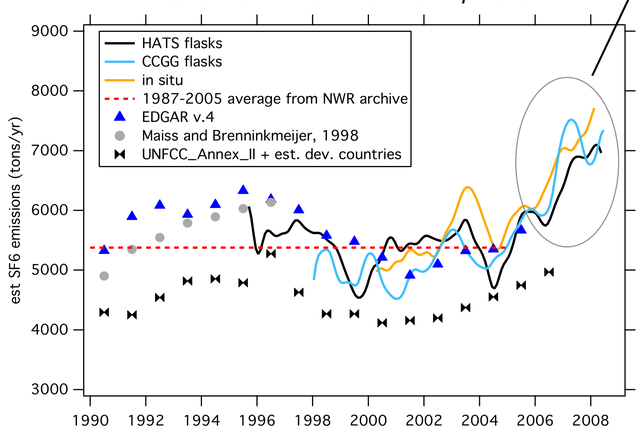


The SF_6 growth rate from 1987-2005 implies an average SF_6 emission rate of ~5400 tons SF_6 yr^{-1}, which is consistent with other measurement-based estimates during this period. Even though some of the early samples are subject to ~0.06 ppt uncertainty, this corresponds to a small uncertainty (~3%) in the inferred emission rate.

SF_6 Growth Rate (3 Networks)



Emissions: Inferred and Reported



All networks show similar growth rates, although some short-term features are not captured by all programs. These differences imply that from 1998 to 2006 the uncertainty in emissions inferred from measured SF_6 is about 15%.

Growth rates (and emissions) over this period may best be estimated by the mean of these three data sets.

Global emissions of SF_6 have increased over the long-term average starting in about 2006. These data also suggest that SF_6 emissions increased slightly from 1999 to 2005. This increase is also seen in the EDGAR emissions estimates, although the timing of the increase appears a little earlier in our data. With many countries making efforts to reduce SF_6 emissions in recent years, it is not clear where the increased emissions (since 2006) are coming from. Improved SF_6 measurements along with modeling efforts will likely be required to infer changes on a regional basis.

What are the prospects for improvement? We have improved precision on one instrument from ~ 0.05 ppt to 0.02-0.03 ppt. It may be possible to achieve this level of improvement on other instruments with modest effort.

History of SF_6 calibration precision

2000-2004:	0.05-0.07 ppt
2004-2006:	0.03-0.05 ppt
2007-present:	0.02-0.03 ppt

References:
Maiss and Brenninkmeijer, Atmospheric SF_6: trends, sources, and prospects, *Environ. Sci. Tech., 32,* 3077-3086 (1998).