

Intercomparisons of Nitrous Oxide and Sulfurhexafluoride within CMDL

G.S. Dutton^{1,2}, E.J. Dlugokencky², P.M. Lang², K.A. Masarie², A.M. Crotwell^{1,2}, T.M. Thompson², and B.D. Hall²

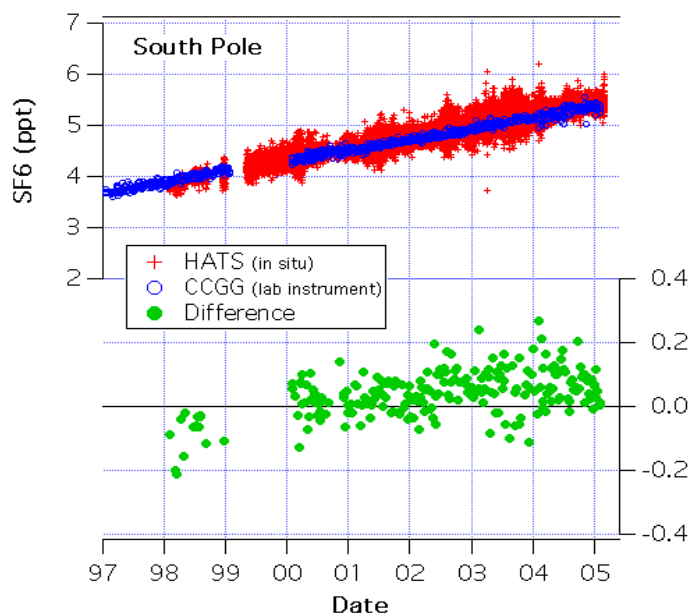
¹Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder 80309; 303-497-6086; Fax: 303-497-6290; E-mail: Geoff.Dutton@noaa.gov

²NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, CO 80305

For the past year, there has been an ongoing measurement intercomparison of nitrous oxide (N₂O) and sulfurhexafluoride (SF₆) within CMDL. The intercomparison focuses on two separate measurement programs, the Carbon Cycle and Greenhouse Gas (CCGG) group flask network and the Halocarbons and other Atmospheric Trace Species (HATS) group in situ program. Both programs use reference gases and a standard scale prepared by the CMDL standards lab. Other similarities include similar chromatographic columns and measurement techniques, namely, gas chromatography with an electron capture detector.

However, the two programs have significant differences in sampling methods and calibration techniques. The CCGG N₂O and SF₆ program utilizes an extensive global flask-sampling network using a pair of flasks that are filled weekly and returned to Boulder for analysis on a dedicated gas chromatograph (GC). A six-point calibration curve is acquired monthly for N₂O whereas, a linear calibration is continuously used for SF₆. The HATS in situ GCs are located at Niwot Ridge, Colorado, and at four CMDL baseline stations (Barrow, Alaska; Mauna Loa, Hawaii; American Samoa; and South Pole, Antarctica). These instruments measure one of two reference tanks and an air sample every hour. Air concentrations are calculated by either a one- or two-point calibration determined by the station reference cylinders.

The intercomparison (Figure 1) has shown some consistent differences between the two programs. In general, the CCGG laboratory instrument is more precise than the HATS field GCs. The precision of the N₂O CCGG



flask measurement is 0.4 ppb (0.1% of ambient) whereas the in situ GCs' precisions can be three times larger. SF₆ precisions are nominally better on the CCGG laboratory instrument (CCGG: 0.04 ppt, HATS 0.03 to 0.1 ppt).

N₂O measurements are systematically different between the two programs. When comparing N₂O data acquired at all five locations, the in situ GCs are 0.1 to 0.5 ppb higher relative to the CCGG flask program. For SF₆ there does not appear to be a consistent bias between the two programs; differences range from -0.1 to 0.1 ppt (Figure 1). Since both programs are using the same calibration scales, measurement differences are likely due to sampling methods.

Figure 1. CCGG flask and HATS in situ SF₆ record from South Pole, Antarctica. Since 2000 there has been a 0.1 ppt difference between the records.