

Atmospheric CFC-11, CFC-12, CFC-113, CCl₄ and SF₆ Histories (1910-2014)

(updated 7 January 2014)

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Table 1 contains a listing of mean northern (NH) and southern (SH) hemisphere tropospheric CFC-11, CFC-12, CFC-113, carbon tetrachloride (CCl₄) and sulfur hexafluoride (SF₆) concentrations for the period 1910 to 2014. The concentrations are given for the mid-point of each year (e.g. 2013.5) and expressed as the mixing ratio (mole fraction) of the trace gas in dry air. All concentration values are reported in parts-per-trillion (ppt).

1.) Details for CFC-11, CFC-12, CFC-113 and CCl₄

The initiation of global atmospheric monitoring programs for CFC-11, CFC-12, CFC-113 and CCl₄ began in the late 1970's and early 1980's. Atmospheric concentrations of these compounds prior to this period are derived from estimates of annual industrial production and release of these compounds, with corrections applied based on the atmospheric lifetimes of each compound. Details on the procedures for deriving annual mean CFC-11, CFC-12, CFC-113 and CCl₄ concentration values (and estimates of errors) for the period 1910-1998 are provided in Walker et al (2000).

Concentration values for CFC-11, CFC-12, CFC-113 and CCl₄ listed in Table 1 from 1910.5 to 2008.5 are based on a 2009 update (bluemoon.ucsd.edu/pub/cfchist) of the Walker et al. (2000) results. Information on the calibration scales used at the Scripps Institution of Oceanography (SIO) is also provided at this website. The most recent (2009.5 to 2013.5) concentration values reported in Table 1 are derived from CMDL atmospheric measurements tabulated at the website: <ftp://ftp.cmdl.noaa.gov/hats/> in 2013. Because of small (typically < 1%) differences in the CMDL and SIO calibration scales for these compounds, the CMDL concentration values reported from 2009.5 to 2013.5 are not directly used in Table 1. Instead, the yearly changes (in ppt) reported by CMDL for each compound during the period 2008.5 to 2013.5 are added to the SIO concentration values for 2008.5 in Table 1 to derive the yearly concentration values for 2009.5 to 2013.5. The CMDL tabulations available (as of December 2013) at the website <ftp://ftp.cmdl.noaa.gov/hats/> only go to November 2013. The 2014.5 concentration values for each compound in Table 1 are extrapolated from the corresponding 2013.5 values, assuming the same changes (in ppt per year) between 2013.5 and 2014.5 as those observed between 2012.5 and 2013.5.

There have been several revisions of the calibration scales used at SIO (e.g. SIO93, SIO98, SIO05) for reporting CFC-12, CFC11, CFC-113 and CCl₄ concentrations (<http://bluemoon.ucsd.edu/pub/cfchist/>). The most recent SIO calibration scale for reporting CFC-12, CFC11, CFC-113 and CCl₄ concentrations is the SIO05 scale, which differs slightly from earlier SIO calibration scales. Since most of the measurements of dissolved CFCs in seawater made as part of the World Ocean Circulation Experiment

(WOCE) and other major studies have been reported on the earlier SIO98 scale, it has been recommended (Bullister and Tanhua, 2010) for consistency that all future measurements of the concentrations of CFCs in seawater continue to be reported (and stored in data centers) on the SIO98 scale. If desired, seawater CFC concentrations on the SIO98 scale can be converted by users to any other SIO scale using simple multiplicative factors (see <https://bluemoon.ucsd.edu/pub/cfchist/>).

All of the atmospheric CFC-11, CFC-12, CFC-113 and CCl₄ concentration values in Table 1 are reported on the SIO98 calibration scale

2.) Details for SF₆

A discussion of the atmospheric history of SF₆ is provided in Bullister et al. (2006). The initiation of global atmospheric monitoring programs for SF₆ began in the 1990's. In Table 1, annual atmospheric concentrations of SF₆ for the period 1953.5-1994.5 are based on the industrial production and release estimates in Maiss and Brenninkmeijer (1998) (MB1988) for this period. To convert these annual release estimates to atmospheric concentrations, the MB1988 cumulative release value for SF₆ in 1995.5 is compared to the measured CMDL (ftp://ftp.cmdl.noaa.gov/hats/sf6/combined/HATS_global_SF6.txt) NH and SH SF₆ atmospheric concentrations in 1995.5. The ratio of the observed CMDL SF₆ atmospheric concentration in 1995.5 to the MB1988 cumulative SF₆ release for 1995.5 is then used to convert the MB1988 derived cumulative release values for each year (from 1953.5 to 1994.5) to atmospheric concentrations.

Note: In Table 1, atmospheric SF₆ concentrations prior to 1953.5 are assumed to be 0. Based on the solubility of SF₆ in seawater (Bullister et al, 2002), the 1953.5 atmospheric concentration of SF₆ (~0.04 ppt) corresponds to a dissolved SF₆ equilibrium concentration of about 0.02×10^{-15} mol/kg seawater. This concentration is at or below the detection limit for dissolved SF₆ in seawater using current measurement techniques (Bullister and Wisegarver, 2008).

In Table 1, SF₆ values for the period 1995.5 to 2013.5 are based on mid-year measurements of SF₆ for the NH and SH reported by CMDL (ftp://ftp.cmdl.noaa.gov/hats/sf6/combined/HATS_global_SF6.txt). The 2014.5 SF₆ concentration values in Table 1 are extrapolated from the corresponding 2013.5 values, assuming the same changes (in ppt per year) between 2013.5 and 2014.5 as those observed between 2012.5 and 2013.5

Because of small differences in the CMDL2006 and SIO2005 SF₆ calibration scales (Miller et al., (2008); Rigby et al (2010)), all SF₆ concentrations reported in Table 1 have been converted to the SIO2005 SF₆ calibration scale.

It has been recommended (Bullister and Tanhua, 2010) that all measurements of the concentrations of SF₆ in seawater be reported (and stored in data centers) on the SIO2005 scale

3.) Additional Notes

There may be very slight differences (<1%) in some of the atmospheric concentrations of CFC-11, CFC-12, CFC-113, CCl₄ and SF₆ reported in this version of Table 1 vs. previous versions, due to small revisions and re-calibration of earlier measurements by the CMDL and SIO groups.

4.) References:

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Maiss, M., and Brenninkmeijer, C. A. M. (1998). Atmospheric SF₆, trends sources and prospects. *Environ. Sci. Tech.*, 32:3077-3086.

Miller, B. R., Weiss, R. F., Salameh, P. K., Tanhua, T., Grealley, B. R., Muhle, J., and Simmonds, P. G. (2008). Medusa: A sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds, *Anal. Chem.*, 80, 1536–1545, doi:10.1021/ac702084k, <http://pubs.acs.org/doi/abs/10.1021/ac702084k>, 2008.

Walker, S. J., Weiss, R. F. and Salameh, P. K. (2000). Reconstructed histories of the annual mean atmospheric mole fractions for the halocarbons CFC-11, CFC-12, CFC-113 and carbon tetrachloride. *J. Geophys. Res.*, 105:14285-14296.

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Table 1. Annual mean tropospheric CFC-11, CFC-12, CFC-113, carbon tetrachloride (CCl₄) and sulfur hexafluoride (SF₆) concentrations in the northern (NH) and southern (SH) hemispheres for the period 1910.5 to 2014.5 The concentrations are expressed as the mixing ratio (mole fraction) of the trace gas in dry air. All concentration values are

reported in parts-per-trillion (ppt). CFC-11, CFC-12, CFC-113 and CCl₄ concentrations are reported on the SIO98 calibration scale; SF₆ concentrations are reported on the SIO2005 calibration scale.