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Changes in atmospheric composition discerned from long-term NDACC measurements: Total atmospheric bromine, chlorine, and fluorine trends and age of the air from the NOAA GMD Cooperating Network

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1. Abstract:

The Montreal Protocol on Substances that Deplete the Ozone Layer and its subsequent amendments has been successful in decreasing the total equivalent chlorine of man-made halocarbons in the atmosphere by ~13% since its peak in 1994-5. The National Oceanic and Atmospheric Administration's Earth System Research Laboratory (NOAA/ESRL) maintains a global in situ and flask network for the measurement and analysis of halocarbons and other atmospheric trace gases. Measurements of nitrous oxide and chlorofluorocarbons -11 and -12 started in 1977. The purpose of this work is to study atmospheric trace gases that affect climate change, stratospheric ozone depletion, and air quality from observations at NOAA and cooperating stations. The analysis of flask samples and data are conducted within the Global Monitoring Division (GMD) in Boulder, Colorado, USA. Through collaborations with the National Aeronautics and Space Administration (NASA) and the National Science Foundation, NOAA/ESRL also operates a number of in situ and flask collection instruments from manned and unmanned aircraft up to 21 km, and balloon platforms up to 32 km . We measure over 40 trace gases in the atmosphere including nitrous oxide (N_2O), chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), methyl halides, numerous halocarbons, sulfur gases (COS, SF_6, CS_2), and selected hydrocarbons. This presentation will highlight our recent observations of halocarbons and other trace gases from the NSF and NOAA sponsored HIAPER Pole-to-Pole Observations over NDACC and NOAA stations from 2009 to 2011 and the NASA and NOAA sponsored Unmanned Aircraft Systems Missions. For more information see http://www.esrl.noaa.gov/gmd/hats and our data are available via anonymous ftp at ftp://ftp.cmdl.noaa.gov/hats .

2. Background:

Measurements of CFC-11, CFC-12, and N_2O began in 1977 from four NOAA/ESRL/GMD baseline observatories (see **Fig.1** large turquoise squares) Barrow, Alaska; Mauna Loa, Hawaii; Cape Matatula, Am. Samoa; and South Pole) and a cooperative station at Niwot Ridge, Colorado with the University of Colorado (**Fig.2**). Over the past 33 years, measurements of these gases and other halocarbons have increased to over fifty stations including ground-based, balloon- and airborne-borne stations and platforms) of >40 gases. Locations of the Network for the Detection of Atmospheric Composition Change (NDACC) Fourier Transform Infrared Spectrometer (FTIR) sites are shown in purple hour-glass symbols (**Fig.1**).

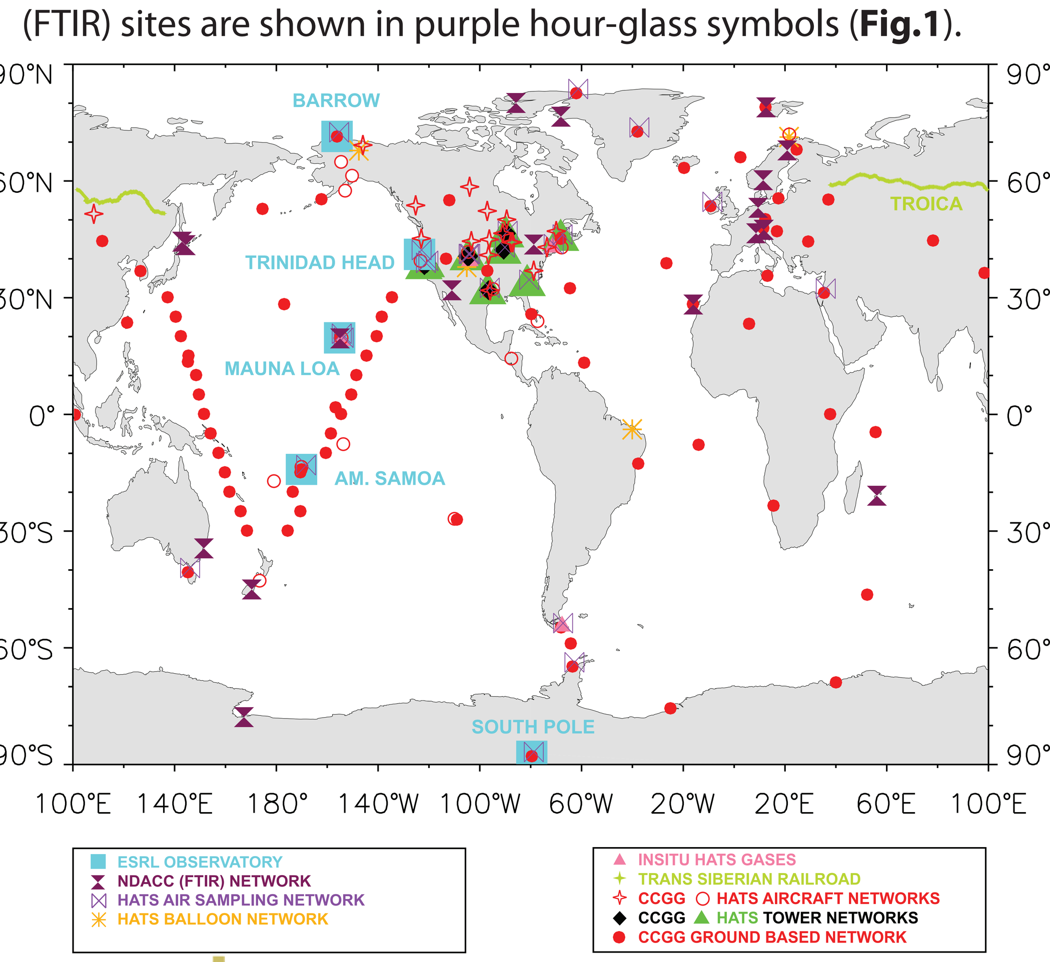

Fig.1 Location of NOAA/ESRL GMD ground-base, balloon- and airborne-borne stations for halocarbon measurements from flask and in situ sampling. Some halocarbons are also measured from flasks from the Carbon Cycle and Greenhouse Gases Group of GMD. Locations of NDACC stations are also noted.

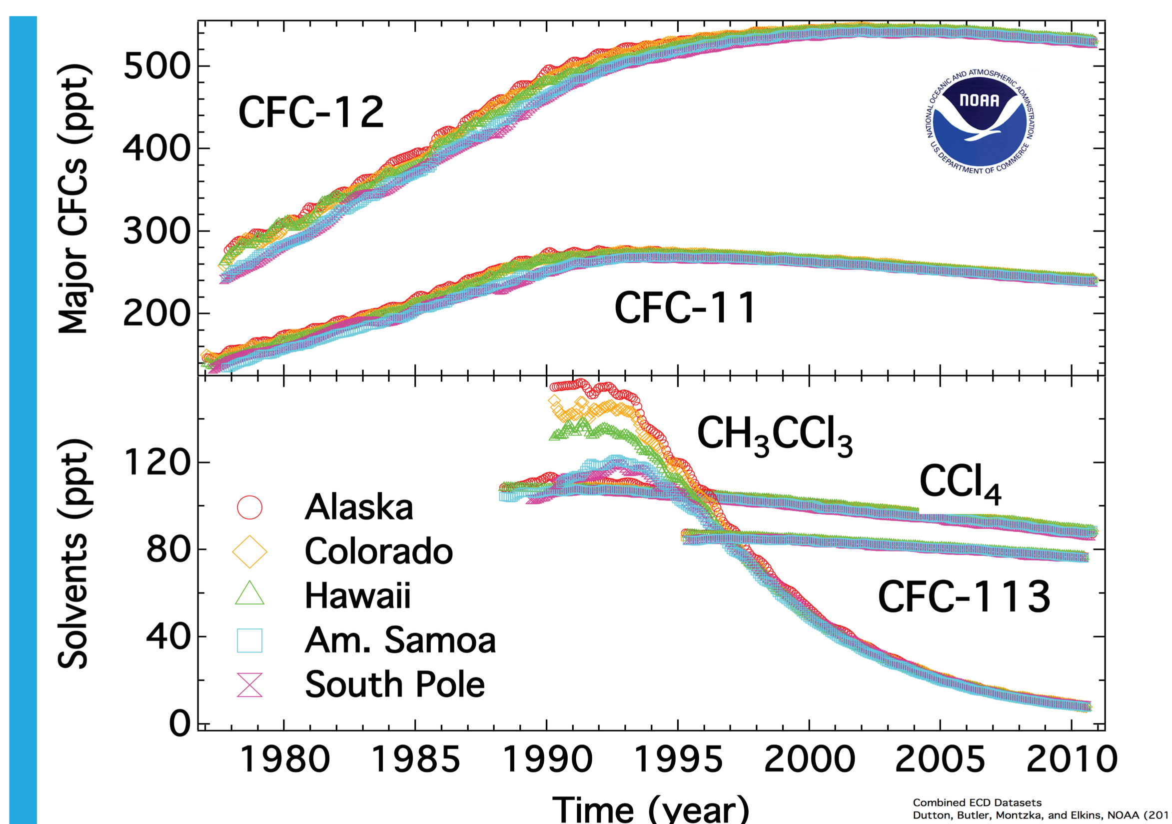

Fig. 2 Mixing ratios of the major CFCs and chlorinated solvents from the four NOAA/ESRL baseline observatories and Niwot Ridge, Colorado.

Decreases in the mixing ratios were observed in the early 1990s in the atmosphere for many of the key compounds following the enactment of the Montreal Protocol (1986) for the shorter lived trace gases, like methyl chloroform and CFC-11 (**Fig.3**). Decreases for the longer lived halocarbons like CFC-12 began later in the early 2000s.

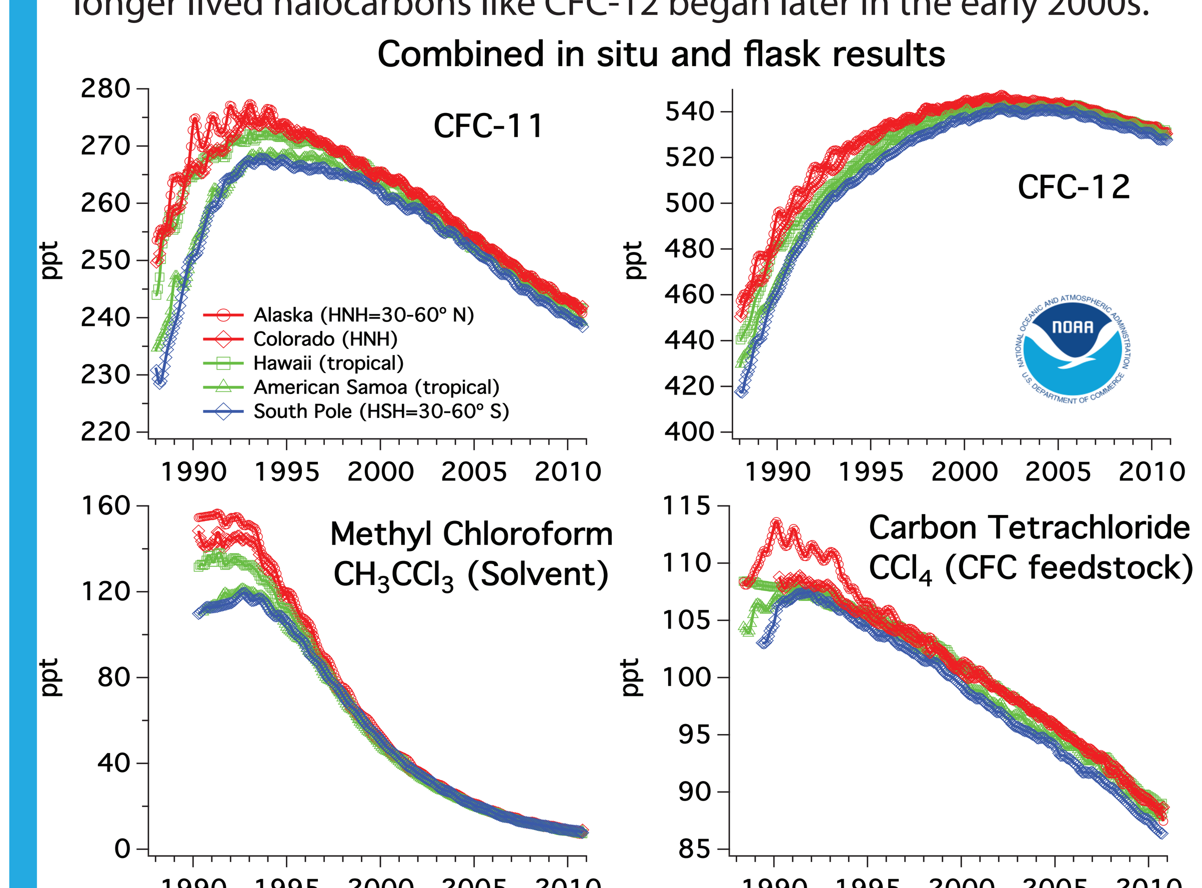

Fig.3 Mixing ratios of major CFCs and chlorinated solvents focused on their peak values after 1990.

Measurement of 10 halocarbons form the basis for the calculation of total chlorine in the atmosphere (**Fig.4**). Measurement of 3 brominated halocarbons form the basis for the calculation of total bromine in the atmosphere (**Fig.5a**). Total chlorine, EECl, and ECL since 1992 are shown in **Fig.5b**. EECl (midlatitude ozone) is down by 13% and ECl (Antarctic ozone) is down by 8.5% from their peak period.

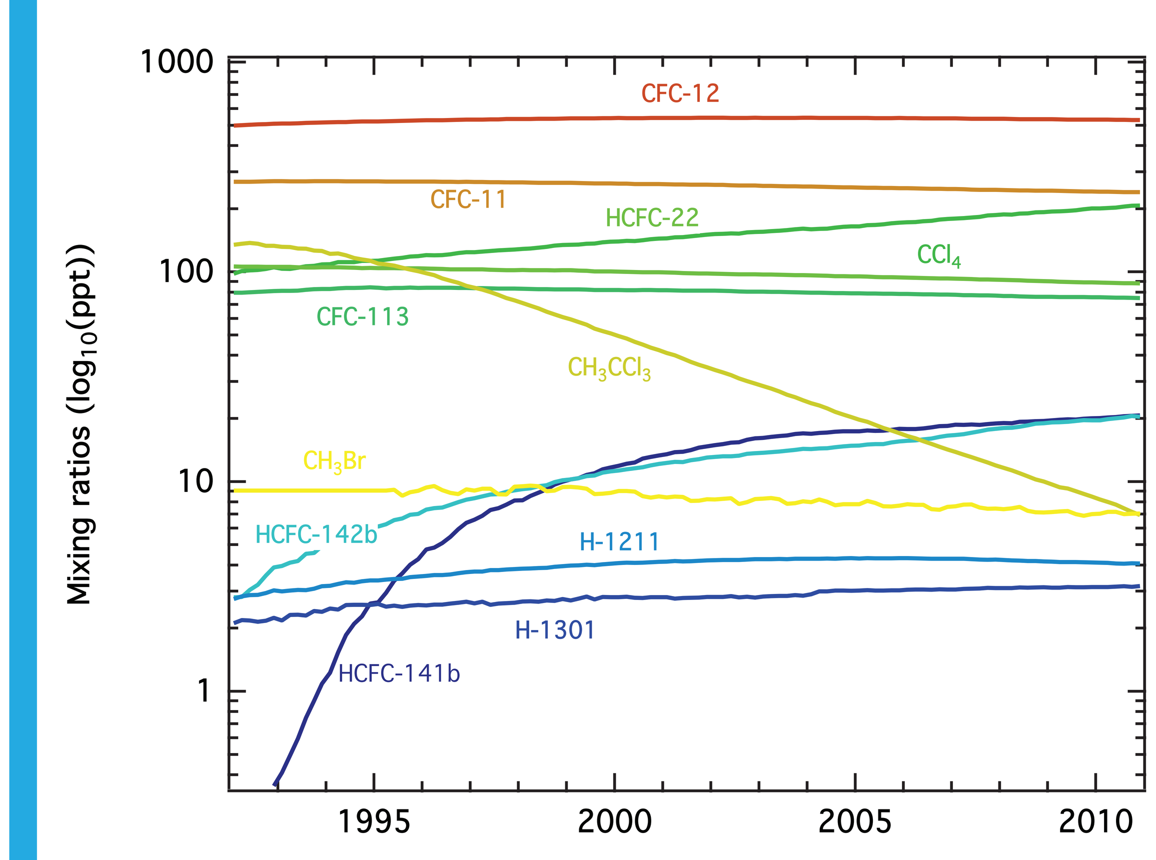

Fig.4 Global mixing ratios in log (base 10 for 11 halocarbons involved in the calculation of total chlorine and bromine in th)e atmosphere. Trends with time are shown after 1992. Measurements include both flask (GC-MSD) and in situ (GC-ECD) from the NOAA/ESRL/GMD Halocarbon network.

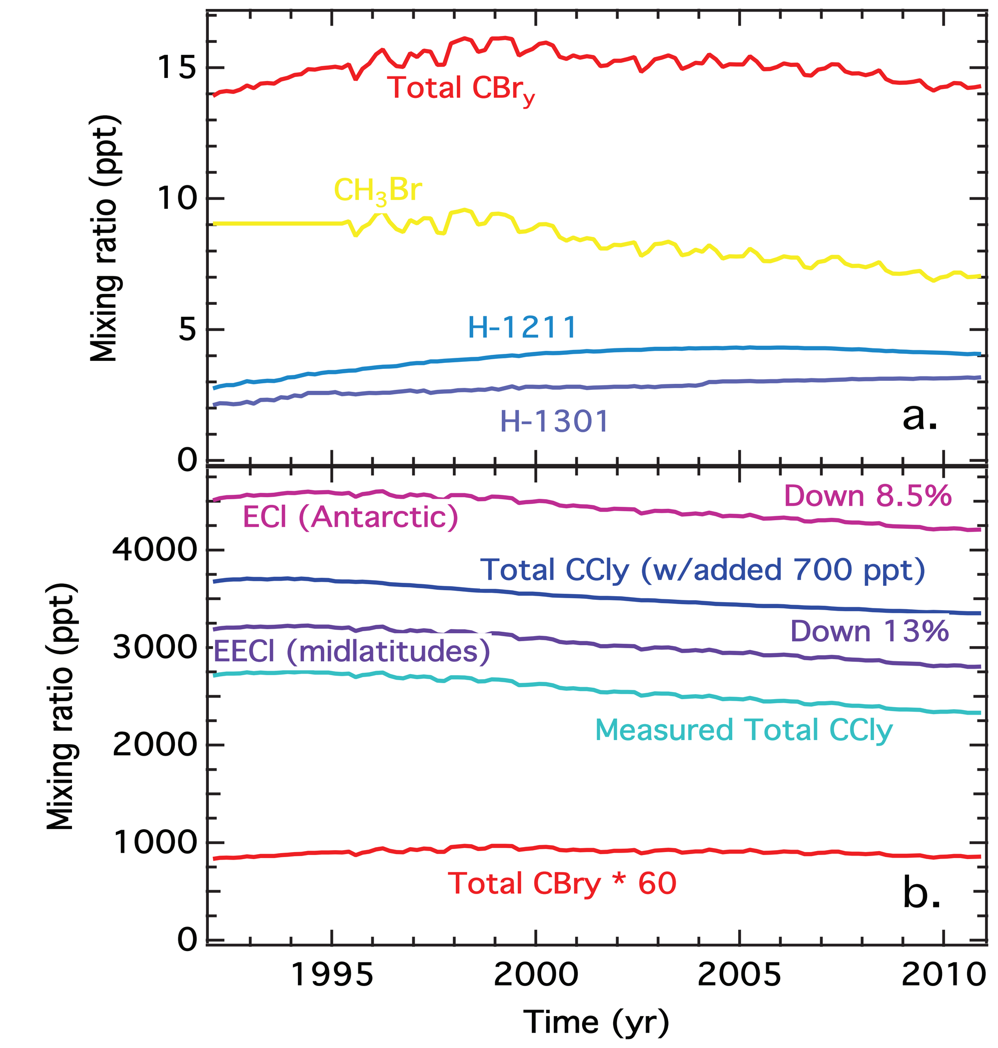

Fig.5 (a) Total organic bromine from the three major measured component species since 1992. **(b)** Total effective equivalent chlorine (EECl, midlatitude ozone), ECl (Antarctic ozone), and total organic chlorine since 1992. Bromine is 60 times more effective in destroying ozone than chlorine per atom basis and is included. (Montzka et al., *Nature, 398*, 690-694, 1999.

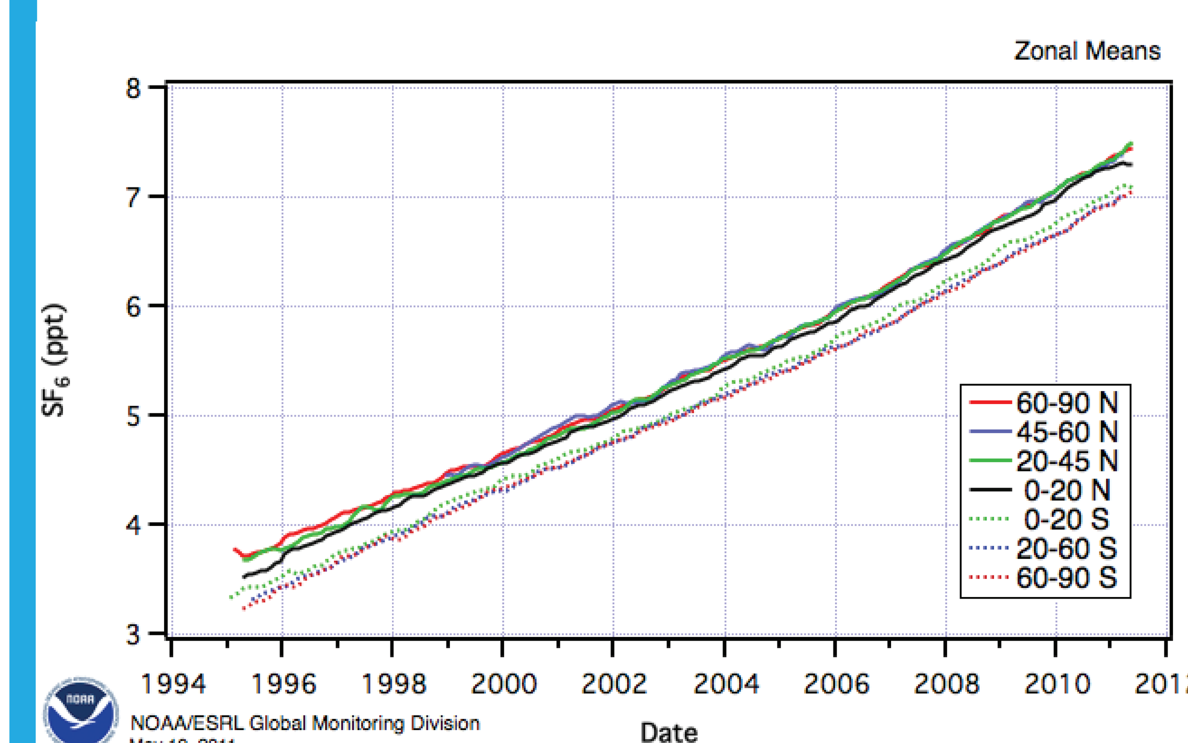

Fig.6 Mixing ratios of sulfur hexafluoride (SF_6) versus time from zonal averages of both in situ and flask sites (**Fig.1**).

Measurements of sulfur hexafluoride (SF_6) have been used as a proxy for the mean age of the air mass in the stratosphere, because it is a long lived gas with almost a linear rate of increase (**Fig.6** or ~0.24 ppt yr^{-1}). The mean age of the midlatitude stratospheric air where ozone is destroyed is about 3 years, while the mean age over the polar regions is 6 years. So, the values of EECl and ECl (**Fig.5**) are delayed by those values in their respective regions.

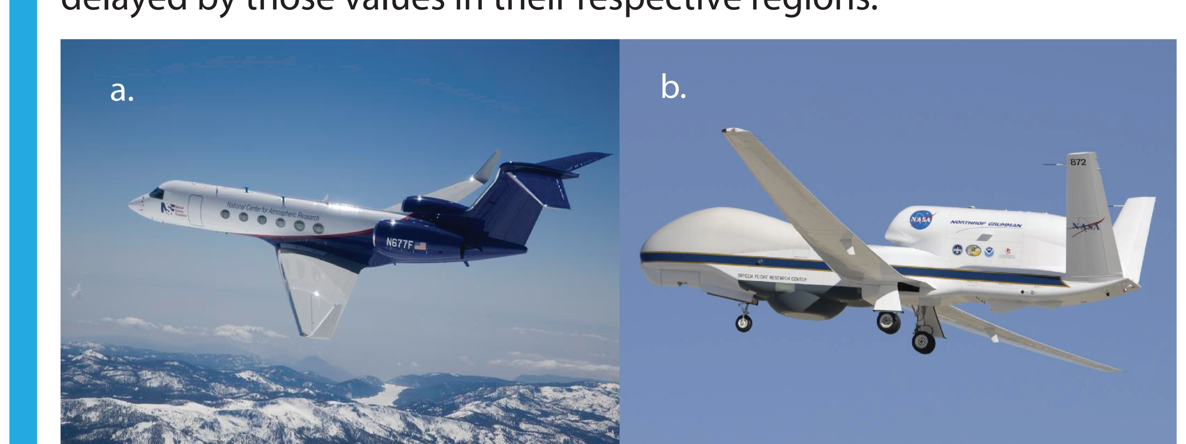

Fig.7 (a). Recent aircraft campaigns have used the manned NSF Gulfstream-V, and **(b).** the unmanned aircraft system (UAS) NASA Global Hawk.

Since many of these halocarbons are destroyed in the upper atmosphere, measurements of vertical profiles are extremely important to the calculation of lifetimes, mixing rates, and photochemical loss. Two airborne campaigns have been useful including the HIAPER Pole-to-Pole Observations of Greenhouse Gases (HIPPO) with the GV (Fig.7a) and the Global Hawk Pacific Experiment (GloPac) (Fig. 7b). HIPPO was a three year study with five north pole to south pole circuits during different seasons (**Fig.8**). GloPac was a series of five flights over the Pacific Ocean to test the new unmanned platform and perform some satellite validation (**Fig.9**).

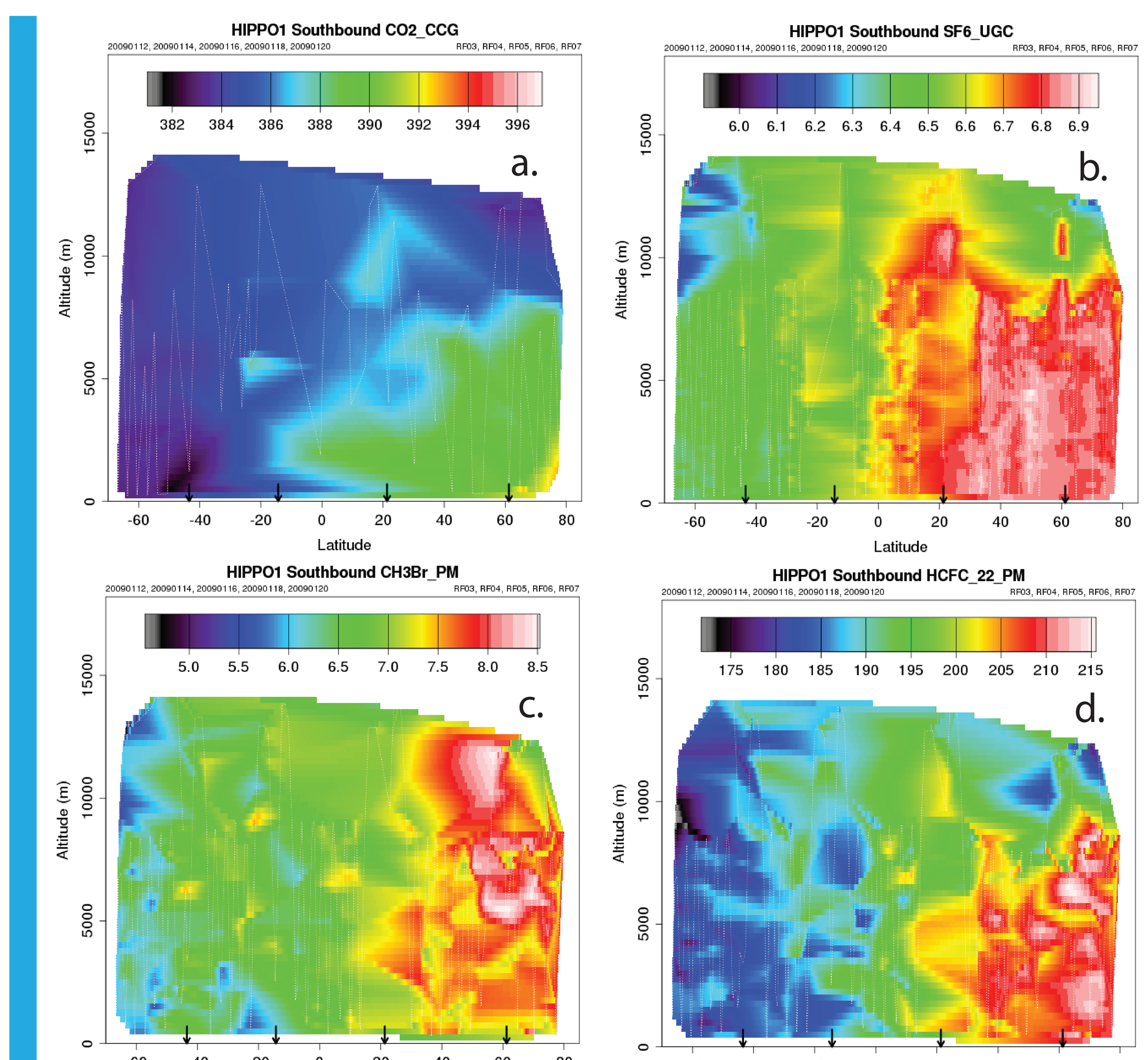

Fig.8 Latitudinal cross sections during the first southbound run of HIPPO/1 in January 2009 of (a) CCGG CO_2 from flasks, (b) in situ SF_6 from UCATS, and (c) methyl bromide (CH_3Br) and (d) HCFC-22 from PANTHER. Note strong N.H. sources in each plot.

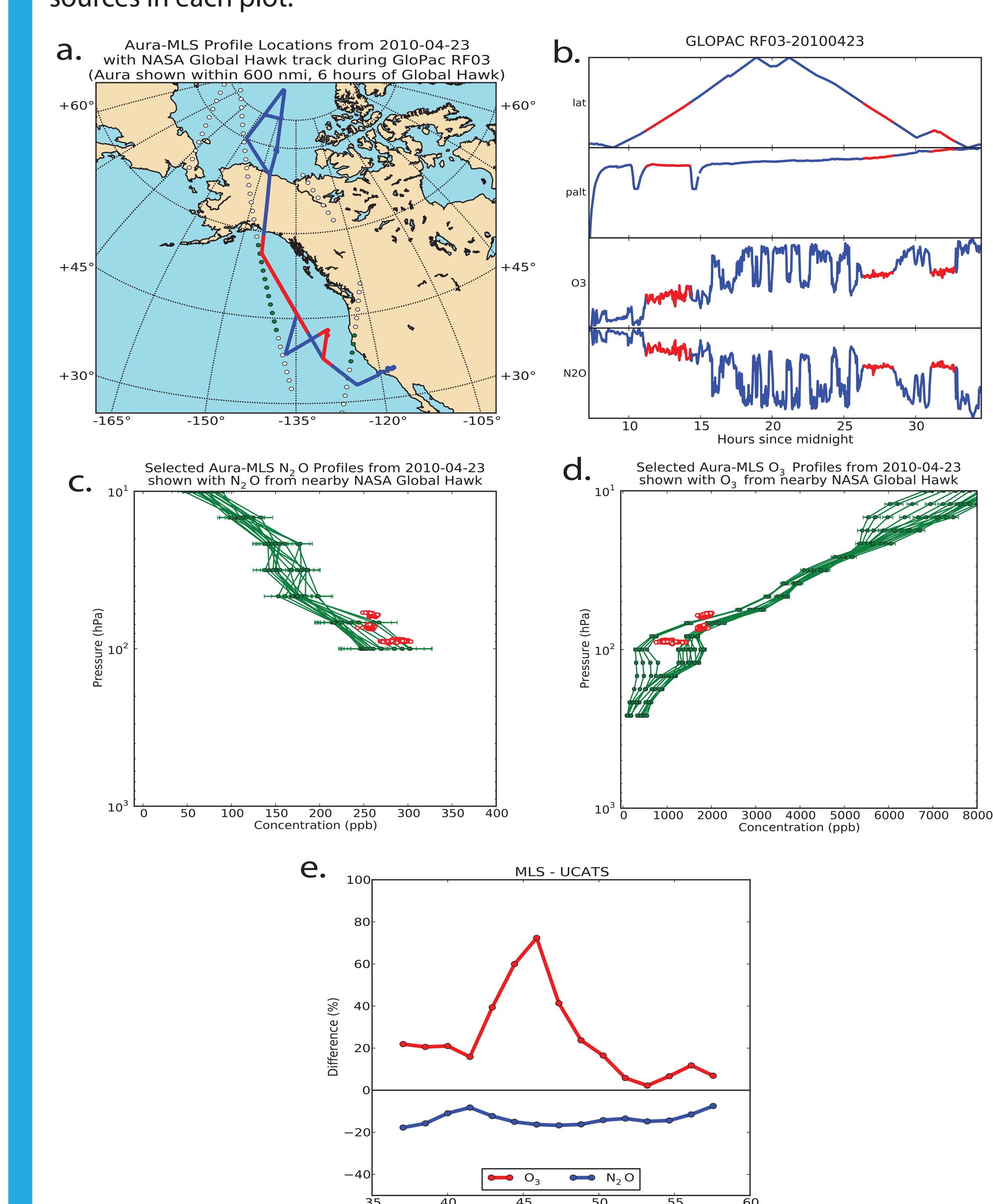

Fig. 9 Comparison of MLS with the UCATS N_2O and O_3 measurement during the 23 April 2010 flight from GloPac. **(a)** Map of sampling locations, **(b)** transect of GloPac flight and values for comparsion in red, **(c)** MLS N_2O (Green) profiles vs. UCATS values (red), **(d)** similar plot for O_3, and **(e)** mean differences of MLS-UCATS.

Conclusions:

Trends of important halocarbons and nitrous oxide that cause ozone depletion are shown, along with trends of total chlorine and bromine. Age of the stratospheric air mass will delay tropopsheric halogen by 3 years in the midlatitude regions and 6 years in polar regions. The goal of NDACC and its cooperating networks like NOAA HATS is to validate their measurements with each other and satellites to obtain global coverage on man's influence on ozone & climate.