

5.1.3. IN SITU GAS CHROMATOGRAPH MEASUREMENTS

Operations Update

Four-channel GC-ECD instruments, developed to replace the aging RITS instruments and add new measurement capabilities, were installed at the CMDL field sites (Barrow Observatory, Alaska (BRW); Mauna Loa Observatory, Hawaii (MLO); Samoa Observatory, American Samoa (SMO); and SPO). This new instrument is called Chromatograph for Atmospheric Trace Species (CATS). Three of the channels have packed gas chromatographic columns and the fourth contains a capillary column. The three packed-column channels are similar to those used in the RITS in situ GCs. They are used to measure three chlorofluorocarbons (CFC-11, CFC-12, and CFC-113), chlorinated solvents (CH_3CCl_3 , CHCl_3 , and CCl_4), N_2O , SF_6 , and halon-1211. The capillary column is used to measure three new compounds for the HATS in situ program: HCFC-22 (CHClF_2) and two methyl halides (CH_3Cl and CH_3Br). The CATS GCs analyze an air sample once every hour.

New techniques were developed by the HATS group to measure HCFC-22 and the methyl halides with an ECD. An ECD is less sensitive to methyl halides than to the CFCs. To enhance the methyl halide response a larger air sample is required. An 80 cm^3 air sample is pre-concentrated on a cold trap held at about -60°C . The trap is subsequently heated to release and inject the sample onto the capillary column for separation. More detailed information on the chromatography of this channel can be found on a Web page at <http://stndstealth.cmdl.noaa.gov/channel4.html>.

The CATS GCs are controlled by a PC-based data acquisition system using the QNX operating system (QNX Software Systems Ltd., Kanata, Ontario). QNX is a multi-tasking UNIX operating system for PC that allows for simultaneous control of the GC, preliminary data processing, data backup and storage, and World Wide Web access. Each CATS GC is accessible via the Internet. System status and preliminary data can be accessed on-line.

The first CATS instrument was installed at SPO in late January 1998. A CATS instrument was installed at BRW in mid-June 1998. After 8 months the data comparison was deemed sufficient, and the RITS instrument was shut off (February 17, 1999). The MLO equipment was deployed in late September 1998, and the SMO instrument was deployed in December 1998. Comparisons of RITS and CATS instruments continue at SMO, SPO, and MLO. It is expected that these RITS instruments will soon be shut down.

Data Analysis – RITS

Trace gas mixing ratios measured by ground-based in situ instruments have shown marked changes over the 10-13 year

record (Figure 5.17). These trends reflect changes in chemical usage, atmospheric lifetimes, and mandated world-wide termination of production and consumption of some chemicals. The RITS data sets, which include individual measurements, daily, monthly, hemispheric and global averages, are available on the Internet at <ftp.cmdl.noaa.gov/hats>.

Mixing ratios of CFC-11 leveled off in late 1993 indicating a temporary balance between source and sink strengths. The average global rate of decrease for the past few years is 1.6 ppt yr^{-1} . With an estimated atmospheric lifetime of 45 years, a global mean mixing ratio of 267 ppt at the beginning of 1999, and assuming negligible sources, the expected decrease in 1999 should have been 5.9 ppt yr^{-1} . Thus CFC-11 continues to be emitted to the atmosphere, albeit at rates that are less than those of the previous decade.

The average global concentration of CFC-12 reached 537 ppt at the end of 1999 and continues to grow in the troposphere at a reduced rate of 2 ppt yr^{-1} . From the average rate of decrease in the growth rate since 1995, it is projected that CFC-12 will peak in the atmosphere in the next 3-4 years (Figure 5.18).

Methyl chloroform emissions have decreased dramatically since early 1993. The effects of reduced emissions can be seen as a decrease in atmospheric mixing ratio (Figure 5.17). The global rate of decrease reached a maximum of 13.5 ppt yr^{-1} in 1996-1997. The interhemispheric difference is now very small (Figure 5.12), indicative of similar emissions in both hemispheres (near zero in this case). As emissions become negligibly small, the atmospheric lifetime can be estimated solely from the trend in atmospheric mixing ratio (Figure 5.19) [Montzka *et al.*, 2000]. Based on in situ measurements from 1998-1999, the globally averaged lifetime is estimated to be 5.6 years. This result is consistent with that obtained from flask-air measurements over the same time period (section 5.1.2). It is encouraging that the flask and in situ programs, employing different sampling methods, different detection methods, and slightly different calibration methods, can provide the same result over this period.

Mixing ratios of carbon tetrachloride have been decreasing globally since 1990 at an average rate near -0.8 ppt yr^{-1} . The interhemispheric difference indicates that sources are located primarily in the northern hemisphere. Because CCl_4 is used mainly as feedstock for the production of CFCs, which were banned in the industrialized nations, developing nations may be responsible for current emissions of CCl_4 .

The tropospheric mixing ratio of N_2O continues to grow at a steady rate near 0.7 ppb yr^{-1} and has reached a global mean of 315.5 ppb at the end of 1999. A north-to-south gradient of 1.2 ppb persists over the period of record because of differences in the balance of sources and sinks in the northern and southern hemispheres.

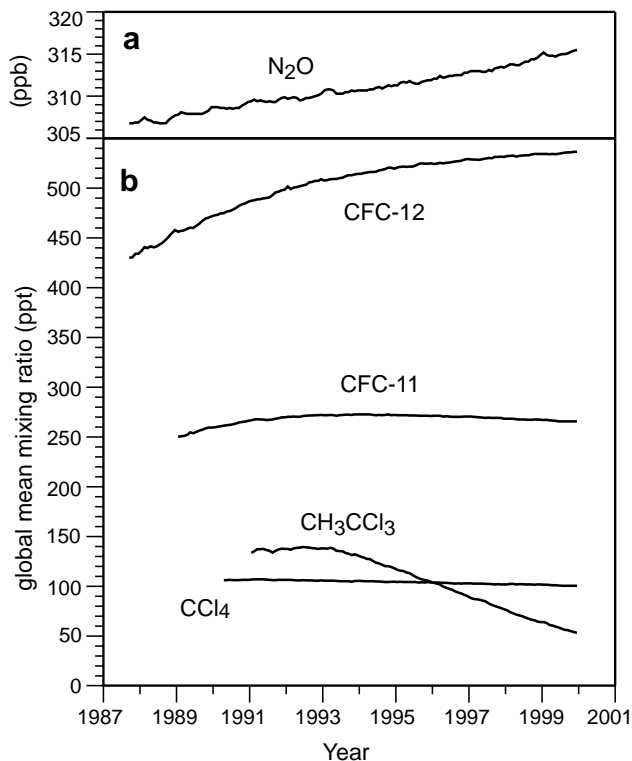


Fig. 5.17. Global monthly mean mixing ratios for (a) N_2O and (b) CFC-12, CFC-11, CH_3CCl_3 , and CCl_4 from the in situ gas chromatographs.

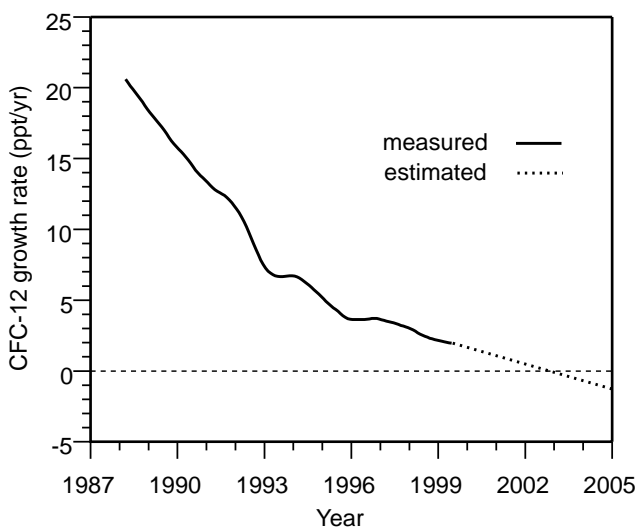


Fig. 5.18. Growth rate of CFC-12 as determined from in situ measurements. The growth rate is projected to reach zero in the next 3-4 years based on the average rate of decrease since 1995.

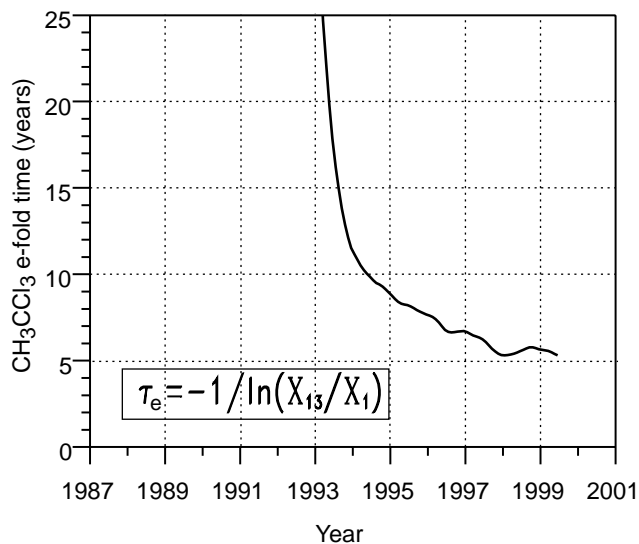


Fig. 5.19. Using a single box model for the atmosphere with emissions assumed to be negligible, the e-fold time (τ_e) is estimated using measured global mean methyl chloroform mixing ratios one year apart. X_1 is the monthly mean global mixing ratio for the first month and X_{13} is the mixing ratio 1 year later (13th month). Calculated values approach a limit as the emissions truly become negligible.

Data Analysis - CATS

Over the past 5 years the HATS instruments have monitored the decrease of several important ozone-depleting gases [Elkins *et al.*, 1993; Montzka *et al.*, 1996a, 1999a]. The new CATS GCs provide insight into additional ozone-depleting gases while still monitoring the trends of the CFCs and chlorinated solvents. HCFC-22 is a refrigerant compound that is replacing some of the phased-out CFCs. The CATS in situ measurements, in corroboration with the HATS flask program, have monitored the global atmospheric increase of HCFC-22 (Figure 5.20a). Emissions of HCFC-22 are solely anthropogenic, dominated by the industrial northern hemisphere. This can be seen as a mixing ratio gradient from north to south.

In situ measurements obtained by the HATS group have traditionally focused on long-lived compounds that have predominately anthropogenic sources. Recent measurements of the methyl halides have added important natural halocarbons to the suite of ozone-depleting gases measured by the HATS group. As the CFCs and other chlorinated compounds are phased out, the natural sources of methyl halides will become more important sources of atmospheric chlorine and bromine. Moreover, the sources of these compounds are not well understood [Butler, 2000]. Monthly mean trends of the CATS in situ data for CH_3Cl and CH_3Br show strong seasonal cycles in the northern hemisphere (Figures 5.20b and 5.20c). The seasonal cycle is at its minimum during the summer in both hemispheres when the dominant sink, hydroxyl radical (OH), is at its maximum.

With the addition of the CATS in situ methyl halide measurements at the CMDL observatories, there is the ability to not only monitor these compounds, but also help locate and quantify their sources. A recent study points to coastal vegetation as a source of CH_3Cl [Yokouchi *et al.*, 2000].

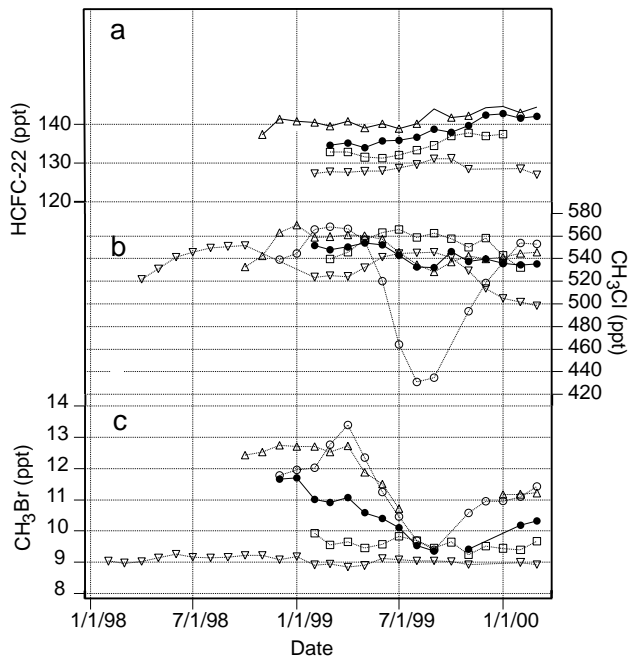


Fig. 5.20. Monthly mean mixing ratios of (a) HCFC-22, (b) methyl chloride, and (c) methyl bromide measured by the CATS in situ gas chromatographs deployed at the CMDL observatories (BRW, triangle; MLO, open circle; SMO, square; SPO, inverted triangle). The solid circles are global averages of the four sites calculated by cosine latitudinal weighting.

Measurements of CH₃Cl at our two tropical coastal sites, MLO and SMO, also point to a coastal terrestrial source. Figure 5.21 shows rapid changes in the CH₃Cl mixing ratio at Mauna Loa (Figure 5.21a) and corresponding changes in wind direction (Figure 5.21b). High concentrations of CH₃Cl are associated with periods of northerly winds (daytime up-slope conditions) that bring CH₃Cl-rich air from the vegetated northern section of the island of Hawaii up to MLO.

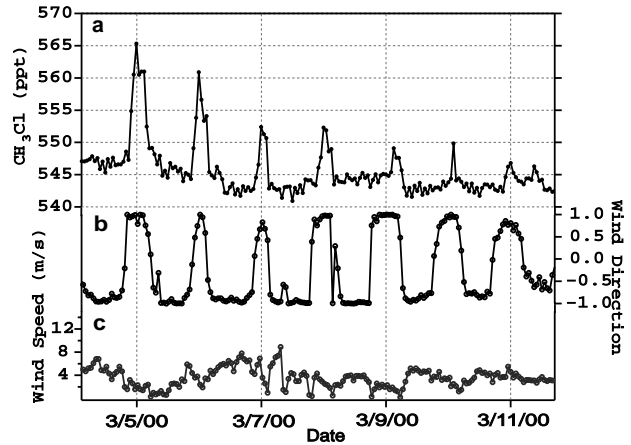


Fig. 5.21. Hourly measurements of CH₃Cl in air at MLO (a) show rapid variability in the CH₃Cl mixing ratio, indicating local sources. The cosine of the wind direction (values near 1 correspond to northerly winds, values near -1 correspond to southerly winds) (b) and wind speed (c) are plotted for comparison.