

## 5.1.2. FLASK SAMPLES

### Overview

No new sampling stations were added in 1998-1999, although Mace Head, Ireland (MHS) and Palmer, Antarctica (PSA) were added at the end of 1997 (Figure 5.1). Sampling at PSA continued throughout 1998-1999, but sampling from MHS was discontinued temporarily because of a high rate of loss of flasks during transit. Efforts were made during the past 2 years to improve the sampling frequency and precision at all sites with considerable success. Progress, however, was delayed somewhat by the CMDL move to the NOAA Broadway site in 1999. One of the analytical instruments (Low Electron Attachment Potential Species (LEAPS) gas chromatograph with electron capture detection (GC-ECD)) experienced considerable difficulties following the move and required the replacement of two electron capture detectors.

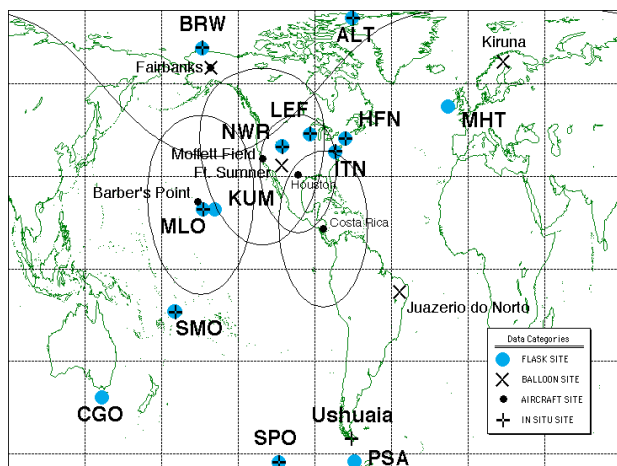


Fig. 5.1. Geographic locations of old and new stations in the HATS flask (gray circles) and in situ (crosses) networks. The sites for balloon launches are noted by "X"s. The location (small black filled circles) and the range of the aircraft operations (arcs and ovals) also are indicated.

Flasks brought into the laboratory were analyzed on two to four instruments depending on the species being examined and the size of the individual sampling flask (Table 5.2). Although all 300-mL flasks were retired from the system, there are still some 850-mL flasks that contain a marginal amount of air for all of the low-level analyses. Most flask analyses were of samples from the network, although many were from research cruises, firn air sampling, and other special projects.

An intercomparison of SF<sub>6</sub> and N<sub>2</sub>O analyses was started with the CCGG group, but it is still in its early stages. Although HATS records extend back into the 1970s for N<sub>2</sub>O and the 1980s for SF<sub>6</sub> (including archived samples), the CCGG network has the advantage of sampling from many more sites per week, thus allowing a better spatial picture of the distributions of these compounds to be obtained.

### Sampling and Analysis

In 1996, 269 flasks from the network were filled and delivered to the Boulder laboratory for analysis. This number has increased each year reaching a total of 399 in 1999 (Figure 5.2). This increase is the result of added sites (1996-1997) and a more efficient turnover of flasks between Boulder and the field sites. This was accomplished through improved record keeping of flasks coming to Boulder and by adding additional flasks to the network

TABLE 5.2. Instrumentation for HATS Flask Analysis

Instrument	Type	Gases	Frequency of Network Data
OTTO	GC-ECD, 3-channel, isothermal	N <sub>2</sub> O, CFCs (3), CCs (2), SF <sub>6</sub>	Weekly
LEAPS	GC-ECD, 1-channel, temperature programmed	halons (2), CH <sub>3</sub> Cl, CH <sub>3</sub> Br, CHCl <sub>3</sub>	Semi-monthly to monthly
HCFC-MS	GC-MS, 1-channel, temperature programmed	HCFCs (3), HFCs (1), CFCs (3), halons (1), CCs (6), BrCs (3)	Semi monthly
HFC-MS	GC-MS, 1-channel, temperature programmed	HCFCs (5), HFCs (2), CFCs (2), halons (2), CCs (6), BrCs (3), ClBrCs (3)	Semi-monthly to monthly

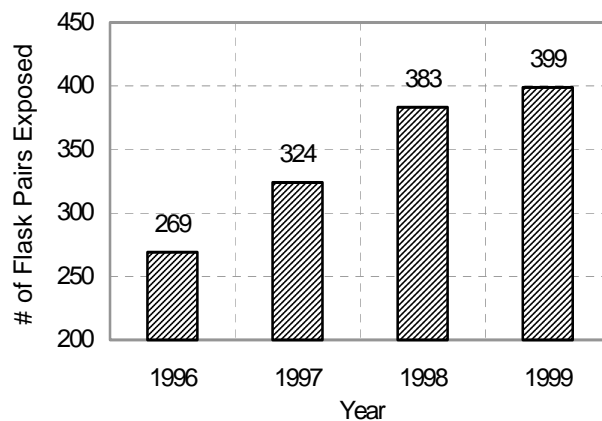


Fig. 5.2. Number of flask pairs filled and returned to Boulder each year from the HATS station network.

in 1996-1997 to accommodate additional sites. Sampling success was improved substantially from that for 1996 at nearly all of our sites (Table 5.3). This was mainly the result of repairing small leaks and replacing valves where necessary on flasks following analysis in Boulder. These repairs greatly improved the agreement in flask pressure within simultaneously sampled pairs (Figure 5.3).

While most of the time the GC-ECD instruments were utilized to process flasks from the station network, 10-20% of the time was devoted to calibrating gas standards, and about 5% of the instruments' operation was dedicated to other quality-control experiments. Special projects involving flask measurements over the past few years included primarily firn air analyses and analysis of flask samples from research cruises.

### Results

Results for most of the major ozone-depleting gases are also discussed in the subsection "Overall Trends in Ozone-Depleting

TABLE 5.3. Flask Sampling Success at CMDL Observatories and Cooperative Sampling Sites

Sampling Station	1996	1997	1998	1999
Barrow, Alaska	69%	94%	88%	87%
Mauna Loa, Hawaii	69%	83%	90%	96%
American Samoa	54%	67%	73%	87%
South Pole	77%	69%	77%	88%
Alert, Canada	52%	46%	67%	67%
Niwot Ridge, Colorado	63%	92%	87%	77%
Cape Grim, Australia	60%	69%	85%	85%
WLEF tower, Wisconsin	12%	35%	69%	92%
Harvard Forest, Massachusetts	46%	62%	69%	69%
Kumukahi, Hawaii	50%	54%	67%	69%
Palmer, Antarctica	--	8%	65%	81%
Mace Head, Ireland	--	--	8%	15%
WITN tower, North Carolina	65%	62%	62%	38%

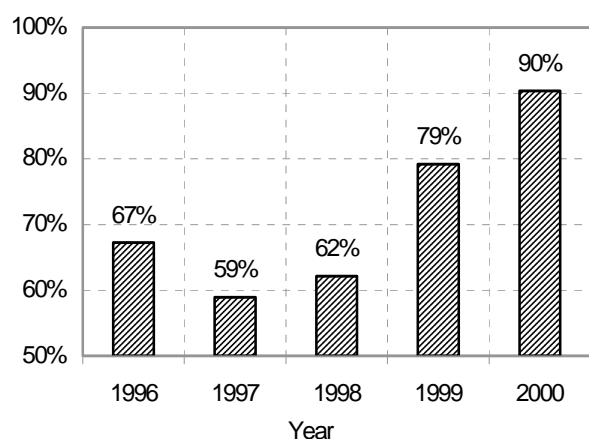


Fig. 5.3. The percentage of flask pairs agreeing within 1 psi in total pressure upon arrival in Boulder.

Gases.” Many of these gases are analyzed by both GC-ECD and gas chromatography with mass selective (GC-MS) detection. CFC-12 continues to increase in the atmosphere while mixing ratios of CFC-11 continue to drop slowly at about  $1\% \text{ yr}^{-1}$  (Figure 5.4). CFC-113 and  $\text{CCl}_4$  are also decreasing at about  $1\% \text{ yr}^{-1}$ , and  $\text{CH}_3\text{CCl}_3$ , which has driven the overall decline in atmospheric chlorine, continues to drop about  $18\% \text{ yr}^{-1}$  (subsection on "Overall Trends"). Gases analyzed only by GC-ECD are  $\text{N}_2\text{O}$ ,  $\text{SF}_6$ , and  $\text{CBrF}_3$  (H-1301). Nitrous oxide has been monitored by the in situ instruments for the past 12 years. The record from flask samples goes back to the mid-1970s (Figure 5.5). The global growth rate of  $\text{N}_2\text{O}$  from 1978 to 2000 was  $0.74 \pm 0.01$  (95% confidence level, C.L.)  $\text{nmol mol}^{-1} \text{ yr}^{-1}$  (parts-per-billion, or ppb,  $\text{yr}^{-1}$ ), which amounts to a mean of about  $0.25\% \text{ yr}^{-1}$ . From 1996 to 2000, the global growth rate was  $0.85 \pm 0.06$  ppb  $\text{yr}^{-1}$ , which differs significantly at the 95% C.L. from the 20-year average. This suggests that  $\text{N}_2\text{O}$  concentrations were increasing more rapidly in the atmosphere near the end of the 20th century. Whether this was a temporary or long-term feature will be borne out in future data.

Sulfur hexafluoride still appears to be increasing linearly in the atmosphere with a growth rate of about  $0.24 \pm 0.01$  (95% C.L.)  $\text{pmol mol}^{-1}$  (parts per-trillion, or ppt,  $\text{yr}^{-1}$ ) since 1996 (Figure 5.6). CMDL measurements of polar firn air confirmed

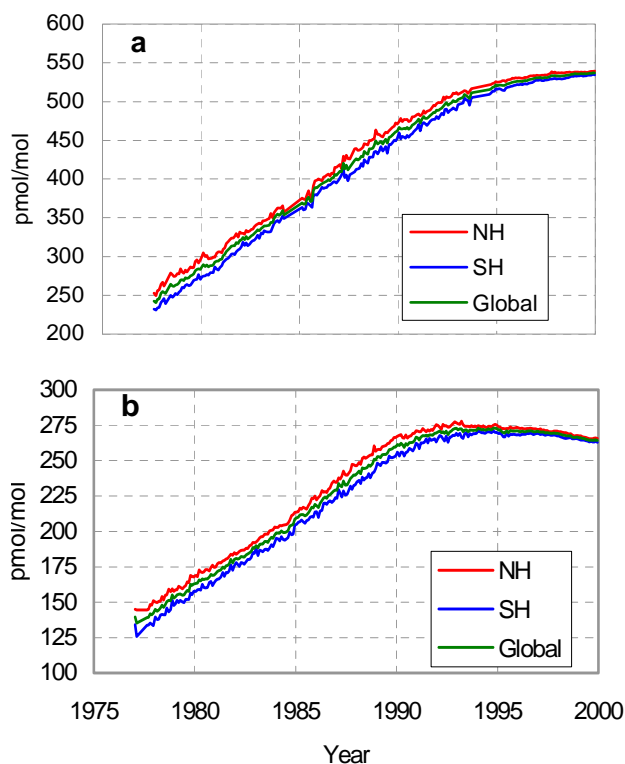


Fig. 5.4. CFC-12 (a) and CFC-11 (b) from flask samples. Data are monthly averages.

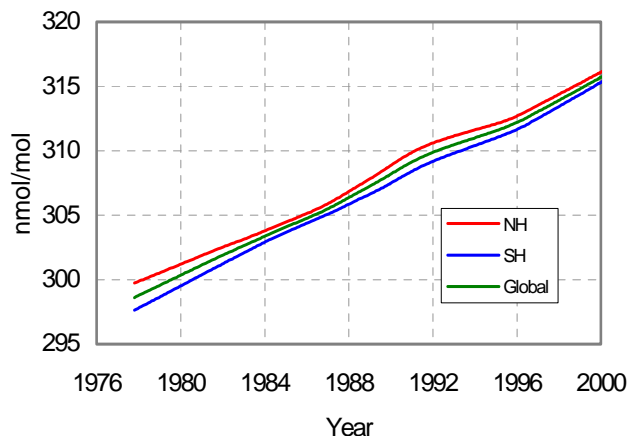


Fig. 5.5. Atmospheric history of  $\text{N}_2\text{O}$  derived from CMDL flask measurements. Data are smoothed with a lowest fit.

the early history of this gas as derived from emission inventories [Butler *et al.*, 1999], indicating natural sources are absent or insignificant in the global  $\text{SF}_6$  budget.

CMDL measurements show that halons are still increasing slowly in the atmosphere in spite of a ban on their production as of 1994. The global growth rate of H-1301 in 1998-1999, at  $0.09 \pm 0.04$  ppt  $\text{yr}^{-1}$ , does not differ significantly at the 95% C.L. from the 1995 to 2000 average of  $0.06 \pm 0.01$  ppt  $\text{yr}^{-1}$ , nor from the 1995-1996 average of  $0.044 \pm 0.011$  ppt  $\text{yr}^{-1}$  reported in Butler *et al.* [1998a] (Figure 5.7). However, at the 90% confidence level,

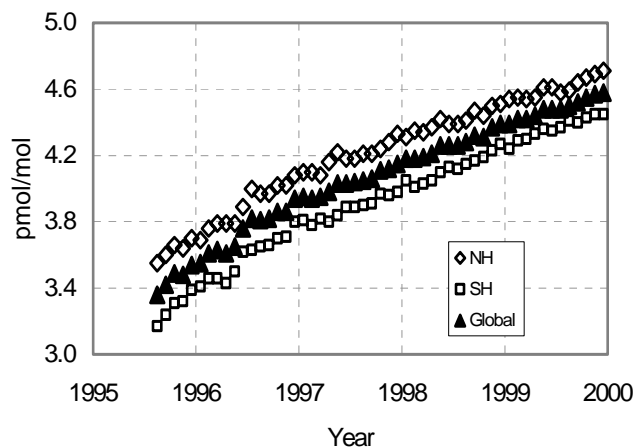


Fig. 5.6. Recent history of atmospheric SF<sub>6</sub> from CMDL flask measurements. Data are monthly averages.

a 30-40% increase in H-1301 emissions is suggested during the past few years. H-1211 is still increasing at a rate of 0.1-0.2 ppt yr<sup>-1</sup>, which means that there has been no curtailment of its global emissions since the 1994 ban on its production in developed countries.

#### Chlorofluorocarbon Alternatives Measurement Program

Measurements of chlorofluorocarbon alternatives from flask air samples continued during 1998-1999. On average nearly three flask pairs per month were sampled and analyzed from nine remote sampling stations across the globe. Slightly fewer than two pairs per month were sampled from the WLEF tower in Wisconsin (LEF), ITN, and Harvard Forest, Massachusetts (HFM). The main change during this period involved building a new inlet isolation box for the instrument and moving the instrument and laboratory to the new building site in Boulder, Colorado, in early 1999. These improvements allow for more precise and reproducible measurements of gases that are present at high levels in laboratory air such as HFC-134a, HCFC-142b, and CH<sub>2</sub>Cl<sub>2</sub>. Moving the instruments does not seem to have caused any unexpected shifts in the results from the GC-MS flask program.

Mixing ratios of HCFCs measured in the flask program (HCFC-22, HCFC-141b, HCFC-142b) continued to increase in the troposphere (Figure 5.8, Table 5.4). Concentrations reported for these gases in past publications have been referenced to a constant set of gravimetric standards (section 5.1.4) [Montzka *et al.*, 1993, 1994, 1996b, 1999a, 2000]. Fairly linear rates of increase were measured for these three HCFCs since the beginning of 1996. In mid-1999 these HCFCs accounted for about 6%, or 170 ppt, of the atmospheric burden of chlorine contained in long-lived anthropogenic halocarbons. When combined with an estimate of atmospheric lifetimes, measurements of anthropogenic halocarbons can be used to infer emission rates. Such an analysis suggests that since 1998, total molar emissions of HCFCs surpassed the aggregate moles emitted of other ozone-depleting substances (CFCs + CCl<sub>4</sub> + halons + CH<sub>3</sub>CCl<sub>3</sub>).

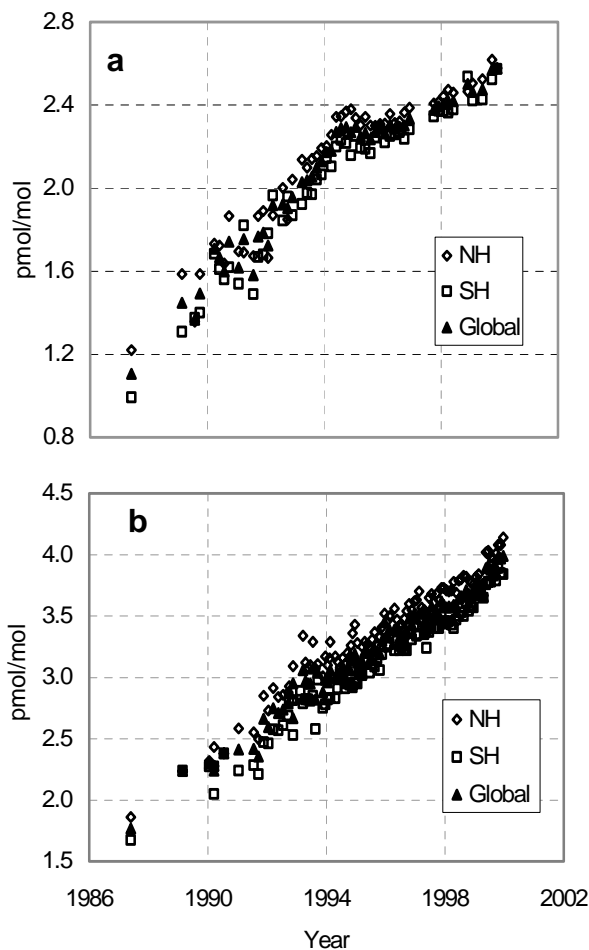


Fig. 5.7. Halons H-1301 (a) and H-1211 (b) from CMDL flask measurements. Data are monthly averages.

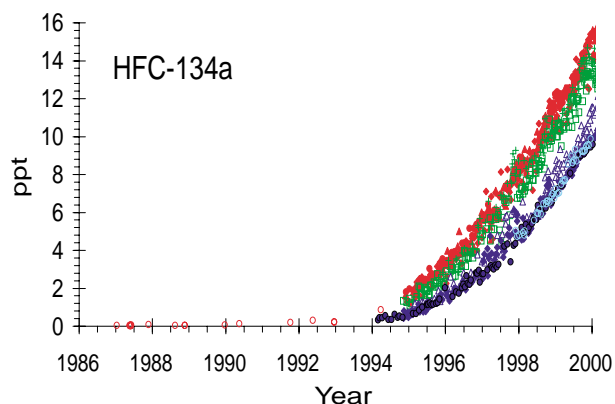
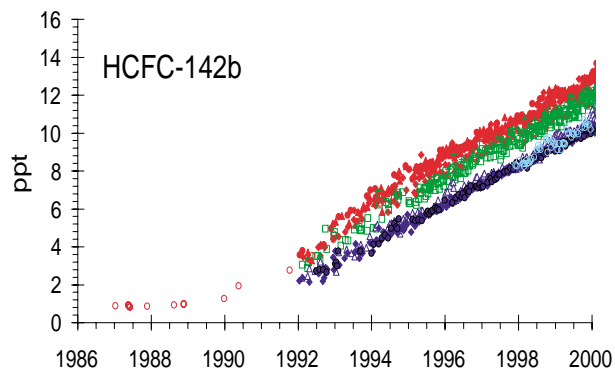
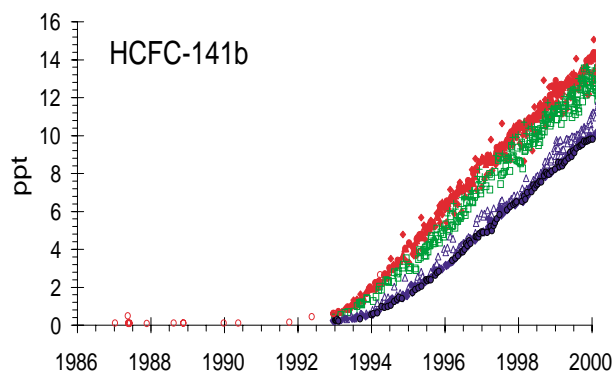
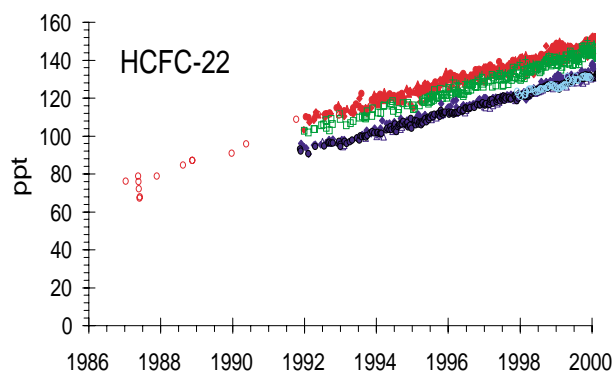


Fig. 5.8. Atmospheric dry mole fractions (ppt) of selected HCFCs and HFC-134a measured by GC-MS in the CMDL flask program. Each point represents the mean of two flasks from one of eight or nine stations: ALT, BRW, NWR, red; KUM and MLO, green; SMO, CGO, PSA, and SPO, blue. Also plotted are results from analysis of archived air samples (open red circles) filled at NWR or on cruises in both hemispheres.

TABLE 5.4. Global Burden and Rate of Change for HCFCs and HFC-134a

Compound	Mean 1998 Mixing Ratio (ppt)	Mean 1999 Mixing Ratio (ppt)	Growth Rate (ppt yr <sup>-1</sup> )
HCFC-22	131.4	136.9	5.1 (1992-1999)
HCFC-141b	9.1	10.9	1.8 (1996-1999)
HCFC-142b	9.7	10.8	1.0 (1996-1999)
HCFC-134a	7.6	10.6	3.1 (1998-1999)

Quantities estimated from latitudinally-weighted measurements at seven remote stations: SPO, CGO, SMO, MLO, NWR, BRW, and ALT.

Continued increases were observed for HFC-134a during 1998-1999 (Figure 5.8, Table 5.4). The observed concentrations are in reasonable agreement with the amounts expected based upon the available industrial production and emission data and an atmospheric lifetime of ~15 years [Montzka *et al.*, 2000].

Continued declines in the concentration of CH<sub>3</sub>CCl<sub>3</sub> were observed from flask measurements during 1998-1999 (Figure 5.9). These data are reasonably consistent with the results from the in situ Radiatively Important Trace Species (RITS) GC-ECD instruments. Accurately describing the atmospheric decline of CH<sub>3</sub>CCl<sub>3</sub> can provide unique information regarding the atmospheric abundance and distribution of the hydroxyl radical, an important atmospheric oxidant [Ravishankara and Albritton, 1995; Montzka *et al.*, 2000; Spivakovsky *et al.*, 2000].

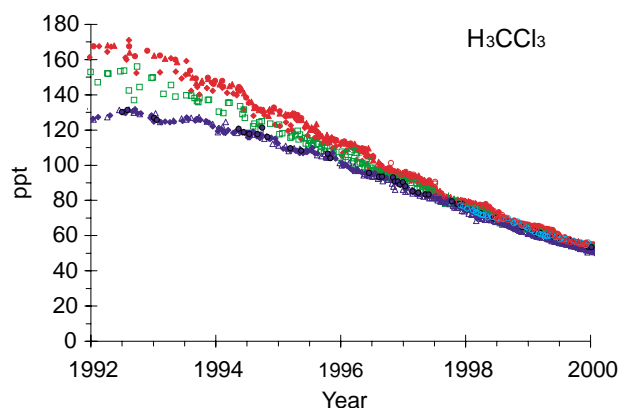


Fig. 5.9. Atmospheric dry mole fractions (ppt) of CH<sub>3</sub>CCl<sub>3</sub> measured by GC-MS in the CMDL flask program. Each point represents the mean of two simultaneously filled flasks from one of eight or nine stations (symbols the same as in Figure 5.8).

### Flask Measurements of $\text{CH}_3\text{CCl}_3$ and Their Implications for Atmospheric Hydroxyl

The analysis of  $\text{CH}_3\text{CCl}_3$  in flask air by GC-MS provides some unique advantages over other techniques, such as linear response (Figure 5.10), good chromatographic resolution (Figure 5.11), and the ability to monitor more than one ion. During 1998-1999 repeat injection precision for GC-MS analysis of flasks was typically 0.4% (the median standard deviation from repeat injections on 1028 flasks during that period); for 95% of all analyses the repeat injection precision was <1.3%. A disadvantage of flask sampling for measurements of  $\text{CH}_3\text{CCl}_3$  is that degradation of  $\text{CH}_3\text{CCl}_3$  during the interim between sampling and analysis can be observed in flasks filled with extremely dry air. This problem is apparent in results from the South Pole, Antarctica, CMDL Observatory (SPO), where poor flask pair agreement and anomalously low mixing ratios are observed from some flask samples. Because the rate of this loss is flask-dependent, its occurrence is readily identifiable by poor agreement between simultaneously filled flasks. Samples in which degradation is suspected are not considered in further data analysis.

In recent years many unique features have appeared in the atmospheric data for  $\text{CH}_3\text{CCl}_3$  that confirm a dramatic decline in emissions. Not only has the mixing ratio decreased exponentially recently (Figure 5.9), but the difference observed between the hemispheres (Figure 5.12) has declined substantially as the emissions, which emanated predominantly from the northern hemisphere, have declined. Furthermore, the gradient observed within each hemisphere is now very similar, suggesting that the atmospheric distribution of  $\text{CH}_3\text{CCl}_3$  in 1998-1999 was controlled by the distribution of loss processes rather than the distribution of sources during this period (Figure 5.13).

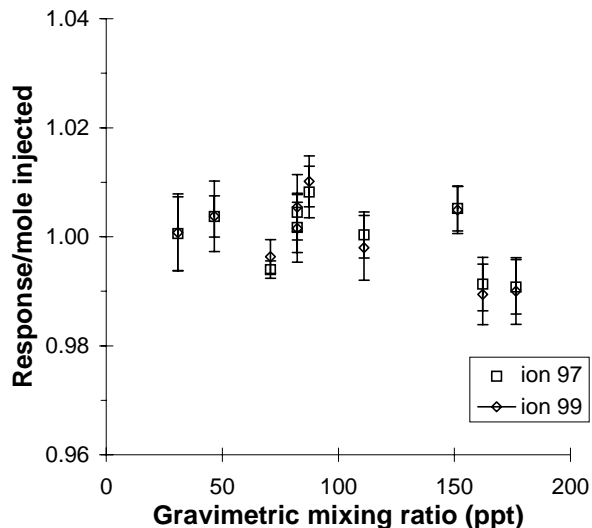


Fig. 5.10. Consistency of gravimetrically prepared standards containing  $\text{CH}_3\text{CCl}_3$  as analyzed on the GC-MS during 1997-1999. For well-made standards analyzed on an instrument with a linear response, the response factor should be independent of mixing ratio. Response factors (measured response divided by the gravimetrically determined mixing ratio) for two different ions are plotted for individual gravimetric standards and are normalized to the mean response factor for all standards. The error bars are one standard deviation of the measured response factor for each tank (from seven to nine measurements of each standard during 1997-1999). The results for one standard at 195.7 ppt (ALM-64596) do not appear in this figure because its response factor was much different from the other standards (0.90 in late 1999), and was changing over time, presumably from slow degradation of  $\text{CH}_3\text{CCl}_3$  in that tank.

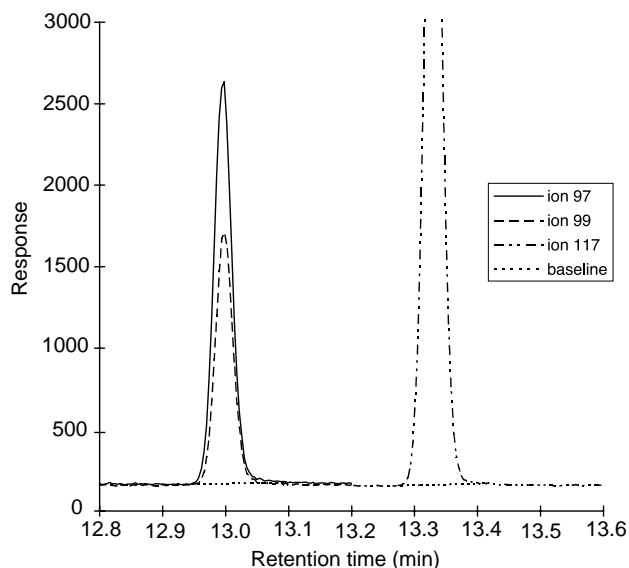


Fig. 5.11. A portion of a chromatogram from the GC-MS flask instrument showing the signals observed for  $\text{CH}_3\text{CCl}_3$  (ions 97 and 99) and  $\text{CCl}_4$  (ion 117; peak maximum not shown) in ambient air collected at Samoa. Concentrations were determined to be 47 ppt  $\text{CH}_3\text{CCl}_3$  and 100 ppt  $\text{CCl}_4$ . The peak height relative to the standard deviation of the baseline was 800 and 600 for  $\text{CH}_3\text{CCl}_3$  at  $m/z = 97$  and  $m/z = 99$  and ~2000 for  $\text{CCl}_4$  at  $m/z = 117$  in this air sample. Also shown are baselines drawn from our custom automatic integration routine (short-dashed line).

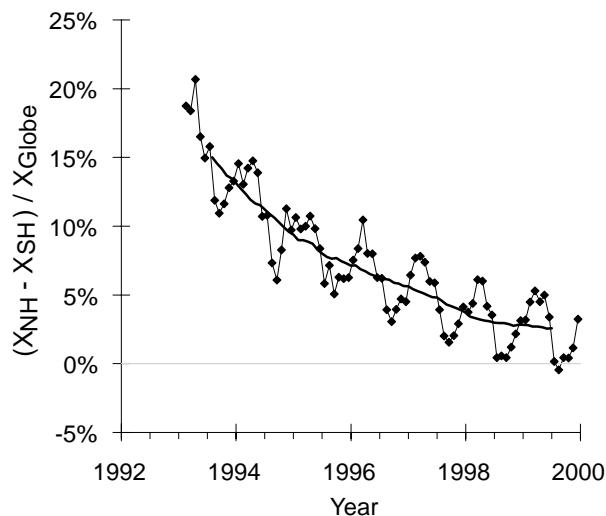


Fig. 5.12. The hemispheric mixing ratio difference for  $\text{CH}_3\text{CCl}_3$  in recent years. The difference was inferred from weighted, monthly mean mixing ratios at three to six sampling stations in each hemisphere. Monthly differences (solid diamonds) are connected with a thin line; the heavy line represents a 12-month running mean difference. The results suggest that northern hemisphere emissions have declined substantially in recent years [Montzka *et al.*, 2000].

The measured rate of decay during 1998-1999 at nine remote stations and LEF allows us to estimate an upper limit to the global lifetime of  $\text{CH}_3\text{CCl}_3$  of 5.5 ( $\pm 0.1$ ) years [Montzka *et al.*, 2000]. Because the decay observed for  $\text{CH}_3\text{CCl}_3$  arises

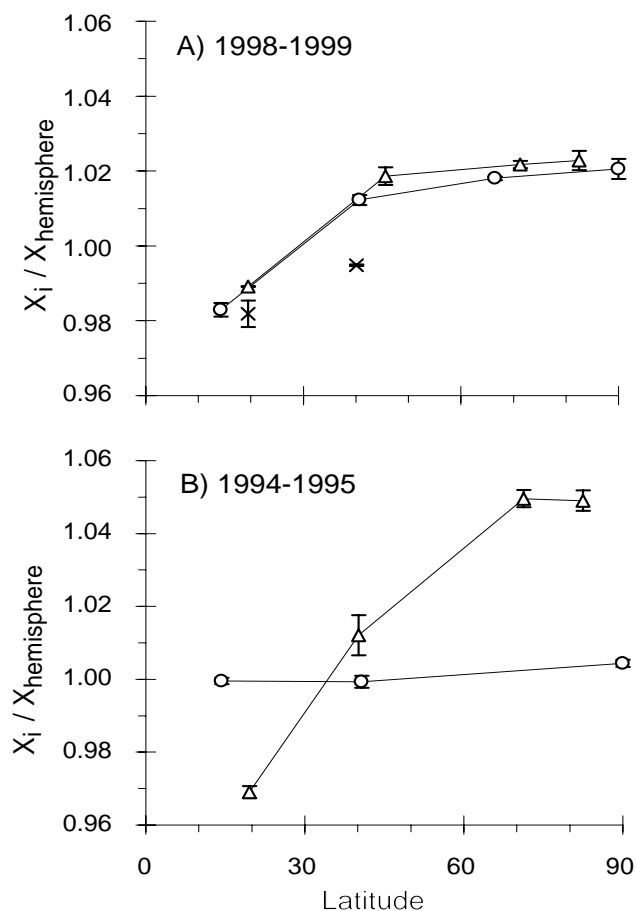


Fig. 5.13. Measured intrahemispheric gradients in annual mean mixing ratios of  $\text{CH}_3\text{CCl}_3$  [Montzka *et al.*, 2000]. (A) Annual means for individual sites ( $X_i$ ) are shown normalized to respective hemispheric annual means for the 2 years 1998-1999. Northern hemispheric data from low altitude sites (<1000m) (triangles) are connected with lines to allow for appropriate comparisons to similar sites in the southern hemisphere (circles). High altitude sites (MLO and NWR) are shown (crosses) but are not connected with lines because there is a clear difference in the intrahemispheric gradient between low and high altitude sites during this period. (B) Same as (A) but for the 2 years 1994-1995 when northern hemispheric emissions were substantial. Because of a lack of measurements from all sites in this earlier period, data from both low and high altitude locations are shown with similar symbols in this panel. Error bars in both panels represent one standard deviation of the annual mean ratios estimated for the 2 years.

predominantly from OH oxidation (Table 5.5), this lifetime limit allows estimation of upper limits to the lifetime of other chemically reduced gases that degrade predominantly by OH oxidation in the atmosphere (Table 5.5). This lifetime limit is completely independent of calibration standard accuracy and emission estimates, but depends upon a consistent calibration reference over time. An uncertainty of  $\pm 0.1$  year is estimated on the measured e-fold time from potential drift of  $0.3\% \text{ yr}^{-1}$  based on comparisons between a reference air sample and ten gravimetric standards (Figure 5.14).

When the magnitude of emissions of  $\text{CH}_3\text{CCl}_3$  during 1998-1999 are considered (A. McCulloch, personal communication, 2000), the rate of decay measured implies that the true global lifetime of  $\text{CH}_3\text{CCl}_3$  is  $5.2 (+0.2, -0.3)$  years [Montzka *et al.*, 2000]. Unlike previous estimates of global lifetime, this estimate is insensitive to calibration standard accuracy and includes a factor of two uncertainty in the magnitude of emissions.

The recent measurements also provide a unique opportunity to discern hemispheric loss rates for  $\text{CH}_3\text{CCl}_3$ . The rate of change observed in the southern hemisphere is determined by emissions within the southern hemisphere, chemical loss in the southern hemisphere, and the  $\text{CH}_3\text{CCl}_3$  delivered from the northern hemisphere through net hemispheric exchange. Because emissions in the southern hemisphere have always been <10% of the total emissions, this term is insignificant compared to the others. From the observed difference in the hemispheric concentration of  $\text{CH}_3\text{CCl}_3$ , the net exchange of this gas between the hemispheres can be estimated. By also including the observed decline of  $\text{CH}_3\text{CCl}_3$  in the southern hemisphere, the lifetime of  $\text{CH}_3\text{CCl}_3$  in the southern hemisphere is estimated to be  $4.9 (+0.2, -0.3)$  years [Montzka *et al.*, 2000]. This estimate is also insensitive to calibration standard accuracy and emission estimate figures.

These results suggest that the mean hemispheric loss frequency for  $\text{CH}_3\text{CCl}_3$  and the mean hemispheric concentration of OH are slightly larger (by  $15 \pm 10\%$ ) in the southern hemisphere than in the northern hemisphere despite the higher levels of precursors for OH such as  $\text{NO}_x$  and  $\text{O}_3$  found in the northern hemisphere. This conclusion hinges on emission figures for 1998-1999 being reasonably accurate; higher mean concentrations of OH in the northern hemisphere could be reconciled with the observations only if emissions were substantially underestimated in 1998-1999 (by about a factor of 3 or more). Higher mean concentrations of OH in the southern hemisphere may result because certain OH sinks, such as CO, are greater in the northern hemisphere, and because the southern hemisphere contains more of the OH-rich tropics compared to the northern hemisphere (given that the intertropical convergence zone (ITCZ) is on average a few degrees north of the equator).

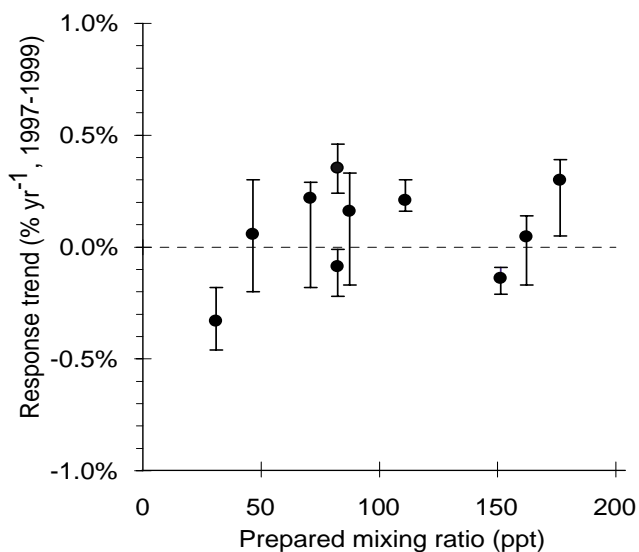


Fig. 5.14. The stability of calibration for  $\text{CH}_3\text{CCl}_3$  during 1997-1999. From multiple (7-9) comparisons of 10 gravimetric standards to a single high-pressure sample of ambient air during 1997-1999, trends in the response ratio (ratio of the response for  $\text{CH}_3\text{CCl}_3$  in the standard to that observed in the high-pressure real-air sample) were calculated and are expressed as linear regression slopes. Error bars represent the range in linear regression slopes calculated when any single response ratio determination was removed from the slope calculation. Drift in the response ratio for ALM-64596 was so large that it does not appear on this figure (the standard at 195.7 ppt drifted at  $-3.2 (\pm 0.1)\% \text{ yr}^{-1}$ ).



TABLE 5.5. Lifetimes of Chemically Reduced Gases (in Years) for 1998-1999

	Partial lifetime with respect to:			Total Lifetime‡ Upper Limit
	OH Loss*	Stratospheric Loss	Total Lifetime†	
CH <sub>4</sub>	10.5 (+0.5, -0.6)	110	9.0 (+0.4, -0.6)	9.5 (±0.2)
HCFC-22	13.6 (+ 0.6, -0.8)	306	13.0 (+0.6, -0.8)	13.8 (±0.3)
HCFC-141b	11.5 (+0.5, -0.7)	81	10.1 (+0.4, -0.6)	10.6 (±0.2)
HCFC-142b	21.8 (+1.0, -1.3)	372	20.6 (+0.9, -1.3)	21.8 (±0.4)
HFC-134a	15.7 (+0.7, -1.0)	377	15.1 (+0.7, -0.9)	16.0 (±0.3)
CH <sub>3</sub> CCl <sub>3</sub>	6.3 (+0.3, -0.4)	45	5.2 (+0.2, -0.3)	5.5 (±0.1)

\*Partial lifetimes with respect to oxidation by OH are derived from the estimate of the total lifetime for CH<sub>3</sub>CCl<sub>3</sub> of 5.2 (+0.2, -0.3) years, a partial lifetime with respect to oceanic loss of 94 years, and with respect to stratospheric loss of 45 years, and from rate constant ratios evaluated at 272 K [Spivakovsky *et al.*, 2000; Prather and Spivakovsky, 1990]. Quoted uncertainties in these lifetime limits do not include uncertainties in rate constants.

†Total lifetimes were calculated as the inverse of summed rate constants. The lifetime quoted for CH<sub>4</sub> also includes a partial lifetime with respect to soil loss of about 145 years.

‡Upper limits to trace gas lifetimes were derived in the same way as the best estimates, except that the upper limit for the total atmospheric lifetime of CH<sub>3</sub>CCl<sub>3</sub> of 5.5 ± 0.1 years is considered. Note that these limits are entirely independent of calibration accuracy and emissions figures.

### Overall Trends in Ozone-Depleting Gases

Emissions of most ozone-depleting gases decreased during the 1990s. The atmospheric response to reduced emissions was most pronounced for the industrial gas CH<sub>3</sub>CCl<sub>3</sub> (Figure 5.9). The global concentration of this gas decreased at an exponential rate of ~18% yr<sup>-1</sup> during 1998-1999. Such a rapid decline is observed for this gas because it has a fairly short atmospheric lifetime, and its past use as a solvent caused changes in emissions to be closely linked to changes in production. This link is not as strong for CFCs and other gases because their emissions can be sustained from devices and foams for years after production has ceased. For example, although similar declines in emissions are inferred for CFC-11 and CFC-12 in the 1990s compared to the 1980s on a relative basis, the atmospheric concentration of CFC-11 is now decreasing but CFC-12 continues to increase. This difference arises because the lifetime of CFC-12 is approximately 100 years or about twice that of CFC-11.

While the tropospheric concentration of some ozone-depleting gases decreased and some increased during 1998-1999, the overall ozone-depleting capacity of the atmosphere has decreased since 1993-1994. Estimates of Effective Equivalent Chlorine (EECl) and Equivalent Chlorine (ECl) [Daniel *et al.*, 1995; Montzka *et al.*, 1996a] from tropospheric measurements provide a very rough estimate of ozone-depleting halogen concentrations in the future stratosphere (once a 3-5 year time lag associated with mixing processes is considered). The EECl and ECl burdens of the troposphere have decreased since 1993-1994 primarily because of the rapid decline in the trace gas methyl chloroform. By the end of 1999, tropospheric EECl was ~5% below its peak and was decreasing at ~1% yr<sup>-1</sup> (Figure 5.15).

As the influence of methyl chloroform on EECl and ECl diminishes, continued declines in EECl and ECl will be realized only if emissions of CFCs and related ozone-depleting gases become smaller than estimated for 1997 [Montzka *et al.*, 1999a]. An update of the Montzka *et al.* [1999a] analysis suggests that overall emissions of ozone-depleting gases have decreased only slightly since 1997 (Figure 5.15).

Emissions of halon-1211 have not decreased significantly during the 1990s despite stringent restrictions on production in developed countries since 1994 [Butler *et al.*, 1998a; Fraser *et*

*al.*, 1999; Montzka *et al.*, 1999a]. The lack of a decline in emissions of this gas likely stems from the large reservoir of this chemical that currently exists in portable fire extinguishers in developed countries. Furthermore, production of halon-1211 in developing nations continued to increase in the 1990s each year through 1998 (the latest year for which production data are available). Production in developing countries is slated for reduction during 2002-2010. Continued emissions from the large amount of halon in existing fire extinguishers, and from new production, have resulted in a steady increase in the atmospheric concentration of halon-1211 through the end of 1999 (Figure 5.7b). This increase continues to retard the decline in EECl and ECl more than other gases. Unless further efforts are made to restrict continued production and emission of this halon, its concentration will likely increase for a number of years into the future because of the substantial reservoir of halon produced but not yet released to the atmosphere.

Emissions of the CFC-substitutes, known as the HCFCs and HFCs, also increased through the 1990s as use of CFCs and related ozone-depleting substances declined. These gases contribute less to reactive halogen in the stratosphere because a large percentage of these gases is removed from the atmosphere in the troposphere, and certain HCFCs (HCFC-22 and HCFC-142b) degrade slowly in the stratosphere.

### Measurements of Shorter-Lived Halogenated Gases

Measurements from flasks of shorter-lived gases continued during 1998-1999 (Figure 5.16). Both CH<sub>3</sub>Cl and CH<sub>3</sub>Br contribute significantly to the halogen burden of the stratosphere. Significant interannual variability was measured for both gases during 1995-1999 [Montzka *et al.*, 1999b]. For CH<sub>2</sub>Cl<sub>2</sub> and C<sub>2</sub>Cl<sub>4</sub> a trend towards lower mixing ratios is evident, particularly in the northern hemisphere. These decreases may result from efforts to reduce emissions of toxic organic compounds in some nations. Although such gases (CH<sub>2</sub>Cl<sub>2</sub>, C<sub>2</sub>Cl<sub>4</sub>, CHCl<sub>3</sub>) contribute some to the halogen burden of the stratosphere, global measurements of them also provide an improved understanding of atmospheric processes such as trace-gas oxidation by OH and Cl atoms and atmospheric transport rates.

CMDL results for CH<sub>2</sub>Cl<sub>2</sub> and C<sub>2</sub>Cl<sub>4</sub> from GC-MS flask measurements were compared to mixing ratios calculated in a three-dimensional model [Spivakovsky *et al.*, 2000]. The

comparison revealed that industrial emissions of  $\text{CH}_2\text{Cl}_2$  are sufficient to account for the amount observed in the atmosphere; the addition of a relatively small oceanic source would cause the model to over-predict the observations in both hemispheres. The data also suggest that the actual loss rate of  $\text{C}_2\text{Cl}_4$  is somewhat greater than can be accounted for by reaction with OH. This additional loss suggests either the bimolecular rate constant for the reaction  $\text{OH} + \text{C}_2\text{Cl}_4$  is underestimated by  $\sim 30\%$ , or additional atmospheric loss arises from significant Cl atom oxidation. The results for  $\text{CH}_2\text{Cl}_2$  also provide unique constraints to the distribution of OH on hemispheric scales provided that air transport rates are well known. Concentrations of shorter-lived gases such as  $\text{CH}_2\text{Cl}_2$  and  $\text{C}_2\text{Cl}_4$  are more sensitive to rates of interhemispheric mixing than longer-lived gases such as CFCs and  $^{85}\text{Kr}$  [Spivakovsky *et al.*, 2000]. Further improvement in our understanding of OH and Cl concentrations on smaller spatial scales from measurements of these gases will require a better understanding of air exchange rates. Measurements of long-lived gases that are increasing rapidly (such as HCFCs and HFCs) may provide this additional constraint.

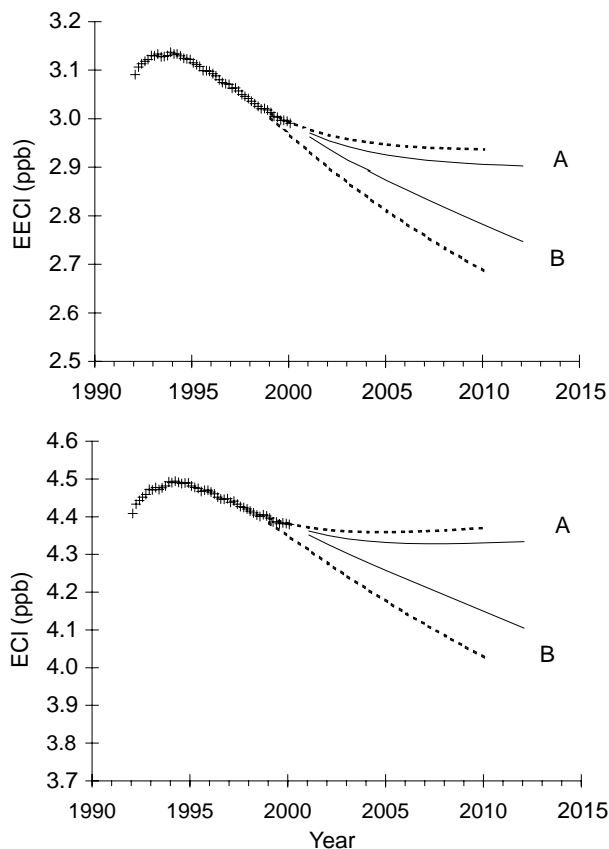


Fig. 5.15. The measured and potential future burden of ozone-depleting halogen in the lower atmosphere. Ozone-depleting halogen is estimated from tropospheric measurements of halocarbons by appropriate weighting factors to calculate Effective Equivalent Chlorine (EECl) for midlatitudes and Equivalent Chlorine (ECl) as an upper limit for polar latitudes [Daniel *et al.*, 1995; Montzka *et al.*, 1996a, 1999a]. Projections into the future are based on two scenarios: (A) emissions of all long-lived halogenated gases (CFCs, HCFCs,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CCl}_4$ , and halons) remain constant at 1999 levels, (B) scenario A with the exceptions that emissions of CFCs,  $\text{CH}_3\text{CCl}_3$ , and  $\text{CCl}_4$  continue decreasing at  $\sim 10\% \text{ yr}^{-1}$ . Future scenarios indicated with dashed lines were formulated with ambient air measurements through 1997 [Montzka *et al.*, 1999a]; scenarios indicated with solid lines incorporated CMDL halocarbon measurements through the end of 1999.

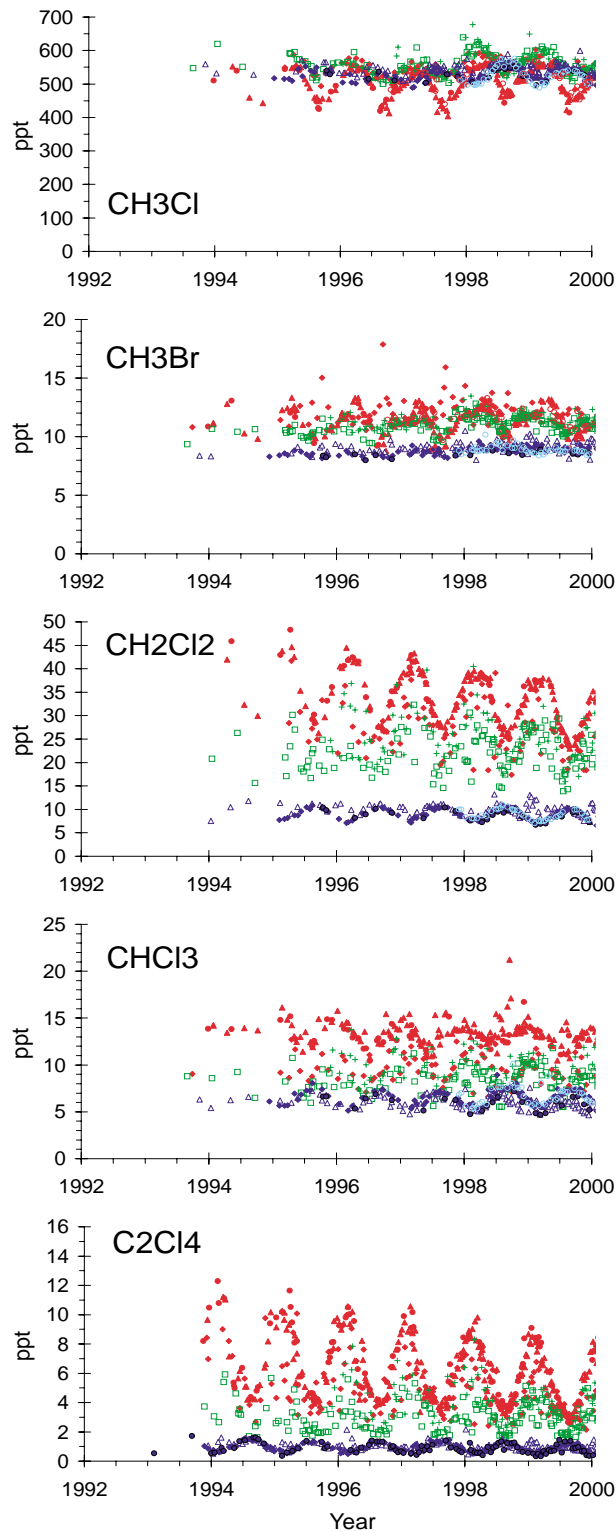


Fig. 5.16. Atmospheric dry-air mole fractions (ppt) determined for selected chlorinated trace gases and  $\text{CH}_3\text{Br}$  by GC-MS in the CMDL flask program. Each point represents the mean of two simultaneously filled flasks from one of eight or nine stations (symbols the same as in Figure 5.8). Results shown for all compounds except  $\text{C}_2\text{Cl}_4$  are from 2.4-L flasks only.