

## 5. Halocarbons and Other Atmospheric Trace Species

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### 5.1. CONTINUING PROGRAMS

#### 5.1.1. INTRODUCTION

The mission of the Halocarbons and other Atmospheric Trace Species (HATS) group, formerly known as the Nitrous Oxide and Halocarbons (NOAH) group, is to study trace atmospheric species that cause chemical and radiative change in the atmosphere. The goal of the HATS group is to measure and interpret the distributions and trends of many halocarbons, nitrous oxide ( $N_2O$ ), sulfur hexafluoride ( $SF_6$ ), fluorocarbons, perfluorocarbons (PFCs), organic nitrates (e.g., peroxyacetyl nitrate (PAN)), organic sulfur gases (e.g., OCS), and hydrocarbons (HCs) in the troposphere, stratosphere, and oceans with the best analytical tools available. The halocarbons include the chlorofluorocarbons (CFCs), chlorocarbons (CCs like  $CCl_4$ ,  $CH_3CCl_3$ ,  $CHCl_3$ ,  $CH_2Cl_2$ ,  $C_2Cl_4$ , etc.), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), methyl halides ( $CH_3Br$ ,  $CH_3Cl$ ,  $CH_3I$ ), bromocarbons ( $CH_2Br_2$ ,  $CHBr_3$ ), and halons.

These trace gases affect the quality of the Earth's atmosphere. All of these trace gases, except the HCs and organic nitrates, produce direct climate forcing on the Earth's atmosphere. Many of these chemicals, including the halocarbons and  $N_2O$ , are involved in stratospheric ozone depletion. The production of some of these compounds is currently restricted for the developed countries by the Montreal Protocol and its amendments [UNEP, 1987]. The hydrocarbons, some sulfur gases, organic nitrates, and CCs play a major role in tropospheric air quality. Recent changes to the U.S. Clean Air Act now restrict the emissions of some CCs and HCs by certain industries and manufacturing processes.

Activities conducted by HATS in 1998 and 1999 included: (1) weekly flask sampling and analysis of air from remote and semi-remote sites, (2) operation of instrumentation for hourly, in situ measurements of trace gases at the four CMDL baseline observatories and four non-baseline sites, (3) preparation and maintenance of trace gas standards, (4) participation on airborne campaigns using in situ gas chromatographs (GCs) on aircraft and balloon payloads, and (5) investigation of oceanic processes influencing trace gas composition of the atmosphere.

Continuing programs within the group are based upon in situ and flask measurements of the atmosphere from the four CMDL baseline observatories and ten cooperative stations (Figure 5.1). Table 5.1 lists the geographic locations and other useful information on all of the sites. There are currently 13 flask sites and 10 in situ sampling sites in the HATS Atmospheric Sampling Network. Flask samples and in situ trace gas measurements obtained in cooperation with the CMDL Carbon Cycle Greenhouse Gases (CCGG) group were ceased at the WITN, Grifton, North Carolina (ITN) tower on June 12, 1999, because the laboratory layout was changed to accommodate only digital television equipment. A high tower site in Texas is being studied as its replacement. A new in situ GC was prepared for installation and operation sometime in early 2001 at Ushuaia,

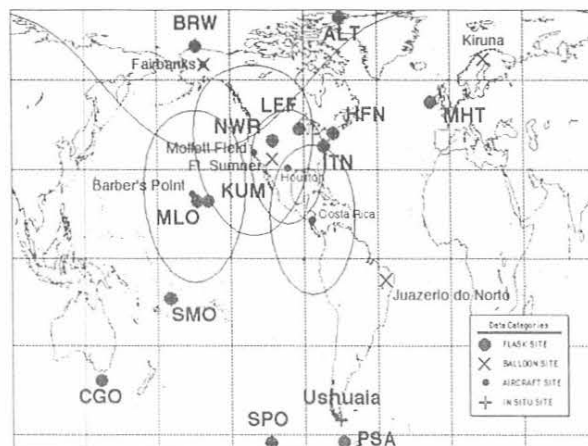


Fig. 5.1. Geographic locations of old and new stations in the HATS flask (gray circles) and in situ (crosses) networks. The sites for balloon launches are noted by "X"s. The location (small black filled circles) and the range of the aircraft operations (arcs and ovals) also are indicated.

Argentina, with funds from the World Meteorological Organization (WMO).

One of the highlights of this report is that the total Effective Equivalent Chlorine (EECl) continues to decrease at about  $1\% \text{ yr}^{-1}$  as a result of the Montreal Protocol. The main reason for this decline is that methyl chloroform ( $CH_3CCl_3$ ) concentrations continued to decline to less than half of the peak levels present in 1992. However, atmospheric concentrations of the halons and CFC-12 are still increasing because of allowed production in the developing countries and the large bank of chemicals present in the developed countries. After  $CH_3CCl_3$  concentrations drop to near zero, continued production and release of the halons may introduce a significant change in the trend of EECl. Other significant results include the observed global increases in atmospheric  $N_2O$  and  $SF_6$  (identified through both flask and in situ monitoring), the continued growth of the CFC replacements (HCFCs and HFCs), and the decline in the northern hemispheric concentrations of  $CHCl_3$ ,  $CH_2Cl_2$ , and  $C_2Cl_4$  as a result of the U.S. Clean Air Act.

Airborne measurements were conducted in the upper troposphere and lower stratosphere in tropical, midlatitude, and polar regions during 1998 and 1999 (Figure 5.1). The exchange of air between the lower stratosphere and the troposphere and midlatitude upper stratosphere was quantified. The development and deployment of the next generation airborne gas chromatograph with electron capture and mass selective detection was funded by the National Aeronautic and Space Administration's (NASA) Instrument Incubation Program to measure trace gases, including acetone and PAN that influence atmospheric chemistry in the upper troposphere.

TABLE 5.1. Geographic and Network Information on HATS Network Sites

Code	Station	Latitude	Longitude	Elevation (m)	LST-GMT (hr)	Type
ALT	Alert, Northwest Territories, Canada (AES)*	82.45°N	62.52°W	210	-4	F, I
BRW	Point Barrow, Alaska	71.32°N	136.60°W	11	-9	F, I
MHT	Mace Head, Ireland (University College)	53.33°N	9.90°W	42	0	F
LEF	WLEF tower, Wisconsin (CMDL-CCGG)	45.95°N	90.28°W	470	-6	F, I
HFM	Harvard Forest, Massachusetts (Harvard University)	42.54°N	72.18°W	340	-5	F, I
NWR	Niwot Ridge, Colorado (University of Colorado)	40.04°N	105.54°W	3013	-7	F, I
ITN†	WITN tower, North Carolina (CMDL-CCGG)	35.37°N	77.39°W	9	-5	F, I
MLO	Mauna Loa, Hawaii	19.54°N	155.58°W	3397	-10	F, I
KUM	Cape Kumukahi, Hawaii	19.52°N	154.82°W	3	-10	F
SMO	Tuluila, American Samoa	14.23°S	170.56°W	77	-11	F, I
CGO	Cape Grim, Tasmania, Australia‡	40.41°S	144.64°E	94	+10	F
TDF	Ushuaia, Tierra Del Fuego, Argentina (WMO GAW station)§	54.82°S	68.32°W	10	-3	I
PSA	Palmer Station, Antarctica**	64.92°S	64.00°W	10	+12	F
SPO	South Pole, Antarctica	89.98°S	102.00°E	2841	+12	F, I

Cooperative sites (F = flasks, I = in situ) with:

\*In situ GC: Only N<sub>2</sub>O and SF<sub>6</sub>; flask sampling for all gases, however.

†ITN site's flask and in situ GC were discontinued on June 12, 1999 (see text).

‡Commonwealth Scientific and Industrial Research Organization (CSIRO) and Bureau of Meteorology, Australia

§Starts collecting data in March 2001.

\*\*Only glass flasks used.

Oceanic measurements of CH<sub>3</sub>Br and other gases were obtained on two research cruises during 1998-1999. Measurements in marine air and surface seawater showed that the oceans are still a significant sink for atmospheric CH<sub>3</sub>Br, but the magnitude of the sink is slightly smaller than previously determined.

### 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.

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, firm 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.

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), CIBrCs (3)	Semi-monthly to monthly

#### 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 in 1996-1997 to accommodate additional sites. Sampling success

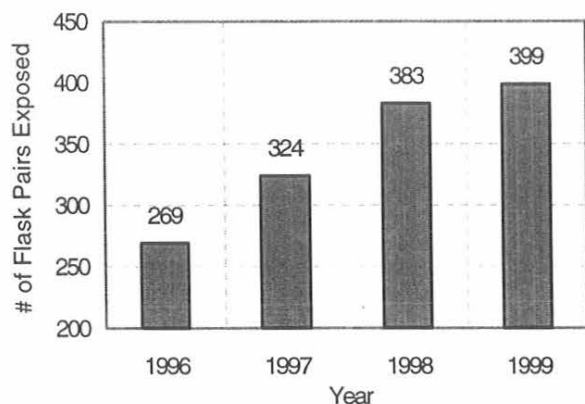


Fig. 5.2. Number of flask pairs filled and returned to Boulder each year from the HATS station network.

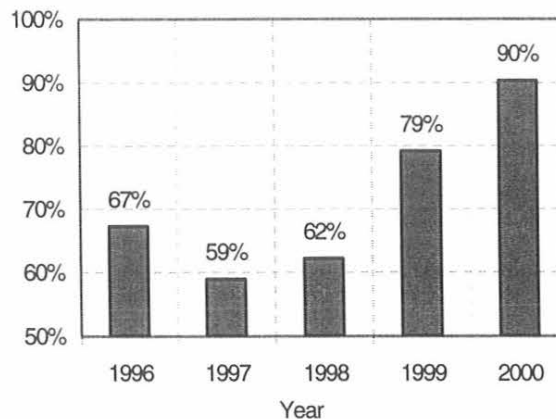


Fig. 5.3. The percentage of flask pairs agreeing within 1 psi in total pressure upon arrival in Boulder.

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 firm 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 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% yr<sup>-1</sup> (Figure 5.4). CFC-113 and CCl<sub>4</sub> are also decreasing at about 1% yr<sup>-1</sup>, and CH<sub>3</sub>CCl<sub>3</sub>, which has driven the overall decline in

atmospheric chlorine, continues to drop about 18% yr<sup>-1</sup> (subsection on "Overall Trends"). Gases analyzed only by GC-ECD are N<sub>2</sub>O, SF<sub>6</sub>, and CBrF<sub>3</sub> (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 N<sub>2</sub>O from 1978 to 2000 was 0.74 ± 0.01 (95% confidence level, C.L.) nmol mol<sup>-1</sup> yr<sup>-1</sup> (parts-per-billion, or ppb, yr<sup>-1</sup>), which amounts to a mean of about 0.25% yr<sup>-1</sup>. From 1996 to 2000, the global growth rate was 0.85 ± 0.06 ppb yr<sup>-1</sup>, which differs significantly at the 95% C.L. from the 20-year

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%

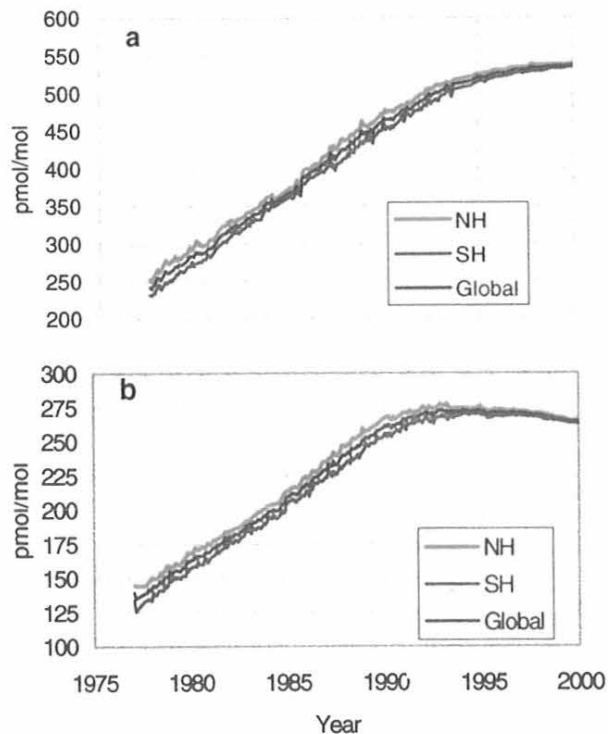


Fig. 5.4. CFC-12 (a) and CFC-11 (b) from flask samples. Data are monthly averages.

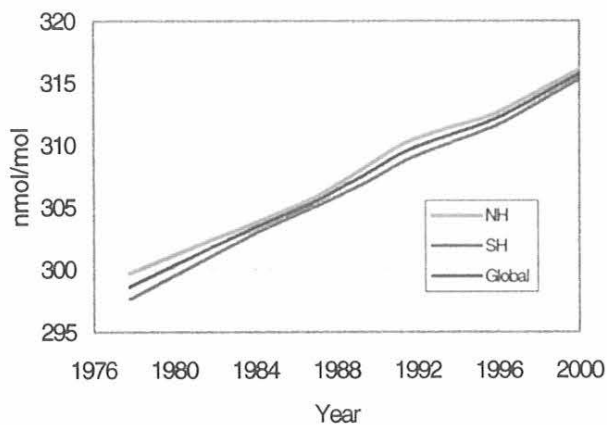


Fig. 5.5. Atmospheric history of  $N_2O$  derived from CMDL flask measurements. Data are smoothed with a lowest fit.

average. This suggests that  $N_2O$  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.)  $pmol\ mol^{-1}$  (parts per-trillion, or ppt,  $yr^{-1}$ ) since 1996 (Figure 5.6). CMDL measurements of polar firn air confirmed 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  $SF_6$  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  $yr^{-1}$ , does not differ significantly at the 95% C.L. from the 1995 to 2000 average of  $0.06 \pm 0.01$  ppt  $yr^{-1}$ , nor from the 1995-1996 average of  $0.044 \pm 0.011$  ppt  $yr^{-1}$  reported in Butler *et al.* [1998a] (Figure 5.7). However, at the 90% confidence level, a 30-40% increase in H-1301 emissions is suggested during the past few years. H-1211 is still increasing at a rate of

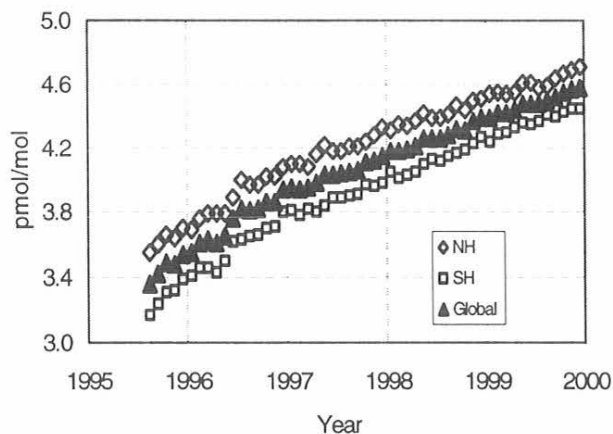


Fig. 5.6. Recent history of atmospheric  $SF_6$  from CMDL flask measurements. Data are monthly averages.

$0.1-0.2$  ppt  $yr^{-1}$ , 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  $CH_2Cl_2$ . 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

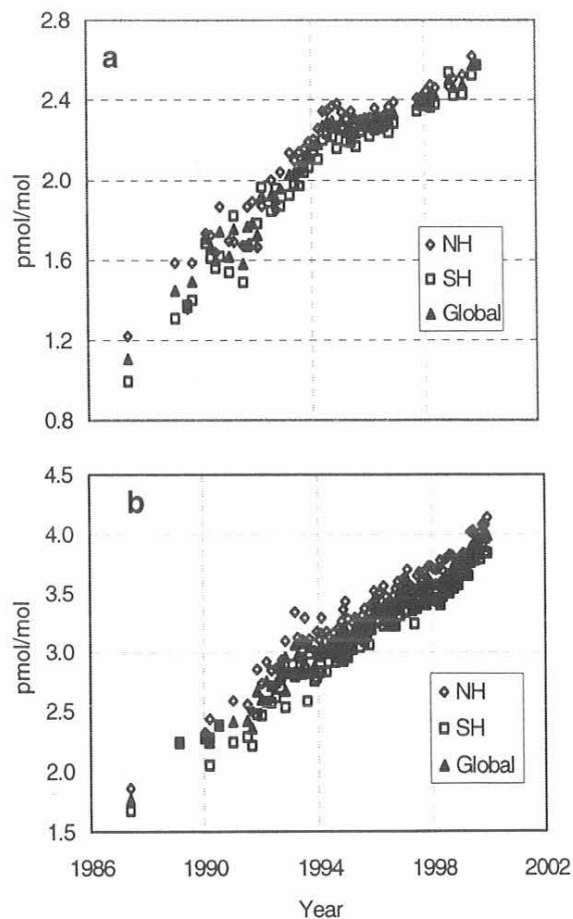


Fig. 5.7. Halons H-1301 (a) and H-1211 (b) from CMDL flask measurements. Data are monthly averages.

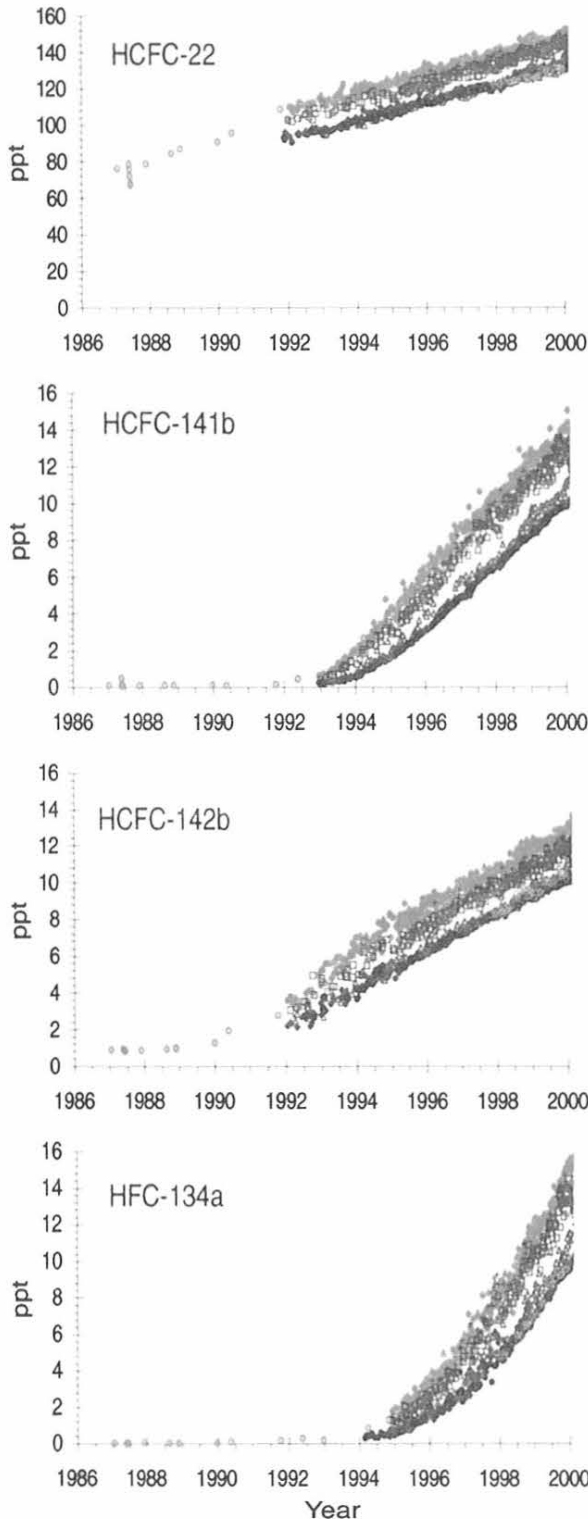


Fig. 5.8. Atmospheric dry mole fractions (ppt) of selected HCFCs and HFC-134a measured by GC-MS in the CMDL flask program. Each point represents the mean of two flasks from one of eight or nine stations: ALT, BRW, NWR, red; KUM and MLO, green; SMO, CGO, PSA, and SPO, blue. Also plotted are results from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

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>).

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

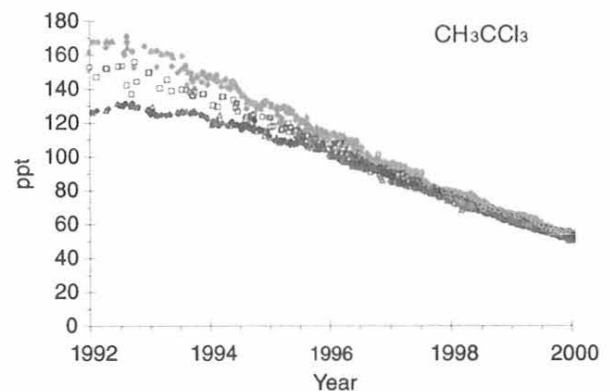


Fig. 5.9. Atmospheric dry mole fractions (ppt) of CH<sub>3</sub>CCl<sub>3</sub> measured by GC-MS in the CMDL flask program. Each point represents the mean of two simultaneously filled flasks from one of eight or nine stations (symbols the same as in Figure 5.8).

atmospheric abundance and distribution of the hydroxyl radical, an important atmospheric oxidant [Ravishankara and Albritton, 1995; Montzka et al., 2000; Spivakovsky et al., 2000].

#### 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

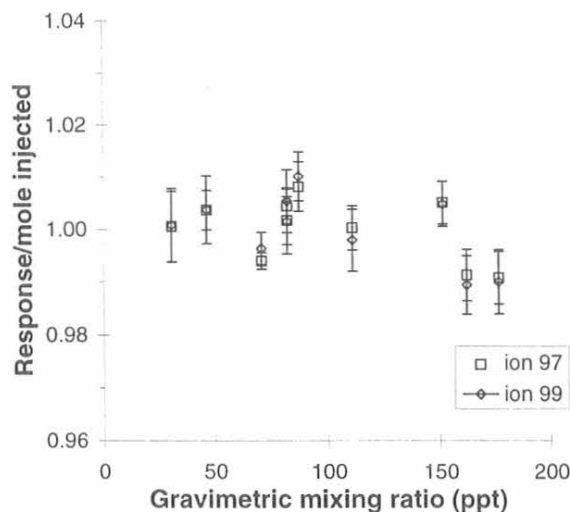


Fig. 5.10. Consistency of gravimetrically prepared standards containing  $\text{CH}_3\text{CCl}_3$  as analyzed on the GC-MS during 1997-1999. For well-made standards analyzed on an instrument with a linear response, the response factor should be independent of mixing ratio. Response factors (measured 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.

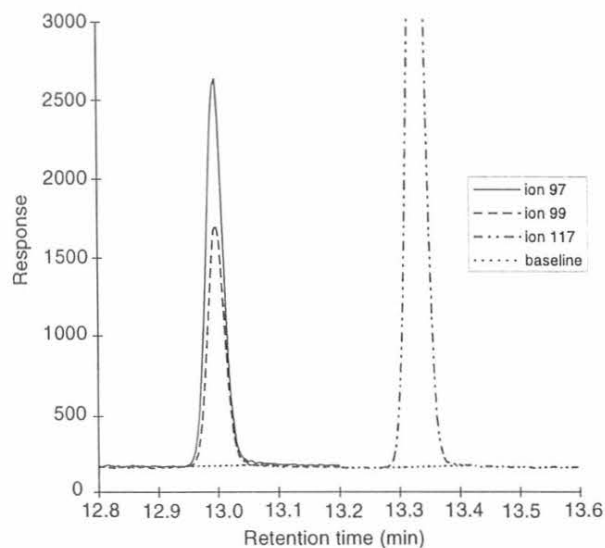


Fig. 5.11. A portion of a chromatogram from the GC-MS flask instrument showing the signals observed for  $\text{CH}_3\text{CCl}_3$  (ions 97 and 99) and  $\text{CCl}_4$  (ion 117; peak maximum not shown) in ambient air collected at Samoa. Concentrations were determined to be 47 ppt  $\text{CH}_3\text{CCl}_3$  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).

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).

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 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.

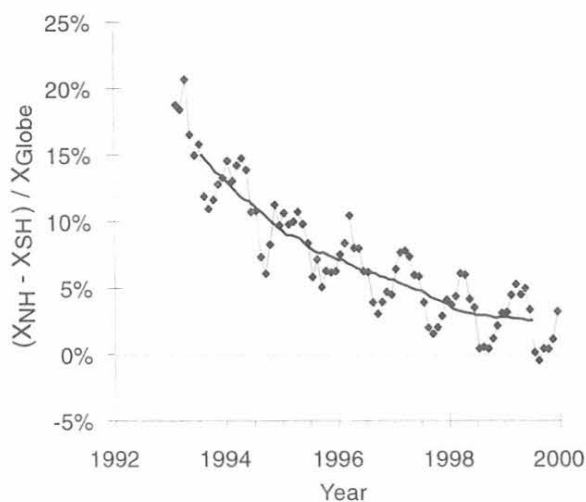


Fig. 5.12. The hemispheric mixing ratio difference for  $\text{CH}_3\text{CCl}_3$  in recent years. The difference was inferred from weighted, monthly mean mixing ratios at three to six sampling stations in each hemisphere. Monthly differences (solid diamonds) are connected with a thin line; the heavy 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 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).

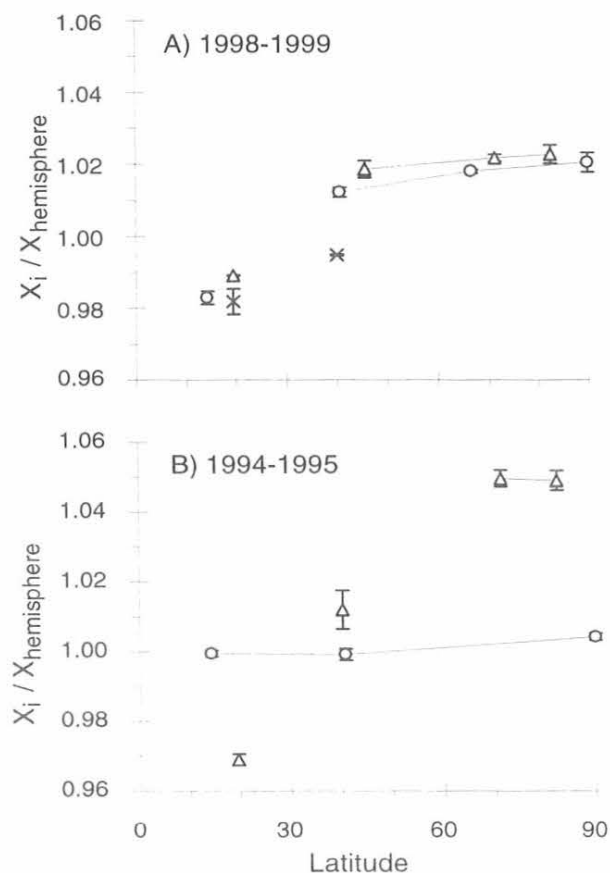


Fig. 5.13. Measured intrahemispheric gradients in annual mean mixing ratios of  $\text{CH}_3\text{CCl}_3$  [Montzka *et al.*, 2000]. (A) Annual means for individual sites ( $X_i$ ) are shown normalized to respective hemispheric annual means for the 2 years 1998-1999. Northern hemispheric data from low 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.

#### 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  $\text{CH}_3\text{CCl}_3$  (Figure 5.9). The global concentration of this gas decreased at an exponential rate of  $\sim 18\% \text{ yr}^{-1}$  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

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.

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

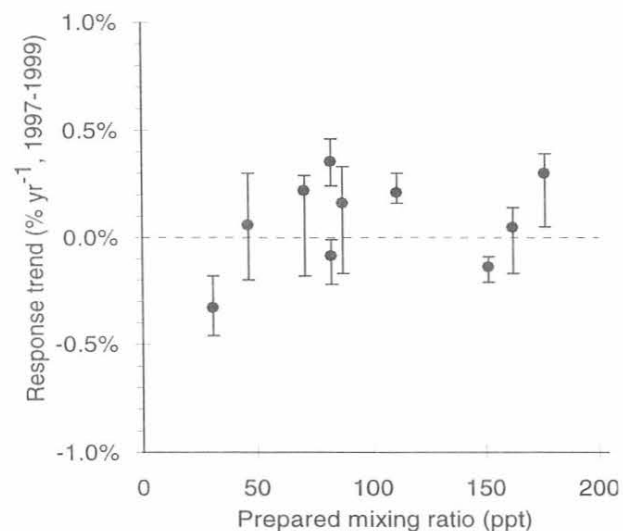


Fig. 5.14. The stability of calibration for CH<sub>3</sub>CCl<sub>3</sub> during 1997-1999. From multiple (7-9) comparisons of 10 gravimetric standards to a single high-pressure sample of ambient air during 1997-1999, trends in the response ratio (ratio of the response for CH<sub>3</sub>CCl<sub>3</sub> 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 (±0.1)% yr<sup>-1</sup>).

decreased since 1993-1994. Estimates of Effective Equivalent Chlorine (EECl) and Equivalent Chlorine (ECI) [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 ECI 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 ECI diminishes, continued declines in EECl and ECI 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 ECI 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



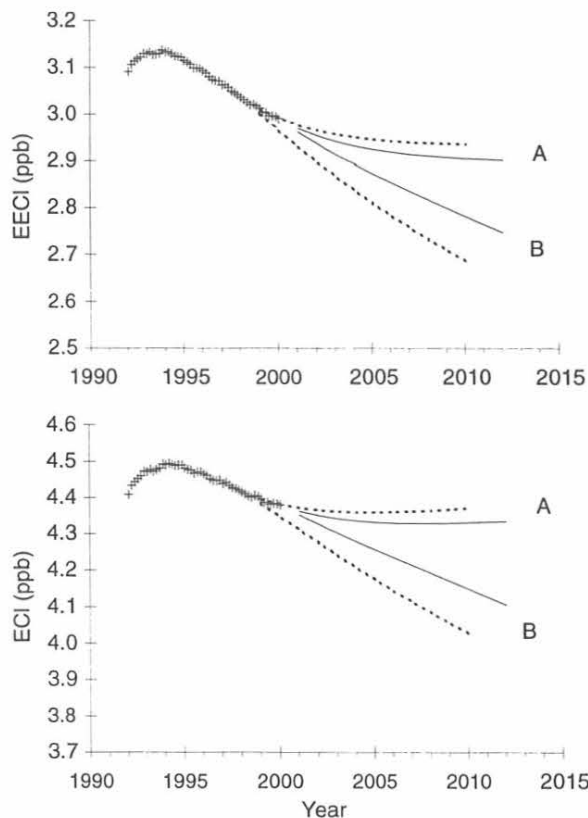


Fig. 5.15. The measured and potential future burden of ozone-depleting halogen in the lower atmosphere. Ozone-depleting halogen is estimated from tropospheric measurements of halocarbons by appropriate weighting factors to calculate Effective Equivalent Chlorine (EECI) for midlatitudes and Equivalent Chlorine (ECI) 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.

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  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  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  $\text{CH}_2\text{Cl}_2$  and  $\text{C}_2\text{Cl}_4$  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 ( $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_2\text{Cl}_4$ ,  $\text{CHCl}_3$ ) contribute some to the halogen burden of the stratosphere, global measurements of them also provide an improved understanding

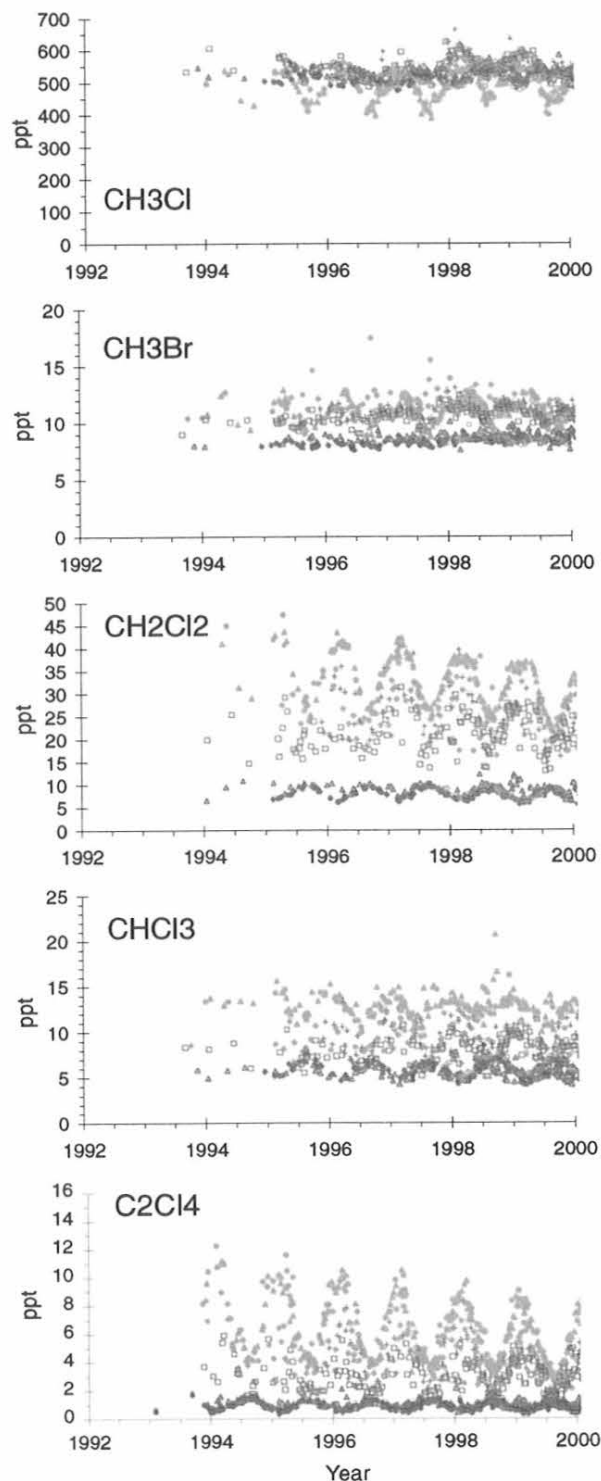


Fig. 5.16. Atmospheric dry-air mole fractions (ppt) determined for selected chlorinated trace gases and  $\text{CH}_3\text{Br}$  by GC-MS in the CMDL flask program. Each point represents the mean of two simultaneously filled flasks from one of eight or nine stations (symbols the same as in Figure 5.8).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

of atmospheric processes such as trace-gas oxidation by OH and Cl atoms and atmospheric transport rates.

CMDL results for  $\text{CH}_2\text{Cl}_2$  and  $\text{C}_2\text{Cl}_4$  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 ~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.

### 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 ( $\text{CH}_3\text{CCl}_3$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$ ),  $\text{N}_2\text{O}$ ,  $\text{SF}_6$ , and halon-1211. The capillary column is used to measure three new compounds for the HATS in situ program: HCFC-22 ( $\text{CHClF}_2$ ) and two methyl halides ( $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$ ). 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  $\text{cm}^3$  air sample is pre-concentrated on a cold trap held at about  $-60^\circ\text{C}$ . 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://stdndstealth.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  $\text{yr}^{-1}$ . 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  $\text{yr}^{-1}$ . 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  $\text{yr}^{-1}$ . 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  $\text{yr}^{-1}$  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  $\text{yr}^{-1}$ . The interhemispheric difference indicates that sources are located primarily in the northern hemisphere. Because  $\text{CCl}_4$  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  $\text{CCl}_4$ .

The tropospheric mixing ratio of  $\text{N}_2\text{O}$  continues to grow at a steady rate near 0.7 ppb  $\text{yr}^{-1}$  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.

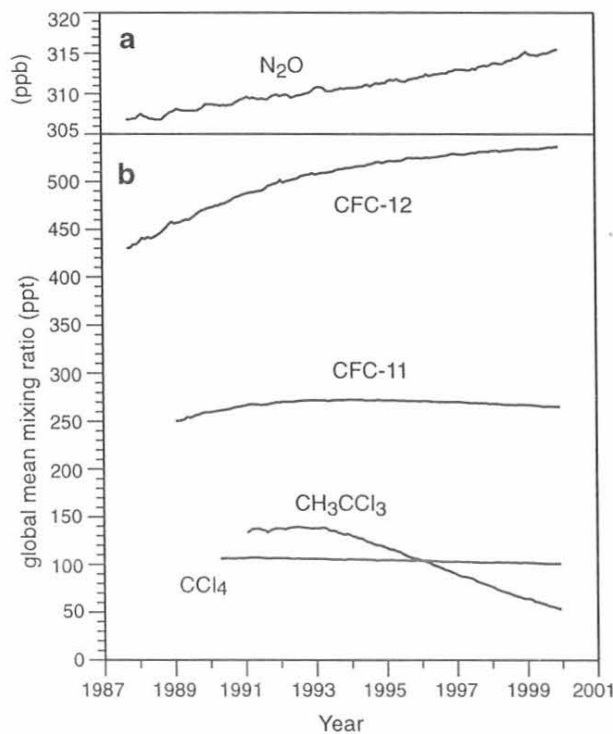


Fig. 5.17. Global monthly mean mixing ratios for (a)  $N_2O$  and (b) CFC-12, CFC-11,  $CH_3CCl_3$ , and  $CCl_4$  from the in situ gas chromatographs.

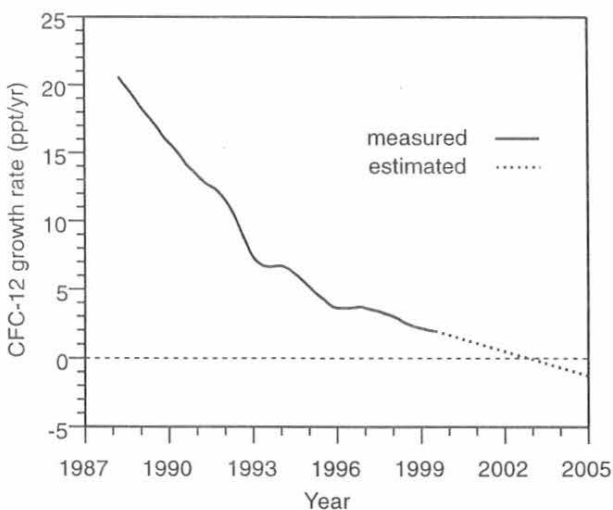


Fig. 5.18. Growth rate of CFC-12 as determined from in situ measurements. The growth rate is projected to reach zero in the next 3-4 years based on the average rate of decrease since 1995.

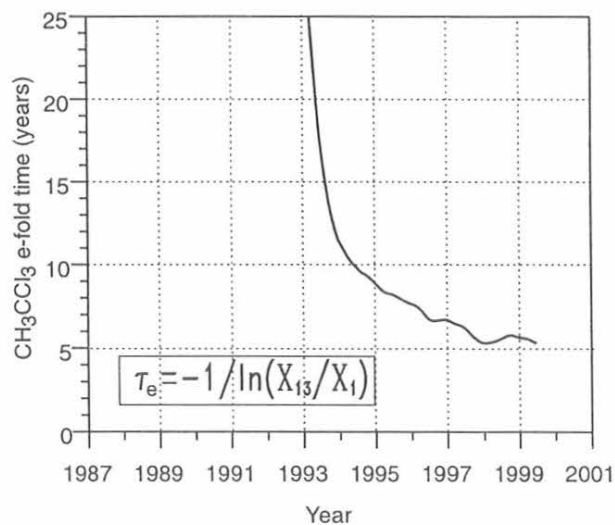


Fig. 5.19. Using a single box model for the atmosphere with emissions assumed to be negligible, the e-fold time ( $\tau_e$ ) is estimated using measured global mean methyl chloroform mixing ratios one year apart.  $X_1$  is the monthly mean global mixing ratio for the first month and  $X_{13}$  is the mixing ratio 1 year later (13<sup>th</sup> 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].

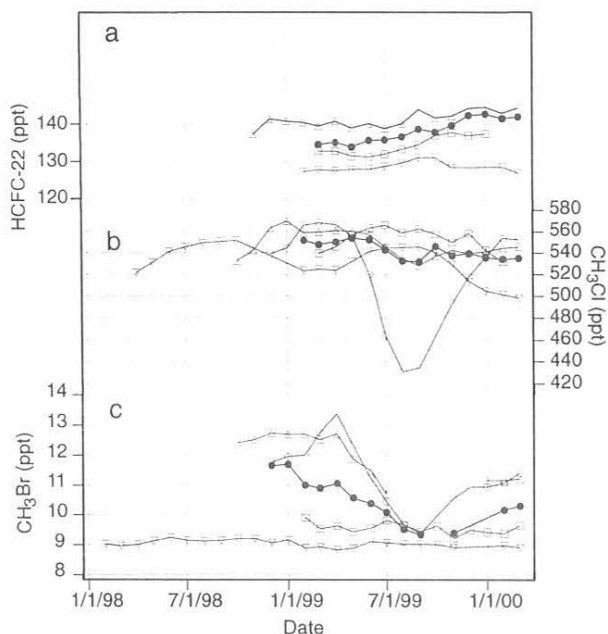


Fig. 5.20. Monthly mean mixing ratios of (a) HCFC-22, (b) methyl chloride, and (c) methyl bromide measured by the CATS in situ gas chromatographs deployed at the CMDL observatories (BRW, triangle; MLO, open circle; SMO, square; SPO, inverted triangle). The solid circles are global averages of the four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

Measurements of  $\text{CH}_3\text{Cl}$  at our two tropical coastal sites, MLO and SMO, also point to a coastal terrestrial source. Figure 5.21 shows rapid changes in the  $\text{CH}_3\text{Cl}$  mixing ratio at Mauna Loa (Figure 5.21a) and corresponding changes in wind direction (Figure 5.21b). High concentrations of  $\text{CH}_3\text{Cl}$  are associated

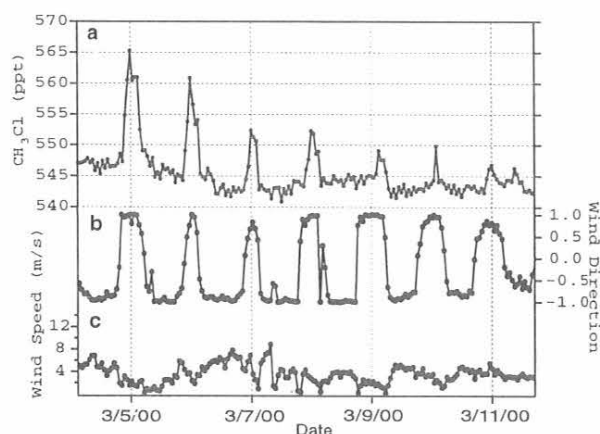


Fig. 5.21. Hourly measurements of  $\text{CH}_3\text{Cl}$  in air at MLO (a) show rapid variability in the  $\text{CH}_3\text{Cl}$  mixing ratio, indicating local sources. The cosine of the wind direction (values near 1 correspond to northerly winds, values near -1 correspond to southerly winds) (b) and wind speed (c) are plotted for comparison.

with periods of northerly winds (daytime up-slope conditions) that bring  $\text{CH}_3\text{Cl}$ -rich air from the vegetated northern section of the island of Hawaii up to MLO.

#### 5.1.4. GRAVIMETRIC STANDARDS

##### Calibration of Working Standards

In May 1999 the three-channel gas chromatograph system used to calibrate standards for the in situ monitoring program was replaced by a four-channel, custom-built GC. The four-channel GC is similar to the four-channel CATS instruments used for in situ monitoring at the observatories. The GC is operated under slightly different conditions compared to those at the observatories in order to optimize chromatography for cylinder calibration (Table 5.6).

The new four-channel instrument was compared to the old GC to ensure that the new GC would provide similar calibration results. For calibrations of ambient-level working standards, the new GC agreed to within 0.1% for  $\text{N}_2\text{O}$ , 0.4% for CFC-113, 0.5% for  $\text{CH}_3\text{CCl}_3$ , and 1% for CFC-11 and  $\text{CCl}_4$ . Initial tests revealed a 2-3% discrepancy for CFC-12. This experiment was repeated several months later, and the discrepancy could not be reproduced. Testing in December 1999 showed that the GCs agreed to within 0.2% for CFC-12. Following this CFC-12 experiment, the old three-channel GC instrument was retired. The four-channel GC is now used to calibrate working standards. Each standard is typically analyzed for 2 full days over a 2-3 week period (8-12 injections each day) (Table 5.7).

##### Preparation of Working Standards

Working standards for use with laboratory and in situ GCs continue to be filled at the C-1 site at Niwot Ridge, Colorado (40.04°N, 105.54°W, elevation 3013 m). Cylinders are filled using a three-stage, SA-6B compressor from Rix Industries (Oakland, California). Cylinders have occasionally been contaminated with trace amounts of unknown compounds that elute near CFC-11 and CFC-113 on the columns used in the CMDL in situ program. Contaminated standards have traditionally been associated with warm temperatures, while clean standards have been obtained during winter when ambient air temperatures are often below 5°C. The contaminants are thought to result from outgassing of material from the piston rings of one or more of the compressor stages (Ray Weiss, personal communication, 1999). Outgassing may be more severe at higher operating temperatures. To reduce the operating temperature of the first stage of the compressor, the compressor was modified in order to allow a small amount of distilled, degassed water to be injected into the air stream just upstream of

TABLE 5.6. Configuration of the Four-Channel GC for Calibration of Working Standards

Channel	Column	Detector	Compounds Resolved
1	Porapak Q	Valco ECD	$\text{N}_2\text{O}$ , $\text{SF}_6$
2	Unibeads 1s	Shimadzu ECD	CFC-12, CFC-11, halon-1211
3	OV-101	Valco ECD	CFC-12, CFC-11, halon-1211, CFC-113, $\text{CHCl}_3$ , $\text{CH}_2\text{CCl}_3$ , $\text{CCl}_4$
4	Poraplot Q	Shimadzu ECD	HCFC-22, $\text{CH}_3\text{Cl}$ , $\text{CH}_3\text{Br}$

TABLE 5.7. Analytical Precision Typically Obtained for a Complete Calibration of a Working Standard on the Four-Channel GC-ECD

Compound*	Precision (%)
N <sub>2</sub> O	0.05
CFC-12	0.08
CFC-11	0.10
CFC-113	0.15
halon-1211†	0.2
CHCl <sub>3</sub>	1.0
CH <sub>2</sub> Cl <sub>2</sub>	0.2
CCl <sub>4</sub>	0.1
SF <sub>6</sub>	0.8

\*Calibration of HCFC-22, CH<sub>3</sub>Cl and CH<sub>3</sub>Br is only performed on the flask GC-MS instrument at this time.

†The calibration scale for halon-1211 is determined on the flask GC-ECD instrument. Halon-1211 calibration on the four-channel instrument is complicated by a co-eluting peak occurring on both channels 2 and 3.

the first stage. Injection of water in this manner reduces the operating temperature of the first stage cylinder head from >100°C to ~50°C. Contamination is substantially reduced by injecting water at a rate of 10-20 mL min<sup>-1</sup> (Figure 5.22).

#### Standards Preparation

A total of 66 natural-air standards were filled at Niwot Ridge during the 1998-1999 period. Fifty-eight of these were used by CMDL or related projects; eight standards were prepared for outside laboratories. A total of 10 gravimetric standards were prepared. Four were prepared for CMDL use, while 6 were prepared for outside laboratories.

#### Calibration Scales

A summary of the calibration scales used in conjunction with measurements performed by the HATS group is reported here. Table 5.8 lists the year that each calibration scale was established. Table 5.9 lists the gravimetric standards and mixing ratios used to define each calibration scale. Factors that

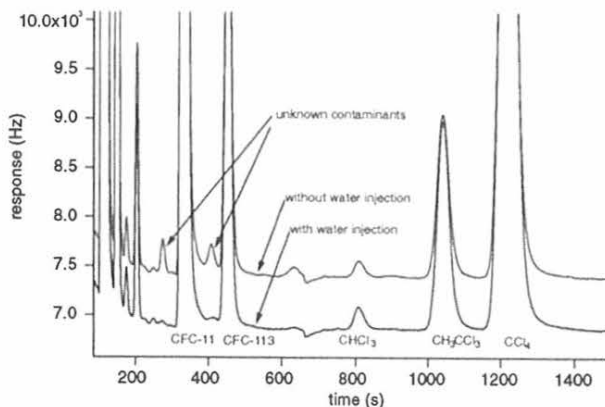


Fig. 5.22. Chromatograms of air samples from tanks pumped at Niwot Ridge, Colorado, with and without water injection (see text). The chromatogram (top) without water injection shows more contamination peaks.

TABLE 5.8. Reference Dates for HATS Calibration Scales

Compound	Year*	Reference‡
N <sub>2</sub> O	1993	Swanson et al. [1993]
CFC-12	1997	Butler et al. [1998b]
CFC-11	1992	Elkins et al. [1993]
CFC-113	1993	Swanson et al. [1993]
CH <sub>2</sub> Cl <sub>2</sub>	1996	Butler et al. [1998b]
CCl <sub>4</sub>	1996	Butler et al. [1998b]
HCFC-22	1992	Montzka et al. [1993]
HCFC-141b	1994	Montzka et al. [1994]
HCFC-142b	1994	Montzka et al. [1994]
HCFC-134a	1995	Montzka et al. [1996b]
CH <sub>3</sub> Cl	1996	Butler et al. [1998b]
CH <sub>3</sub> Br	1996	Butler et al. [1998b]
CH <sub>2</sub> Cl <sub>2</sub> †	1992	Spivakovsky et al. [2000]
C <sub>2</sub> Cl <sub>4</sub> †	1992	Hurst et al. [1997]
CHCl <sub>3</sub> †	1992	Hurst et al. [1997]
halon-2402†	1992	Butler et al. [1998b]
halon-1211	1996	Butler et al. [1998a]
halon-1301	1990	Butler et al. [1998a]
SF <sub>6</sub>	1994	Geller et al. [1997]
H <sub>2</sub>	1995	Novelli et al. [1999]
CO	1991	Novelli et al. [1991]

\*Calibration scales are defined by a particular set of gravimetric standards (see Table 5.9). In some cases only a single standard is used. The year shown for each species refers to either the year during which the standards were prepared or the year in which a significant change in calibration scale occurred. Thus data reported prior to the year listed are associated with a different calibration scale than those reported in subsequent years.

†These species are measured by CMDL, but their calibration is defined only by an incomplete set of standards.

‡The reference listed for each species refers to a publication that describes a calibration change or a publication that includes recent results.

influence the number of gravimetric standards used to define a particular scale include the time-history of the measurements, the range of concentrations investigated, and the linearity of response (e.g., CFC-12 measurements were made over more extensive spatial and temporal scales than CH<sub>3</sub>Br, thus a large number of CFC-12 standards were prepared over the years). All of the standards listed in Table 5.9 were prepared in 5.9-L or 29.5-L Aculife-treated aluminum cylinders (Scott Specialty Gases, Plumsteadville, Pennsylvania).

Examples of calibration response curves determined on the CATS GC instrument are shown in Figure 5.23. The uncertainty associated with the calibration curves (expressed as the standard error of the residuals) is typically 0.2-0.5%.

The number of gravimetric standards used to define scales for N<sub>2</sub>O and SF<sub>6</sub> will be expanded in the near future. A number of standards with N<sub>2</sub>O and SF<sub>6</sub> mixing ratios near ambient levels will be prepared. The addition of numerous standards at near-ambient concentrations will enable high-precision maintenance of the scales over time.

## 5.2. AIRBORNE PROJECTS

### 5.2.1. AIRBORNE CHROMATOGRAPH FOR ATMOSPHERIC TRACE SPECIES (ACATS-IV)

#### Overview

Airborne Chromatograph for Atmospheric Trace Species (ACATS-IV) is a four-channel gas chromatograph designed to

TABLE 5.9. Gravimetric Standards Used to Define Calibration Scales for the HATS Group

Compound	Cylinder Number	Prepared Gravimetric Concentration	Compound	Cylinder Number	Prepared Gravimetric Concentration
N <sub>2</sub> O	*ALM-38408	96.2 ppb	SF <sub>6</sub>	*CLM-7506	3.1 ppt
	*ALM-26738	172.0 ppb		*CLM-7519	23.2 ppt
	*ALM-26743	331.0 ppb		*CLM-7494	60.6 ppt
	*ALM-26737	359.9 ppb		*CLM-7503	107.6 ppt
	*CLM-30135	801.1 ppb		†CLM-7490	5.3 ppt
CFC-11	*ALM-38408	25.5 ppt	CH <sub>3</sub> Br	†ALM-62626	5.3 ppt
	*CLM-2431	49.5 ppt		†ALM-39771	25.6 ppt
	*ALM-38417	80.9 ppt	CH <sub>3</sub> Cl	†ALM-39971	1024 ppt
	*CLM-2482	69.2 ppt		†ALM-26738	105 ppt
	*ALM-26735	75.16 ppt	HCFC-22	†ALM-26743	145 ppt
	*CLM-2413	136.3 ppt		†ALM-26735	105 ppt
	*ALM-26743	288.2 ppt		†ALM-38417	111.6 ppt
	*ALM-26737	313.6 ppt		†ALM-26737	158 ppt
CFC-12	*CLM-2426	77.8 ppt	HCFC-141b	†ALM-39758	5.0 ppt
	*CLM-2431	163.5 ppt		†ALM-39744	25.5 ppt
	*CLM-9015	189.2 ppt		†ALM-39749	51.3 ppt
	*CLM-2482	228.8 ppt	HCFC-142b	†ALM-39758	5.0 ppt
	*CLM-9041	274.4 ppt		†ALM-39744	25.4 ppt
	*CLM-9018	370.3 ppt	HCFC-134a	†ALM-39749	51.1 ppt
	*CLM-2413	450.7 ppt		†CLM-8952	5.44 ppt
	*CLM-9038	646.9 ppt		†CLM-9036	10.22 ppt
CFC-113	*CLM-2482	19.1 ppt	halon-1211	*†CLM-9039	3.02 ppt
	*CLM-2413	37.5 ppt		*†CLM-9024	5.41 ppt
	*†ALM-26735	48.0 ppt	halon-1301	*†CLM-2416	95.4 ppt
	†ALM-26738	48.0 ppt		*†FF-30071	6.08 ppb
	*†ALM-26743	82.8 ppt	halon-2402	†ALM-26748	47.5 ppt
	*†ALM-26737	90.0 ppt	CH <sub>2</sub> Cl <sub>2</sub>	†ALM-26748	122.0 ppt
	*†ALM-52792	30.9 ppt	C <sub>2</sub> Cl <sub>4</sub>	†ALM-26748	157.0 ppt
	*†ALM-52788	70.8 ppt	CHCl <sub>3</sub>	†ALM-26748	141.0 ppt
CH <sub>3</sub> CCl <sub>3</sub>	*†ALM-59967	111.0 ppt			
	*†ALM-52811	151.4 ppt			
	*†ALM-52792	22.1 ppt			
	*†ALM-52788	50.6 ppt			
	*†ALM-59967	79.4 ppt			
	*†ALM-52811	108.3 ppt			
CCl <sub>4</sub>					

\*These standards are used to define the calibration scales associated with GC-ECD instruments.

†These standards are used to define the calibration scales associated with GC-MS instruments.

measure atmospheric trace gases in the upper troposphere and lower stratosphere onboard the NASA high-altitude ER-2 aircraft [Elkins *et al.*, 1996]. ACATS-IV measures six chlorinated trace gases (CFC-12, CFC-11, CFC-113, CHCl<sub>3</sub>, CH<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub>) in addition to halon-1211, N<sub>2</sub>O, CH<sub>4</sub>, H<sub>2</sub>, and SF<sub>6</sub>. ACATS-IV has been part of the ER-2 payload for studies of stratospheric transport and ozone depletion since 1994, and in 1997 participated in the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) study. The principal objective of POLARIS was to determine the roles of photochemistry and transport in summertime decreases of stratospheric ozone over the arctic. Nineteen instruments onboard the NASA high-altitude ER-2 aircraft made in situ measurements of trace gases, radicals, aerosols, radiation, and meteorology in the upper troposphere and lower stratosphere of the northern hemisphere during spring, early summer, and late summer. The edge of the arctic polar vortex was penetrated during one flight in late April, and fragments of the eroding vortex were sampled during several other flights in May and June. The observed 35% decrease of the ozone column above Fairbanks, Alaska, was largely attributed to photochemistry, predominantly catalytic reactions between O<sub>3</sub> and NO in air parcels continuously exposed to sunlight for up to 10 days. ACATS-IV data from POLARIS

were incorporated in several publications that appeared during 1999 [e.g., Hurst *et al.*, 1999; Romashkin *et al.*, 1999; Sen *et al.*, 1999; Toon *et al.*, 1999].

#### Hydrogen Budget

The total hydrogen budget of the northern hemisphere lower stratosphere was recently evaluated for closure from in situ measurements of H<sub>2</sub>O, CH<sub>4</sub>, and H<sub>2</sub> onboard the NASA ER-2 aircraft during POLARIS and the 1995-1996 Stratospheric Tracers of Atmospheric Transport (STRAT) mission [Hurst *et al.*, 1999]. Budget closure requires that measured abundance relationships between these principal hydrogen reservoirs corroborate theoretical hydrogen partitioning predicted by reactions that oxidize CH<sub>4</sub> to H<sub>2</sub>O and H<sub>2</sub>, and oxidize H<sub>2</sub> to H<sub>2</sub>O. A simple evaluation of these reactions predicts that H<sub>2</sub>O production ( $\Delta\text{H}_2\text{O}$ ) should equal two times CH<sub>4</sub> loss ( $-2\cdot\Delta\text{CH}_4$ ) plus the net change in H<sub>2</sub> ( $\Delta\text{H}_2$ ). ACATS-IV measurements revealed that H<sub>2</sub> mixing ratios are relatively constant in the lower stratosphere (Figure 5.24). From the measured  $\Delta\text{H}_2/\Delta\text{CH}_4 = -0.027 \pm 0.003$  (Figure 5.24), the ratio of H<sub>2</sub>O production to CH<sub>4</sub> destruction ( $\Delta\text{H}_2\text{O}/\Delta\text{CH}_4$ ) was predicted to be  $-1.973 \pm 0.003$  [Hurst *et al.*, 1999].

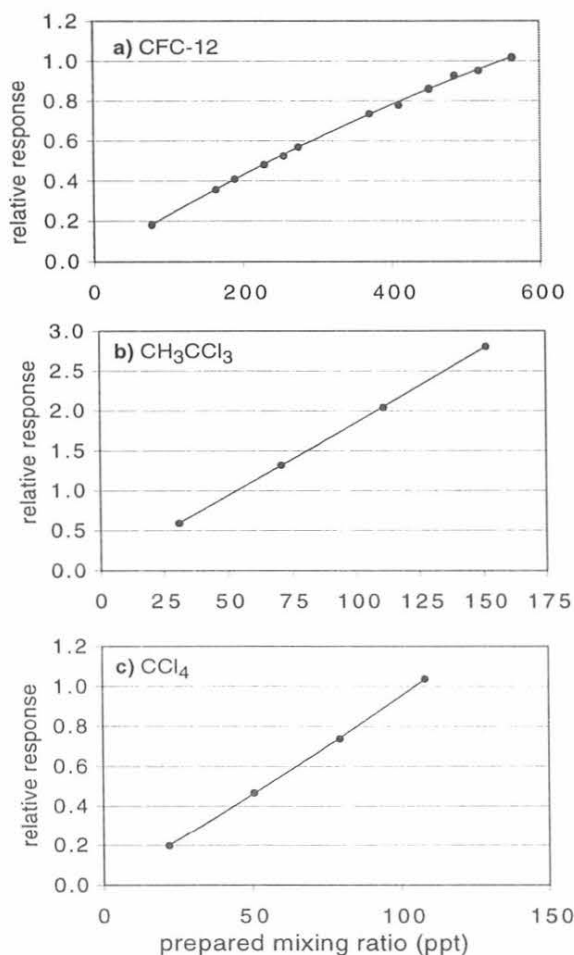


Fig. 5.23. Sample calibration curves for CFC-12 (a), CH<sub>3</sub>CCl<sub>3</sub> (b), and CCl<sub>4</sub> (c). Each filled circle represents the response of a gravimetric standard relative to a working standard. Solid lines are second-order polynomial fits to response data.

This predicted relationship was compared to the slope of the anticorrelation between H<sub>2</sub>O and CH<sub>4</sub> mixing ratios measured in the lower stratosphere during STRAT and POLARIS. H<sub>2</sub>O was measured during both campaigns by the Harvard University Lyman- $\alpha$  hygrometer [Hintsa *et al.*, 1999] and also by the Jet Propulsion Laboratory (JPL) tunable diode laser (TDL) hygrometer during POLARIS. CH<sub>4</sub> was measured by ACATS-IV and a JPL TDL spectrometer. The anticorrelation between H<sub>2</sub>O and CH<sub>4</sub> in the lower stratosphere was found to be tight and linear for air masses with mean ages greater than 3.8 years (Figure 5.25). In younger air masses large variations in H<sub>2</sub>O mixing ratios degrade the compactness of the anticorrelation. These variations result from the seasonal cycle of temperature near the tropical tropopause, the entry point for most stratospheric air masses. Air masses passing through the tropical tropopause are regularly imprinted with an H<sub>2</sub>O mixing ratio dictated by the lowest temperature they encounter [e.g.,

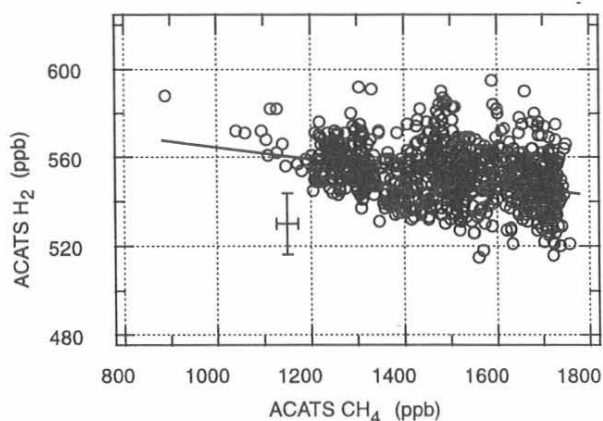


Fig. 5.24. H<sub>2</sub> and CH<sub>4</sub> measured by ACATS-IV in the lower stratosphere between 3°S and 60°N latitude during STRAT (1995-1996). The solid line is an ODR fit to the data with a slope of  $-0.027 \pm 0.003$ , indicating that H<sub>2</sub> production slightly exceeds H<sub>2</sub> destruction in the stratosphere. The crossed error bars represent the average random errors (1 $\sigma$ ) of the measurements.

Mote *et al.*, 1996]. As young air masses age in the stratosphere, they gradually lose their H<sub>2</sub>O imprint as they mix with air masses of different H<sub>2</sub>O content.

Data from each unique combination of H<sub>2</sub>O and CH<sub>4</sub> instruments were fit with an orthogonal distance regression (ODR). Data for air masses with mean ages <3.8 year (or alternately CH<sub>4</sub> >1450 ppb) were excluded from the fits. For all instrument combinations the mean slope ( $\Delta\text{H}_2\text{O}/\Delta\text{CH}_4$ ) was  $-2.15 \pm 0.18$  (1 $\sigma$ ). The mean slope using only ACATS-IV CH<sub>4</sub> data,  $-2.02 \pm 0.17$ , is in excellent agreement with the predicted  $\Delta\text{H}_2\text{O}/\Delta\text{CH}_4 = -1.973$ . The annual mean mixing ratio of H<sub>2</sub>O in air masses entering the stratosphere was estimated from the slope and intercept values from each ODR and a CH<sub>4</sub> mixing ratio of 1.7 ppm (the annual mean CH<sub>4</sub> mixing ratio entering the stratosphere). The result,  $4.0 \pm 0.4$  ppm H<sub>2</sub>O, agrees well with the  $3.8 \pm 0.3$  ppm H<sub>2</sub>O deduced from a recent re-evaluation of radiosonde temperature data near the tropical tropopause [Dessler, 1998].

#### Tracer Correlations

Measurements of CH<sub>3</sub>CCl<sub>3</sub> and CFC-11 in the lower stratosphere during POLARIS revealed significant differences in the CH<sub>3</sub>CCl<sub>3</sub>-CFC-11 correlation between spring and summer, 1997 [Romashkin *et al.*, 1999]. These differences were associated with the rapid decrease of tropospheric CH<sub>3</sub>CCl<sub>3</sub> that began in 1992 (see sections 5.1.2, 5.1.3) and the fact that the mean ages of the air masses observed during spring and summer differed by up to 1 year.

Before the CH<sub>3</sub>CCl<sub>3</sub>-CFC-11 correlations could be used to gain insight into stratospheric transport, the influences of the large tropospheric CH<sub>3</sub>CCl<sub>3</sub> trend on the lower stratospheric CH<sub>3</sub>CCl<sub>3</sub> distribution had to be minimized. Initially, the CH<sub>3</sub>CCl<sub>3</sub> mixing ratio in each air mass sampled by ACATS-IV was normalized to the CH<sub>3</sub>CCl<sub>3</sub> mixing ratio in air masses that entered the stratosphere on January 1, 1997. The normalization was based on the well-documented trend of tropospheric CH<sub>3</sub>CCl<sub>3</sub> (Figure

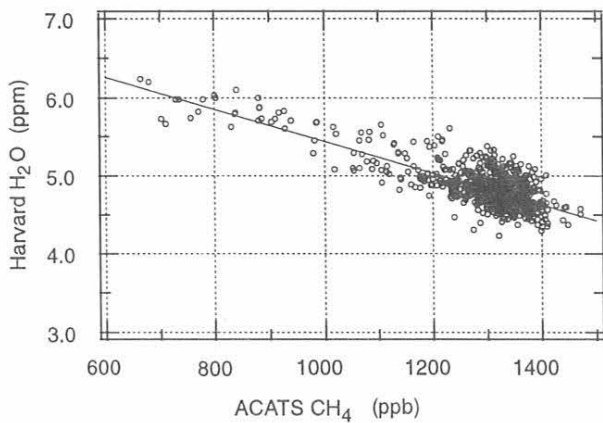


Fig. 5.25. A tight, linear anticorrelation between Harvard H<sub>2</sub>O and ACATS-IV CH<sub>4</sub> was observed in the lower stratosphere during STRAT (1995-1996) and POLARIS (1997). The solid line is an ODR fit to the data with a slope of  $-2.01 \pm 0.16$ . Data for air masses with mean ages  $<3.8$  years were omitted from this analysis.

5.9) and the mean ages of stratospheric air masses calculated from ACATS-IV measurements of SF<sub>6</sub>.

This normalization procedure, based solely on mean age, is inexact because an air mass is better characterized by a spectrum of ages [Hall and Plumb, 1994]. Two methods were used to quantify the effect of age spectra width on the initial normalization. In the first method, the stratospheric entry mixing ratio of CH<sub>3</sub>CCl<sub>3</sub> was expressed as the mean tropospheric mixing ratio of CH<sub>3</sub>CCl<sub>3</sub> over  $\pm 1.25$ -year intervals, the estimated width of the age spectrum [Volk et al., 1997]. For the second method, a 10-year-wide age spectrum (Green's) function based on a one-dimensional diffusive model (equation 21 of Hall and Plumb [1994] with diffusion coefficient  $K = 1.5 \text{ m}^2 \text{ s}^{-1}$ ) was used to weight the CH<sub>3</sub>CCl<sub>3</sub> tropospheric trend. The model-derived, weighted trend was used in combination with mean ages from ACATS-IV because the model underpredicts mean ages by a factor of two or more. The two normalization methods were similar in their influences on lower stratospheric CH<sub>3</sub>CCl<sub>3</sub> mixing ratios.

Correlations between normalized CH<sub>3</sub>CCl<sub>3</sub> and CFC-11 mixing ratios (Figure 5.26c) exhibit greater curvature than the raw correlations (Figure 5.26b). The induced curvature reveals straight lines of data between different parts of the correlation, evidence that air has mixed between the polar vortex and the midlatitudes (lines  $\alpha$  and  $\beta$  on Figure 5.26c). These mixing lines were not visible in the linear, un-normalized correlations (Figure 5.26b). The study confirms that stratospheric correlations between trace gases can be significantly altered by a strong tropospheric trend in one of the gases.

#### Total Inorganic Chlorine

Sen et al. [1999] compared two methods of determining the total inorganic chlorine content (Cl<sub>y</sub>) of air masses sampled in the arctic stratosphere during POLARIS. In the first method, Cl<sub>y</sub> was calculated as the difference between the total chlorine content (Cl<sub>tot</sub>) of an air mass when it entered the stratosphere and the total organic chlorine content (CCl<sub>y</sub>) of the same air mass at the time it was sampled by the ER-2. CCl<sub>y</sub> was determined from ACATS-IV in situ measurements of chlorinated source gases

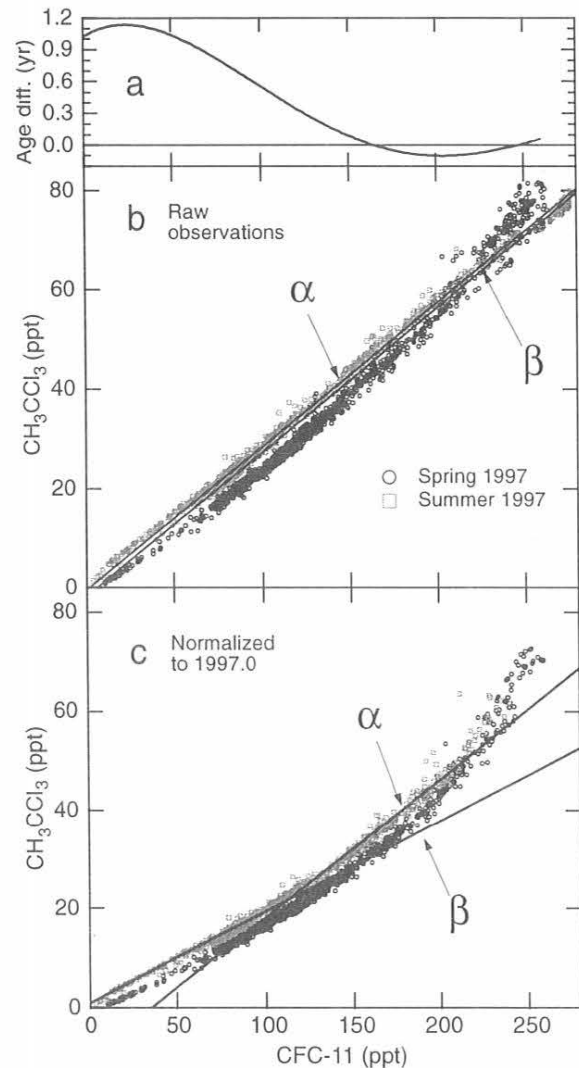


Fig. 5.26. Results from CH<sub>3</sub>CCl<sub>3</sub> and CFC-11 measurements made during the POLARIS campaign (1997): (a) differences between the SF<sub>6</sub>-based mean ages of air masses sampled by ACATS-IV (summer-spring), (b) correlations between CH<sub>3</sub>CCl<sub>3</sub> and CFC-11 during spring and summer, and (c) same correlations as (b) with the effects of the tropospheric CH<sub>3</sub>CCl<sub>3</sub> trend removed using 10-year-wide age spectrum, normalized to January 1, 1997. Solid lines in (b) and (c) are least squares fits to the following data subsets:  $\alpha$ , 100 ppt < CFC-11 < 225 ppt measured on June 26, 1997;  $\beta$ , 0 ppt < CFC-11 < 125 ppt measured on June 29, 1997.

near 20 km altitude (lower stratosphere) during the ER-2 flight of April 26, 1997. Cl<sub>tot</sub> values for the sampled air masses were compiled from time series of source gas mixing ratios measured at the Earth's surface in flasks and at NOAA observatories [Woodbridge et al., 1995; Montzka et al., 1996a]. The date of stratospheric entry of each sampled air mass was determined from its mean age calculated from ACATS-IV SF<sub>6</sub> data. Cl<sub>y</sub> was also calculated as the sum of remotely sensed solar occultation Fourier transform infrared (FTIR) measurements



of HCl, ClONO<sub>2</sub>, and HOCl by the JPL MkIV interferometer and estimates of ClO from a photochemical model. The MkIV observations were made during a balloon flight on May 8, 1997. These two methods of estimating Cl<sub>y</sub> agree to within 10% (Figure 5.27), adding confidence to both the in situ and remotely sensed data and suggesting that the photochemical model estimates of ClO are realistic for the sunlit lower stratosphere.

#### Intercomparison of Trace Gas Measurements

ACATS-IV measurements of CFC-11, CFC-12, CFC-113, CCl<sub>4</sub>, and SF<sub>6</sub> during POLARIS were compared to remotely sensed solar occultation FTIR measurements by the JPL MkIV interferometer on a balloon floating at 38 km altitude [Toon *et al.*, 1999]. Both sets of tracer data were correlated with N<sub>2</sub>O to account for the different dynamical histories of air masses sampled several days apart by the two instruments. Differences were less than 2% for both CFC-11 and CFC-12, well within the experimental uncertainties of the MkIV measurements. CFC-113 and CCl<sub>4</sub> data agreed to within experimental uncertainties (11-15%) between 13 and 21 km altitude, but the MkIV mixing ratios of both gases increased anomalously below 13 km. The anomalous increases were not observed for other long-lived tracers and were attributed to interfering absorption lines in the spectral regions used to quantify these gases. ACATS-IV SF<sub>6</sub> mixing ratios were on average 0.5 ppt (14%) lower than the MkIV values. This bias is surprising given that there was no discernable bias between SF<sub>6</sub> data from ACATS-IV and the Atmospheric Trace Molecule Spectroscopy (ATMOS) FTIR instrument aboard the space shuttle during 1993 and 1994 [Chang *et al.*, 1996; Michelson *et al.*, 1999]. The reason for this discrepancy has not yet been determined.

#### Instrument Modifications for TIES and SOLVE

ACATS-IV was modified twice during the second half of 1999 in preparation for the 2000 Stratospheric Aerosol and Gas Experiment-III (SAGE) Ozone Loss and Validation Experiment

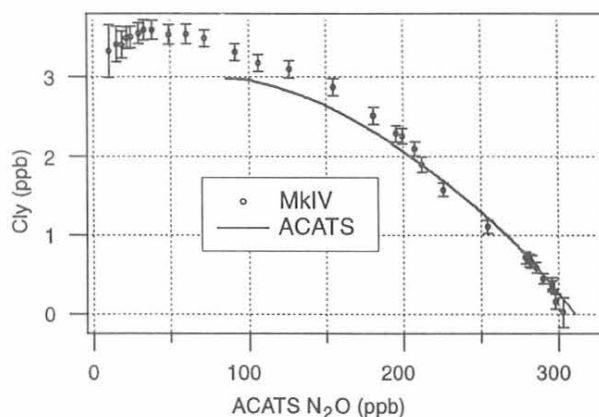


Fig. 5.27. Two independent methods were used to determine the total inorganic chlorine content (Cl<sub>y</sub>) of stratospheric air masses during POLARIS (1997). One method (solid line) utilized CMDL surface measurements of chlorinated source gases and ACATS-IV (1997) measurements of organic chlorine compounds in the lower stratosphere. The other method (open circles) combined MkIV measurements of HCl, ClONO<sub>2</sub>, and HOCl and modeled estimates of ClO. The two methods agree to within 10%.

(SOLVE) in Kiruna, Sweden. The first modifications were made for the 1999 Tracer Intercomparison Experiment for SOLVE (TIES) mission, a side-by-side intercomparison of coincident measurements by the three in situ N<sub>2</sub>O and CH<sub>4</sub> instruments selected for the SOLVE ER-2 payload. TIES was conducted at NASA Dryden, Edwards Air Force Base, California, during September-October 1999. The mission was a critical evaluation of N<sub>2</sub>O and CH<sub>4</sub> measurements by the JPL TDL spectrometer and a new, lightweight, compact TDL spectrometer that will replace a heavy, large TDL spectrometer that provided high quality N<sub>2</sub>O data aboard the ER-2 for many years. ACATS-IV was modified to include a new, rapid chromatography channel to measure N<sub>2</sub>O and SF<sub>6</sub> every 70 seconds. The new channel was operated in parallel with the "old" 250-s N<sub>2</sub>O and SF<sub>6</sub> channel during TIES, and the coincident data were in excellent agreement. ACATS-IV measurements of N<sub>2</sub>O and CH<sub>4</sub> were used to assess the reliability of higher-frequency measurements by the TDL instruments. The assessment demonstrated that the quality of TDL N<sub>2</sub>O data was, at times, inadequate for the upcoming SOLVE mission, and that further refinements of the spectrometers and their retrieval algorithms were necessary.

ACATS-IV was again modified after the TIES mission by replacing the "old" N<sub>2</sub>O and SF<sub>6</sub> channel with a new, rapid chromatographic channel to measure CFC-12 and halon-1211 every 70 seconds. This channel was thoroughly tested in the laboratory for artifacts, flown during SOLVE test flights in December 1999 and then adopted as part of the final instrument configuration for SOLVE. The two modifications to ACATS-IV enabled 70-s measurements of N<sub>2</sub>O, SF<sub>6</sub>, CFC-12, and halon-1211, 140-s measurements of CFC-11, CFC-113, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CCl<sub>4</sub>, CH<sub>4</sub>, and H<sub>2</sub>, and improved the precision of SF<sub>6</sub> and halon-1211 measurements to about ±1% during SOLVE.

#### 5.2.2. LIGHTWEIGHT AIRBORNE CHROMATOGRAPH EXPERIMENT (LACE)

LACE is a three-channel gas chromatograph that operates on the NASA-sponsored Observations in the Middle Stratosphere (OMS) gondola and the NASA WB-57F aircraft. The OMS platform represents a collaboration with scientists from CMDL, Cooperative Institute for Research in Environmental Sciences (CIRES), NOAA Aeronomy Laboratory (AL), JPL, NASA Ames Research Center, Harvard University, and Penn State University. The WB-57F platform represents collaboration with scientists from CMDL, CIRES, AL, National Center for Atmospheric Research (NCAR), University of Denver, JPL, NASA, and California Institute of Technology.

OMS deployments at Fairbanks, Alaska, and Brazil were reported in Ray *et al.* [1999]. On May 18, 1998, CMDL participated in a midlatitude OMS balloon flight out of Fort Sumner, New Mexico, as a follow-up to the STRAT and POLARIS campaigns. After finalizing the data from this flight, the LACE instrument was modified for the Atmospheric Chemistry and Combustion Effects Near the Tropopause (ACCENT) campaign designed to investigate the effects of rocket and aircraft combustion in the upper troposphere and lower stratosphere and the SOLVE campaign designed to examine the processes controlling ozone levels at mid- to high latitudes.

A new chromatography channel was developed that proved advantageous for both campaigns. This channel measures molecular hydrogen, methane, and carbon monoxide once every

140 seconds. Carbon monoxide was included on the ACCENT mission to help identify rapid convection in the troposphere. Molecular hydrogen and carbon monoxide were included on the SOLVE campaign because of their strong mesospheric sources, and methane was included to help close the hydrogen budget [Hurst *et al.*, 1999].

The ACCENT campaign in Houston, Texas, (September 1999) utilized an unpressurized chamber in a WB-57F aircraft. Substantial thermodynamic, mechanical, and electrical modifications of the LACE instrument were required in order to participate in the ACCENT mission. LACE operated successfully on all eight ACCENT science flights, including a tropical flight, a flight over the eye of hurricane Floyd, a flight within the commercial airline flight corridor, and a rocket plume intercept. The ACCENT data were finalized and submitted to the NASA archive. Following the ACCENT campaign, LACE was reconfigured to fly on the balloon platform as part of the OMS SOLVE campaign in Kiruna, Sweden.

The SOLVE campaign began with a balloon flight well inside the northern vortex just days after the vortex had formed (November 19, 1999). Preliminary analysis of these data revealed many interesting features of atmospheric transport such as the rate of descent of air within the vortex, the degree of entrainment of midlatitude air into the vortex, and mixing characteristics within the vortex.

Tracers such as CO, H<sub>2</sub>, and SF<sub>6</sub> that have large vertical gradients in the mesosphere can also provide an estimate of the distribution of altitudes from which air originated before descending into the vortex. Estimates of the mesospheric sources and sinks for these molecules can also be made. After quantifying the mesospheric losses of SF<sub>6</sub> and CO<sub>2</sub>, limits on the corrections to the age profiles calculated from these molecules can be quantified. In addition to providing information on vortex air descent, these measurements contributed to ongoing studies of transport in the lowermost stratosphere [Ray *et al.*, 1999].

### 5.2.3. PAN AND OTHER TRACE HYDROHALO-COMPOUNDS EXPERIMENT (PANTHER)

The next step in evolution for the HATS airborne gas chromatographs is the development of the PANTHER instrument. ACATS-IV and LACE instruments use packed columns and electron capture detectors. In addition to these technologies, PANTHER will incorporate cryogenic trapping to collect larger samples, capillary columns to increase separation and signal-to-noise, and a Hewlett Packard (HP, now Agilent Technologies) model 5973 quadrupole mass selective detector (MSD). These added technologies will enable PANTHER to make in situ measurements of the CFC replacement molecules, methyl halides, peroxyacetyl nitrate (PAN, CH<sub>3</sub>C(O)OONO<sub>2</sub>), and one of PAN's precursors, acetone.

Initial activities focused on proof of concept studies. Three basic concepts (chromatography, calibration, and data acquisition) had to be addressed before design and construction of the flight instrument could begin.

The first objective was to show that adequate chromatography could be achieved. Reliable chromatography of the CFC replacements and the methyl halides has already been demonstrated within the HATS group by the flask, ocean, and in situ projects. Chromatography for PAN and acetone are new concepts for the HATS group. This year, in collaboration with NOAA Aeronomy Laboratory, PAN was successfully separated from the air peak using a 5-m, 0.53-mm inside diameter, megabore column with a 1- $\mu$ m thick RTX 200 coating, cooled to 15°C.

Output from this column was directed into the HP-G1533A anode-purged ECD and the MSD. A detection limit of better than 3 ppt was demonstrated for the ECD, and an impressive detection limit of better than 0.8 ppt was demonstrated for the MSD using the chemical ionization source, with a flow of 1 sccm CH<sub>4</sub>. Peroxypropionyl nitrate (PPN, CH<sub>3</sub>CH<sub>2</sub>C(O)-OONO<sub>2</sub>) was also detected.

A modest sensitivity to acetone was detected on the MSD; the ECD has no sensitivity to acetone. However, large (100 cm<sup>3</sup>), cryo-focused samples are needed. A 30-m, 0.25-mm inside diameter HP-5MS capillary column was used with a 0.25- $\mu$ m thick 5% PH ME siloxane film to separate acetone and many of the HCFCs from the air peak. Using an electron ionization source and running the quadrupole in single ion mode, tuned to mass/charge (*m/z*) ratios of 58 and 43, a detection limit of 1 ppt was obtained for acetone. A detection limit of 0.3 ppt for HCFC-141b at *m/z* of 81 was verified. No chromatographic interference was found when 50 ppm of O<sub>3</sub> was dynamically mixed with the inlet stream. For ease, this work was done with a liquid N<sub>2</sub> cryogen. Thermal electric coolers will be employed in the flight instrument.

Calibration of ACATS-IV and LACE systems was achieved by in situ analysis of gas mixtures stored in Aculife-treated aluminum cylinders. This method will not work for PAN because it cannot be reliably stored as a gas mixture. An in-flight PAN source will be required for calibration. The generation of PAN from a calibrated NO source dynamically diluted to the ppt level was studied. PAN was produced by photolyzing acetone at 285 nm in the presence of NO. Carbon monoxide was added to quench competing reactions.

The third proof of concept area was to resolve incompatibilities between the HP MSD instrument control, data acquisition involving Chemstation on a Windows NT operating system utilizing an HPIB bus, and the airborne HATS approach using DOS with a metabite bus. The most recent GCs built within the HATS group are the CATS GCs with QNX. Substantial development of reliable GC control and data acquisition was invested in this operating system. QNX requires a relatively small memory overhead compared to the NT operating system and is less prone to system crashes prevalent with the Windows NT environment. Both HP-IB (IEEE) and RS-485 drivers for the QNX operating system exist. Using these drivers the HP MSD runs entirely from QNX. The new smart electrometers, gas-sample valves, and the stream-selection valve were moved off of the stack built by Tommy Thompson and onto RS-232 and RS-485 serial communication lines, reducing wiring and power requirements. This should result in an instrument that is lighter, easier to work with, and more dependable.

With these three issues resolved, the design and construction phase of the project will proceed in 2000. Validation flights onboard the ER-2, WB-57F, or both will take place in 2001.

## 5.3. OCEAN PROJECTS

### Observations

The oceans play an important role in the atmospheric budgets of halogenated, organic gases, both as sources and sinks. Natural halocarbons contribute a substantial amount of chlorine and bromine to the troposphere and, in some cases, the stratosphere. Methyl bromide (CH<sub>3</sub>Br) and methyl chloride (CH<sub>3</sub>Cl) together contribute about one quarter of the total equivalent chlorine to the atmosphere [Butler, 2000]. As the production and use of the anthropogenic, halogenated gases are phased out, methyl halides, which are primarily natural in origin, will play an increasingly important role in regulating stratospheric ozone.

Other halogenated compounds, such as dibromomethane ( $\text{CH}_2\text{Br}_2$ ) and bromoform ( $\text{CHBr}_3$ ), could be important sources of bromine to the stratosphere. While these compounds are generally present at low concentrations in the atmosphere and have short lifetimes, rapid vertical transport, particularly in the tropics, could provide a mechanism by which they could participate in stratospheric ozone depletion. An understanding of the sources and sinks of these compounds is needed to predict recovery of stratospheric ozone in the event of climate change.

The HATS group participated in two research cruises during 1998-1999 with the goal of quantifying the fluxes that constitute the oceanic cycle of  $\text{CH}_3\text{Br}$ . On both cruises, conducted aboard the NOAA ship *Ronald H. Brown*, the group made saturation measurements in conjunction with  $\text{CH}_3\text{Br}$  production and degradation measurements made by other groups. The first cruise, RB-98-02, Gas Exchange Experiment (GasEx 98), focused on the North Atlantic and coastal northeastern Pacific Oceans during May-July 1998 [King *et al.*, 2000]. The cruise departed from Miami, Florida, and ended in Newport, Oregon, with port stops in Lisbon, Portugal, Ponta Delgada, Azores, and Miami, Florida (Figure 5.28). The focal point of this cruise was a month-long air-sea exchange experiment in a cold-core eddy northeast of the Azores. The second cruise, RB-99-06, Bromine Air-Sea Cruise Pacific (BACPAC 99), was conducted in the North Pacific during September-October 1999, departing from Kwajalein, Marshall Islands, and ending in Seattle, Washington, with port stops in Oahu, Hawaii, and Dutch Harbor, Alaska (Figure 5.28).

During GasEx 98  $\text{CH}_3\text{Br}$  was supersaturated in temperate waters and undersaturated in tropical and subtropical waters (Table 5.10). Supersaturation implies a net flux from the ocean to the atmosphere, while undersaturation implies the reverse. These trends were particularly evident during the third leg of the cruise from the Azores to Miami, as the saturation anomaly became more pronounced with decreasing latitude (Figure 5.29). The  $\text{CH}_3\text{Br}$  supersaturations in the temperate northeastern

Atlantic Ocean during GasEx 98 differed from previous observations [Lobert *et al.*, 1996; Groszko and Moore, 1998]. Direct comparison of springtime supersaturations ( $23 \pm 8\%$ , standard error of the mean, s.e., King *et al.* [2000]) and fall undersaturations ( $-15 \pm 4\%$ , s.e., Lobert *et al.* [1996]) in the same region of the North Atlantic ( $37\text{-}45^\circ\text{N}$ ,  $17\text{-}26^\circ\text{W}$ ) suggests that there may be a seasonal cycle in temperate North Atlantic waters. When seasonal cycling in temperate waters is incorporated into global flux calculations, estimates of the net, global, air-sea flux of  $\text{CH}_3\text{Br}$  range from  $-11$  to  $-20 \text{ Gg yr}^{-1}$  [King *et al.*, 2000]. This net  $\text{CH}_3\text{Br}$  sink is not as strong as previously reported [Lobert *et al.*, 1997], but the oceans are still estimated to provide an overall net sink for atmospheric methyl bromide.

Methyl bromide was undersaturated throughout most of the BACPAC 99 cruise with supersaturations observed primarily in coastal regions (Table 5.10, Figure 5.29c). In general  $\text{CH}_3\text{Br}$  was more undersaturated in the subtropics and closer to equilibrium in the temperate waters. The undersaturations in the temperate North Pacific during fall are consistent with the existence of a seasonal cycle in temperate waters as suggested by observations in the temperate North Atlantic. The data from BACPAC 99 showed less variability than that from GasEx 98. While the precision during BACPAC 99 was significantly better than during GasEx 98 (2.6% versus 5.8%,  $1\sigma$ ), this difference cannot completely explain the increased variability in the GasEx 98 data. It is likely that the remaining variability was a result of natural processes in the North Atlantic at that time of year.

Mean saturation anomalies for  $\text{CH}_3\text{Cl}$ , methyl iodide ( $\text{CH}_3\text{I}$ ),  $\text{CH}_2\text{Br}_2$ , and  $\text{CHBr}_3$  are provided from both GasEx 98 and BACPAC 99 on a regional basis (Table 5.10). In contrast to  $\text{CH}_3\text{Br}$ , these trace gases were generally more supersaturated in the subtropics and tropics than in the temperate waters. Higher supersaturations of these compounds in the tropics are particularly important as tropical deep convection could transport these short-lived compounds to the upper troposphere and lower stratosphere, where they could participate in stratospheric ozone depletion.

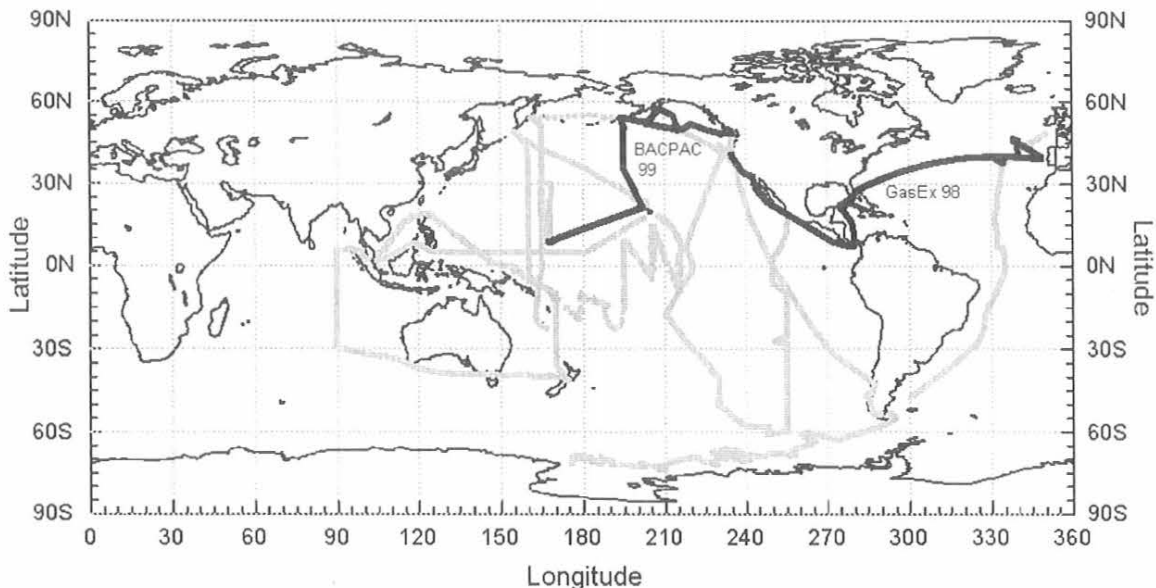


Fig. 5.28. Cruise tracks from RB-98-02 (GasEx 98) and RB-99-06 (BACPAC 99) and previous cruises (light gray) by the HATS group between 1987 and 1996.

TABLE 5.10. Average Measured Saturation Anomalies and Associated Standard Errors for Two Oceanic Regions From CMDL Cruises in 1998 (GasEx 98) and 1999 (BACPAC 99)

Compound	Saturation Anomaly (%) Spring/Summer 1998		Saturation Anomaly (%) Fall 1999	
	Subtropics/Tropics*	Temperate*	Subtropics/Tropics*	Temperate*
CH <sub>3</sub> Br	-12 ± 2	37 ± 3	-35 ± 1	-19 ± 1
CH <sub>3</sub> Cl	122 ± 3	37 ± 1	71 ± 3	2 ± 1
CH <sub>3</sub> I	5067 ± 110	3351 ± 65	2603 ± 78	1113 ± 37
CH <sub>2</sub> Br <sub>2</sub>	334 ± 75	76 ± 3	33 ± 3	37 ± 2
CHBr <sub>3</sub>	173 ± 11	69 ± 3	230 ± 17	69 ± 6

\*Subtropics and tropics are defined as the region between 0° and 30°N, and temperate regions are defined to be between 30° and 60°N.

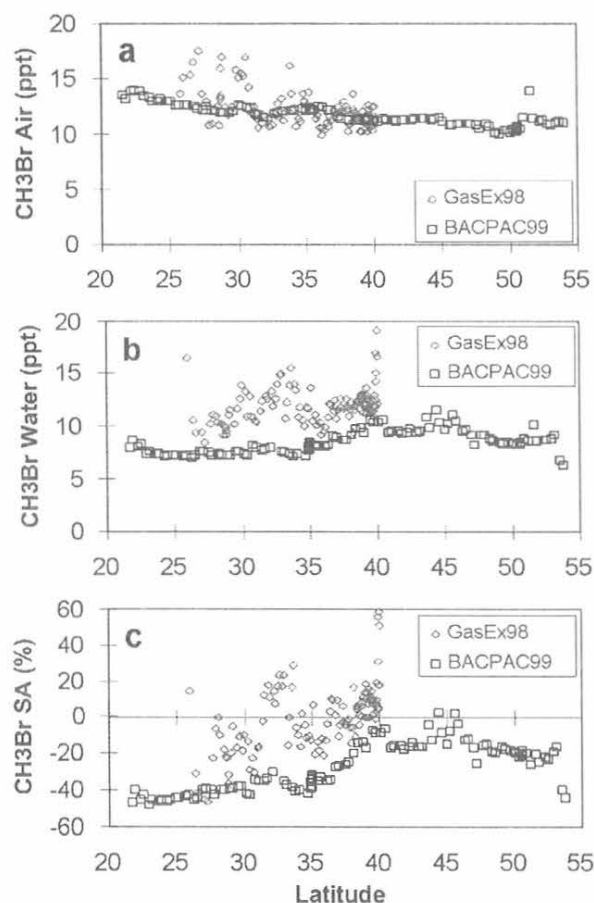


Fig. 5.29. Methyl bromide measurements in air (a) and air equilibrated with surface seawater (b). Saturation anomaly (c) is the percent difference between the partial pressure in water and air. Data from GasEx 98 are only shown from the third leg, between the Azores and Miami, Florida. Data from BACPAC 99 are only shown from the second leg, between Hawaii and Dutch Harbor, Alaska.

### Temperature Dependence

*Groszko and Moore* [1998] suggested that there is a relationship between methyl bromide concentrations in the surface water and sea surface temperature. CH<sub>3</sub>Br saturation anomalies were used from five CMDL research cruises to test this relationship for a wider range of waters (Figure 5.30a). The correlation observed from the CMDL data is similar to that reported by *Groszko and Moore* [1998] with CH<sub>3</sub>Br supersaturated in ocean waters between 11° and 21°C. Based on this relationship, sea surface temperature can account for 40-70% of the variability in CH<sub>3</sub>Br saturation anomaly on a global basis. However, only a small fraction of the observed seasonal cycle in temperate waters can be accounted for by the change in sea surface temperature [*King et al.*, 2000].

A global oceanic net flux of methyl bromide of -14 Gg yr<sup>-1</sup> can be calculated with the temperature relationship shown in Figure 5.30a and a global map of sea surface temperature, wind speed, solubility from *De Bruyn and Saltzman* [1997], and a gas exchange coefficient based on the equation from *Wanninkhof* [1992]. This estimate falls within the range predicted by other methods [*Lobert et al.*, 1997; *King et al.*, 2000]. However, it does not accurately describe the temporal and spatial distribution of dissolved CH<sub>3</sub>Br, especially in temperate waters, where widespread supersaturations are predicted year-round. Predicted supersaturations in temperate waters are not supported by data obtained from several field campaigns [*Lobert et al.*, 1995, 1996; *Groszko and Moore*, 1998], which indicates temperature is not the only variable controlling the concentration of CH<sub>3</sub>Br in surface waters.

Methyl chloride and methyl iodide have a different relationship to sea surface temperature than that of methyl bromide (Figures 5.30b and 5.30c). For both of these compounds, this relationship is best described with a linear regression. About three-quarters of the variability in the saturation anomaly of CH<sub>3</sub>Cl can be explained by the variability in sea surface temperature. For CH<sub>3</sub>I, only about one-half of the variability in the saturation anomaly can be explained by the variability in sea surface temperature. Global maps of both CH<sub>3</sub>Cl and CH<sub>3</sub>I will be created in the near future to estimate global air-sea fluxes for these compounds.

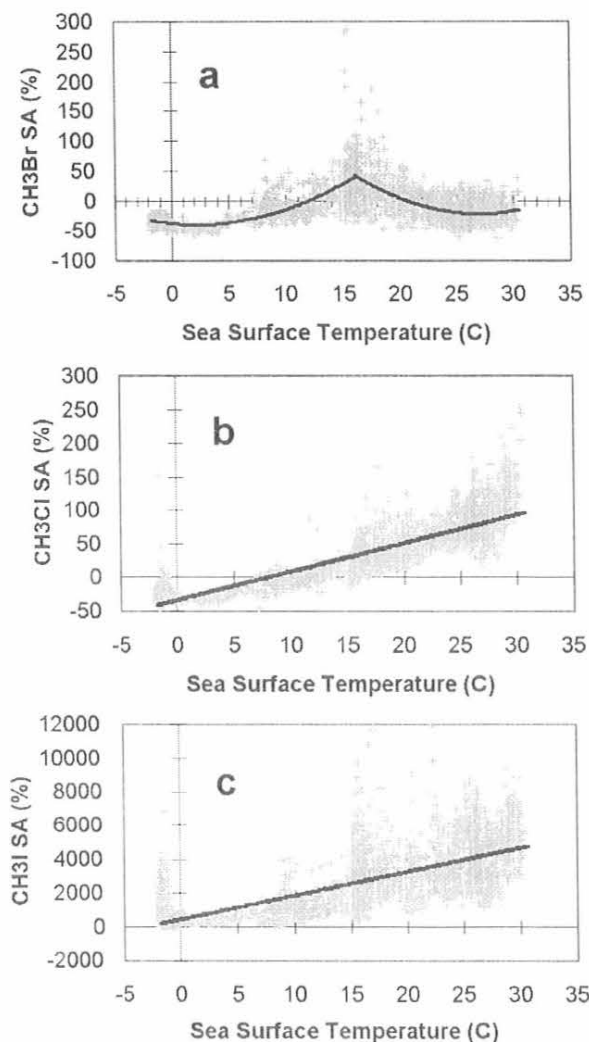


Fig. 5.30. Correlations between the saturation anomalies of the methyl halides (methyl bromide (a), methyl chloride (b), and methyl iodide (c)) and sea surface temperature based on data from five CMDL research cruises between 1994 and 1999.

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