5. Halocarbons and other Atmospheric Trace Species

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5.1. Overview

The mission of the Halocarbons and other Atmospheric Trace Species (HATS) group is to study halocarbons and other trace gases that cause chemical and radiative change in the atmosphere. The goal of HATS is to measure and interpret the distributions and trends of these species in the troposphere, stratosphere, and ocean with the best analytical instrumentation available. The species studied include nitrous oxide (N_2O); many halogenated species, such as halocarbons, fluorocarbons, perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6); organic nitrates, such as peroxyacetyl nitrate (PAN); organic sulfur gases, such as carbonyl sulfide (COS); and hydrocarbons (HCs). The halocarbons include the chlorofluorocarbons (CFCs); chlorocarbons (CCs), such as carbon tetrachloride (CCl_4), methyl chloroform (CH_3CCl_3), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), and tetrachloroethene (C_2Cl_4); the replacement CFCs hydrochlorofluorocarbons (HCFCs); hydrofluorocarbons (HFCs); methyl halides (CH_3Br, CH_3Cl, and CH_3I); bromocarbons (CH_2Br_2 and $CHBr_3$); and halons.

Three primary research areas involving these trace gases are stratospheric ozone depletion, climate forcing, and air quality. For example, the CFCs, HCFCs, halons, chlorinated solvents, and N_2O are significant ozone-depleting and greenhouse gases. The trace gas, SF_6, is a greenhouse gas with a large global warming potential and a very long lifetime (600-3500 years). It may become a significant greenhouse gas in the later part of this century. Short-lived halocarbons, PAN, and HCs play an important role in global and regional pollution. PAN is a major precursor of tropospheric ozone in the remote marine atmosphere. COS is a relatively stable sulfur molecule that contributes significantly to the background stratospheric aerosol layer, and its main sink is the same as carbon dioxide (CO_2), the strongest permanent greenhouse gas.

Research conducted by HATS in 2002 and 2003 included (1) weekly flask sampling and analysis of air from remote and continental-influenced sites including the five CMDL baseline observatories, (2) operation of gas chromatographs (GCs) for hourly, in situ measurements of trace gases at four of the five CMDL baseline observatories and at four cooperative sites, (3) preparation and maintenance of trace gas standards, (4) participation on airborne campaigns with in situ GCs on aircraft and balloon platforms, (5) investigation of oceanic processes that influence the trace gas composition of the atmosphere, and (6) measurement of many trace gases in firn air from the South Pole Observatory (SPO).

Sustained measurement programs within HATS are based upon in situ and flask measurements of the atmosphere from the five CMDL baseline observatories and ten cooperative stations (Figure 5.1). Table 5.1 lists the geographic locations and other sampling information for all the sites. There are currently 13 flask sites and 8 in situ sampling sites in the HATS atmospheric sampling network. The in situ sampling site at Ushuaia, Argentina, went offline after March 2003 because of station construction and funding cut backs. Flask samples have not been filled there because of logistical problems. Hopefully, the station will be fully operational by late spring of 2004.

The most significant result to report is the decrease of global mixing ratios of CH_3Br and total tropospheric bromine as a result of decreased emissions mandated by the Montreal Protocol [*Montzka et al.*, 2003a]. The total equivalent tropospheric chlorine (ETCl $\sim$ Cl + 45 $\times$ Br) has decreased at a faster rate than was predicted by scenarios described in the last World Meteorological Organization's (WMO) Scientific Assessment of Ozone Depletion [*WMO*, 2003]. Most major CFCs and CCl_4 are decreasing at a slow rate, while CH_3CCl_3 has decreased in the troposphere to mixing ratio levels below 25 parts per trillion (ppt, 10^{-12}). The global atmospheric growth rate of halon-1211 is still positive but is gradually slowing down, whereas the growth rate of halon-1301 is not significantly different than zero. With good precision, our in situ gas chromatographs are monitoring the increase of the CFC replacement compounds (the HCFCs) that continue to supply chlorine to the stratosphere. The slowing of the growth rate of equivalent chlorine is observed in the lower stratosphere (where most of the ozone depletion occurs) by our airborne projects.

Future plans include participation in the TRans-siberian Observations Into the Chemistry of the Atmosphere (TROICA-8) in March 2004 (see track in Figure 5.1). The Max Planck Institute (MPI) in Mainz, Germany, and the Institute of Atmospheric Physics in Moscow, Russia, [*Crutzen et al.*, 1998] created the TROICA expedition plan. HATS participation with an automated airborne GC (ACATS-IV) is a continuation of our measurements of 11 source gases in the summer of 2001 [*Hurst et al.*, 2004]. This expedition will involve the collection of over 220 flask samples for the more unusual gases, including the carbon isotopes, HFCs, HCFCs, CFCs, halogenated solvents, and HCs with the cooperation of the National Center for Atmospheric Research (NCAR), University of Miami, MPI, and the CMDL Carbon Cycle Greenhouse Gases (CCGG) group.

5.2. Flask Sample Programs

5.2.1. Overview

CMDL's halocarbon flask sampling network of 13 globally distributed sites continued to function successfully allowing the routine, weekly or biweekly analysis of samples for over 25 gases and providing the basis for analyses of worldwide trends of a comprehensive suite of greenhouse, ozone-depleting gases, and air quality (Figure 5.1, Table 5.1). Of the two stations added to the sampling network in 2001, Trinidad Head, California (THD), the new CMDL Baseline Observatory, has become an integral part of the halocarbon flask network providing reliable data from a
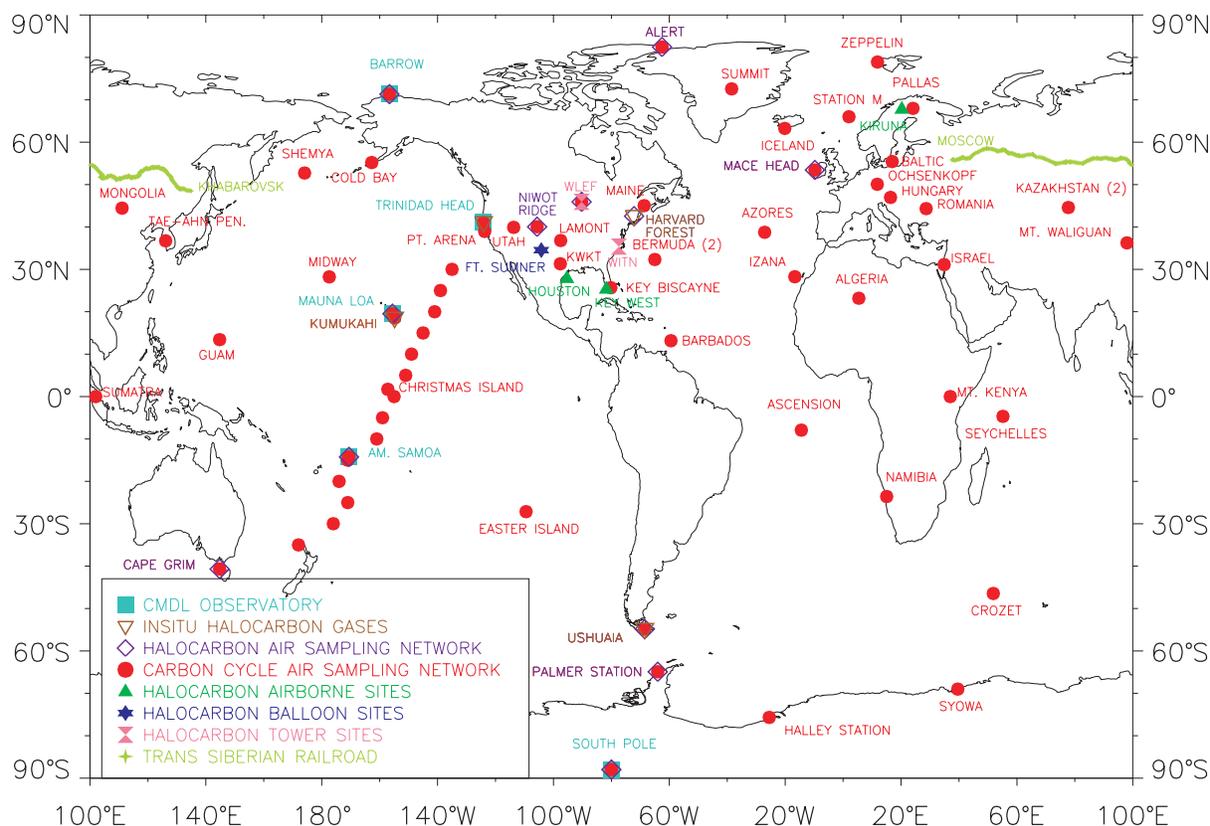
Figure 5.1. Geographic locations of stations in the CMDL/HATS flask and in situ networks. Airborne (aircraft and balloon) sampling locations and the route of the TRans-Siberian Observations Into the Chemistry of the Atmosphere (TROICA) Experiment in 2001 and planned for March 2004.

Table 5.1. Geographic and Network Information for HATS Network Sites

Code	Station	Latitude	Longitude	Elevation (m)	LST-GMT (h)	Type
ALT	Alert, Northwest Territories, Canada (AES)	82.45°N	62.52°W	210	-4	F
BRW	Point Barrow, Alaska, USA	71.32°N	156.60°W	11	-9	F, I
MHD	Mace Head, Ireland (University College)	53.33°N	9.90°W	15	0	F
LEF	WLEF tower, Wisconsin (CMDL-CCGG), USA	45.95°N	90.28°W	470	-6	F, I
HFM	Harvard Forest, Massachusetts (Harvard University), USA	42.54°N	72.18°W	340	-5	F, I
THD	Trinidad Head, California (Humboldt State University), USA	41.05°N	124.15°W	107	-8	F
NWR	Niwot Ridge, Colorado (University of Colorado), USA	40.05°N	105.59°W	3472	-7	F, I
ITN∗	WITN tower, North Carolina (CMDL-CCGG), USA	35.37°N	77.39°W	9	-5	F, I
MLO	Mauna Loa, Hawaii (WMO GAW station), USA	19.54°N	155.58°W	3397	-10	F, I
KUM	Cape Kumukahi, Hawaii, USA	19.52°N	154.82°W	3	-10	F
SMO	Tutuila, American Samoa	14.23°S	170.56°W	77	-11	F, I
CGO	Cape Grim, Tasmania, Australia†	40.68°S	144.68°E	94	+10	F
TDF	Ushuaia, Argentina (WMO GAW station)‡	54.85°S	68.31°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:

∗ITN site's flask and in situ GC instrument closed down on June 12, 1999.

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

‡Data from October 2001 to March 2003 (see text).

§Only glass flasks used.

midlatitude, Northern Hemisphere (NH) site under marine influence. CMDL accelerated the sampling rate at this location during the Intercontinental Transport and Chemical Transformation 2002 (ITCT 2K2) study, conducted in the spring of 2002, to provide support for a large-scale, multinational effort to detect the influence of Asian air on North America. Unfortunately, CMDL had difficulty in obtaining flask samples of air from Ushuaia, Tierra Del Fuego, Argentina (TDF) in the far Southern Hemisphere (SH), the other site added in 2001. This is a cooperative site with the Argentine government and is a Global Atmospheric Watch (GAW) station sponsored by the WMO. Sampling at Mace Head, Ireland (MHD), which was suspended for almost a year in 2000, was reinstituted biweekly near the end of 2001 and has since generated a reliable record of measurements. Efforts to improve sampling frequency and precision at all sites continued throughout 2002-2003.

Flasks brought into the laboratory are analyzed on two to three instruments, depending upon the species being examined (Table 5.2). A gas chromatograph with electron capture detection (GC-ECD) or a gas chromatograph with mass spectrometric detection (GC-MSD) is used to perform analyses. Although all 300-ml flasks have been retired, 850-ml flasks still remain that contain a marginal amount of air for all of these low-level analyses. Most flask analyses are of network samples with the remainder from research cruises, firn air sampling, and other special projects. One hundred new electro-polished, stainless steel flasks were recently purchased from LabCommerce, Inc., to supply the new sites, to upgrade flask quality and quantity at old sites, and to use for special projects.

In 1996 and 1997 an average of nearly 350 flasks from the network were filled each year and delivered to the Boulder laboratory for analysis. This number has increased each year, reaching a total of 578 in 2003 (Figure 5.2). This increase is the result of added sites and a more efficient turnaround of flasks between Boulder and the field sites. The improved turnaround of flasks was accomplished through better record keeping, additional flasks, and automated analysis. Sampling success has steadily improved since 1996 at all sites (Table 5.3). This was mainly the result of small leak repairs and valve replacements on

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

flasks where necessary. These repairs greatly improved the agreement in flask pressure between simultaneously sampled flasks (Figure 5.3).

5.2.2. GC-ECD RESULTS

The global atmospheric growth rate of CFC-12 (CCl_2F_2) from flask samples (Figure 5.4) for 2002-2003 was virtually zero (0.10 ± 0.09 ppt yr^{-1}), although the in situ analyses suggest that the CFC-12 concentrations in the atmosphere have begun to decline. Mixing ratios of CFC-11 (CCl_3F) continued to decrease between 2002 and 2003 (Figure 5.5); the linear global growth rate for CFC-11 during this period was -2.6 ± 0.1 ppt yr^{-1}. A new ECD was installed on the N_2O and SF_6

Table 5.2. Instrumentation for HATS Flask Analyses

Instrument	Type	Gases	Frequency of Network Data
OTTO	GC-ECD (three-channel, isothermal)	N_2O, CFCs (3), CCs (2), SF_6	Weekly
LEAPS	GC-ECD (one-channel, temperature–programmed)	Halons (2), CH_3Cl, CH_3Br, $CHCl_3$	Semimonthly to monthly
HCFC-MS	GC-MSD (one-channel, temperature-programmed)	HCFCs (4), HFCs (2), CFCs (3), halons (1), CCs (6), BrCs (3), COS, benzene	Semimonthly

OTTO, not an acronym; Low Electron Attachment Potential Species (LEAPS); bromocarbons (BrCs).

Table 5.3. Percentage Sampling Success for Flasks Filled at CMDL Observatories and Cooperative Sampling Sites

Site	1996	1997	1998	1999	2000	2001	2002
BRW	92%	94%	88%	87%	90%	90%	77%
MLO	98%	83%	90%	96%	94%	83%	98%
SMO	71%	67%	73%	88%	88%	83%	94%
SPO	92%	73%	77%	88%	81%	92%	92%
ALT	73%	48%	67%	67%	65%	88%	94%
NWR	94%	92%	87%	77%	88%	85%	77%
CGO	77%	69%	85%	87%	85%	71%	83%
LEF	12%	35%	69%	92%	108%*	150%*	173%*
HFM	54%	62%	73%	69%	88%	96%	108%*
KUM	62%	54%	69%	69%	83%	94%	90%
PSA	—	08%	100%	88%	104%*	81%	96%
MHD†	—	—	15%	31%	—	27%	50%
ITN‡	81%	62%	62%	38%	—	—	—

Sampling success is defined as the fraction of flasks analyzed relative to the number expected (i.e., one pair per week).

*Sampling more than required, e.g., the biweekly site LEF is sometimes sampled weekly.

†Sampling was discontinued temporarily in 2000 due to loss of flasks in shipments.

‡Site was discontinued indefinitely in 1999.
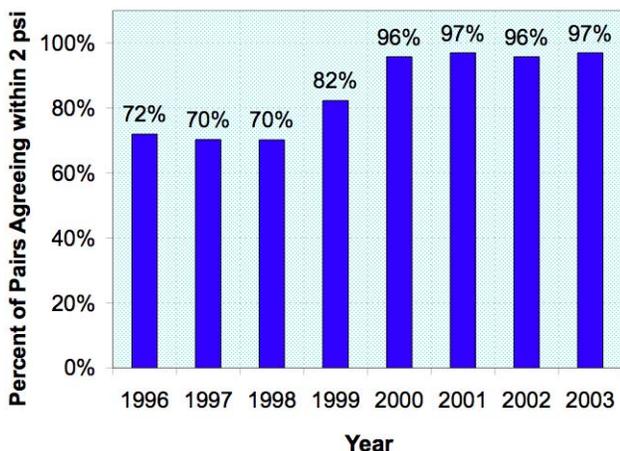
Figure 5.3. Percentage of flask pairs agreeing within 2 psi in total pressure upon arrival in Boulder.
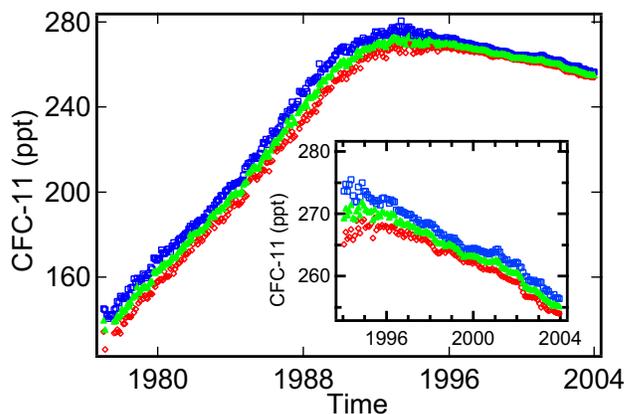
Figure 5.5. Historical and recent (inset) measurements of CFC-11 flask measurements in the atmosphere showing a steady loss rate since 1997 (GC-ECD monthly means; northern hemispheric means (blue squares), global means (green triangles), and southern hemispheric means (red diamonds)).
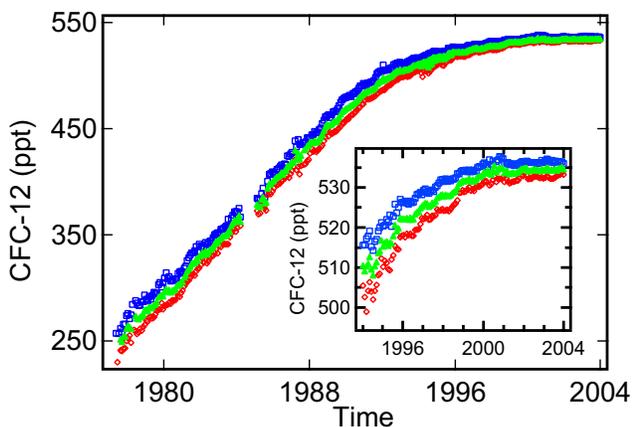
Figure 5.4. Historical and recent (inset) measurements of CFC-12 in the atmosphere. Measurements are monthly averages of GC-ECD data; northern hemispheric means (blue squares), global means (green triangles), and southern hemispheric means (red diamonds). Data for the first 6 months of 1994 and 2000 were replaced by measurements from flasks using the GC-MSD system because of problems with the GC-ECD system. RITS data are used for 1992-1993 because of a drifting flask standard.
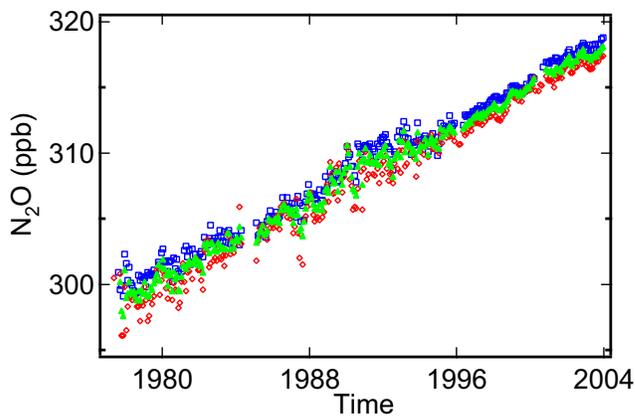
Figure 5.6. Atmospheric history of N_2O since 1977 from flask measurements (GC-ECD monthly means; northern hemispheric means (blue squares), global means (green triangles), and southern hemispheric means (red diamonds)). A new GC-ECD instrument has been used since 1994 with a new detector added in 2003.

channel of the flask GC in 2003. The atmospheric growth rate of N_2O from the flask data during 2002-2003 was 0.37 ± 0.10 parts per billion (ppb, 10^{-9}) yr^{-1} (Figure 5.6). This rate, calculated over a shorter time span, is lower than the mean 1997-2004 global atmospheric growth rate of 0.81 ± 0.01 ppb yr^{-1}. The mean global atmospheric growth rate for SF_6 for 2002-2003 was 0.237 ± 0.005 ppt yr^{-1} (Figure 5.7). This is significantly higher than 0.201 ± 0.002 ppt yr^{-1} during the previous 4-year period (1998-2001).

5.2.3. GC-MSD ANALYSIS OF FLASKS

Measurements of CFC alternatives and other trace gases continued during 2002-2003 from flasks collected at 13 locations. In both years, three samples per month, on average, were filled and analyzed on GC-MSD instrumentation from these sites. During this period flasks were sampled for the first time at THD and more regular sampling was achieved at MHD.
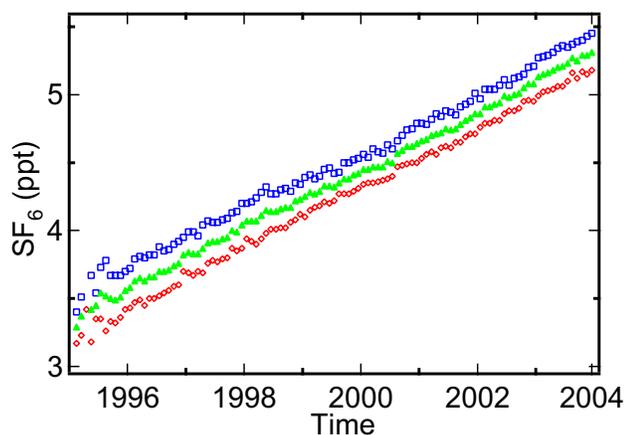
Figure 5.7. Recent history of atmospheric SF_6 from CMDL HATS flask measurements (GC-ECD monthly means; northern hemispheric means (blue squares), global means (green triangles), and southern hemispheric means (red diamonds)).

Tropospheric mixing ratios of HCFCs and HFCs continued to increase during 2002-2003 (Table 5.4, Figure 5.8). Although the rate of increase of HCFC-22 ($CHClF_2$) remained fairly constant at 5.1 ppt yr^{-1} since 1992, the rates of increase for HCFC-141b CCl_2FCH_3) and HCFC-142b ($CClF_2CH_3$) slowed significantly during 2002-2003. The growth rate of HFC-134a (CF_3CH_2F) continues to become larger each year; the mean linear rate of increase during 2002-2003 was 4.3 ppt yr^{-1}. Some discussion of these updated CMDL measurement data and results from another sampling network appeared in the work of *O'Doherty et al.* [2004]. CMDL flask network measurements were also incorporated into an analysis of the stratospheric chlorine budget and halocarbon degradation rates in the stratosphere [*Schauffler et al.*, 2003].

In late 2003 minor instrument changes allowed for improved measurements of CFC-12 and better integration of the entire peak of COS.

Figure 5.8. Atmospheric dry mole fractions (ppt) of selected HCFCs and HFC-134a measured by GC-MSD in the CMDL flask program. Each point represents a monthly mean at one of 8-10 stations: ALT, BRW, NWR, red; KUM, MLO, green; SMO, CGO, PSA, SPO, blue. Also plotted are results from analysis of archived air samples (open red circles) filled at NWR and in past cruises from both hemispheres. Results from PSA (light blue circles) are from glass flasks; no measurements of HCFC-141b are included from this site since the glass flask stopcock seals are contaminated with this gas.

Table 5.4. Global Mixing Ratios (MR) and Rate of Change for Selected Trace Gases Measured in the CMDL Flask Sampling Network

Compound	Mean 2001 MR, ppt	Mean 2002 MR, ppt	Mean 2003 MR, ppt	Growth Rate ppt yr^{-1}
HCFC-22	147.5	153.1	158.1	5.1 (1992-2003)*
HCFC-141b	14.1	15.5	16.5	1.2 (2002-2003)*
HCFC-142b	12.6	13.4	14.0	0.7 (2002-2003)*
HFC-134a	17.4	21.3	25.5	4.3 (2002-2003)*
Halon-1211	4.04	4.09	4.13	0.04 (2002-2003)†
CH_3Br	8.3	8.1	8.0	-0.07 (2002-2003)†
CH_3CCl_3	38.0	31.7	26.5	-5.2 (2002-2003)†
CFC-113	81.7	81.2	80.5	-0.67 (2002-2003)†

Quantities are estimated from latitudinally weighted flask measurements on GC-MSD instrumentation at seven to ten remote CMDL stations.

*Mean linear growth rate estimates over the period indicated.

†Growth estimated from a difference between annual means (2003 minus 2002).

5.2.4. TRENDS IN CHLORINATED GASES AND TOTAL CHLORINE FROM FLASK AND IN SITU ECD INSTRUMENTS

Total tropospheric chlorine from ozone-depleting gases (for which the Montreal Protocol restricts production) decreased at a mean rate of 21 ppt yr^{-1} during 2002 to 2003. This represents a slowdown in the decline of atmospheric chlorine observed since

the early 1990s; the maximum decline of ~35 ppt yr^{-1} was observed during 1997-1998. Diminished mixing ratios of CH$_3$CCl$_3$ are the main reason for the slowdown in this decline. Although atmospheric CH$_3$CCl$_3$ continues to decrease with an exponential decay time constant of ~5.5 years in the global troposphere, during 2002-2003 this corresponded to an absolute rate of decrease of only 5 ppt yr^{-1} (compared to nearly three times this in the late 1990s, Table 5.4).

Despite the lessening influence of CH$_3$CCl$_3$ on the decline in total Cl, chlorine from some of the most abundant CFCs (CFC-11 and CFC-113) declined at nearly 10 ppt Cl yr^{-1} during 2002-2003. Global mixing ratios of CFC-12, however, were essentially constant over this period.

By mid-2003, chlorine from the three most abundant HCFCs amounted to 205 ppt, or 7.4% of all chlorine carried by long-lived, purely anthropogenic halocarbons. Total chlorine from the HCFCs increased at 8 ppt yr^{-1} during 2002-2003, which is slightly slower than the mean rate of increase of 9.3 ppt yr^{-1} observed since 1992.

Methyl chloride (CH$_3$Cl) is a gas with little industrial production; its atmospheric mixing ratios are maintained predominantly by natural sources. As a result, the Montreal Protocol does not restrict industrial production of this gas. However, CH$_3$Cl is one of the most abundant chlorine-containing gas in the remote atmosphere and trends for this gas could affect the decline in atmospheric chlorine. Long-term changes in atmospheric CH$_3$Cl mixing ratios were inferred with CMDL measurements of CH$_3$Cl in firn air and the University of California at Irvine's measurements of CH$_3$Cl in air bubbles trapped in ice [*Aydin et al.*, 2004]. The results suggest a cyclic variation in past mixing ratios for this gas. More recently, CMDL flask measurements have shown no systematic trend for CH$_3$Cl since 1995 (Figure 5.9). However, significant interannual variability was observed for CH$_3$Cl with enhanced mixing ratios during 1998 and 2003.

For the shorter-lived and lesser abundant chlorinated gases (CH$_2$Cl$_2$, CHCl$_3$, and C$_2$Cl$_4$), large seasonal changes are observed. Significant and sustained interannual declines continue for C$_2$Cl$_4$ (Figure 5.9).

5.2.5. TRENDS IN BROMINATED GASES AND TOTAL BROMINE FROM FLASK MEASUREMENTS

The sum of Br from the most abundant halons and methyl bromide (CH$_3$Br) peaked in 1998 and declined through 2002 in the troposphere at a mean rate of –0.25 ± 0.09 ppt yr^{-1} (Figure 5.10) [*Montzka et al.*, 2003a]. This decline is driven entirely by the decreases observed for CH$_3$Br. The results suggest that the total amount of Br entering the stratosphere reached a plateau in 1998 and has since decreased. In 2002 tropospheric Br from CH$_3$Br, halon-1211, and halon-1301 was about 5% (or 0.8 ± 0.2 ppt) below the amounts measured in 1998-1999.

Measurements from the CMDL flask network show global mean mixing ratios of CH$_3$Br at Earth's surface declined steadily from 1998-2002 (Figure 5.11) [*Montzka et al.*, 2003a]. The global mean of 8.1 ± 0.1 ppt estimated from measurements at ten sites during 2002 was about 1.2 ± 0.3 ppt (or about 10%) lower than the mean during 1995-1997. The global mean rate of change from
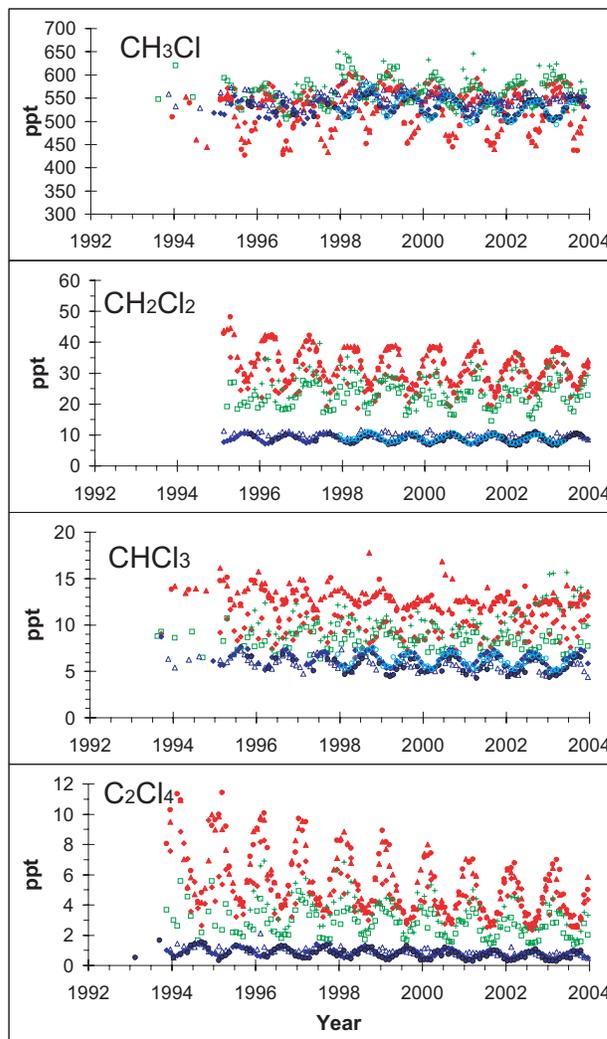
Figure 5.9. Atmospheric dry mole fractions (ppt) of selected chlorinated gases measured by GC-MSD in the CMDL flask program. Each point represents a monthly mean at one of 8-10 stations: ALT, BRW, NWR, red; KUM, MLO, green; SMO, CGO, PSA, SPO, blue. Results from PSA (light blue circles) are from glass flasks; no measurements of C$_2$Cl$_4$ are included from this site because stopcock seals on glass flasks appear to be contaminated with this gas.

mid-1999 to mid-2002 was –0.35 ± 0.05 ppt yr^{-1}, which is a sharp contrast to the continuous increases reported for atmospheric CH$_3$Br throughout most of the 20th century [*Khalil et al.*, 1993; *Miller*, 1998; *Butler et al.*, 1999; *Sturges et al.*, 2001]. The observed decrease is substantially faster and larger than expected based upon reported declines in industrial production.

Methyl bromide mixing ratios have not declined similarly at all sites across the globe; overall declines at NH surface sites ranged from 1.5 to 1.9 ppt during 1995-2002 or about two times larger than the concurrent changes observed in the SH. As a result, the hemispheric ratio (north/south) as estimated from CMDL surface sites, decreased from a value of 1.30 ± 0.03 during 1995-1997 to 1.23 ± 0.03 in 2002. The declines observed at Arctic and midlatitude sites since 1999 are similar to those observed by

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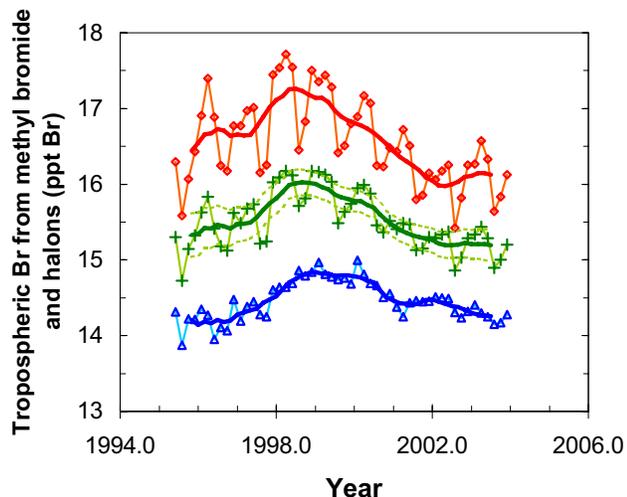
Figure 5.10. Mean tropospheric organic Br from CMDL flask measurements of CH₃Br and the most abundant halons for the hemispheres (open red diamonds=NH, open blue triangles=SH) and mean global troposphere (green plus symbols). Thin lines connect bimonthly means; thick lines are 12-month running means. To better approximate tropospheric means from surface measurements, tropospheric vertical gradients of 0-15% for CH₃Br [*Schauffler et al.,* 1999] were accounted for by multiplying measured surface mixing ratios by 0.93; no correction was applied to halon measurements. In this figure mixing ratios of halon-2402 were assumed constant after 1997 [*Fraser et al.,* 1999]. Trend uncertainty is shown only on the smoothed global results.

Yokouchi et al. [2002] at Alert, Canada (82°N), and above Sagami Bay (35°N) from aircraft at 4000-7000 m.

During 2003 the steady decline observed for CH₃Br during the preceding 4 years slowed down (Figure 5.11). The global mean surface mixing ratio in 2003 was only 0.05 ppt lower than that measured in 2002. This slowdown was driven predominantly by changes in the NH, where mixing ratios in 2003 were 0.06 ppt larger than in 2002. In the SH, however, mixing ratios continued to decrease in 2003 at a rate similar to that observed during 1998-2002. If countries continue to adhere to the Montreal Protocol, enhanced emission of CH₃Br from industrial production and use is not expected in 2003; however, global production figures for 2003 are not yet available. The slower decline in 2003 may reflect enhanced nonindustrial sources such as biomass burning or reduced losses during this year. A similar temporary increase was observed from 1997 to 1998, perhaps because of the enhanced burning (a source of CH₃Br) during that unusually warm El Niño year.

Mixing ratios of halon-1211 (CBrClF₂) and halon-1301 (CBrF₃) increased less rapidly in 2002-2003 than in earlier years (Figure 5.12). The mean global rate of halon-1301 for 2002 to 2003 is not significantly different than zero. From mid-1999 to mid-2002 atmospheric Br from the sum of these halons increased at a mean rate of 0.1 ppt Br yr⁻¹. Most of this growth comes from increases in halon-1211. This is a slower rate than was observed in the mid-1990s when Br from these gases increased at between 0.2 and 0.3 ppt yr⁻¹. The mean rate of increase for halon-1211 during 2002-2003 was 0.04 ppt yr⁻¹ (Table 5.4).
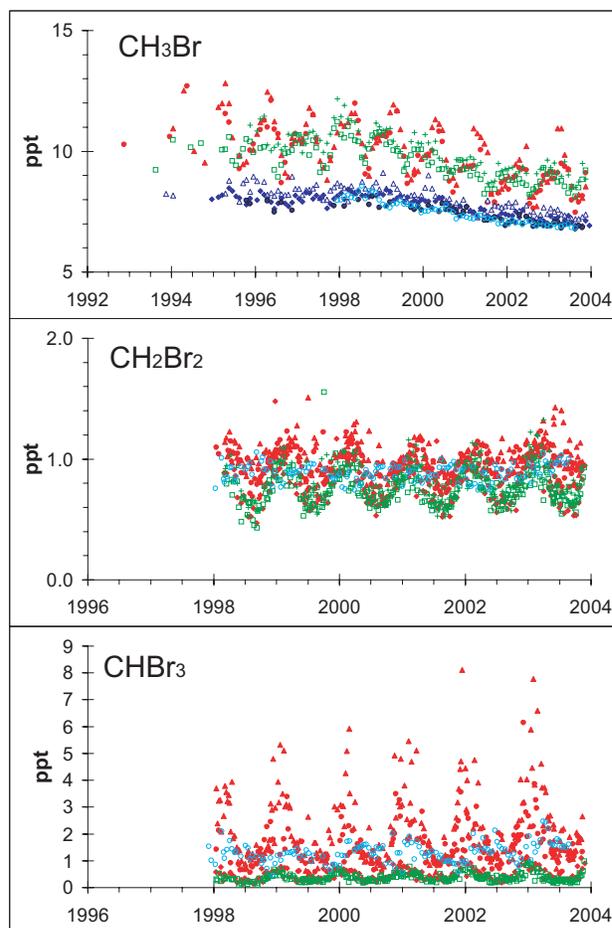
Figure 5.11. Atmospheric dry mole fractions (ppt) of selected brominated gases measured by GC-MSD in the CMDL flask program. For methyl bromide (CH₃Br), each point represents a monthly mean at one of 8-10 stations: ALT, BRW, red; KUM, MLO, green; SMO, CGO, PSA, SPO, blue. For CH₂Br₂ and CHBr₃ each point represents the mean of two simultaneously filled flasks from selected stations (symbols the same as in panel for CH₃Br).

Halon scenarios from past WMO Scientific Assessments of Ozone Depletion reports are roughly consistent with currently observed mixing ratios and trends (Figure 5.12), although large uncertainties regarding the size of stocks that have not been emitted and the lifetime of halon-1211 make accurate projections difficult [*Madronich et al.,* 1999; *Montzka et al.,* 2003b]. Despite this, the projections, and the fact that halon production in both developed and developing countries is now limited [*WMO,* 2003], suggest that accumulation rates for halons will continue to decrease in the coming years.

Short-lived gases with mostly natural sources, such as CHBr₃ and CH₂Br₂, can be transported rapidly to the stratosphere and contribute to ozone-depleting Br [*Schauffler et al.,* 1999; *Pfeilsticker et al.,* 2000]. Some Br (0-6 ppt) may also reach the stratosphere as inorganic Br from the oxidation of short-lived gases as they are transported through the troposphere [*Pfeilsticker et al.,* 2000; *Ko et al.,* 2003]. Although atmospheric
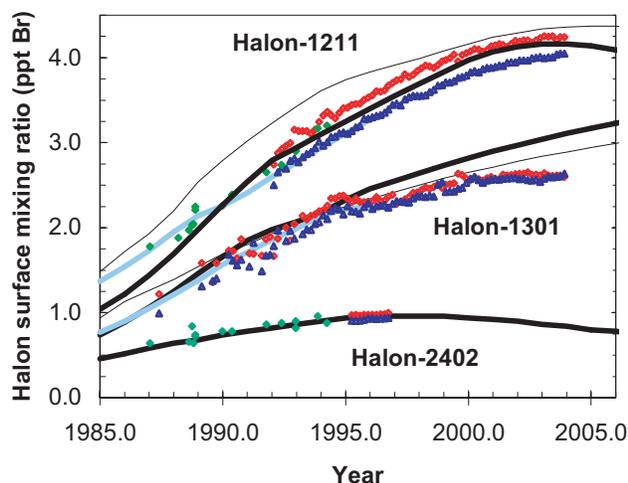
Figure 5.12. Measured hemispheric mixing ratios (NH in red, SH in blue) of the most abundant halons at Earth's surface (as ppt Br; points are bimonthly means unless from archive samples and ocean cruises in green) compared to results from WMO scenarios (thin black lines are from the work of *Madronich et al.* [1999]; thick black lines are from the work of *Montzka et al.* [2003b]. Thick light blue lines are the global history inferred from firn samples [*Butler et al.*, 1999].

Br from these gases may be variable on interannual time scales, Antarctica firn air data suggest minimal long-term changes throughout the second half of the 20th century [*Sturges et al.*, 2001]. Measurements from flasks collected as part of the CMDL flask network suggest no substantial trends since 1998 (Figure 5.11). These measurements are currently referenced to new standards prepared in 2002-2003 at CMDL.

5.2.6. TRENDS IN EQUIVALENT CHLORINE

Ground based measurements provide an indication of the burden and trend of individual ozone-depleting gases. The sum of chlorine and bromine atoms in long-lived trace gases provides an estimate of the ozone-depleting power of atmospheric halocarbons after the enhanced efficiency of bromine to destroy ozone compared to chlorine is included (a factor of 45 is used here [*Daniel et al.,* 1999]). This sum is often expressed as equivalent tropospheric chlorine (ETCl). Until CMDL's recent trends of CH_3Br became published [*Montzka et al.,* 2003a], assessments of changes in ETCl included the assumption that mixing ratios of this gas were constant over time. Declines in ETCl for ozone-depleting gases other than CH_3Br, for which production was restricted under the Montreal Protocol, were estimated at between 0.5 and 1.0% yr^{-1} since 1995 [*Montzka et al.,* 1999; *Hall et al.,* 2002]. The observed decline in CH_3Br, however, substantially affects our understanding of changes in ETCl during recent years. Considering that Br is about 45 times more efficient at depleting stratospheric ozone than Cl on average, the observed rate of change in tropospheric organic Br during 1998-2002 corresponds to a decline of about 11 ppt yr^{-1} in Cl equivalents, or about half as large as the mean decline observed for Cl contained in long-lived chlorinated gases during this period. An updated calculation of tropospheric equivalent chlorine (ECl = Cl + Br × 45), which includes CMDL global measurements of CH_3Br, shows an overall decline in ETCl by

2002 that is 25-30% larger than when constant CH_3Br mixing ratios are assumed (Figure 5.13). Although mixing ratios of CH_3Cl vary substantially from year to year, they appear not to have substantially influenced trends in ETCl in recent years (Figure 5.13).

5.2.7. ANALYSIS OF CALIBRATION TANKS ON THE FLASK GC-MSD

Secondary standards are regularly calibrated for selected gases by the flask GC-MSD for use by Chromatograph for Atmospheric Trace Species (CATS) instruments at remote sites. In/out values for HCFC-22, HCFC-142b, H-1211, and COS were quite consistent in these analyses (Table 5.5). Results for methyl halides are less consistent because decreases in CH_3Br and increases in CH_3Cl are often observed in Aculife-treated aluminum tanks. For these gases the GC-MSD calibration provides an estimate of drift during use of the secondary standard.

5.2.8. ANALYSIS OF FIRN AIR

During 2002-2003 air was routinely sampled through tubes permanently inserted into the upper 15 m of the snow pack at South Pole. These data are used to better understand how gases become incorporated into the snow. Enhancements for gases such as CH_3Br and COS were observed in the uppermost firn air as the sun rises at South Pole, and the implications of these enhancements for interpreting trace gas atmospheric histories from firn air measurements and ice core measurements are being studied.
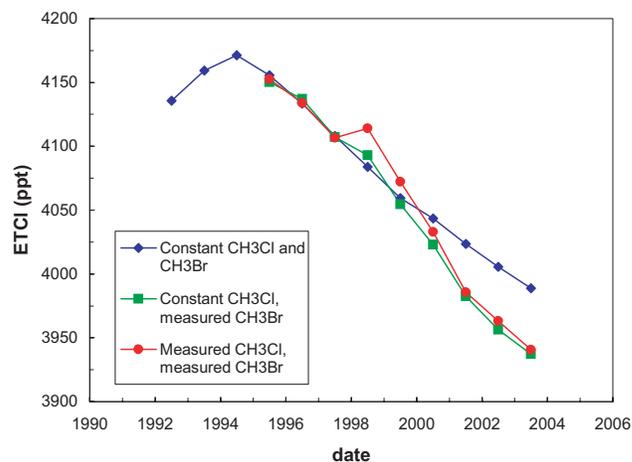
Figure 5.13. Changes in the global tropospheric burden of both brominated and chlorinated ozone-depleting gases in recent years expressed as equivalent tropospheric chlorine (where ETCl= Cl + 45× Br). Data for Cl included in this calculation are updates to measurements described previously [*Montzka et al.*, 1996, 1999] of CFC–11, –12, and –113; methyl chloroform; carbon tetrachloride; and HCFC–22, –141b, and –142b. ETCl is calculated by considering measured tropospheric mixing ratios of these gases plus those of halon-1211 and halon-1301, and either (1) constant mixing ratios for CH_3Br and CH_3Cl (mixing ratios were scaled by the measured global mean for these gases over 1995-1997), or (2) constant CH_3Cl and measured changes in CH_3Br, or (3) measured changes in both CH_3Br and CH_3Cl.

Table 5.5. Initial Versus Final Mixing Ratios Assigned to Secondary Standards Used by In Situ Instrumentation (CATS) at Remote Sites from Flask GC-MSD Analyses

| | Initial/Final Result Ratio* | | | No. of Tanks |
Compound	Median	Average	Std. Dev.	Analyzed
HCFC-22	0.999	0.998	0.009	49
HCFC-142b	1.001	1.003	0.022	49
Halon-1211	1.001	1.004	0.015	47
COS	1.001	1.025	0.20	20
COS†	1.001	1.001	0.05	18

*Mean elapsed time between initial and final analysis was 2.2 years.

†Results from two tanks that showed exceptionally large losses of a number of gases, including COS, were removed.

5.3. IN SITU GAS CHROMATOGRAPH PROGRAM

5.3.1. CATS PROGRAM

Introduction

The HATS in situ program has been active since 1986 when the first Radiatively Important Trace Species (RITS) GC was installed at the American Samoa Observatory (SMO). The RITS program was expanded to the three other CMDL baseline observatories and the Niwot Ridge (NWR) cooperative site. As the RITS systems aged CATS was developed and replaced the RITS GCs by October 2000 [*Hall et al.,* 2002]. Both the RITS and CATS instruments measure CFC-11, CFC-12, CH_3CCl_3, CCl_4, and N_2O. Other trace gases measured by CATS instruments include COS and the halogenated species: CFC-113, $CHCl_3$, H-1211, SF_6, HCFC-22, HCFC-142b, CH_3Cl, and CH_3Br.

The CATS and RITS instruments sample air once an hour for a total of nearly 750 samples per month per site. Monthly means of the in situ data are used to generate Figures 5.14-5.20. For molecules measured by both instruments, a weighted average is used during the overlapping period that ranged from 8 to 34 months depending on the station. Hemispheric means are calculated by using a latitudinal weighted average of each station in a hemisphere. The global mean is the average of both hemispheres. Growth rates are 12-month differences. For example, the growth rate for February 2002 is February 2002 minus February 2001.

Chlorine-Containing Compounds

All major CFCs are now in decline. The most abundant chlorine containing compound, CFC-12, reached sustained negative growth beginning in October 2002 (Figures 5.14 and 5.15). CFC-12's average annual global growth rate for 2002-2003 is 0.0 ± 0.4 ppt yr^{-1}. The maximum global mixing ratio for CFC-12 was 536.4 ± 0.7 ppt in January 2002. The 2002-2003 growth rate for CFC-11 is -2.0 ± 0.2 ppt yr^{-1} and CFC-113 is -0.7 ± 0.1 ppt yr^{-1}. The CFCs are the major source of chlorine to the stratosphere; in 2003 they accounted for 63% of the total chlorine burden (Figure 5.16).

Chlorinated solvents continue to decrease. Methyl chloroform's growth rate for 2002-2003 is -6.0 ± 0.7 ppt yr^{-1} and the CCl_4 growth rate is -1.0 ± 0.2 ppt yr^{-1}. Once a major source of chlorine to the stratosphere, CH_3CCl_3's chlorine burden is now less than
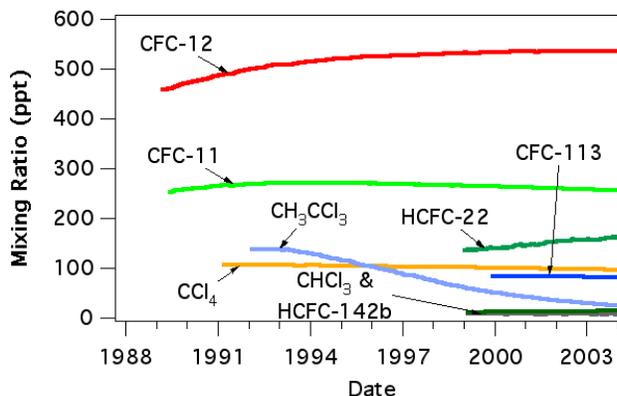
Figure 5.14. Global monthly means of chlorine containing compounds measured by the in situ program. CFC-12 and CFC-11 are two of the major components to the total chlorine budget. Quality CATS HCFC data started in 2000.
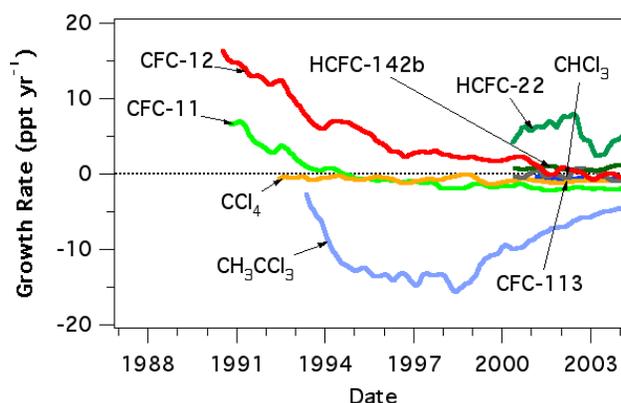
Figure 5.15. Global growth rates of chlorine containing compounds measured by the in situ program. CFC-12 recently reached sustained negative growth.
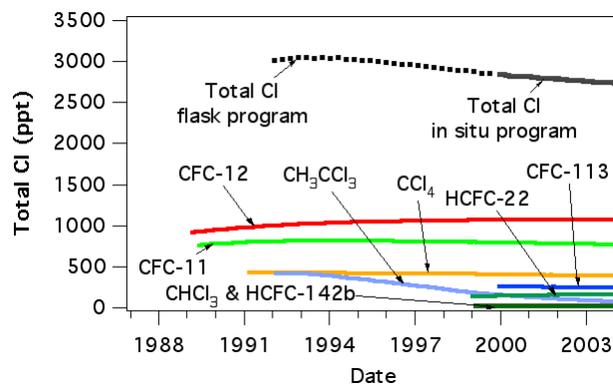
Figure 5.16. Estimate of the total chlorine burden. For individual compounds total chlorine is calculated as the product of the mixing ratio and the number of chlorine atoms in the molecule. Total chlorine is the sum of these products plus an estimate of CH_3Cl at a constant level of 550 ppt.

the major CFCs and HCFC-22. These two solvents make up about 14% of the total chlorine burden in 2003.

As the atmospheric mixing ratios of CFCs and chlorinated solvents decline, the CFC replacement compounds, HCFCs, are contributing relatively more chlorine to the global chlorine burden. The CATS instruments measure two HCFCs (HCFC-22 and HCFC-142b). HCFCs make up about 6% of the total 2003 chlorine burden. The global annual growth rate from 2000 to 2003 for HCFC-22 is 5.4 ± 1.6 ppt yr^{-1}, slightly higher than estimated by the flask program.

The remaining 17% of the 2003 chlorine burden is comprised of CH_3Cl. The CATS instruments have been measuring CH_3Cl, however, there are a number of outstanding problems with reliability of this particular channel and calibration, therefore, these data are not provided. A constant global mean value of 550 ppt is used in estimating the trends in total chlorine.

N_2O and SF_6

The in situ program has been measuring N_2O since 1987. SF_6 was added in 1998. There were a number of improvements in instrumentation and chromatography that aided in the detection of these gases. The CATS instruments use Valco Instruments, Inc. (Houston, Texas) ECDs. This detector replaced the Shimadzu (Tokyo, Japan) mini-II ECDs which resulted in an improvement in sensitivity and precision. Better ECD temperature control (temperature deviations of less than 0.1°C) also improved N_2O precision, and to a lesser extent, SF_6 precision. Both instruments use 5% methane 95% argon (P5) carrier gas with 3.2-mm diameter Porapak Q packed columns (pre-column is 2-m long and the main is 3-m). Average daily precision on the CATS systems ranges from 0.3-0.6 ppb for N_2O and 0.02-0.08 ppt for SF_6.

Like many greenhouse gases, the mixing ratio of N_2O continues to increase. As of September 2003, the global N_2O mixing ratio was 318.2 ppb (Figure 5.17). However, the growth rate of N_2O has varied from 0.2 to 1.3 ppb yr^{-1} while interhemispheric differences varied from 0.4 to 1.4 ppb (Figure 5.18) .

As of September 2003, the global SF_6 mixing ratio was 5.23 ppt (Figure 5.19). SF_6 is growing steadily at a nearly constant rate of 0.2 ppt yr^{-1} (Figure 5.20).

Conclusion

Over the past decade there was steady improvement in the HATS in situ program. In the late 1980s, only five molecules were measured, but by 1998 nine additional compounds were measured by the CATS instruments. Substantial progress in chromatography, instrumentation, and software has significantly improved precision and accuracy of the in situ data. Therefore, differences in the mixing ratios of the HCFCs and other gases between the GC-MSD and in situ data need to be resolved in the near future.

5.3.2. THE RITS DATASET

Much work was done over the past few years to improve the RITS dataset. Three-channel RITS GC-ECDs were operational within a period of 15 years from 1986 to 2001 at the four baseline observatories and the NWR cooperative site measuring N_2O, CFC-12, CFC-11, CH_3CCl_3, and CCl_4 with dual-channel redundancy for N_2O and CFC-11. The highest sample injection rate at all five field sites was one injection every 30-minutes for a
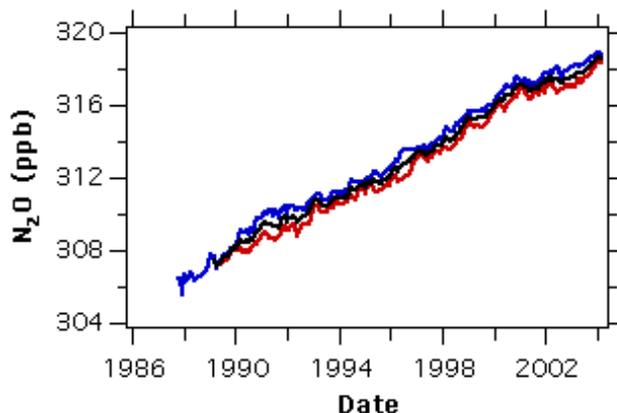
Figure 5.17. Northern Hemisphere (blue), Southern Hemisphere (red), and global monthly means (black) of N_2O.
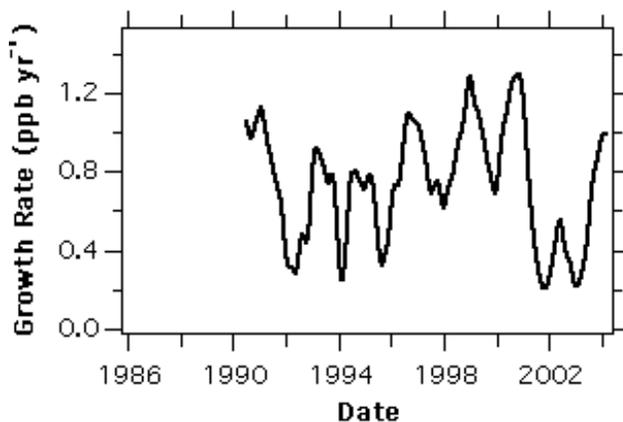
Figure 5.18. Interannual variability in the N_2O global atmospheric growth rate has varied from 0.3 to 1.4 ppb yr^{-1}. On average the N_2O growth rate is 0.7 ppb yr^{-1}.
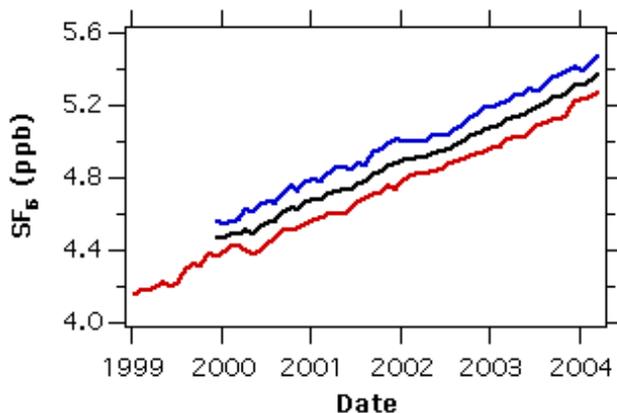
Figure 5.19. Northern Hemisphere (blue), Southern Hemisphere (red), and global monthly means (black) of SF_6.

124
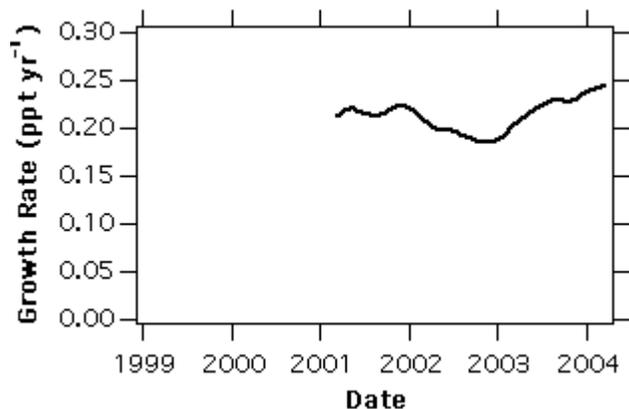
Figure 5.20. The SF_6 growth rate is fairly constant over the HATS in situ record, averaging 0.2 ppt yr^{-1}.

combined maximum analysis burden of ~13,000 chromatographic peaks per week.

Especially during the early years of operation, RITS chromatography, hardware, software, and analysis procedures used to record and manipulate the data evolved over time. Consequently, several file formats were used for storing both the raw data (~2.5 million saved chromatograms) and the database of chromatographic-peak analysis outputs (areas and heights). Long-term storage media for these data files included several computer hard drives, 48 DC600 6.4 mm (1/4 inch) tape cartridges, 17 magneto optical disks, and several hundred diskettes.

It is also worth noting that early chromatogram analysis and quality-control measures were significantly constrained by limitations in processing power. The labor requirements involved in simply keeping up with the new data coming in and remotely troubleshooting the inevitable equipment problems arising at the field sites limited the time available for revisiting earlier data reductions. Accordingly, the computation of atmospheric concentrations from the area/height measurements was largely performed in a piecewise fashion on an annual basis.

The primary purpose of this upgrade effort (funded by a grant from the Environmental Services Data and Information Management Program) was to implement an enhanced system of quality-control procedures and graphical techniques to reexamine the RITS data in its entirety while concurrently standardizing to common formats the chromatogram files and the area/height database files for renewed storage on CDROM. Particular emphasis was given in identifying and recovering data inadvertently lost or degraded during the original reduction.

The Raw Data

The initial phase of the upgrade effort involved the standardization and inventory of the RITS raw data. Chromatograms were converted to a common format and exposed to a series of thorough consistency checks prior to storage renewal on CDROM.

Chromatogram recording errors involving the timestamp and/or source-label of the sample injection often occurred for a variety of reasons. The format-standardizing program checked for "time folds" (regions of overlapping data caused by an improper system clock setting) and other inconsistencies between the internal (file header) and external (filename) descriptors. Sample-source labeling errors were detected graphically by plotting ratios of processed peak response measures for nearby environmental and calibration sample injections. Cross-channel inconsistencies were detected by passing the chromatograms through an inventory program that recorded the station, timestamp, sample-source, and channel of each chromatogram found within a 30-minute time slot. Inconsistencies were found in ~1% of the chromatograms processed. These were corrected and reanalyzed to recover the data.

The Area/Height Database

The outputs generated during original chromatogram analyses were assembled in record-oriented binary or text format database files for later retrieval during the computation of atmospheric mixing ratios. Each of the original database files was structured in accordance with one of several multiple-injection sampling cycles. Data records were designed to accommodate a full cycle of injections to which a single timestamp was assigned. The details of the sampling cycle and the form of the timestamp both changed over time.

Newly developed graphical displays of the original database found significant data loss and degradation that occurred during chromatogram processing because of analysis software limitations. Problems included the misidentification of peaks, peaks that were missed altogether because of an excessively constrained analysis method, and temporal instabilities associated with an insufficiently constrained analysis method. These problems ultimately resulted from the inability of the analysis software to focus all of its limited resources on one peak at a time. The software was modified to give it this ability and then the affected peaks were reanalyzed.

Another problem was discovered that related to the coarse time-resolution of the original database files. The grouping of an entire sampling cycle into a single data record with a single timestamp led to spurious timestamp modification and data loss by overwriting after interruptions to the normal sampling cycle. The problem was addressed by restructuring the area/height database to include timestamps for every sample injection. This was accomplished by initializing the restructured database with timestamps and sample-source identifiers from the chromatogram inventory and employing an algorithm that matched the peak analysis outputs stored in the original database with the corresponding initialized data records in the new database. Although this problem was relatively minor, restructuring the database offered several important additional advantages.

First, the restructured database is compatible with all structural variants found among the original database files. Thus all of the data associated with a given peak was able to be collected into a single file without regard to the details of the sampling cycle.

Second, upon scanning the new database in search of overwritten samples (initialized records not corresponding to any peak analysis outputs in the original database), which typically numbered on the order of a thousand per station, tens of thousands more good quality samples were discovered that were overlooked during the original reduction. All overwritten and overlooked chromatograms were fetched and analyzed to fill in the gaps.

Finally, storage space was added to each data record to facilitate the flagging of individual injections for equipment problems. Because a single calibration sample of poor quality can adversely affect several individual calculations of a compound's atmospheric mixing ratio, marking these samples prior to final reduction is a powerful way to enhance the overall quality of the dataset. A combination of graphical and statistical methods was used to scan the entire restructured area/height database and flag well-known chromatography problems.

The Final Calibration

The final computation of atmospheric mixing ratios for RITS compounds is proceeding according to the calculation methods described for in situ measurements in the work of *Hall et al.* [2002].

RITS working calibration gas standards (stored in high pressure gas cylinders) were filled with atmosphere at or above 3000-m of altitude at NWR. These working standards were referenced in the laboratory against calibration scales derived from a series of gravimetrically developed, primary gas standards. As discussed in more detail in the next section and in previous summary reports, gravimetrically developed calibration scales are periodically updated each time a new gravimetric standard is developed, and each new scale differs, often negligibly but sometimes significantly, from its predecessors. For each of the RITS compounds, multiple gravimetric scales were used to calibrate the many working standards shipped to field sites over the 15-year history of measurements. The primary issue remaining involves how to best reconcile cases where changing calibration scales produced significant shifts in the measured atmospheric signals of RITS compounds.

5.4. GRAVIMETRIC STANDARDS

5.4.1. IMPROVEMENTS IN N_2O ANALYSIS

The WMO GAW program recently adopted the CMDL N_2O calibration reference scale. Five secondary standards were calibrated at CMDL for use by the N_2O World Calibration Center in Garmisch-Partenkirchen, Germany. Concurrent with this work was an effort to improve our ability to calibrate secondary N_2O gas standards.

From 1999-2003, N_2O and SF_6 standards were calibrated with a custom made GC-ECD (Valco detector) as part of a multi-ECD GC system (hereafter referred to as the old system). The reproducibility (relative agreement between the results of measurements of the same compressed gas standard carried out under changed conditions of measurement) of N_2O analysis on this instrument was approximately ±0.8 ppb [*Hall et al.*, 2002]. Although the old system was sometimes capable of reproducibility better than 0.3 ppb, this level of performance could not be maintained over long periods. In order to resolve latitudinal and longitudinal gradients in N_2O with different instruments, the instruments must be intercalibrated to within 0.1 ppb. A short-term goal of 0.3 ppb was established with 0.1 ppb as an eventual target.

The reproducibility of the old system was thought to be limited by (a) cleanliness and consistency of the P5 carrier gas, (b) ECD

temperature control, and (c) frequency of analysis and calibration. Because this system is also used for analysis of CFCs, chlorinated solvents, and some halons, the frequency of analysis and calibration is determined in part by the operating requirements for the other gases. Consequently, a separate instrument was dedicated to N_2O and SF_6 to provide more flexibility in analysis and calibration frequency.

The new N_2O/SF_6 calibration system uses an Agilent GC-ECD. Gases are separated on a Porapak Q packed column (4.76-mm O.D., 2-m pre-column, 3-m main), similar to that used in the old system. The carrier gas is ultra-high purity N_2 doped with approximately 0.05 ml min^{-1} CO_2 just before the ECD inlet. The sample volume is 9 ml at 85.7 kPa (620 torr). The ECD temperature is 340°C and the column temperature is 56°C. Nitrogen carrier gas was chosen over P5 because the quality of commercial N_2 is often better than that of P5 and should lead to better performance over the long term. The frequency of analysis is five injections per hour compared with two injections per hour on the old system.

The reproducibility of the new system, when calibrated in a manner similar to the old system, is approximately ±0.3 ppb N_2O at near-ambient N_2O based on monthly analyses of a 314 ppb secondary whole air standard. The reproducibility of the old system was ±0.8 ppb based on monthly analysis of the same standard. The reason for the improvement is not entirely known, although it is suspected that improvements in instrumental precision and carrier gas consistency are the major factors. The precision $(2\sigma/N^{1/2})$ of the new instrument is typically better than 0.05% and ranged from 0.02-0.12% during a 10-month test phase. This is about twice as good as that of the old system (0.05-0.2%). Improved precision is also the result of better ECD temperature control and increased analysis frequency. In addition, reproducibility has remained relatively constant with changes in carrier gas cylinders. The reproducibility of SF_6 calibrations is the same as that achieved with the old system.

During the testing phase the new system employed a single working standard with an N_2O mixing ratio of 314 ppb. A series of secondary standards (125, 192, 256, 283, and 315 ppb) was analyzed every 2-4 weeks to maintain calibration. These are the same standards used to calibrate the old system. Mixing ratios for the secondary standards were determined by comparison to 17 gravimetrically prepared primary standards. Operation of the new system is currently under revision and will soon include weekly calibration with six secondary standards having N_2O mixing ratios of 262, 290, 314, 333, 345, and 358 ppb N_2O. All samples will be compared to a single working standard at 318 ppb. It is hoped that increased frequency of analysis and calibration, and consistent carrier-gas quality, will result in a reproducibility of 0.2 ppb or better within the next year.

5.4.2. CALIBRATION SCALES

Current calibration scales for a number of trace species measured by CMDL are summarized in Table 5.6. Several new primary standards were prepared in 2002-2003. The scales shown in Table 5.6 are tied to specific sets of primary standards [*Hall et al.,* 2002] and named according to the year they were adopted. Thus the preparation and use of new primary standards for a particular compound results in a new scale for that compound.

Table 5.6. Current Calibration Scale Definitions

Species	Previous Scale	Current Scale	N[a]	Range[b]
N_2O	1993	2000[c]	17	100-360 ppb
SF_6	1994	2000[c]	17	1-8 ppt
CFC-12	1997	2001[d]	15	150-650 ppt
CFC-11	1992	1992	8	20-320 ppt
CFC-113	1993	2003[e]	16	20-120 ppt
CH_3CCl_3	1996	2003[f]	10	10-180 ppt
CCl_4	1996	1996[g]	12	20-150 ppt
Halon-1211	1996	1996[h]	2	3-6 ppt
Halon-1301	1990	1990[i]	2	1-6 ppt
HCFC-22	1992	1992	5	105-160 ppt
HCFC-141b	1994	1994	3	5-50 ppt
HCFC-142b	1994	1994	3	5-50 ppt
HFC-134a	1995	1995	2	5-10 ppt
CH_3Cl	1996	2003[j]	9	280-810 ppt
CH_3Br	1996	2003[k]	9	8-390 ppt
$CHCl_3$	1992	1992[l]	1	4-13 ppt
CH_2Cl_2	1992	1992[m]	1	6-35 ppt
C_2Cl_4	1992	2003[n]	8	5-14 ppt
COS	None	2002	7	260–730 ppt
$CHBr_3$	None	2003	2	5-11 ppt
CH_2Br_2	None	2003	2	10-20 ppt

[a] Number of primary standards used to define scale.

[b] Approximate range of primary standards.

[c] Eight new standards prepared in 2003 are currently being evaluated. A scale update is expected in 2004.

[d] Six primary standards were prepared in 2001 and added to the set of eight that defined the 1997 scale. In addition, one 1997 standard was discovered and added to the scale. The 2001 scale is 1.2 ppt higher than the 1997 scale at ambient CFC-12 mixing ratio.

[e] Eleven new standards were prepared in 2002-2003. The new 2003 scale is equivalent to the 1993 and interim 2002 scales at ambient CFC-113 mixing ratio.

[f] The 2003 scale is, on average, 4.6% lower than the 1996 scale over the range 50-150 ppt. The 1996 scale (ppt) can be converted to the 2003 (ppt) scale by the function $y = -1.6120 \cdot 10^{-4} x^2 + 0.9654x + 0.2$, where x = mixing ratio on 1996 scale. Calibration results reported on the interim 2002 scale from measurements by GC-ECD can be updated to the 2003 scale (ppt) using $y = -2.0022 \cdot 10^{-4} x^2 + 1.0402x - 2.68$. No correction is required for GC-MSD.

[g] Eight primary standards were added to the set of four used to define the 1996 scale and are being evaluated. A scale update is expected in 2004.

[h] One new primary standard was prepared in 2000.

[i] Five new primary standards were prepared in 2001-2002 and are being evaluated.

[j] Nine new primary standards were prepared in 2001-2003. The 1996 and 2003 scales differ by, at most, 5% (the primary standard used to define the 1996 scale drifted upward by 5% from 1994 to 2002).

[k] The CH_3Br scale was updated in 2003 by preparing nine new primary standards and by quantifying CH_3Br drift (-1.5% yr^{-1}) that occurred in a 25 ppt primary standard used to define the scale from 1995-2002 [*Montzka et al.*, 2003a].

[l] Eight new primary standards were prepared in 2001-2003. These standards agree with the 1992 scale.

[m] Eight new primary standards were prepared in 2001-2003 but have not yet been adopted.

[n] The 2003 scale, based on eight standards prepared in 2001-2003, is 1.6% higher than the 1992 scale.

Also shown in Table 5.6 is the number of primary standards used to define each scale and the concentration range of those standards. Scales for CFC-11, CCl_4, $CHCl_3$, CH_2Cl_2, HCFC-22, HCFC-141b, HCFC-142b, and HFC-134a remain the same as those described in the work of *Hall et al.* [2002]. For some compounds, the addition of new standards resulted in only minor scale changes (1.2 ppt for CFC-12 for example). The most significant scale changes occurred for CH_3CCl_3 and CH_3Br. New primary CH_3CCl_3 standards were prepared from new reagent-grade CH_3CCl_3. The change in the CH_3CCl_3 scale (–4.6% over the range 25-150 ppt) corresponds closely to the difference in purity between the new reagent (99.8%) and that used to prepare the 1996 standards (~94%). The change in CH_3Br resulted from preparation of new primary standards in humidified air in stainless steel cylinders. By analyzing the new standards and a number of archive air samples, the drift rate of a key CH_3Br primary standard prepared in 1994 was quantified [*Montzka et al.*, 2003a].

5.5. AIRBORNE PROJECTS

5.5.1. ACATS-IV, LACE, AND PANTHER GAS CHROMATOGRAPHS

Three GC instruments, the Airborne Chromatograph for Atmospheric Trace Species (ACATS-IV) [*Romashkin et al.*, 2001], the Lightweight Airborne Chromatograph Experiment (LACE) [*Moore et al.*, 2003], and the PAN and other Trace Hydrohalocarbons Experiment (PANTHER) [*Elkins et al.*, 2001, 2002], continue to monitor ozone-depleting substances (CFCs, CH_3CCl_3, CCl_4, $CBrClF_2$) and greenhouse gases (N_2O, CH_4, SF_6) in the troposphere and stratosphere. In 2002-2003 these instruments made stratospheric measurements during five missions aboard four different airborne platforms. ACATS-IV was deployed on the National Aeronautics and Space Administration (NASA) ER-2 aircraft in June 2002, LACE was launched on the NASA Observations of the Middle Stratosphere (OMS) balloon gondola in October 2002 and September 2003, and PANTHER was deployed on the NASA WB-57F aircraft in July 2002 for the Cirrus Regional Study of Tropical Anvils and Cirrus Layers - Florida Area Cirrus Experiment (CRYSTAL-FACE) and on the NASA DC-8 in January 2003 for the Stratospheric Aerosol and Gas Experiment III-Ozone Loss and Validation Experiment (SOLVE II). In addition, ACATS-IV was flown aboard a small jet aircraft over the United States and Canada during May-June 2003 as a part of the CO_2 Budget and Regional Airborne-North America (COBRA-NA) study.

ACATS-IV was modified in early 2002 to add carbon monoxide (CO) detection to an existing GC channel that measured H_2 and CH_4 with an N_2O-doped electron capture detector. The N_2 carrier gas for this channel was replumbed to bypass the hot zirconium catalytic purifier and is now scrubbed of CO and other impurities by hopcalite (MnO_2 and CuO) and molecular sieve traps. Reductions of the sample loop volume (from 7.5 to 2.5 ml) and lengths and diameters of chromatography columns (pre-column: from 2.0 to 0.7-m length; main column: from 3.3 to 2.0-m length; both columns: from 3.8- to 2.2-mm inner diameter) now permit elution of H_2, CH_4, and CO into the ECD within 140 seconds while maintaining adequate resolution between peaks. The N_2O doping level in the ECD was raised from ~30 to ~50 ppm to increase sensitivity to CO. The minimum

detection limit for CO is 8 ppb, precision is ±4 ppb, and detector response to CO is nearly linear below 500 ppb.

5.5.2. MONITORING OF STRATOSPHERIC CHLORINE AND BROMINE

The tropospheric mixing ratios of several chlorinated and brominated source gases (CH_3CCl_3, CFC-11, CFC-113, CCl_4, and CH_3Br) are currently in decline as a result of the 1987 Montreal Protocol for Substances that Deplete the Ozone Layer and its Amendments [*Montzka et al.*, 1996, 2003a; *Yokouchi et al.*, 2002]. These decreases have brought about significant reductions in the total amounts of tropospheric organic chlorine (Cl_{TOT}) starting in ~1994 and organic bromine (Br_{TOT}) beginning in ~1999 [*Montzka et al.*, 1999, 2003a]. Cl_{TOT} and Br_{TOT} denote the total amounts of organic chlorine (CCl_y) and bromine (CBr_y) that enter the stratosphere where they are converted into inorganic chlorine and bromine species (Cl_y and Br_y) that participate in catalytic ozone destruction. The detection of trends in stratospheric CCl_y and CBr_y is complicated by this continuous conversion of organic to inorganic species.

Semiannual to annual flights of LACE, ACATS-IV, or PANTHER on high-altitude balloons or aircraft provide CMDL with the opportunity to monitor trends in stratospheric CCl_y and CBr_y. Also, it is possible to infer temporal changes in Cl_y and Br_y by calculating the difference between the amount of Cl_{TOT} (Br_{TOT}) measured at the surface by CMDL and the amount of CCl_y (CBr_y) measured in the stratosphere by ACATS-IV, LACE, or PANTHER. Since these three airborne instruments do not measure all the source gases contributing to CCl_y and CBr_y in the stratosphere, unmeasured gases are inferred from tracer-tracer correlations obtained from the NCAR whole air sampler [*Woodbridge et al.*, 1995; *Wamsley et al.*, 1998; *Schauffler et al.*, 2003].

The conversion of chlorine and bromine from organic CCl_y (CBr_y) to inorganic Cl_y (Br_y) reservoirs in the stratosphere is illustrated in Figure 5.21. Generally, the longer an air parcel has resided in the stratosphere, as depicted by its mean age, the greater the ratio of Cl_y (Br_y) to CCl_y (CBr_y). The crossing point of CCl_y and Cl_y (50% of each) occurs at a mean age of 3.5 years while CBr_y and Br_y cross at 2.3 years, reflecting the longer stratospheric lifetime of CCl_y than CBr_y. The downward slope of Cl_{TOT} towards younger mean age (upper panel) illustrates the decreasing tropospheric trend since ~1994 as described previously. This trend is likewise indicated by the lower values of Cl_{TOT} in 2002-2003 than in 2000 for a given mean age. This same feature is evident in stratospheric CCl_y values but only for younger air masses because stratospheric mixing gradually erodes the tropospheric trend as air masses age. Br_{TOT} (lower panel) levels off at younger mean ages in the 2000 data but shows a discernable decrease in the 2002-2003 data. Similar trends in CBr_y are complicated by the fact that the peak of Br_{TOT} in the troposphere was recent enough that values of Br_{TOT} are the same in both younger and older air masses sampled in 2002 and 2003, increasing the effectiveness of stratospheric mixing in eroding the tropospheric trend.

The determination of stratospheric trends of nonconserved source gases must only utilize air masses with similar exposures to their photochemical sinks, such that similar fractions of CCl_y
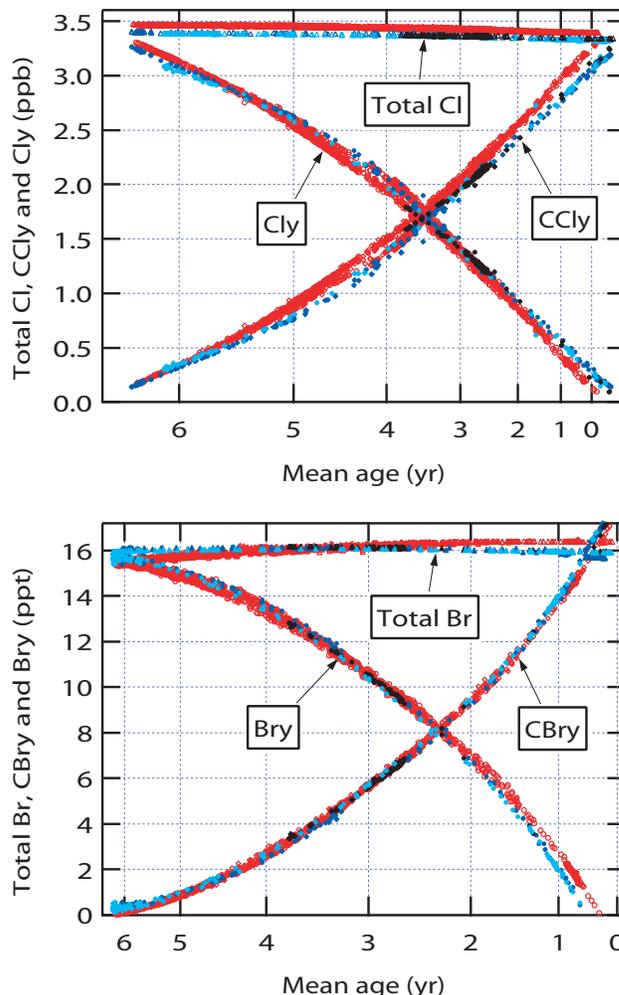
Figure 5.21. The stratospheric partitioning of total chlorine (top) and bromine (bottom) between organic (CCl_y, CBr_y) and inorganic (Cl_y, Br_y) species as a function of mean age. CCl_y and CBr_y data shown are from ACATS-IV flights in January-March 2000 (red) and June 2002 (black), and from LACE flights in October 2002 (blue) and September 2003 (cyan). Total chlorine and bromine are the CMDL surface trends lagged by the mean ages of stratospheric air masses calculated from ACATS-IV and LACE in situ measurements of SF_6. Inorganic chlorine and bromine (Cl_y, Br_y) are calculated as the differences between total chlorine (bromine) and CCl_y (CBr_y).

to Cl_y (CBr_y to Br_y) conversion have occurred. A reasonable surrogate of this conversion fraction is the mixing ratio of N_2O, a long-lived gas having only surface sources and stratospheric sinks. Stratospheric air masses with lower N_2O mixing ratios have had greater exposure to the photochemical sinks of N_2O that also convert CCl_y (CBr_y) to Cl_y (Br_y). When binned by concurrently measured N_2O mixing ratios, stratospheric CCl_y and CBr_y data can be analyzed for temporal trends as is done for >11 years of ACATS-IV and LACE data (Figure 5.22). The downturn in CCl_y is apparent for all N_2O bins, while recent reductions in CBr_y are observable only for the highest N_2O mixing ratios bins (which represent the youngest air masses). It is expected that a
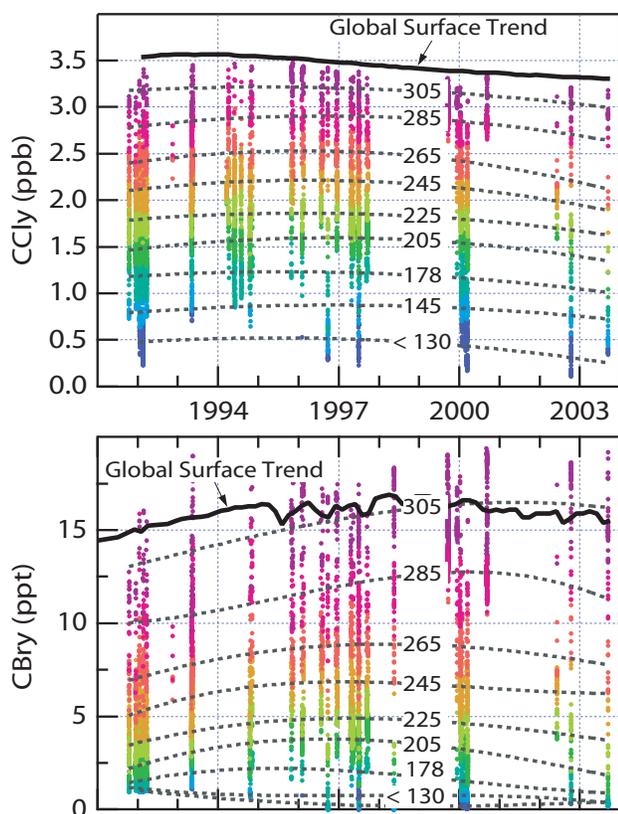
Figure 5.22. Trends in organic chlorine (top) and bromine (bottom) in the stratosphere from ACATS-IV and LACE flights during 1991-2003. CCl_y and CBr_y data are colored according to their N_2O mixing ratio bin with bin midpoints labeled on the plot. The six highest bins are 20 ppb N_2O in width (i.e., midpoint 305 for 295-315 ppb bin), the next lowest two bins are 30 ppb wide, and the lowest bin incorporates all N_2O mixing ratios <130. N_2O bins group the air masses sampled according to their photochemical histories (see text). Dashed curves are 3rd-order polynomial fits to binned data for the 12-year period.

reduction in CBr_y will be evident within a few years in air masses represented by the lowest N_2O bins.

5.5.3. 2003 COBRA-NA

This study of large-scale sources and sinks of greenhouse and ozone-depleting gases was carried out during May-June 2003 in conjunction with Harvard University, the University of North Dakota (UND), Scripps Institution of Oceanography, the Cooperative Institute for Research in Environmental Sciences (CIRES), and NCAR. Two 11,000-km flight racetracks encompassing large regions of the United States and Canada were completed with the UND Cessna Citation II jet aircraft along with several regional flights in the northeastern and southern central United States. ACATS-IV measured seven halocarbons (CFC-11, CFC-12, CFC-113, CH_3CCl_3, CCl_4, $CHCl_3$, and $CBrClF_2$) and five other trace gases (N_2O, CH_4, SF_6, CO, and H_2) in the planetary boundary layer and free troposphere during 38 flights. Carbon dioxide, carbon monoxide, ozone, and water vapor were

also measured in situ, and air was sampled in flasks for assay of O_2/N_2, Ar/N_2, $^{13}C/^{12}C$ in CO_2 and CH_4, $^{18}O/^{16}O$ in CO_2.

The emissions of many halocarbons have become increasingly weaker and more difficult to estimate as worldwide production diminished, especially in developed countries where production was mandated to cease prior to 1996. Weaker and perhaps less uniformly distributed halocarbon sources in these nations have greatly widened the uncertainties of regional- to continental-scale emission estimates derived from measurements of polluted air masses at only one or a few sites. Accurate appraisals of large-scale halocarbon emissions now require geographically extensive measurements of polluted air masses like those made by ACATS-IV during COBRA-NA.

ACATS-IV data from COBRA-NA reveal that some halocarbons are still emitted in many regions of the United States and Canada. In the absence of production, the halocarbons must have emanated from existing stockpiles or banks of these chemicals (functioning and discarded refrigerators, air conditioners, fire extinguishers, and blown foam products). The elevated halocarbon mixing ratios detected during COBRA-NA were typically correlated with emissions of CO from fossil fuel combustion (Figure 5.23), so halocarbon emission ratios were determined relative to CO. When analyzed on a flight-by-flight basis, halocarbon emission ratios are statistically significant (95% confidence level) for ≥50% of flights for CFC-12, $CBrClF_2$, CH_3CCl_3, and $CHCl_3$, and ≥25% of flights for CFC-11 and CFC-113 [*Hurst et al.*, 2003]. Statistically significant CCl_4 emission ratios were found for only four flights (Figure 5.24).

A detailed analysis of halocarbon emissions in the United States and Canada is ongoing. Individual pollution plumes sampled by ACATS-IV during COBRA-NA were identified and emission ratios for each plume will be quantified. Emission ratios will be transformed to regional emission estimates by mapping gridded CO emissions onto plume back-trajectories simulated by the Stochastic Time-Inverted Lagrangian Transport model [*Lin et al.*, 2003].

5.5.4. 2003 SOLVE-II

The first flight of the PANTHER instrument occurred during the CRYSTAL-FACE mission. Science-quality data from PANTHER was first obtained on the following SOLVE II mission. During SOLVE II the three ECD channels measured five halocarbons (CFC-11, CFC-113, CH_3CCl_3, CCl_4, and $CHCl_3$), N_2O, SF_6, CH_4, and H_2. The mass spectrometer channel measured HCFC-22, HCFC-142b, HFC-134a, COS, CH_3Br, CH_3Cl, and CFC-12. Flights out of Edwards Air Force Base, California, and the transit flights to and from Kiruna, Sweden, sampled midlatitude air in the troposphere and lower-most stratosphere, some of which was of recent origin from south of the InterTropical Convergence Zone (ITCZ). Flights out of Kiruna sampled the lower-most parts of the 2002/2003 Arctic vortex core and edge region. Representative mixing ratios of CH_3Cl from the GC-MSD channel and CCl_4 using one GC-ECD channel during the flight on 20 January 2003 are shown in Figure 5.25.

The 2002/2003 Arctic vortex separated into two stable pieces that later recombined to transport midlatitude air across the vortex edge. This transport was absent in the stable 1999/2000 Arctic vortex investigated in the original SOLVE campaign. Also
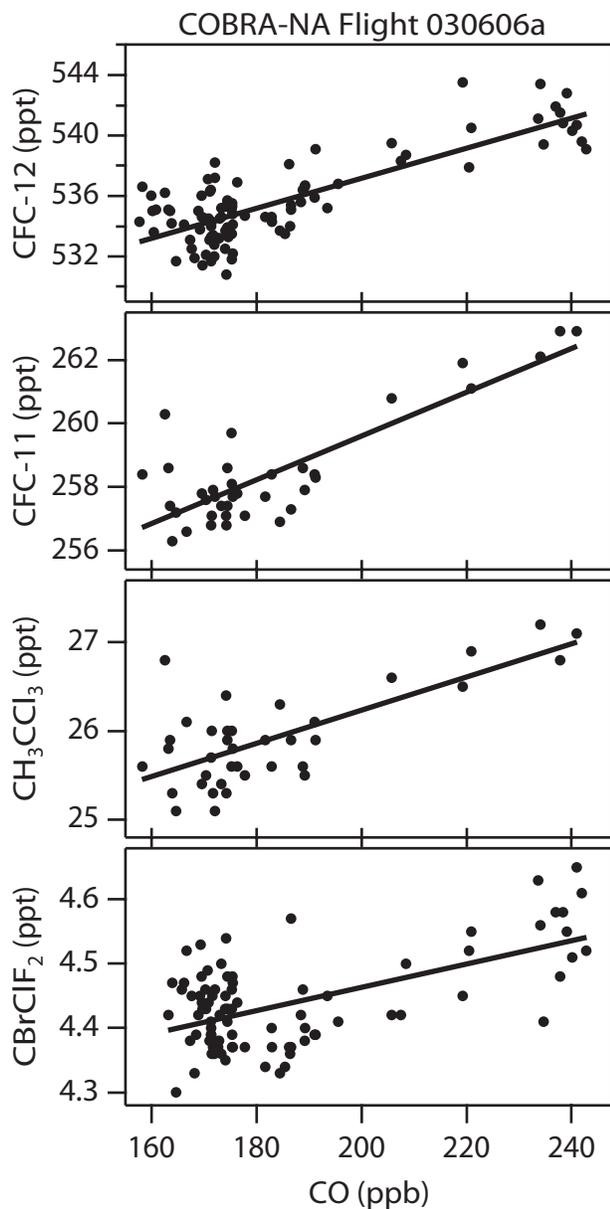
Figure 5.23. Correlation plots of selected halocarbons versus CO mixing ratios measured during the COBRA-NA morning flight of 6 June 2003. Polluted air masses were sampled in the boundary layer near Harvard Forest, Massachusetts. Data in each panel were fit using linear orthogonal distance regression (gray line). Slopes of fit lines, assessed for statistical significance at the 95% confidence level (2σ), depict emission ratios for the entire flight.

Figure 5.24. Flight-by-flight emission ratios for the seven halocarbons measured by ACATS-IV during the 2003 COBRA-NA campaign. Only emission ratios significantly different from zero are shown. There were 38 flights between 23 May and 28 June 2003; on some days there were two or three flights.
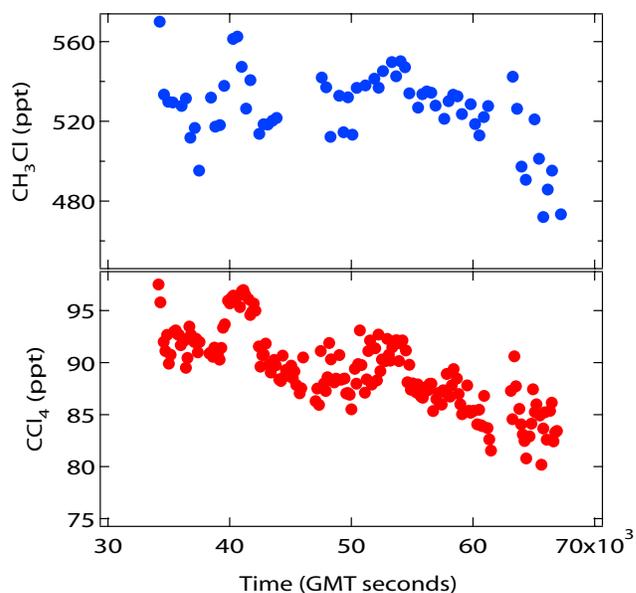
Figure 5.25. Mixing ratios of CH_3Cl using the GC-MSD channel and CCl_4 using one GC-ECD channel versus flight time are shown for 20 January 2003.

absent in the original SOLVE campaign was the SAGE III satellite that was operational and available for validation studies in the SOLVE-II campaign. The PANTHER data are currently being finalized.

Several new studies using LACE and ACATS data from the original SOLVE campaign were published since the last CMDL report. In the work of *Plumb et al.* [2002] a comparison was made of LACE and ACATS tracer/tracer data to the three-dimensional chemical NCAR transport model [*Mahowald et al.*, 1997; *Rasch et al.*, 1997]. This study looks into the formation and dynamics of the Arctic vortex. It highlights the mesosphere as an important factor in stratospheric transport and chemistry. Two other studies that concentrate on descent and mixing in the 1999/2000 Arctic vortex were also published [*Piani et al.*, 2002; *Greenblatt et al.*, 2002].

5.6. SPECIAL PROJECT—IN SITU GAS CHROMATOGRAPHY

5.6.1. MASS SELECTIVE DETECTOR SYSTEM

In September 2002 the development of an automated, three-channel GC with a mass selective detector (MSD) and two ECDs began. The instrument will be placed at a Pacific CMDL station to make hourly measurements of a variety of atmospheric species with a wide range of lifetimes. The primary goal is to characterize the episodic long-range transport of pollution from Asia. From this characterization, Asian emission inventories will be

constructed and the implications for air quality in North America will be assessed. This section reports progress on several aspects of the measurement system as well as a discussion of the scientific basis for the choice of deployment location.

The instrument (Figure 5.26) consists of an MSD channel to measure CFCs, HCFCs, HFCs, methyl halides, and selected hydrocarbons; an ECD channel to measure N_2O and SF_6; and an ECD channel to measure PAN and peroxypropionyl nitrate (PPN). Thus the instrument will provide unparalleled long-term, in situ measurements of key chemical species with important roles in the radiative balance of the atmosphere, air quality, and stratospheric ozone depletion.
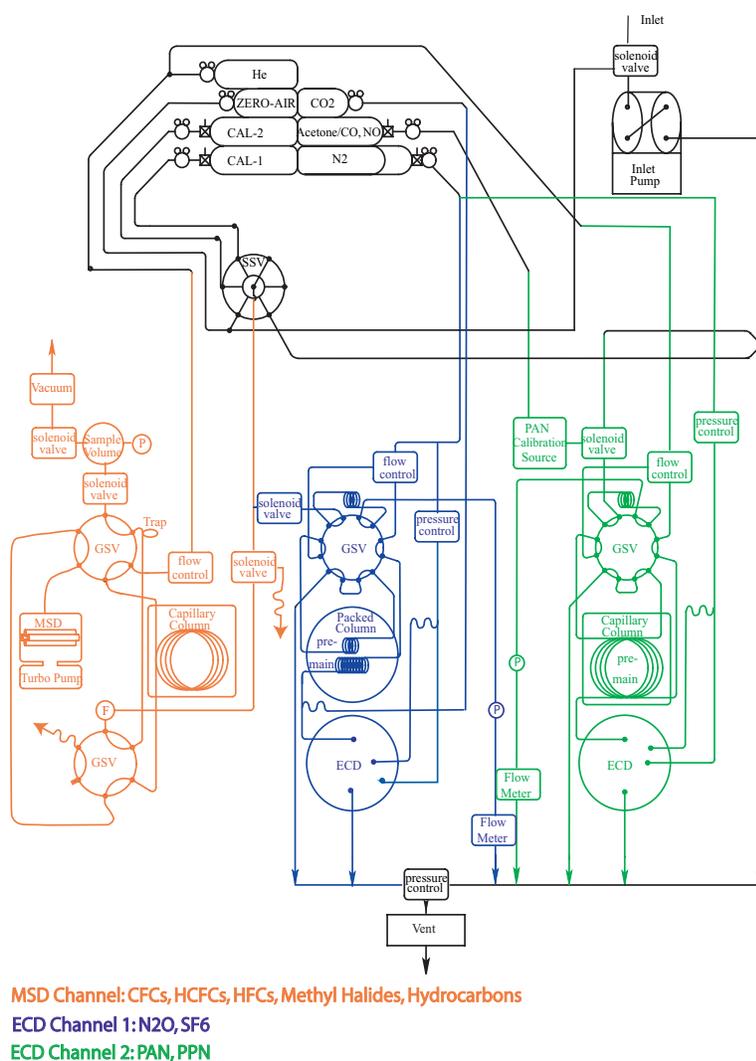
Figure 5.26. Plumbing diagram showing the major components of the in situ GC-MSD. The cryogenic trapping system is labeled "trap" on the MSD channel, and the dynamic dilution system is labeled "PAN calibration source" on the PAN ECD channel.

5.6.2. Development of Key Systems

Efforts thus far have been focused on the development of two key components of the instrument, one of which is the calibration system for the PAN/PPN channel. The instability of these two gases in high-pressure cylinders necessitates that calibration standards must be produced in situ for long-term deployment of the instrument. There is ongoing development of a dynamic dilution system to produce PAN and PPN photochemically at a known concentration using gravimetrically prepared mixtures of the precursor gases.

The other key component is a module that pre-concentrates air samples using a cold trap prior to analysis by the MSD channel. To avoid the use of cryogens at the station, a trapping system was developed that uses chemical adsorbents to trap the gases of interest at a moderately cool temperature (–50°C) attainable with three-stage Peltier thermoelectric coolers (Figure 5.27a). The trap (Figure 5.27b) is heated directly using the resistance of the stainless steel tubing. It is flash-heated from –50°C to 130°C in ~5 seconds and is then cooled to –50°C within 10 minutes. The small dimensions of the trap and the ability to heat it rapidly help to ensure the sample is instantaneously introduced onto the column so that the chromatographic peaks are well-resolved.
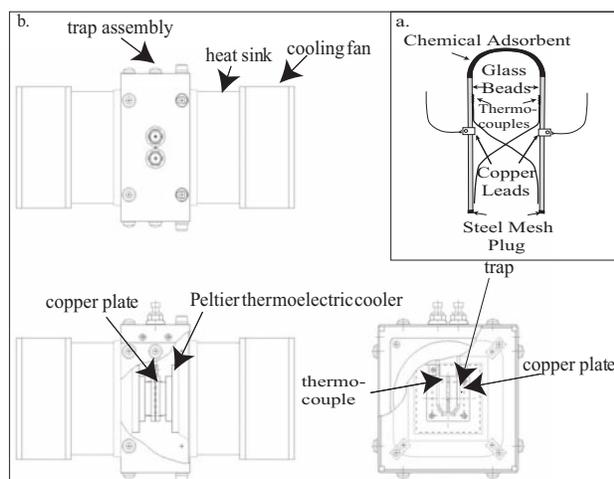
Figure 5.27. (a) Schematic of the trap. The trap is constructed using 1.59-mm OD, 1.02-mm ID stainless steel tubing. The adsorbent material is packed in the center of the trap with inert glass beads filling the remaining volume and the ends plugged with steel mesh. Thermocouples are spot-welded on both sides of the trap to provide an accurate measure of the trap temperature. (b) Schematics of the Peltier assembly. The trap is sandwiched between two copper plates with grooves cut to accommodate the thermocouples. Two copper leads that provide the electricity to heat the trap are attached to the trap just outside the copper plates via small clamps. The trap is encased in a Teflon sheath to electrically isolate it from the copper plates. A three-stage Peltier thermoelectric cooler is attached to each copper plate, followed by a heat sink and cooling fan. The trap is connected to electrically isolated bulkhead fittings, and polyamide reducing ferrules are used to connect the tubing from the gas sampling valve to the bulkhead fittings.

5.6.3. Testing of Adsorbent Trapping Materials

The use of Peltier coolers for the MSD channel-trapping system necessitates the use of adsorbent trapping materials that quantitatively trap the gases of interest at –50°C. The ideal adsorbent must also fully desorb these gases during flash heating without background contamination or chemical reaction. Three types of trapping materials were investigated for suitability on the MSD channel: HayeSep D, Porapak Q, and a combination of Carboxen 1000 and Carboxen 1003. The Carboxen materials were tested only for the most volatile gases to be measured, because they require heating of the trap to 240°C for full desorption of all of the gases. The power required for heating to this temperature while the trap is in the Peltier assembly exceeds the limitations of the current heating system. In addition, there is evidence that Carboxen produces sulfuric acid in the presence of moisture. Thus it may be reactive and/or corrosive (P. Simmonds, personal communication, 2003). Porapak Q proved useful for most of the lighter gases of interest, but at the highest desorption temperature used thus far (140°C) it appears to have a memory for many of the lower volatility gases. In addition, this trap showed contamination and nonzero blanks of several gases.

Figure 5.28 shows the total ion chromatogram for a trap using 4.5 ml of HayeSep D as the adsorbent material and a DB-624 capillary column. All of the target gases present in the sample cylinder, except acetone, were measured with precisions ranging from 0.16 to 8% (with the large values only for the very smallest peaks). While there does not appear to be any nonzero blanks of acetone in the trap, as is the case with Porapak Q, the abundance and characteristics of the acetone peak change dramatically during a succession of runs. Current efforts are focused on improving the acetone measurement by removing gases that may interact with acetone in the trap. *Neu et al.* [2003] presented an analysis of the peak abundances from the HayeSep D trap for the gases of interest over a range of desorption temperatures from 50°C to 150°C. It was shown that 130°C is an adequate desorption temperature for all gases of interest. Determinations of breakthrough volumes and dependence on adsorption temperature are in progress.

5.6.4. Scientific Issues Regarding the Choice of Deployment Location

While instrument development is an important and necessary part of any measurement project, it is critical that scientific issues drive the decision-making process. The primary goal of this research is to study the long-range transport of Asian pollution; the choice of deployment location is critical to the success of the project. The Mauna Loa Observatory (MLO), Hawaii or THD provide an opportunity to measure air masses transported across the Pacific from Asia. The choice of location must be based on the potential scientific value of data collected there.

While THD could potentially provide information about changes to background levels of pollution in the United States caused by Asian influence, it is likely that the elevation of the site (107 m) is too low to observe Asian air masses on a regular basis. Long-range transport usually results from a frontal passage that lofts pollutants into the free troposphere. While subsidence in
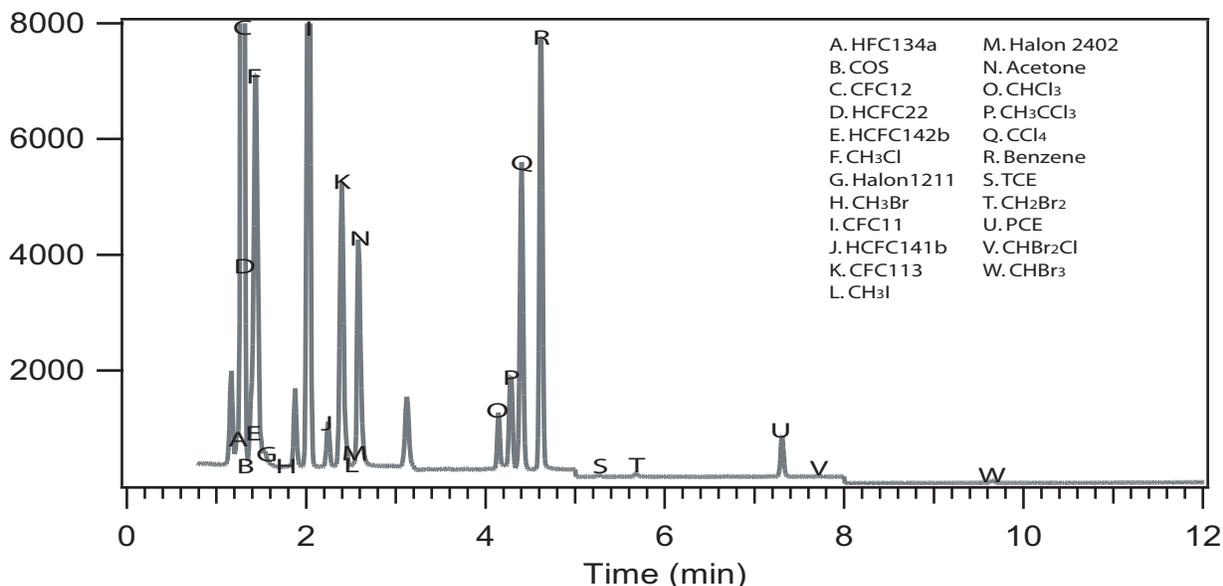
Figure 5.28. Total ion chromatogram for the HayeSepD trap using 220 ml of NWR air as the sample. The trap was heated from –48°C to 130°C for 5 s and held at 130°C for 25 s. The column temperature was ramped from 30°C to 150°C at a rate of 10°C min^{-1}. The sample was run in single ion mode to distinguish co-eluting peaks. The gases of interest are listed at their retention times. The sample contains no COS, CH$_3$Br, or CH$_3$I.

high-pressure systems can bring the pollutants back to the surface, there is no persistent high-pressure system along the California coast that would provide a semi-continuous feed of Asian air to this low altitude station. In fact, A. H. Goldstein et al. (manuscript in preparation, 2003) found that the variability in carbon monoxide (CO) measured at THD during the ITCT 2K2 study that took place in April and May 2002 was largely driven by North American emissions carried to the site by large-scale recirculations. They found no evidence for episodic enhancements of pollutant concentrations caused by the transport of Asian pollution plumes despite the fact that the study took place during the peak season for such transport. While trajectory analyses showed the mean concentration of CO was largely influenced by Asian emissions, not a single identifiable Asian pollution plume was observed and emission inventories could not be calculated.

The observatory at MLO (3397 m), on the other hand, is sufficiently high in altitude to regularly sample the free troposphere and is free from North American continental influence (as well as generally free from local influence). In fact, the CMDL CATS instrument has identified Asian air masses throughout the year at Mauna Loa. Placing this new instrument at the site will greatly expand the number of species measured by CMDL and will provide the first long-term measurements of many of these species within Asian air masses. Such measurements will help to calculate emission inventories and improve our understanding of the conditions under which long-range transport events occur.

The development and deployment of this instrument will provide an invaluable tool for monitoring the growth in key chemical species and understanding how Asian emissions are influencing the regional and global atmosphere. The data will be used to validate chemical transport models, constrain model parameters, and identify source regions for inverse modeling.

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