5. Nitrous Oxide and Halocarbons


5.1. Continuing Programs

5.1.1. Introduction

Research conducted by the Nitrous Oxide and Halocarbons Group (NOAH) of CMDL in 1996 and 1997 included: (1) weekly flask sampling and analysis of air from remote locations and regionally influenced sites, (2) operation of instrumentation for hourly, in situ measurement of trace gases at the four CMDL observatories and at four regionally influenced sites, (3) preparation and maintenance of calibration gases for all measurements, (4) participation on campaigns requiring in situ stratospheric measurements from high-altitude aircraft and balloons, (5) investigation of oceanic processes influencing trace gas composition of the atmosphere, (6) in situ monitoring of air at multiple elevations from tall towers, and (7) measurement of gases in air that is archived in consolidated polar snow in Antarctica and Greenland.

The main mission of NOAH is to measure and to evaluate the distribution and trends of nitrous oxide (N₂O) and many halogenated gases in the atmosphere and ocean with the best analytical tools available. The halogenated gases, or halocarbons, include the chlorofluorocarbons (CFCs), chlorinated solvents (CCl₄, CH₂CCl₃, CHCl₃, etc.), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), methyl halides, halons, and sulfur hexafluoride (SF₆). The recent motivations for measuring these compounds are: (1) that many of the brominated and chlorinated compounds that cause ozone depletion are being phased out of production as required by the amended and adjusted Montreal Protocol [United Nations Environmental Programme (UNEP), 1987, 1997], and (2) that these compounds are introduced to replace them contribute to global warming. The Protocol of the Third Conference of Parties to the United Nations (UN) Framework Convention on Climate Change, held in Kyoto, Japan, December 1997, recommended future limits on the emissions of six compounds or compound groups: (1) carbon dioxide (CO₂), (2) methane (CH₄), (3) nitrous oxide (N₂O), (4) HFCs, (5) SF₆, and (6) the perfluorocarbons (PFC). The last four of these six categories are within the domain of NOAH's research.

Continuing programs within NOAH are based upon in situ or flask air sample measurements from four CMDL observatories and nine cooperative sampling sites (Figure 5.1, Table 5.1). These stations provide a robust network for evaluating global atmospheric change and hemispheric relationships for the various compounds.

One of the more significant discoveries in the past 2 years is the turnover of total anthropogenic chlorine in the atmosphere. This finding came from the combined results of flask and in situ sampling, in situ monitoring, and standards programs and is discussed in the following sections.

Other significant results include the observed global increases in atmospheric N₂O and SF₆, again in both flask and in situ monitoring, the continued growth of atmospheric HCFCs and HFCs as they increasingly are used as replacements for the ozone-depleting CFCs, and the surprising, protracted growth of the halons in the atmosphere years after the cessation of their production in developed countries.

5.1.2. Flask Samples

Overview

The flask sampling program has undergone a few changes in 1996-1997 with the new automated system. The new automated instrument is designed to facilitate processing of samples and data. Over the past 16 years, the number of gases analyzed by this group has risen from 3 to over 25, and the number of weekly sampling sites has more than doubled, from 5 to 11 (Figure 5.1, Table 5.1). Additional flasks are collected as part of special projects, including oceanic expeditions, polar firm sampling, and aircraft missions. Flasks that once were analyzed by one instrument are now analyzed by four instruments, two of which are mass spectrometers (Table 5.2). This increase in the number of flasks sampled and gases measured has resulted in a considerable increase in the laboratory workload. Attempts to offset this have focused on automation of instruments, streamlining of data processing, and improvement of quality control. In 1991 the first of the automated instruments, a multi-channel gas chromatograph (GC) electron capture detector (ECD) system capable of measuring seven gases, was put in service. This service replaced the old manual, one-channel method.
TABLE 5.1. Geographic and Network Information on NOAH Network Sites

<table>
<thead>
<tr>
<th>Code</th>
<th>Station</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Elevations (m)</th>
<th>LST-GMT (hr)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALT</td>
<td>Alert, Northwest Territories, Canada (AES)*</td>
<td>82.45°N</td>
<td>62.52°W</td>
<td>210</td>
<td>-4</td>
<td>F, I</td>
</tr>
<tr>
<td>BRW</td>
<td>Point Barrow, Alaska</td>
<td>71.32°N</td>
<td>136.60°W</td>
<td>11</td>
<td>-9</td>
<td>F, I</td>
</tr>
<tr>
<td>MHT</td>
<td>Mace Head, Ireland (University College)</td>
<td>53.33°N</td>
<td>9.90°W</td>
<td>26</td>
<td>0</td>
<td>F</td>
</tr>
<tr>
<td>LEF</td>
<td>WLEF tower, Wisconsin (CMDL-CGG)</td>
<td>45.95°N</td>
<td>90.28°W</td>
<td>470</td>
<td>-6</td>
<td>F, I</td>
</tr>
<tr>
<td>HFM</td>
<td>Harvard Forest, Massachusetts (Harvard University),</td>
<td>42.54°N</td>
<td>72.18°W</td>
<td>340</td>
<td>-5</td>
<td>F, I</td>
</tr>
<tr>
<td>NWR</td>
<td>Niwot Ridge, Colorado (University of Colorado)</td>
<td>40.04°N</td>
<td>105.54°W</td>
<td>3013</td>
<td>-7</td>
<td>F, I</td>
</tr>
<tr>
<td>ITN</td>
<td>WITN tower, North Carolina (CMDL-CGG)</td>
<td>35.37°N</td>
<td>77.39°W</td>
<td>9</td>
<td>-5</td>
<td>F, I</td>
</tr>
<tr>
<td>MLO</td>
<td>Mauna Loa, Hawaii</td>
<td>19.54°N</td>
<td>155.58°W</td>
<td>3397</td>
<td>-10</td>
<td>F, I</td>
</tr>
<tr>
<td>KUM</td>
<td>Cape Kumukahi, Hawaii</td>
<td>19.52°N</td>
<td>154.82°W</td>
<td>3</td>
<td>-10</td>
<td>F</td>
</tr>
<tr>
<td>SMO</td>
<td>Tulaia, American Samoa</td>
<td>14.23°S</td>
<td>170.56°W</td>
<td>77</td>
<td>-11</td>
<td>F, I</td>
</tr>
<tr>
<td>CGO</td>
<td>Cape Grim, Tasmania, Australia†</td>
<td>40.41°S</td>
<td>144.64°E</td>
<td>94</td>
<td>+10</td>
<td>F</td>
</tr>
<tr>
<td>PSA</td>
<td>Palmer Station, Antarctica‡</td>
<td>64.92°S</td>
<td>64.00°W</td>
<td>10</td>
<td>+12</td>
<td>F</td>
</tr>
<tr>
<td>SPO</td>
<td>South Pole, Antarctica</td>
<td>89.98°S</td>
<td>102.00°E</td>
<td>2841</td>
<td>+12</td>
<td>F, I</td>
</tr>
</tbody>
</table>

Cooperative sites (F = flasks, I = in situ) with:
*In situ GC: Only N₂O and SF₆ flasks sampling for all gases, however.
†Commonwealth Scientific and Industrial Research Organization (CSIRO) and Bureau of Meteorology, Australia
‡Only glass flasks used.

GC/ECD that measured only three gases [Thompson et al., 1985]. After a few years of debugging and intercomparison, the old, manual GC/ECD was retired in 1996. Software for running the automated GC/ECD system was upgraded in 1995. In the past 2 years quality control programs were written and a database developed that now allows evaluation of data from samples immediately following analysis.

TABLE 5.2. Instrumentation for NOAH Flask Analysis

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Type</th>
<th>Gases</th>
<th>Frequency of Network Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTTO</td>
<td>GC/ECD, 3-channel, isothermal</td>
<td>N₂O, CFC’s (3), CIC’s (2)</td>
<td>Weekly</td>
</tr>
<tr>
<td>LEAPS</td>
<td>GC/ECD, 1-channel, temperature programmed</td>
<td>Halons (2), C₂H₅Cl, C₂H₅Br, CFC’s (1)</td>
<td>Semi-monthly to monthly</td>
</tr>
<tr>
<td>HCFC-MS</td>
<td>GC/MS, 1-channel, temperature programmed</td>
<td>HCFCs (3), HFCs (1), CFCs (3), Halons (1), CICs (6), BrCs (3)</td>
<td>Semi-monthly</td>
</tr>
<tr>
<td>HFC-MS</td>
<td>GC/MS, 1-channel, temperature programmed</td>
<td>HCFCs (5), HFCs (2), CFCs (2), Halons (2), CICs (6), BrCs (3), ClBrCs (3)</td>
<td>Semi-monthly to monthly</td>
</tr>
</tbody>
</table>

Other efforts at automation included the GC mass spectrometer (MS) mainly responsible for measurement of HCFC’s and methyl halides and an additional GC electron capture detector (ECD) system, Low Electron Attachment Potential Species (LEAPS), mainly used for measurement of halons and methyl bromide. Programs also have been written to speed up processing of data from these instruments. Peak integration is now fully automated on both GC/MS instruments, although manual integration of peaks is still necessary on the LEAPS GC/ECD system.

Thirty-two new, 3-L sampling flasks from Meriter Corporation (San Jose, California) were purchased for inclusion in our sampling network. These flasks are constructed from no. 316 stainless steel, are highly electropolished, and have minimal internal weld exposure. Stability is excellent for most gases in these flasks, although CCl₄ and, to a lesser extent, CH₂CCL₃ can degrade over the long term as they do in all stainless steel flasks filled with dry air. Recent work with glass flasks in sampling firm air has shown that glass flasks identical to those used in the carbon cycle network can be used for sampling halocarbons over the short term. Further tests of flasks already in the network showed that many of them, depending upon their history, can be contaminated. We continue to purchase and test these in small lots as a possible option for use in special projects and for measuring gases that are less stable in selected stainless steel flasks.

A number of improvements at our flask sampling sites during 1996 and 1997 were made. At SMO the sample inlet was moved from the stack to the pump board Air-Cadet inlet system of the Radiatively Important Trace Species (RITS) GC to avoid cross contamination from other observatory instruments with inlets attached to the stack. Samples are now collected from the continuous flow, pressurized inlet at all sites except CGO, which will be changed over in 1998. Because of concerns about the durability of the Air-Cadet pumps for use with the RITS
inlet system and flask sampling, existing pumps were replaced with KNF Neuberger N-05 pumps during visits to the South Pole Observatory, Antarctica (SPO), Mauna Loa Observatory, Hawaii (MLO), Cape Kumukahi, Hawaii (KUM), and SMO. Pumps at the remaining sites will be upgraded in 1998. At KUM before November 1997, a pump system was connected upstream of the continuously flowing, Air Cadet pump to facilitate flask sampling. In November 1997 the Air cadet pump was replaced by a continuously flowing KNF Neuberger pump. Flasks can now be sampled from a simple manifold. BRW and CGO will be visited in 1998 to receive the same improvements. At NWR, AC power was installed at T-van. The battery-powered pump system will be replaced by a new system that allows flasks to be filled to higher pressures.

In addition to improvements at these sites, sampling with glass flasks was initiated at Palmer Station, Antarctica (PSA) at the end of 1997 in an attempt to understand the seasonal cycling of some of the more reactive halogens at a southern hemispheric coastal site. The objective is to compare results from this site with those from BRW where seasonal cycles are pronounced and perhaps influenced by the springtime breakup of ice. With assistance from CMDL’s Carbon Cycle Group (CCG), samples are collected in glass flasks twice per month. The glass flasks are filled to about 1.3 kPa with the CCG MAKS sampling apparatus by personnel trained by CCG. Although contamination is observed for some halocarbons, pump tests and preliminary results suggest good data can be obtained for many other compounds with this technique.

CFCs and Chlorocarbons

Measurements from the automated flask GC (OTTO) show that atmospheric mixing ratios of CFC-11 and CFC-113 continued to decline through 1996 and 1997 at rates similar to those previously reported for earlier years [Montzka et al., 1996], while the growth rate of CFC-12, although still positive, decreased from 5.9 to around 4 ppt yr⁻¹ (see cover figure). As a result of declining concentrations and growth rates for CFCs, methyl chloroform, and CCl₄, the amount of chlorine, equivalent chlorine (chlorine + bromine weighted by an efficiency factor), and effective equivalent chlorine (equivalent chlorine weighted by destruction rates in the midlatitude stratosphere) contained within long-lived, halogenated gases (CFCs, HCFCs, CH₂CCl₃, CCl₄, and halons), peaked in 1992-1994 and declined through 1995 [Montzka et al., 1996]. Cunnold et al. [1997] found similar results for chlorine-containing compounds measured by the Advanced Global Atmospheric Gases Experiment (AGAGE). The measurements suggest that declines in these quantities continued during 1996-1997 at rates similar to those observed in mid-1995 (Figure 5.2). Amounts observed at the end of 1997 represent a decrease of 2.4% from the peak Cl, ECI, and EECI delivered to the atmosphere from these gases in earlier years. Relative declines in the total atmospheric burden of Cl, ECI, and EECI are smaller because other gases (e.g., CH₂Cl and CH₂Br) also contribute significantly to the atmospheric burden of these quantities.

The gas contributing the most to this decline is CH₂CCl₃, which has an atmospheric lifetime of less than 5 years. As this gas is removed from the atmosphere, the overall rate of the decline in total chlorine will become slower. However, distributions and trends of this gas allow understanding of other atmospheric processes. For example, the difference in the atmospheric mixing ratio of CH₂CCl₃ between hemispheres has become dramatically smaller since 1992 as emissions have declined. The global latitudinal distribution of CH₂CCl₃ in 1992 and earlier years reflected the distribution of sources; mixing ratios in the northern hemisphere were higher than in the southern
hemisphere because this solvent was emitted pre-
dominantly in the northern hemisphere. As emissions
become insignificant, the distribution of CH$_3$CCl$_3$ will
instead reflect the latitudinal distribution of sinks for this
compound, which is dominated by the reaction of CH$_3$CCl$_3$
with the hydroxyl radical (Figure 5.3). Since the summer
of 1996, mixing ratios at SMO have been lower than at
CGO, likely as a result of the greater abundance of OH in
the tropics. Continued monitoring of methyl chloroform as
emissions diminish further should allow for refined
estimates of the global lifetime of CH$_3$CCl$_3$ and, therefore,
of other trace gases that react with OH. It also will be
useful in estimating the relative mean OH abundance in the
northern and southern hemispheres.

The global mixing ratio of CCl$_4$ is more difficult to
determine from flask samples because CCl$_4$ (and to a much
lesser extent CH$_3$CCl$_3$ and CH$_3$Br) can be degraded in dry
air samples stored for extended periods in stainless steel
flasks. This is indicated by anomalously low mixing ratios
and poor flask pair agreement in many of the samples
collected at SPO and less frequently from wintertime
samples collected at ALT, BRW, MLO, and NWR.

Nevertheless, measurements from reliable flask samples
(those for which pair agreement is within acceptable
limits) support the trends and abundance determined by the
RITS program, showing a continued decrease of 0.8 ppt
yr$^{-1}$ for atmospheric CCl$_4$ through 1996 and 1997.

$\text{SF}_6$

$\text{SF}_6$ is a trace gas only recently introduced into the
atmosphere. It has a lifetime of ~3200 years
(Ravishankara et al., 1993) and a greenhouse warming
potential (GWP) of 15,000-35,000 (Schimel et al., 1996),
making it an extraordinarily strong greenhouse gas on a per
molecule basis. $\text{SF}_6$ is used mainly as an insulator in
electrical transformers and circuit breakers. Once leaked
into the atmosphere, it will persist for millennia. Al-
though present at low ppt levels in today's atmosphere
and currently of little global consequence, $\text{SF}_6$ has been
increasing in abundance since the early 1970s (Geller et
al., 1997; Maiss and Levin, 1994). $\text{SF}_6$ data, which
include archived air samples and recent samples from the
flask network, show that the growth rate has not changed
much over the past decade (Figure 5.4). The growth rate
of $0.20 \pm 0.03$ (95% C.L.) ppt yr$^{-1}$ from the flask network
samples, which run from 1995-1998, does not differ

![Fig. 5.3. The annual mean abundance of methylchloroform relative to the abundance at Cape Grim, Tasmania, for that year. Similar years are connected with lines to guide the eye. Mixing ratios are determined from GC/MS analysis of paired flask samples.](image)

$\text{N}_2\text{O}$

The growth rate of atmospheric $\text{N}_2\text{O}$ over the past two
decades has ranged from under 0.5 to over 1.0 ppt yr$^{-1}$. The
mean, globally-averaged growth rate of this gas from
flask measurements during this time was 0.75 ± 0.03 (95% con-
fidence limits (C.L.)) ppt yr$^{-1}$, which amounts to about
0.25% yr$^{-1}$. These data and growth rates are from 20 years
of flask analyses and are corroborated by measurements
with RITS in situ instrumentation over the past 11 years
(section 5.1.3). The factors that cause this increase and
determine the isotopic composition of atmospheric $\text{N}_2\text{O}$ are
currently unexplained (Bowman et al., 1995; Cicerone,
1989; Kim and Craig, 1993). However, our measurements
of firm air (Battle et al., 1996) and other ice-core records
(Khalil and Rasmussen, 1989; Leuenberger and Siegenthaler,
1992; Machida et al., 1995) show clearly that $\text{N}_2\text{O}$ has been increasing in the atmosphere for at least
the past 100 years.

![Fig. 5.4. CMDL measurements of atmospheric $\text{SF}_6$. (a) Global and hemispheric averages of the dry mole fraction of $\text{SF}_6$ in flask samples dating back to 1995. (b) Annual growth rates calculated from year-to-year differences in the global mean $\text{N}_2\text{O}$. The dark line is a loess smooth of the data.](image)
significantly from the $0.22 \pm 0.03$ (95% C.L.) ppt yr$^{-1}$ determined from archived NWR samples which go back to 1987. Northern hemisphere (NH), southern hemisphere (SH), and global growth rates for this gas are identical, which is to be expected for a gas with constant source strength and long lifetime.

**Halons**

Measurements show that the atmospheric burden of halons H-1301 and H-1211 has doubled and that of H-2402 has increased by over half during the past decade (Figure 5.5) [Butler et al., 1998]. Halon mixing ratios continued to increase in recent years despite an international ban on their production and sales in developed nations effective January 1, 1994. The growth rate of H-1301 appears to have slowed recently, but it remains significant (Table 5.3, Figure 5.5a) and, within stated uncertainties, the 1997 growth rate does not differ from that reported for the end of 1996 [Butler et al., 1998]. Atmospheric H-1211 is increasing at a much higher rate than H-1301 and has not shown much sign of slowing over the past decade (Table 5.3, Figure 5.5b). The 1997 tropospheric growth is virtually identical to growth over the past decade. Although the growth rate of H-2402 is substantially slower than that of the other two halons, H-2402 contains two bromine atoms per molecule. Thus the increase of Br due to growth of H-2402 in the atmosphere in 1996 is almost half that of H-1301 and about one-tenth that of H-1211.

Few measurements of halons that allow for accurate comparisons to the results presented here have been reported over the past decade. Usually such reports are associated with field missions that are limited in geographic distribution, period of sampling, or both. Some are part of stratospheric investigations, so contribute only a few values for the troposphere. Even if these differences in sampling are taken into account, it is still clear that measurements from these studies in the past have not agreed well (Figure 5.6). Such widespread disagreement among laboratories underscores the need for extensive intercalibration among investigators making these measurements. Small offsets in calibration can lead to large errors in estimates of potential ozone depletion because of the possibility of the halons offsetting gains in stratospheric ozone protection resulting from reductions in chlorocarbon emissions [e.g., Montzka et al., 1996]. Small errors in estimating the atmospheric burden of halons can lead to significant errors in estimates of the atmospheric burden or trend of equivalent chlorine in the atmosphere [Daniel et al. 1996].

Evaluations of the growth rates and the amounts of “banked” halon available for use suggest that H-1301 emissions could continue at the present rate for another 40 years before depleting the bank of H-1301 [Butler et al., 1998]. This would leave an atmospheric mixing ratio of 3.6 ppt, or 57% higher than observed today. Under the same scenario, reserves of H-1211 would be depleted in 8 to 12 years leaving an atmospheric mixing ratio of 4.6-5.0 ppt, or 31-43% higher than observed today. However, there is a significant discrepancy between H-1211 emissions calculated from production and use and emissions deduced from atmospheric measurements. The discrepancy can be reconciled by lowering estimated emissions by ~25%, reducing the atmospheric lifetime of H-1211 from the 20 years given in Kaye et al., [1994] to 11 years or some combination of the two [Butler et al., 1998]. These uncertainties cause considerable doubt in

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**Fig. 5.5.** Hemispheric and global bimonthly averages of tropospheric mole fractions of (a) H-1301, (b) H-1211, and (c) H-2402. Data are taken from the CMDL flask network (squares), research cruises (triangles), and cylinders of archived air (diamonds). Northern hemispheric results are shown as shaded symbols, southern hemispheric results as open symbols, and global means as solid symbols. Bimonthly, hemispheric averages are calculated by weighting measurements by the cosine of the sampling latitude within each hemisphere. Global averages are computed as means of the hemispheric averages.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Tropospheric Mole Fraction (pmol mol⁻¹)</th>
<th>Global Growth Rate (pmol mol⁻¹ yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1301</td>
<td>2.4 ± 0.1</td>
<td>0.044 ± 0.015</td>
</tr>
<tr>
<td>H-1211</td>
<td>3.6 ± 0.1</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td>H-2402</td>
<td>0.45 ± 0.03</td>
<td>0.009 ± 0.001</td>
</tr>
</tbody>
</table>

**Table 5.3. Atmospheric Halons**

Fig. 5.6. Measurements of tropospheric halons over the past decade. Solid lines are CMDL global averages for (a) H-1211 and (b) H-1301. Symbols signify measurements by other laboratories and research groups. Filled squares represent work by Khalil and Rasmussen [Ehhalt et al. 1988, Khalil and Rasmussen, 1992], open triangles are from a study by Singh et al. [1988], open squares represent measurements by Oertel [1992], filled circles are measurements by C.J.L. Wang, D.R. Blake, N. Blake, and F.S. Rowland, as given in Lorenzen-Schmidt [1994], filled diamonds are values from Lorenzen-Schmidt [1994], open circles are from Schaeffler et al. [1993], and filled triangles are from Fabian et al. [1994].

Chlorofluorocarbon Alternatives Measurement Program (CAMP)

Measurements of chlorofluorocarbon alternatives continued on two instruments during 1996 and 1997. On average, one to three flask pairs per month from eight remote and three regional sampling locations were analyzed on the older GC-MS instrument. In addition, about one sample flask pair per month was analyzed from the remote locations on the instrument dedicated to making measurements of HFC-134a. The main changes made in this program involved automated data manipulation on both instruments as of January 1997 and automated analysis of larger flasks on the older GC-MS instrument as of September 1997.

Automated data manipulation allows results to be calculated and compiled more efficiently. This is achieved through the use of macros that determine chromatographic peak areas and calculate and compile results with a commercially-available spreadsheet software package. Automation allows for unattended analysis of up to eight flasks or four high-pressure cylinders. Flasks and secondary air standards are connected via a 16-port stream selection valve to the instrument inlet. Flows from flasks are regulated with different lengths of small diameter stainless steel tubing that are matched to the initial flask pressures. With automated analysis, agreement between replicate injections and between simultaneously filled flasks is similar to or improved over manual analysis. Results from a subset of flasks analyzed by both methods agreed for nearly all compounds. Some small offsets were observed for HCFC-142b and HCFC-141b and appear to result from problems associated with manual analysis of flasks. Protocols for routine checking of sample integrity as it passes through the multiple sampling ports are being implemented.

Mixing ratios of the most abundant HCFCs (HCFC-22, -141b, and -142b) continue to increase throughout the troposphere (Figure 5.7, Table 5.4). In mid-1997 these three gases accounted for about 5% or 150 ppt of the atmospheric burden of chlorine contained within long-lived, anthropogenic halocarbons. This amount was increasing by about 10 ppt per year in 1997 or similar to that reported for earlier years [Ehuiks et al., 1996a; Montzka et al., 1996].

Continued increases were also observed for HFC-134a, a gas for which restrictions on future use are being considered as part of the Kyoto Protocol (Figure 5.7, Table 5.4). Global mixing ratios of this CFC replacement are currently below 10 ppt. Because of laboratory air contamination and other issues, the number of good measurements made in 1997 was limited, but improvements are being implemented to avoid these problems in the future.
TABLE 5.4. Global Mid-Year Burden and Rate of Change for HCFCs, and HFC-134a

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mid-1996 Mixing Ratio (ppt)</th>
<th>Mid-1997 Mixing Ratio (ppt)</th>
<th>1996-1997 Growth Rate (ppt yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCFC-22</td>
<td>121.6</td>
<td>126.0</td>
<td>4.9*</td>
</tr>
<tr>
<td>HCFC-141b</td>
<td>5.4</td>
<td>7.4</td>
<td>1.9</td>
</tr>
<tr>
<td>HCFC-142b</td>
<td>7.7</td>
<td>8.7</td>
<td>1.0</td>
</tr>
<tr>
<td>HFC-134a</td>
<td>3.1</td>
<td>5.4</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Quantities estimated from latitudinally weighted measurements at seven remote sampling locations.

CH₂Cl₂ and CHCl₃, and reliable measurements of CH₃Cl and CH₃Br (Figure 5.8). These MPI flasks are larger (2.4 L versus 0.8 L), made out of a higher grade stainless steel, and do not contain any seals that require Teflon tape. Results from simultaneously filled pairs of these flasks generally agree to within the instrument measurement capabilities, suggesting that mixing ratios of gases contained within the flasks do not change during storage and transport. This was not true for some gases, particularly CH₃Cl and CH₃Br in the older, 0.8-L flasks.

5.1.3. Radiatively Important Trace Species (RITS) Measurements

Operations Update

The major operational change in this program over the 2-year period of this report was the relocation of equipment to new buildings at three sites. The air line intakes were not moved during this period, but in November 1995 the tower at SPO was moved and the lines extended to accommodate construction of the Atmospheric Research Observatory (ARO). Normal equipment and software maintenance continued as usual based on failures and problems reported by the site personnel.

At the C-1 site on Niwot Ridge, Colorado, a 3 m x 5 m Tall Ranch Tuff Shed was placed at the site in early October 1995 east of the existing facility. Over the next 6 months as time and weather permitted, a window was installed and the interior of the structure was wired for electricity. The building was insulated and wall board, flooring, heating equipment, and air conditioning were installed. Finish work was done by NOAA staff. University of Colorado personnel brought power to the building and installed a fiber optic computer network. On April 3, 1996, all of the equipment was moved into the new building. As the air lines were moved, one of the lines was found to have a small hole in it about 1 m from where it entered the old building. The Dekabon tubing was cut at that point and attached to the pump in the new building. A comparison of the previous month’s data shows no significant difference between the two air lines for any of the chemicals measured.

The new building at SMO was completed in early July 1996 and our equipment was the first to be moved from the old EKTO building. The equipment was checked and then

Fig. 5.7. Atmospheric dry mole fractions (ppt) of the most abundant HCFCs and HFC-134a. Each point represents the mean of two simultaneously filled flasks from one of eight stations: ALT, filled circle; BRW, filled triangle; NWR, filled diamond; KUM, crosses; MLO, open square; SMO, open triangle; COO, filled diamond; SPO, filled circle. Also plotted are results from analysis of archived air samples (open circles) filled at NWR and in a past cruise from both hemispheres (mid-1987).

Short-Lived Gases

Measurements of CH₂Cl₂, CHCl₃, and C₃Cl₃ by GC-MS techniques continued from remote flask sampling locations during 1996-1997 (Figure 5.8) and as part of CAMP. Beginning in 1995 the use of a new type of flask built at Max Planck Institute for Chemistry (MPI), Mainz, Germany, allowed for more reliable measurements of
Fig. 5.8. Atmospheric dry mole fractions (ppt) determined for selected chlorinated trace gases and CH$_3$Br. Symbols are identical to those described in Figure 5.7. Results shown for CH$_3$Cl, CH$_3$Br, and CHCl$_3$ are from 2.4-L flasks only. Results plotted for CH$_2$Cl$_2$ and C$_2$Cl$_4$ are from both 2.4-L and 0.8-L flask samples. All results are based on preliminary calibration scales.

turned off on July 20, 1996, moved and tested, and was operational on July 25th. Because the existing air lines were too short to reach into the new building, a union fitting was put in each line and about 9 m of new Dekabon tubing was added to reach the pump board.

On January 21, 1997, the computer and GC equipment were shut down in the Clean Air Facility at SPO, crated for transport, and quickly moved to the new ARO. By January 27 all of the equipment was operational again. The very long air sampling lines were moved and cable tied above the snow with other lines on poles to avoid being crushed by people and equipment. Since the distance from the ARO to the sampling tower was closer than the Clean Air Facility to the tower, the excess air line was coiled up in the crawl space below the first floor where the equipment is located.

Three 4-channel Chromatograph for Atmospheric Trace Species (CATS) (old STEALTH system) type gas chromatographs are currently in operation at HFM, ITN, and Lef. A fourth single-channel version measures N$_2$O and SF$_6$ at ALT. The RITS 3-channel GCs will be phased out after a 6-month comparison with the CATS system. This period will be used to ensure comparable results. The first CATS system was shipped in December 1997 and was installed at SPO in January 1998.

**Data Analysis**

A thorough review of our current calibration scale for CFC-12 was undertaken before an intercomparison meeting with AGAGE staff in May 1997. This resulted in changes on the order of -2% to assigned mixing ratios for all calibration tanks used at the field sites from 1993 to the present. Likewise, by applying the same techniques to other gases, the calibration scales for CFC-11, nitrous oxide, methyl chloroform, and carbon tetrachloride have changed, though not dramatically. All data presented here have had these corrections applied and are our current best estimates of what is happening in the global tropospheric atmosphere.

The revised, globally averaged maximum CFC-11 mixing ratio was 272.5 ppt in late 1993 (Figure 5.9). The mixing ratio was 268.8 ppt at the end of 1997, the growth rate was -1.3 ppt yr$^{-1}$, and the interhemispheric difference was 2.6 ppt. The global CFC-12 mixing ratio at the end of 1997 was 531.4 ppt (Figure 5.10). The growth rate slowed until mid-1996 and now appears to be holding steady at 3.6 ppt yr$^{-1}$. The average interhemispheric difference continues to decline and was 7.9 ppt in late 1997.

Carbon tetrachloride has been decreasing in the troposphere over the last 6 years at the rate of -0.7 ppt yr$^{-1}$. At the end of 1997 the global mixing ratio was 102.0 ppt and the interhemispheric difference about 1.4 ppt (Figure 5.11). The revised calibration scale has increased mixing ratios by approximately 1% from 1993 and the rate of decrease is less than previously reported.

As noted in section 5.1.2, methyl chloroform mixing ratios continue to decrease in the atmosphere (Figure 5.12). At the end of 1997 the global mixing ratio was 76.9 ppt, and the interhemispheric gradient was near zero. The global distribution in 1997 reflects the distribution of sinks more than sources now that emissions have dropped substantially.
Fig. 5.9. (a) Monthly average CFC-11 mixing ratios in ppt from the in situ GCs, (b) hemispheric and global average mixing ratios, and (c) global average growth rate in ppt yr⁻¹.

Fig. 5.10. (a) Monthly average CFC-12 mixing ratios in ppt from the in situ GCs, (b) hemispheric and global average mixing ratios, and (c) global average growth rate.

Fig. 5.11. (a) Monthly average carbon tetrachloride mixing ratios in ppt from the in situ GCs, (b) hemispheric and global average mixing ratios smoothed using a LOWESS routine, and (c) global average growth rate in ppt yr⁻¹.

Fig. 5.12. (a) Monthly average methyl chloroform mixing ratios in ppt from the in situ GCs, (b) hemispheric and global average mixing ratios, and (c) global average growth rate.
The atmospheric burden of nitrous oxide continued to increase at an average rate of 0.68 ppb yr\(^{-1}\) (RITS measurements) over the past 4 years (Figure 5.13). The global mixing ratio at the end of 1997 was 313.1 ppb and the average hemispheric difference over the 1987-1997 period was 1.2 ppb. There is an annual cycle in the southern hemisphere that is in phase with the annual cycle in the northern hemisphere, generally peaking in the first quarter of each year.

![Graph showing monthly average nitrous oxide mixing ratios in ppt from the in situ GCs, (b) hemispheric to global average mixing ratios, and (c) global average growth rate.](image)

**Fig. 5.13.** Monthly average nitrous oxide mixing ratios in ppt from the in situ GCs, (b) hemispheric to global average mixing ratios, and (c) global average growth rate.

### Chromatography and Software

Each in situ gas chromatograph system is custom designed specifically for each site. Table 5.5 lists the compounds to be sampled by the new in situ gas chromatograph at the CMDL observatories.

Chromatography is controlled and data acquired with custom programs developed on the QNX operating system run on personal computers. QNX is a UNIX-based operating system with structured C programming language support. As a multitasking operating system, QNX provides simultaneous programming functions that allow for concurrent control, data acquisition, user interface operation, and data retrieval. The enhanced capabilities of QNX have allowed the addition of features that take advantage of available technology.

### TABLE 5.5. Peak Characteristics on Four-Channel GC at SPO

<table>
<thead>
<tr>
<th>Compound</th>
<th>Channel</th>
<th>Retention Time (sec)</th>
<th>Peak Window Size (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)O*</td>
<td>1</td>
<td>250</td>
<td>40</td>
</tr>
<tr>
<td>SF(_6)*</td>
<td>1</td>
<td>310</td>
<td>20</td>
</tr>
<tr>
<td>N(_2)O†</td>
<td>2</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>CFC-12†</td>
<td>2</td>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>CFC-11†</td>
<td>2</td>
<td>215</td>
<td>70</td>
</tr>
<tr>
<td>CFC-114‡</td>
<td>3</td>
<td>200</td>
<td>20</td>
</tr>
<tr>
<td>CFC-113‡</td>
<td>3</td>
<td>235</td>
<td>20</td>
</tr>
<tr>
<td>CH(_3)Cl‡</td>
<td>3</td>
<td>350</td>
<td>20</td>
</tr>
<tr>
<td>CH(_2)CCl(_2)‡</td>
<td>3</td>
<td>425</td>
<td>30</td>
</tr>
<tr>
<td>CCl(_4)‡</td>
<td>3</td>
<td>485</td>
<td>30</td>
</tr>
<tr>
<td>TCE‡</td>
<td>3</td>
<td>590</td>
<td>40</td>
</tr>
<tr>
<td>PCE‡</td>
<td>3</td>
<td>1230</td>
<td>80</td>
</tr>
<tr>
<td>HCFC22‡</td>
<td>4</td>
<td>640</td>
<td>30</td>
</tr>
<tr>
<td>CH(_3)Cl§</td>
<td>4</td>
<td>710</td>
<td>40</td>
</tr>
<tr>
<td>CH(_2)Br§</td>
<td>4</td>
<td>1148</td>
<td>60</td>
</tr>
</tbody>
</table>

*Porapak Q column
†Unibeads 1s column (replacing old Porasil A column)
‡OV101 column
§Capillary column (Poraplot Q)

The control functions of the in situ gas chromatograph fall into two categories: those controlled by a custom digital interface and those controlled by an RS-485 network. Sample selection, chromatographic valves, cut-off solenoids, and flow controllers are controlled by a custom digital interface. Temperature controllers use an RS-485 network. Two data acquisition circuit boards handle input from the gas chromatograph electrometers, temperature sensors, and pressure sensors. Chromatographic data from the electrometers and engineering data are stored in a file buffer on the hard drive of the computer. Raw chromatograms and a representative subset of the engineering data are extracted from the buffer, compressed, and stored in a retrieval sub-directory, set up as a first-in-first-out (FIFO) on the hard drive and archived on 100 mb Iomega Zip disks at the site.

A computer workstation at CMDL Boulder automatically retrieves the chromatographic and engineering data from the in situ gas chromatograph on a daily basis for processing. Routines for this retrieval were programmed using TCP/IP - Internet links. Additional programs for use in trouble-shooting and routine maintenance have been included in the QNX software. A World Wide Web (WWW) site allows scientists and technicians to determine the operational status of the instrument system over the Internet. The WWW page includes real-time and near real-time engineering and chromatographic data displayed in tabular and graphic formats. This user interface, accessed with widely available WWW browser software, adds considerable flexibility for scientists and technicians to anticipate problems to resolve quickly.

### 5.1.4. Gravimetric Standards

The NOAA standards project was expanded in 1996 with the addition of one full-time research assistant. A new gas chromatograph, similar to the CATS GC, was tested and
calibrated. The new GC will provide measurement of CH3Br, CH3Cl, and HCFC-22 in the standards laboratory and eliminate the need for three separate GCs for measuring the other seven gases. Thirty gravimetric standards were prepared during 1996-1997. A total of 132 secondary and primary gravimetric standards were analyzed in the standards laboratory. Thirty-three standards were made for outside organizations and other NOAA laboratories. The leader of the standards project left for a new position at NIST at the end of 1997.

One of the major goals of the standards program was to provide a uniform standardization between the major networks responsible for monitoring N2O and many halocarbons in the atmosphere. A workshop was held during May 1997 in Boulder to begin this process. A series of round-robin tanks are being distributed for intercomparison. A number of tests involving cylinder stability are underway.

Calibrations for CFC-12, methyl chloroform, and carbon tetrachloride were revised since the last report [Elkins et al., 1996b]. All atmospheric CFC-12 data reported after 1993 were about 2.3% higher than actual. The reason for the error was the reliance on a set of 1993 standards that deviated from the rest of the standards which were made in 1991 and 1997 (Figure 5.14). Removal of that set resulted in a better agreement (within 1%) for atmospheric measurements of CFC-12 between the CMDL and AGAGE networks. New gravimetric standards were prepared for CH2CCL and CCL4 in 1996. After comparing standards for all gases, the same 1993 set was found to have problems with these gases too (Figure 5.15). The values of the 1993 CCL4 standards are on average 4% lower near ambient levels (102 ppt) than those made in 1991 and 1997. The net effect to atmospheric CCL4 values (RITS GCs) reported in the last summary report is small, because a calibration tracking error in the opposite direction was found. The 1993 CH2CCL3 standards exhibited greater imprecision than the combined 1991 and 1996 sets but no significant offset. The atmospheric values are relatively unchanged from the last summary report. The new scales for CH2CCL3 and CCL4 give atmospheric values that are about 8 ppt and 3 ppt higher in 1997 than those measured by AGAGE. An exchange of weighed pure solvents in sealed microtubes is planned to test methods used by both networks.

![Graph](image)

Fig. 5.14. The relative difference in percent (observed-gravimetric value) for CFC-12 standards versus the gravimetric value for those standards made in 1993 and those prepared in 1991 and 1997 for the complete range of ambient ppt mixing ratios.

Fig. 5.15. The relative difference (%) in the observed-gravimetric value for (a) CCL4 and (b) CH2CCL3 standards versus the gravimetric value for those standards made in 1993 and those prepared in 1991 and 1997 for the complete range of ambient ppt mixing ratios.

### 5.2. STRATOSPHERIC MEASUREMENTS

#### 5.2.1. AIRCRAFT PROJECTS-ACATS-IV

**ASHOE/MAESA: Stratospheric and Atmospheric Lifetimes of Source Gases**

The environmental impact of the measured anthropogenically-produced source gases depends, among other factors, on the rate at which they break down, releasing ozone-depleting chemicals in the stratosphere, i.e., on their stratospheric lifetimes. For many compounds studied here, there exist no significant tropospheric sinks (e.g., N2O, CCL4, CPCs 11, 12, and 113), so the stratospheric lifetime, defined here as the atmospheric lifetime with respect to stratospheric loss, is identical to the atmospheric lifetime for these species. A long atmospheric lifetime means a greater ozone depletion potential and a greater global warming potential than similar source gases with shorter lifetimes.

Plumb and Ko [1992] showed that in the “global diffuser” model, stratospheric transport can be described by a simple one-dimensional flux-gradient relationship. If the mixing ratios of two long-lived tracers, \( \sigma_1 \) and \( \sigma_2 \), are in steady state, then the slope of their correlation in the lower stratosphere equals the ratio of their stratospheric removal rates. Thus,

\[
\frac{\tau_1}{\tau_2} = \frac{d\sigma_1}{\sigma_2} \frac{dL}{B_2}
\]
where \( B_i \) is the total atmospheric burden for species \( i \), and \( \tau_i \) is its steady-state stratospheric lifetime, equal to the steady-state atmospheric lifetime for species without tropospheric sinks. **Volk et al.,** [1997] showed that under the same conditions, steady-state stratospheric lifetimes may be derived from the gradient of the steady-state tracer mixing ratio, \( \sigma \), with respect to the mean age of stratospheric air [Hall and Plumb, 1994], \( \Gamma \), in the measured air parcels:

\[
\frac{B}{\tau} = -\frac{\partial \sigma}{\partial \Gamma} M_u
\]  

(2)

where \( M_u \) is the total number of molecules above the tropopause, and the tracer gradient with respect to age, \( \partial \sigma/\partial \Gamma \), needs to be evaluated at \( \Gamma = 0 \) which is assumed to be the extratropical tropopause.

If the tropospheric mixing ratio of the tracer is changing with time, part of the tracer gradient at the tropopause is due to accumulation in the troposphere and \( 1/\tau_i \) in either equation (1) or (2) has to be replaced with \( \tau_i^{-1} + B_i' \), where \( B_i' \) is the total accumulation rate above the tropopause. **Volk et al.,** [1997] proposed an alternative method of accounting for tropospheric growth and non-steady-state mixing ratios, \( \chi_i \), to obtain steady-state lifetimes. In this method, one deduces the correction factors \( C(\chi_i) \) for each species using the tracer gradient with respect to age at the tropopause, \( d\chi/d\Gamma \), the time series of tropospheric mixing ratios of the respective species during a 5-year period prior to the stratospheric observations, and estimates of the width of the stratospheric age spectrum from three-dimensional transport models [Hall and Plumb, 1994].

**Volk et al.,** [1997] showed that corrected steady-state correlation slopes defined as:

\[
\frac{\partial \sigma_i}{\partial \sigma_{CFC-11}} = \left( \frac{\text{observed}}{d\chi_{CFC-11}} \right) \cdot \frac{C_i}{C(\text{CFC-11})}
\]

(3)

can be used in equation (1) to derive steady-state lifetimes based on a given CFC-11 reference lifetime. Mixing ratios of \( N_2O \) from the Airborne Tunable Laser Absorption Spectrometer (ATLAS) [Loewenstein et al., 1989] and ACATS CFC-113 plotted against ACATS IV CFC-11 (Figure 5.16a, b) are used to calculate the observed gradient \( d\chi/d\chi_{CFC-11} \) in Table 5.6. ATLAS \( N_2O \) measurements were calibrated from CMDL \( N_2O \) standards and agreed with onboard ACATS \( N_2O \) measurements to within ±2%. ATLAS \( N_2O \) data are used here to increase the number of measurements used by a factor of 2. The steady-state stratospheric lifetime for a source gas using the reference lifetime for CFC-11 is:

\[
\tau = \left( \frac{\tau_{CFC-11} - \frac{\sigma}{\sigma_{CFC-11}}}{C_i \frac{\partial \chi}{\partial \chi_{CFC-11}}} \right)
\]

(4)

\[
\frac{C_i}{C(\text{CFC-11})} = \frac{\tau_{CFC-11}}{d\chi_{CFC-11}}
\]

where \( \sigma \) is the mean atmospheric mixing ratio with the gradient calculated at the tropopause. From Figure 5.16 and Table 5.6, the steady-state atmospheric and stratospheric lifetime for \( N_2O \) is 122 ± 22 years and for CFC-113 is 100 ± 32 years using a CFC-11 reference lifetime of 45 ± 7 years using equation (4).

The steady-state gradient, \( \partial \sigma / \partial \Gamma \) defined as (observed \( d\chi/d\Gamma \) times \( C(\chi_i) \)), is used in equation (2) to obtain the steady-state lifetime using the “mean age” technique. The steady-state stratospheric lifetime for a source gas based on mean age becomes:

\[
\tau = -\frac{\partial \sigma M_a}{d\Gamma_{\tau=0}}
\]

(5)
TABLE 5.6. Stratospheric Steady-State Lifetimes From Volk et al. [1997] Compared to Current Reference Values

<table>
<thead>
<tr>
<th>Source Gas</th>
<th>Observed $\frac{d\phi}{dt}$ (ppt yr$^{-1}$ ± %)</th>
<th>Steady-State Lifetime Based on Age (year)$^*$</th>
<th>Observed $\frac{d\phi}{dt}$ CFC-11 (ppb ppt, ± %)</th>
<th>Steady-State Lifetime Based on CFC-11 (year) $t_{CFC-11} = 45$ ± 7 yr$^+$</th>
<th>WMO/IPCC Reference Lifetimes (year)</th>
<th>Correction Factor (Cd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>-13.000 ± 38%</td>
<td>124 ± 49</td>
<td>436 ± 11%</td>
<td>122 ± 22</td>
<td>120±</td>
<td>0.97 ± 0.02</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>-109.0000 ± 48%</td>
<td>84 ± 35</td>
<td>3230 ± 10%</td>
<td>93 ± 14</td>
<td>120±</td>
<td>0.96 ± 0.02</td>
</tr>
<tr>
<td>CFC-12</td>
<td>-43.8 ± 25%</td>
<td>77 ± 26</td>
<td>1.29 ± 7%</td>
<td>87 ± 17</td>
<td>105±</td>
<td>0.77 ± 0.07</td>
</tr>
<tr>
<td>CFC-113</td>
<td>-7.3 ± 22%</td>
<td>89 ± 35</td>
<td>0.212 ± 20%</td>
<td>100 ± 32</td>
<td>85±</td>
<td>0.65 ± 0.12</td>
</tr>
<tr>
<td>CCl$_2$</td>
<td>-33.5 ± 28%</td>
<td>41 ± 12</td>
<td>(1)</td>
<td>(45 ± 7)</td>
<td>50±</td>
<td>0.96 ± 0.02</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>-16.3 ± 35%</td>
<td>32 ± 11</td>
<td>0.515 ± 3.6%</td>
<td>32 ± 6</td>
<td>42±</td>
<td>1.03 ± 0.02</td>
</tr>
<tr>
<td>H-1211</td>
<td>-0.84 ± 31%</td>
<td>20 ± 9</td>
<td>0.472 ± 10%</td>
<td>34 ± 8</td>
<td>45±</td>
<td>1.14 ± 0.13</td>
</tr>
</tbody>
</table>

where $M_A$ is the total atmospheric mass (5.13 x 10$^{18}$ kg) and $M_a$ is the total atmospheric mass in the upper atmosphere above the tropopause (1.1 x 10$^{18}$ kg). From Figure 5.16 the steady-state and stratospheric lifetime for N$_2$O is 124 ± 49 years and for CFC-113 is 89 ± 35 years based on “mean age” calculated using equation (5) (Table 5.6). The uncertainties on the lifetimes using mean age are less precise than those calculated from the reference lifetime method because SF$_6$ was only measured during the last quarter of the flights during ASHAE/MAESA.

Lifetime results from the two methods presented in Volk et al., (1997) are consistent with each other (see Table 5.6). In most cases the calculated stratospheric lifetimes from observations are shorter than the World Meteorological Organization (WMO) or the Intergovernmental Panel on Climate Change (IPCC) reference lifetimes derived from photochemical models. Since the derived stratospheric lifetimes are identical to the atmospheric lifetimes for many of the source gases in Table 5.6, the shorter lifetimes also would imply a faster-than-predicted recovery of the ozone layer following the complete phase out of industrial halocarbons.

**STRAT CAMPAIGN**

The primary goal of the Stratospheric Tracers of Atmospheric Transport (STRAT) mission was to measure the morphology and dynamic properties of long-lived tracers as functions of altitude, latitude, and season to help determine the rates for global-scale transport and future stratospheric distributions of high-speed civil transport (HSC) exhaust. ACATS-IV participated in four out of six STRAT deployments and was flown on a total of 31 flights that spanned a range of latitudes (2.1°S to 59.1°N), predominantly at 15 to 21 km altitudes (potential temperature, $\theta = 360$ to 510 K). These flights included four southbound survey flights into the tropics from Barbers Point, Hawaii (22°N), four northbound survey flights to nearly 60°N from Moffett Field, California (38°N), and 23 midlatitude flights from both locations.

Sulfur hexafluoride has no known sinks below the stratosphere ($\tau = 3200$ years, [Ravishankara et al., 1993]) and has exhibited a steady rate of growth of 6.7% yr$^{-1}$ in recent years [Geller et al., 1997]. It is used to study atmospheric transport processes and the age of air masses in the upper atmosphere [Geller et al., 1997; Volk et al., 1997; Wamsley et al., 1998]. The age of air masses at the tropical tropopause is defined as zero. Tropospheric air masses that have not yet reached the tropopause are associated with negative ages. ACATS-IV measurements of SF$_6$ in the northern midlatitude upper troposphere during November 1995 and December 1996 show that mixing ratios increased by approximately 0.28 ppt in 13 months, which is close to the 0.26 ppt expected from the documented growth rate (Figure 5.17). Figure 5.18 shows the convergence of the November 1995 and December 1996 data sets above $\theta = 450$ K that are due to the increased effects of stratospheric mixing with age of the air.

In the tropics (2°S to 20°N) vertical profiles of the mixing ratios of trace gases with different lifetimes conform to the results of Volk et al. [1996] (that is, entrainment into a “leaky tropical pipe”). This entrainment of midlatitude air results in “proportionally mixed” tropical profiles, which for CFC-11 are shifted about 15% from the unmixed tropical model line of Volk et al., [1996] shown in Figure 5.18. In the altitude range important for HSC (16-20 km), ACATS-IV tropical data show several intrusions of midlatitude air into the tropics, denoted by several measurements that lie far to the left of the proportionally mixed tropical profiles ($\theta = 410-450$ K and at 480 K, Figure 5.19). The trace gas mixing ratios of the intruding air masses are about 50% lower than the proportionally mixed profiles and are more typical of midlatitude air from much further aloft ($\theta > 440$ K; the midlatitude data are shown by a red line and a 95% prediction band on Figure 5.18). Similar, but weaker intrusions of midlatitude air at the same $\theta$ can also be seen in other tropical data [Elkins et al., 1996a; Volk et al., 1996].

The entrainment of midlatitude air into the tropics is illustrated further by looking at the age of the air in the tropical region. The age measured during the flight of December 11, 1996, reaches 1.2-2.3 years at both 410-450 and 480 K surfaces in the latitude range from 12°N to...
during POLARIS (Figure 5.23), calculated from ACATS-IV SF₆ measurements, demonstrates that the tropical lower stratosphere is characterized by young air (0.3 to 0.8 year average) and that the lines of stable tracer mixing ratios (isopleths) typically follow θ surfaces. Air masses older than 4 to 5 years are generally found poleward of 50°N, but in some cases were observed around 40°N. The oldest air masses encountered during POLARIS were 6.7 years at about 60-65°N in late June 1997.

5.2.2. High Altitude GC Tracer Measurements Project: OMS/STRAT/POLARIS

LACE is a relatively new, three-channel GC instrument (Figure 5.24). It was constructed to extend real time GC measurements of atmospheric tracers such as those measured with the ACATS instrument, to higher altitudes of up to 32 km where, particularly in the tropics, a larger portion of ozone production and loss takes place. The LACE instrument has also made improvements on the spatial and temporal resolution by speeding up the chromatography to obtain a sampling period of 70 seconds. Many of these improvements have now been incorporated into the ACATS instrument. During 1997 LACE obtained high-quality data from four balloon flights onboard the Observations of the Middle Stratosphere (OMS) gondola. As part of the STRAT campaign, LACE flew one midlatitude flight out of New Mexico at 35°N and two tropical flights out of Brazil at 7°S. There was also one polar flight out of Fairbanks at 65°N as part of the POLARIS campaign.

The OMS package is currently configured to make measurements pertinent to stratospheric transport issues. Toward this end, LACE has made in situ measurements from the surface to the middle stratosphere of the long-lived tracers H-1211, CFC-11, -113, -12, N₂O, and SF₆.
with a typical precision of between 1\% and 4\%. The stratospheric lifetimes of these halocarbons and nitrous oxide are dominated by simple photolysis. Their global atmospheric lifetimes span several orders of magnitude. The local photolytic lifetimes of some gases are reduced by 4 orders of magnitude from the tropopause to 32 km. This range in lifetimes covers the dynamic time scales of stratospheric transport. Gas mixing ratios are extremely sensitive to this transport with a strong dependency on vertical flow. Sulfur hexafluoride, however, does not have this altitude-dependent photo-disassociation and has a global atmospheric lifetime greater than 3200 years. Spatial and temporal gradients in the mixing ratio of SF\(_6\) are, therefore, driven by surface emissions which are predominantly in the northern hemisphere. This leads to a large interhemispheric surface gradient and, in this instance, a nearly linear surface growth rate [Geller et al., 1997]. Because there is no known stratospheric sink for SF\(_6\), its sensitivity to transport is driven entirely by the mean transit time from this growing tropospheric source. Unlike the halocarbons, the measured gradients in the value of SF\(_6\) in the stratosphere have only a passive sensitivity to altitude, yet maintain a strong dependency on the time scales of transport [Volk et al., 1997]. Our current precision of SF\(_6\) in the stratosphere is 2\%, which translates to 3.5 months of growth.

Although this 3.5 month resolution is adequate to track stratospheric dynamics by defining a mean age of the air parcel since entering the stratosphere, it is not adequate to track transport within the free troposphere other than interhemispheric exchange. Nonetheless, tropospheric vertical gradients with both temporal and latitudinal dependence appear to persist. The interhemispheric surface gradient is believed to be transported into the free troposphere between 30\(^\circ\)N and 30\(^\circ\)S in a time scale comparable to or faster than this 3.5-month resolution. A measurement of these vertical gradients in the SF\(_6\) mixing ratio below the 380 K isotherm coupled
Finally the CFCs and H-1211 mixing ratios represent a significant fraction of the total chlorine and bromine entering the stratosphere. As with the ACATS instrument, an estimate of total chlorine and bromine and their organic-inorganic partitioning can be made from LACE measurements.

**Stratospheric Dynamics**

Major strides in understanding the interactions between pollutants, production to loss of ozone, and climate forcing have been made in the last decade. Today, uncertainties in transport appear to be the limiting parameter in predictive three-dimensional models. The quality of the upcoming assessment on the environmental impact of existing aircraft and the proposed High Speed Civilian Transport (HSCT) fleet is, therefore, limited by our ability to quantify stratospheric transport. In evaluating LACE data, estimates have been made of entrainment of air from midlatitudes into the tropics, the mean age of an air parcel after crossing the tropical tropopause, and mean flow. Breakdown of the arctic vortex and the resulting cross theta “mixing surface” was also observed in the LACE measurements.

As discussed by Plumb and Ko [1992], tracer-tracer correlations between simple photochemical species are robust as long as quasi-horizontal mixing dominates over vertical advection, as in the global diffuser model. In the “tropical pipe” model of Plumb [1996] the concept of a weak tracer-tracer correlation is also valid in the midlatitudes and, to a large degree, in the tropics on the other side of the tropical barrier. Mixing across this barrier, the so-called leaky pipe, connects these two regions. This mixing is a major mechanism for transport of midlatitude, lower stratospheric air into the middle and upper stratosphere. This midlatitude mixing into the tropics is also a key uncertainty in the HSCT assessment and has been a primary focus of the OMS platform.

A modified Volk et al. [1996] analysis, which quantifies the mixing of air from the extratropical stratosphere into the tropical pipe, has been extended to 32 km by using the new LACE CFC and SF$_6$ profiles. Two approaches have proven fruitful. The first approach relies on mean vertical advection rates ($Q$). Local chemical losses of the CFCs are dominated by simple photolysis; therefore, assuming no midlatitude influence, isolated tropical profiles can be calculated given the advection rate, photochemical lifetimes ($\tau$), tropospheric growth rates ($\gamma$), and mixing ratios ($\chi$) of the CFCs entering the tropical tropopause (Figure 5.25a,b; dotted black line). These isolated tropical profiles can then be evolved a second time to incorporate mixing from midlatitudes along constant potential temperature ($\Theta$) surfaces. This is done with the entrainment time ($\tau_{in}$) assumed to be constant. The tracer continuity is governed by equation (6).

$$\frac{\partial \chi}{\partial t} = Q - \frac{\chi}{\tau} - \gamma \chi - \frac{(\chi - \chi_{mid})}{\tau_{in}}$$

(6)

These profiles have also been corrected for weak O($^1\Sigma$) chemistry and photochemical production ($P$) (Figure 5.25a,b).
LACE data are consistent with a constant entrainment time of $1.5^{19}/_{12}$ months over the entire range up to 32 km (Figure 5.25c). By 32 km, 90% of the air in the tropical upwelling region is of midlatitude origin because of the total integrated entrainment. A comparison of the first approach (equation 6), which is sensitive to Q, with the second approach (equation 7), which is independent of Q, may help to constrain mean flow in the tropics. This work is consistent with the Volk et al. [1996] earlier analysis and is expected to generate a more complete picture of midlatitude intrusions into the tropics when finalized.

Data taken recently in the tropics also revealed air masses that were of midlatitude origin showing the characteristic signature of lower mixing ratios. Surprisingly, the ozone profile did not show the same midlatitude signature and remained representative of tropical air. The chemical equilibrium time for ozone at these locations is fast (weeks to a month), apparently much faster than the mixing time over the spatial scale of these midlatitude intrusions during this time of weak upwelling. These data and the chemical equilibrium time of ozone can, therefore, set lower limits on mixing within the tropical upwelling region.

Sulfur hexafluoride has proven to be useful for evaluating transport in the lower and middle stratosphere. Measurements of stratospheric SF$_6$ permit an accurate determination of the mean age of an air parcel after it crosses the tropical tropopause. Mean age estimates are shown in Figure 5.26 for all LACE flights and threedimensional model estimates. In general, these models underestimate the age of air as defined by SF$_6$ distributions. Although increased mixing from midlatitudes could account for the older measured age in the tropics, the excessively young midlatitude model estimates imply that mean flow in these models is too high.

One important lesson from our OMS balloon launch from POLARIS in Fairbanks was the observation of unmixed and mixed remnants of the polar vortex from the earlier March 1997 arctic ozone depression. Because the remnants of this vortex lasted as late as July, these measurements show one reason why we should continue to sample the arctic. As shown in Figure 5.27, this mixed air is clearly not representative of a typical midlatitude distribution and must continually be monitored to quantify both the chemistry and dynamics that are taking place at the pole.

**Atmospheric Dynamics Below the 380 K Isentropic Surface**

LACE has taken highly precise measurements of several trace gases in the lowermost stratosphere and upper troposphere, regions for which very little tracer data exist. Measurements of SF$_6$ and CFC-11, in particular, reveal many interesting features in these regions and their vertical gradients offer constraints on transport time scales. Simulation of these tracer gradients by models is important for an accurate assessment of tracer transport in the lower stratosphere and troposphere where the impact of aircraft exhaust and the transport of greenhouse gases play a key role.
Fig. 5.26. Profiles of mean age of the air from zonally-averaged models (supplied by D. Waugh [private communication, 1998]). This modeled age is plotted with (a) ACATS measured age (triangles) against latitude, and LACE measured age (diamonds) against altitude for (b) the tropics at -5° latitude, (c) the midlatitudes at 35° latitude, and (d) the polar regions at 65° latitude. The shaded region indicates the dominant range of model results. Mean age is taken to be zero at the equator at 20.0 ± 0.5 km.

The lowermost stratosphere is that part of the stratosphere that lies between the tropopause and the 380 K potential temperature surface. The lowermost stratosphere is a unique part of the stratosphere, since air can be exchanged isentropically between the stratosphere and troposphere. Thus the lowermost stratosphere contains a mixture of older stratospheric air that has been advected downward by the mean meridional circulation and tropospheric air that has been transported isentropically. The relative importance of downward advection and isentropic transport largely depends on season and location.

Figure 5.28 shows profiles of SF₆ and CFC-11 from the Ft. Sumner flight on September 21, 1996. The 380 K and tropopause heights are indicated on the figure and lines are drawn through the data in each height region. The two profiles have different vertical gradients in the lowermost stratosphere. CFC-11 has almost no vertical gradient below the 380 K surface, while SF₆ has a large vertical gradient in the lowermost stratosphere and a small but still noticeable gradient in the upper troposphere. The constant CFC-11 mixing ratio suggests that the gradients seen in the SF₆ profiles are of tropospheric origin. Downward advection would have a larger effect on CFC-11 because of its more rapid decrease above the 380 K surface. Weak downward flow across the 380 K surface at the time of our flight is consistent with the seasonality of the mean meridional circulation in the stratosphere and the midlatitude location.

The vertical gradient in SF₆ from the Ft. Sumner flight is, therefore, assumed to be due to an interplay between

isentropic mixing from the tropical upper troposphere and residence time of air in the lowermost stratosphere. Were it the result of growth, the vertical gradient in SF₆ would
represent a 9-month age difference over the depth of the lowermost stratosphere. The time scale of isentropic mixing between the tropopause and the northern midlatitudes is on the order of a month or less and the flushing time of the northern hemisphere lowermost stratosphere is thought to be roughly 4 or 5 months. Therefore, some of the vertical gradient in the lowermost stratosphere could be caused by transport of the interhemispheric gradient of surface SF$_6$ to the upper troposphere. Some portion of the interhemispheric gradient in SF$_6$ is likely to be mapped along the tropopause from the tropics to the midlatitudes. As tropospheric air is isentropically mixed into the midlatitude lowermost stratosphere, the latitudinal tropopause gradient will contribute to the vertical gradient of SF$_6$ in the lowermost stratosphere.

This gradient in SF$_6$ along the tropopause may have a strong dependence upon seasonal variability of tropospheric transport, coupled with the interhemispheric gradient of SF$_6$ at the surface. Profiles of SF$_6$, which have been normalized to remove the growth rate for the two Brazil flights, are shown in Figure 5.29. The February Brazil flight has SF$_6$ mixing ratios in the upper troposphere that are close to the global mean surface value and decrease toward the southern hemisphere surface average with decreasing height (Figure 5.29). This profile is consistent with a significant amount of northern hemisphere surface air entering the tropical upper troposphere during February. The monthly mean position of the Hadley circulation was estimated by Oort and Yienger [1996]. In January and February the northern hemisphere Hadley cell is shifted south and is also consistent with a significant amount of northern hemisphere surface air being transported into the tropical upper troposphere as suggested by our data.

The November flight has a nearly constant mixing ratio in the upper troposphere that is close to the southern hemisphere surface average. In October and November the northern hemisphere Hadley cell is weak and shifted north of the equator so the tropical upper troposphere should be dominated by southern hemispheric air at a 7°S, again consistent with our data.

These tropical profiles suggest that the seasonal cycle of the Hadley circulation causes a seasonal cycle in the SF$_6$ mixing ratios in the tropical upper troposphere. This seasonal cycle will likely cause a seasonal cycle in the latitudinal gradient of SF$_6$ mixing ratios along the tropopause, since the mean Hadley circulation flow in the upper troposphere is poleward. For the northern hemispheric tropopause we would expect a large gradient during summer, when more southern hemispheric surface air is transported into the tropical upper troposphere, and a weak gradient during winter when mostly northern hemispheric surface air is transported into the tropical upper troposphere. Our midlatitude flight was in September at the beginning of fall when a remnant of the tropopause gradient caused by the summer tropospheric transport could have been present. This also suggests that a small seasonal correction to the connection between stratospheric age of air and the CMDL global average may be needed.

The effects of significant mean downward motion across the 380 K surface on trace gas profiles in the lowermost stratosphere can be seen in Figure 5.30. CFC-12, -11, H-1211, and SF$_6$ measurements from the June 30, 1997, flight over Fairbanks are shown in this figure along with the heights of the 380 K and tropopause surfaces. Mixing ratios of all four tracers decrease above the tropopause.

This decrease and the vertical gradient in the lowermost stratosphere are largest in the shortest lived tracer, H-1211, which is consistent with the expected effect of downward advection. Subsequently smaller decreases above the tropopause and vertical gradients in the lowermost stratosphere are seen in CFC-11 and CFC-12 which have longer photochemical lifetimes. SF$_6$ also has a large decrease above the tropopause due not to photolysis but to its growth rate. Air advected down across the 380 K surface in the high latitudes is 2 years older on average, than northern tropospheric air. Therefore the sharp decrease in SF$_6$ above the tropopause is a result of the growth of SF$_6$ in the northern high-latitude troposphere during the time air was transported to the high-latitude lowermost stratosphere.

Even though June is a time of relatively weak mean downward flow in the northern hemisphere high latitudes, the tracer data suggest that this flow is the dominant transport into this part of the lowermost stratosphere. It is interesting to note the relative compactness of the profiles above and below the 380 K surface. The lowermost stratosphere appears to be relatively well mixed compared with the stratosphere above the 380 K surface.
5.3. OCEAN PROJECTS

5.3.1. SOUTHERN OCEAN EXPEDITION - BLAST III

The flux of CH$_3$Br from the world’s oceans has been a source of considerable controversy over recent years. Although earlier studies suggested the ocean was a large, net source of atmospheric CH$_3$Br [Singh et al., 1983; Singh and Kanakidou, 1993; Khalil et al., 1993], recent widespread examinations by CMDL of the saturation of CH$_3$Br in the east Pacific and Atlantic Oceans showed that most of the ocean was undersaturated in this gas [Lobert et al., 1995, 1996; Butler et al., 1995]. Extrapolation of these data indicated that the global oceans were a net sink for atmospheric CH$_3$Br.

Two subsequently published numerical models, however, suggested that polar and sub-polar oceans might be a large, net source of atmospheric CH$_3$Br [Pilinis et al., 1996; Anbar et al., 1996]. The two models used production rates based on data published by Lobert et al. [1995], presuming them to be either constant over the entire oceanic regions or a function of chlorophyll-a concentration. With chemical degradation being very slow in cold, polar waters, and a very high biological productivity during the austral summer, the predicted saturation anomalies were positive and ranged up to 500%, indicating this polar source could globally outweigh the sinks estimated by Lobert et al. [1995]. To resolve this question, CMDL conducted a study to measure the saturation of CH$_3$Br in the Southern Ocean during a time of high biological productivity (Bromine Latitudinal Air-Sea Transect (BLAST) III, Figure 5.31, Lobert et al. [1997]).

The shipboard GC/MS and sampling system was virtually identical to that used during the two previous cruises. On this cruise CH$_3$Br was also measured with a custom-built GC equipped with an ECD and different columns. Mole fractions from MS and ECD systems agreed, on average, within 0.2 ppt (Figure 5.32, Table 5.7). Measured, dry mole fractions of CH$_3$Br in the atmosphere were consistent with data from the BLAST I and BLAST II cruises. Most important, however, is that the ocean in this region was consistently undersaturated in CH$_3$Br with a mean saturation anomaly corrected for physical effects of $-33 \pm 8\%$ (Figure 5.32c, Table 5.7).

Maintaining a steady-state, $-35\%$ undersaturation of CH$_3$Br in the surface waters in the presence of air-sea exchange requires a minimum in situ degradation rate of about 5.8% d$^{-1}$, which is a factor of 10 larger than that for chemical degradation alone. The most likely explanation of these findings is that dissolved CH$_3$Br is being degraded by an additional mechanism other than reaction with H$_2$O.

Fig. 5.30. Profiles of CFC-12, CFC-11, H-1211, and SF$_6$ from the Fairbanks, Alaska, flight. The tropopause and 380 K surfaces are indicated. The three distinct regions, the middle stratosphere (above 380 K), the lowermost stratosphere, and the troposphere, are clearly defined by both the gradients and spread in the data. Relationships between the time scales of mean flow and mixing can be inferred.

Fig. 5.31. BLAST III cruise track from McMurdo, Antarctica, to Punta Arenas, Chile, aboard the RV Nathaniel Palmer, Cruise 96-02. Numbers along the cruise track indicate the Julian day of year 1996.
and Cl\(^{-}\). A significant biological sink for CH\(_3\)Br in subtropical waters has been identified recently [King and Saltzman, 1997], suggesting that the additional sink might be biological.

Several conclusions can be drawn from this study. First, the Southern Ocean, and probably most high-latitude waters, are a net sink for atmospheric CH\(_3\)Br. Second, biological processes, or some chemical processes other than reaction with H\(_2\)O or Cl\(^{-}\), rapidly remove CH\(_3\)Br from surface waters. Third, CH\(_3\)Br production is neither constant over the global ocean nor strictly dependent upon chlorophyll concentration. The data from this expedition and those from BLAST I and BLAST II suggest that the global ocean is a net sink of 21 \((11-31)\) Gg yr\(^{-1}\) for CH\(_3\)Br.

### 5.3.2. Oceanic Uptake of Atmospheric Trace Gases

The atmospheric lifetime of a trace gas is derived from the sum of its sinks or loss rates. Loss to the ocean is a significant sink for some gases. Over the past few years a gridded, finite-increment model was developed to determine the uptake rate constant and partial atmospheric lifetime with respect to oceanic degradation for any trace gas that reacts in seawater. The model, originally developed to study the oceanic uptake of atmospheric methyl bromide (CH\(_3\)Br) [Butler, 1994; Yvon and Butler, 1996; Yvon-Levis and Butler, 1997], is used here to calculate the oceanic uptake rate and partial atmospheric lifetime of chlorocarbons, HCFCs, and HFCs (Figure 5.33, Table 5.8). The oceanic uptake rate (mol yr\(^{-1}\)) is defined in the following equation:

\[
\text{Uptake} = \frac{K_{W}A}{H} \left( \frac{r}{n_{tr}} \right) \left( \frac{k_{d} + K_{biod} + \sqrt{D_{k}z}}{k_{d} + k_{biod} + \frac{D_{k}z}{z} + \left( \frac{K_{W}}{z} \right)} \right)
\]

The rate constant \((k_{ocn})\) and lifetime \((\tau_{ocn})\) for this removal process can then be calculated from the following equation:

\[
k_{ocn} = \frac{1}{\tau_{ocn}} = \frac{K_{W}A}{H} \left( \frac{r}{n_{tr}} \right) \left( \frac{k_{d} + K_{biod} + \sqrt{D_{k}z}}{k_{d} + k_{biod} + \frac{D_{k}z}{z} + \left( \frac{K_{W}}{z} \right)} \right)
\]

![Schematic of the air-sea flux of a trace gas. Terms are as described in Table 5.8.](image)

**TABLE 5.7. Mean Mixing Ratios of CH\(_3\)Br in Air and Equilibrated Water during BLAST III**

<table>
<thead>
<tr>
<th></th>
<th>GC/MS (ppt)</th>
<th>GC/ECD (ppt)</th>
<th>Mean Saturation Anomaly*</th>
<th>Corrected Saturation Anomaly†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>8.3 ± 0.3</td>
<td>8.5 ± 0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrated</td>
<td>5.5 ± 0.6</td>
<td>5.6 ± 0.8</td>
<td>-36 ± 7%</td>
<td>-33 ± 8%</td>
</tr>
</tbody>
</table>
Initially this equation was applied to a $2^a \times 2^b$ grid of physical properties in and over the global ocean for the calculation of the partial atmospheric lifetime with respect to oceanic uptake for CH$_3$Br (Figure 5.34). The inclusion of both the chemical and biological degradation rates for CH$_3$Br in the ocean resulted in a partial atmospheric lifetime of 1.8 (1.1-3.9) years, which is substantially shorter and more certain than the 3.7 (1.4-14) year estimate calculated by Butler [1994], owing to the inclusion of spatial variability in oceanic physical properties and biological degradation rates. The corresponding atmospheric lifetime, including soil to atmospheric sinks for CH$_3$Br, is 0.7 (0.5-1.2) years.

Oceanic uptake does not appear to be a significant sink for many of the HCFCs and the HFCs (Table 5.9). Because biological degradation processes have not been investigated for most of these trace gases, the term ($k_{biol}$) was null in these calculations. Model results for these gases depend upon chemical degradation rates alone. The presence of any biological degradation would result in substantially reduced lifetimes. Evidence for the presence of degradation mechanisms other than the hydrolysis reaction used in this model has been observed in the saturation anomaly data for CH$_3$Br, CH$_3$Cl, and CCl$_4$.

The $\tau_{ocean}$ values calculated by Wine and Chameides [1989] are shorter than those determined by this model because the investigators neglected stratification below the mixed layer [e.g., Butler et al., 1991]. At this time there are no available data on the degradation rate constants...
and/or solubilities for many of the halocarbons found in the atmosphere. This lack of data prevents us from calculating the effect of oceanic degradation processes on the lifetimes and budgets of many trace gases. Accounting for the oceanic uptake of CHCl and OCS resulted in reductions of 3% and 25% in the total atmospheric lifetimes for these species.

5.4. GC Measurements at Two Tall Towers in the U.S.

Automated, four-channel GCs have been in operation at the 610 m WITN tower in eastern North Carolina (NC) since November 1994 and at the 447-m WLEF tower in northern Wisconsin (WI) since June 1996. Every hour these instruments measure 12 trace gases (CFC-11, CFC-12, CFC-113, CHCl, CCl, CCl, N,O, SF, H, CH, and CO) at 51, 123, and 496 m above ground on the NC tower and at 30, 76, and 396 m on the WI tower. The GCs are calibrated hourly with two standards of dried, whole air stored in AcuLife-treated aluminum cylinders, one of which has been diluted by 10% with zero air. The design and operation of the GC at the NC tower were described previously [Elkins et al., 1996a; Hurst et al., 1997a].

Trace gas mixing ratios at the two towers are variable on diurnal, synoptic, seasonal, and longer time scales. Diurnal variations result primarily from the daily development of the planetary boundary layer (PBL), which defines the mixing depth of ground-based source emissions. At night, local and regional emissions augment mixing ratios beneath a shallow (100-200 m) inversion and create significant vertical gradients. During the late morning and afternoon, this vertical structure disappears as emissions are rapidly mixed into a 1-2 km deep PBL by convection [Hurst et al., 1997a, 1998]. Diurnal variability at the lower two sampling levels on each tower is greater than at the top because the nocturnal inversion consistently lies between the middle and top sampling levels.

Synoptic-scale variability is driven predominantly by the transport of pollution plumes from regional urban centers to the measurement sites. Daily mean mixing ratios (and daily standard deviations) at 496 m on the NC tower during 1996-1997 illustrate day-to-day (and diurnal-scale) variability (Figure 5.35). Daily means 5-10% above the majority of the data are regular features, especially for CCl. Significant long-term trends in CHCl and SF are mixing ratios at the NC tower are also evident (Figure 5.35). Linear fits to regional "background" mixing ratios during 1996-1997 at the NC tower imply trends of -16.5 ± 0.5 ppt yr for CHCl and 0.24 ± 0.01 ppt yr for SF [Hurst et al., 1997b] which are in good agreement with background trends at remote northern hemispheric sites (Figure 5.4) [Montzka et al., 1996; Geller et al., 1997].

Synoptic-scale variability of trace gases at the NC tower was analyzed to identify regional-scale emission ratios [Bakwin et al., 1997]. CCl was chosen as the reference compound because of its high ratio of atmospheric variability to measurement precision at the NC tower and its reasonably well-known emissions [McCulloch and Midgley, 1996]. Several statistical approaches were used for the analysis, including a method where "scores" for each trace gas were computed as the sum of its mixing ratios during pollution events >4 hours in duration. For December 1994 through August 1996, 211 pollution events of 4 to 273 hours duration were identified [Bakwin et al., 1997]. Event scores for each trace gas were plotted against those for CCl and fit with a linear, orthogonal distance regression (Figure 5.36) to determine a regional-scale emission ratio. CCl correlated well with CFC-12, -11, CHCl, SF, and several other gases (r >0.85). North American source strengths estimated from this "score" method and a time-domain analysis of the data are in good agreement with industry estimates for CHCl and CO but are 35-75% lower for CFCs. Discordance in CFC estimates may indicate that CFC emissions from the region surrounding the NC tower are not representative of North America (although CHCl and CO emissions appear to be) or that industry estimates of CFC emissions during 1995-1996 are too high. The latter scenario is supported by Elkins et al. [1993] and Cunnold et al. [1997] who demonstrated that global-scale observations of CFC-11 and CFC-12 mixing ratios during the 1990s are significantly lower than those calculated from emission inventories.

The synoptic-scale variability of several halogenated trace gases recently decreased at both the NC and WI towers reflecting reductions in regional-scale emissions [Hurst et al., 1998]. Mixing ratio variability at all sampling heights on the towers was examined, but trends were deduced using only nighttime data from the top sampling level of each tower. This was done to minimize the influences of local sources and diurnal-scale variability, leaving regional emissions as the primary source of variability. Monthly variability, calculated as one standard deviation of monthly-binned mixing ratios with measurement errors subtracted in quadrature, was plotted as a
time series and fit with a linear least-squares regression (Figure 5.37). Variability at the remotely-located WI tower was generally lower than at the NC tower, which is closer to large urban centers.

Fig. 5.35. Time series of daily mean mixing ratios of CH$_3$CCl$_3$ (circles), C$_2$Cl$_4$ (crosses), and SF$_6$ (inverted triangles) at the NC tower during 1996-1997. The mean mixing ratio ± one standard deviation for each day are represented by vertical bars (solid for CH$_3$CCl$_3$ and SF$_6$, dashed for C$_2$Cl$_4$).

Significant decreases in the synoptic-scale variability of CFC-12, CFC-113, CH$_3$CCl$_3$, and C$_2$Cl$_4$ were observed at both towers (Table 5.10). With the exception of CH$_3$CCl$_3$, variability trends at the two towers agreed within their quoted uncertainties. The variability trend for CH$_3$CCl$_3$ at the NC tower, $-1.31 \pm 0.19$ ppt yr$^{-1}$, represents a $72 \pm 11\%$ decrease in regional emissions between early 1995 and late 1997. Trends for CFC-11, CCl$_4$, and SF$_6$ at both towers did not differ significantly from zero. However, because of the low ratios of atmospheric variability to measurement precision for these gases, only trends $>25\%$ over the entire measurement period at each tower could have been detected at a $75\%$ level of confidence. Reductions in CFC-12, CFC-113, and CH$_3$CCl$_3$ emissions are attributed to production restrictions imposed by the Montreal Protocol. Reduced emissions of C$_2$Cl$_4$ are probably the result of recent requests to industry by the U.S. Environmental Protection Agency (EPA) to voluntarily reduce emissions of this compound because of its toxicity.

5.5. Firn Air Measurements

Past success in analyzing for halocarbons in air samples collected from firn (unconsolidated snow) at the South Pole [Elkins et al., 1996a] prompted us to continue these investigations in Greenland and Antarctica. Our initial measurements of South Pole firn air were from low pressure glass flasks used in collecting air for carbon-cycle gases. Although these measurements seemed reasonable and the samples generally uncontaminated, they could only be run on two of our instruments; GC MS measurements were precluded for the South Pole samples because of a lack of available air. In April 1996 we assisted in the collection of samples from two holes at Tunu, Greenland (78°01’N, 33°59’E) and filled our usual 2.5-L stainless steel flasks to 375 kPa (yielding about 9 L of air) in
addition to the glass flasks (150 kPa, yielding only 3.8 L air, most of which is used in analyses for carbon-cycle gases by the CMDL Carbon Cycle Group). Samples were returned to Boulder for analysis on all four instruments used in flask analyses (Table 5.2). Both glass flasks and steel flasks were run on the two GC/ECD systems and steel flasks were run on the two GC/MS systems. Similarly we obtained samples in both steel and glass flasks from deep and shallow holes drilled at Siple Dome, Antarctica (81°40'S, 148°49'W), in December 1996.

Data from these sites showed that CFCs, CH₃CCl₃, CCl₄, SF₆, halons, and HCFCs were essentially absent in the early 20th century atmosphere (Figures 5.38, 5.39, and 5.40). This is not surprising information, but these samples, which, unlike the initial South Pole samples, were collected in such a way as to avoid low-level contamination of halocarbons, are the first verification of levels of CFCs and the major chlorocarbons that do not differ significantly from zero. The data demonstrate that if natural sources of these gases do exist, they are insignificant.

Results for methyl halides were more ambiguous, although it still may be possible to derive 20th century atmospheric histories for them (Figure 5.39b and Figure 5.41). Methyl chloride in the diffusive zone is about 10% higher than it is at the bottom of the profiles suggesting that activities over the past century have elevated the mixing ratio of this gas in the atmosphere by about 30 ppt. This is consistent with seasonal cycles of CH₃Cl which are associated with photochemical cycles of tropospheric OH.

Data for CH₃Br from Siple Dome agreed well with those from the South Pole, both suggesting that atmospheric CH₃Br in the earlier part of this century was about 25% lower than it is today (Figure 5.41a). However, at Tunu, Greenland, a warmer and more coastally influenced site, CH₃Br was high near the bottom of the profile, reaching mixing ratios of nearly 50 ppt at the firm-ice transition (Figure 5.41b). Tests confirm that this elevation in concentration at depth is not an artifact of sample collection, storage, or analysis. This leads us to believe that the observed high values for CH₃Br in the firm at Tunu are real, although not necessarily of atmospheric origin. (This feature was also observed at Tunu for at least one other marine biogenic gas, CH₄I, and it was observed for CHBr₃ at Siple Dome where CH₃Br and CH₄I do not appear to have been produced.) A model of the

![Graph](image-url)

**Fig. 5.37.** Trends in monthly nighttime variability at the top sampling level of the North Carolina (NC) tower (circles) and Wisconsin (WI) tower (crosses). Variability was calculated as one standard deviation of nighttime mixing ratios during each month with random measurement noise removed. Lines fit to variability time series at the NC (solid) and WI (dashed) towers with least-squares regressions reflect trends in regional-scale emissions [Hurst et al., 1998].
Fig. 5.38. "Conservative" gases of anthropogenic origin in Tuna firm air. (a) CFC's, (b) halons, (c) SF6. CO2 in air at the bottom of the Tuna, Greenland, profile corresponds to atmospheric CO2 in the early 1930s.

Fig. 5.39. Chlorocarbons in Siple Dome firm air. (a) CH3CCl3 and CCl4, (b) CH3Cl. CO2 in air at the bottom of the Siple Dome profile corresponds to atmospheric CO2 in the early 1950s.

Fig. 5.40. Replacement compounds for CFCs in Tuna firm air.
fim profiles strongly suggests that CH$_3$Br is produced near the firm-ice transition, a process that could not have been happening at South Pole or Siple Dome and yield the observed profiles.

Processes in the upper 10 m of firm also may affect CH$_3$Br concentrations. At each Antarctic site, the CH$_3$Br concentration was elevated by as much as 1 ppt (10-15%) in samples just below the surface. This feature was consistent, though at present unexplained. Such variations did not appear throughout the profiles which suggests this may be a phenomenon limited to the upper 10 m. How this affects the overall profile is difficult to ascertain without first understanding the process. All firm samplings were conducted during the summer months thus precluding any evaluation of seasonal effects in the surface. In the fall of 1997, flasks were sent to SPO for sampling from a 15 m deep hole in winter and summer of 1998.

5.5. References

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