

SECTION 5 – HALOCARBONS AND OTHER TRACE ATMOSPHERIC SPECIES (HATS) RESEARCH GROUP

RESEARCH OVERVIEW

The GMD Halocarbons and Other Trace Atmospheric Species (HATS) Research Group and its predecessors began making measurements of atmospheric trace gases that influence stratospheric ozone and climate, such as halogenated gases and nitrous oxide, in the late 1970s. What began as a program to measure a handful of trace gases at three NOAA observatories (section 2) has grown into one in which more than 40 trace gases are measured. NOAA and cooperative organizations (starting with the Institute of Arctic and Alpine Research (INSTAAR); Commonwealth Scientific and Industrial Research Organization (CSIRO), Australia; and Environment Canada) make measurements routinely at surface sites, from aircraft platforms, and periodically as part of focused field campaigns, employing both flask sample and in situ methods. Many of these measurements complement those obtained by other GMD research efforts, such as those made by the Carbon Cycle and Greenhouse Gases and Ozone and Water Vapor groups.

The HATS group's primary objective is the study of trends and distributions of atmospheric trace gases that influence stratospheric ozone, climate, and air quality. Key outcomes include: a) monitoring changes in halogenated compounds controlled by the Montreal Protocol on Substances that Deplete the Ozone Layer and its amendments and adjustments to provide feedback on the effectiveness of various control measures, b) characterizing sources and sinks of ozone-depleting substances (ODS) and radiatively important gases, c) using information on trends and distributions of trace gases to improve our knowledge of atmospheric chemistry and transport, and d) development of gas standards and calibration methods (see section 8).

We perform sample analyses with various instruments; including gas chromatography with electron capture detection (GC-EC), gas chromatography with mass spectrometric selective detection (GC-MS), tunable diode laser absorption spectroscopy (airborne water vapor), and UV absorption spectroscopy (airborne ozone). We describe changes and improvements in sampling, analysis, and data processing in the subsections below.

5.1 FLASK AND IN SITU PROGRAMS

The flask program is one of the cornerstones of the HATS sampling efforts. We obtain routine surface measurements at sites across much of the Western Hemisphere and through much of the troposphere above North America by sampling using flasks. Samples are analyzed on dedicated instruments under controlled conditions, thus limiting calibration and inter-instrument issues that can influence in situ measurements made under field conditions. By combining efforts with other research groups in GMD, approximately 50 compounds are measured on some flask samples. Flask samples have also been collected during special projects such as HIPPO, involving the NCAR Gulfstream V aircraft (see section 5.2, Table 5-4).

We started the in situ program in the late 1980s to complement the flask program by providing high-frequency measurements of fewer compounds at a relatively small number of sites. We upgraded the original in situ Radiatively Important Trace Species (RITS) program in the late 1990s with custom-built gas chromatographs with electron capture detectors.

We can obtain a comprehensive view of atmospheric trace gas mole fractions and distributions, and insight into the natural and anthropogenic processes controlling changes in the chemical composition of the atmosphere over seasonal to decadal periods, with a combination of surface in situ measurements and flask sampling from a variety of platforms. GMD creates and uses combined data in indices such as the NOAA Annual Greenhouse Gas Index (AGGI) and Ozone Depleting Gas Index (ODGI), as well as international assessments and reports.

FLASK MEASUREMENTS - HATS

Current operations

We made a number of improvements to the flask program during 2004–2013. These improvements allow better characterization of concentrations and emissions of ozone depleting substances and non-CO₂ greenhouse gases throughout the globe and in particular over the U.S. The HATS global flask sampling network consists of sixteen ground-based sites, with two new sites added since 2004 and continuing at present. Paired flask samples are collected weekly or biweekly at these sites. The total number of flask sample pairs collected per year has

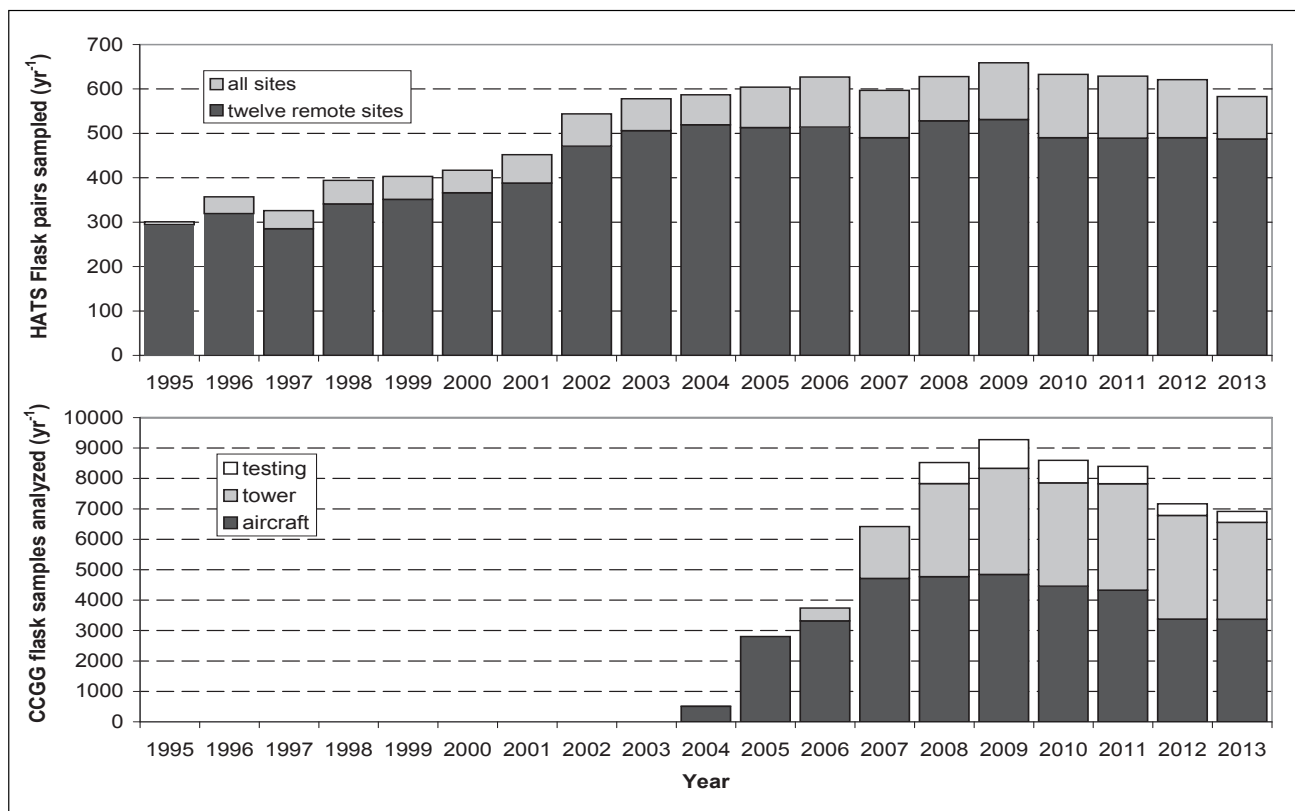


Fig. 5-1: The number of flasks collected annually in the HATS or CCGG sampling networks that were analyzed by GCMS instrumentation. Top panel: Paired flask samples collected from the HATS group's ground-based sampling network (at all sites and 12 remote background sites). Bottom panel: The number of flasks collected by the CCGG group that were analyzed on GC-MS instrumentation. The CCGG samples are collected at tower and aircraft platforms in North America and over the Pacific Ocean, typically as single flasks

ranged between 583 and 659 since 2004 (Figure 5-1); the sampling pair frequency at the 12 baseline sites has ranged between 487 and 531, which amounts to 0.78–0.85 pairs per week. Sampling frequencies are sometimes below one per week at the remote baseline sites because of out-of-sector wind conditions, flask shortages, and pump malfunctions. We routinely analyze HATS-paired flasks with two aliquots per flask surrounded by reference gas injections.

For this program, we update data that have been documented in peer-reviewed publications approximately once every two weeks on the web at <ftp://ftp.cmdl.noaa.gov/hats/>. These compounds include: CFC-113, CH₃CCl₃, HCFC-22, HCFC-142b, HCFC-141b, H-1211, H-2402, HFC-134a, HFC-152a, CH₃Cl, CH₃Br, COS, CH₂Cl₂, and C₂Cl₄.

We also began to make higher frequency flask measurements (~daily) at 13 additional U.S. sites in collaboration with the CCGG tall tower network and semimonthly to monthly at 19 additional sites

with 12-flask aircraft profiles as part of the CCGG aircraft network (Table 5-1a & b). We collect these samples as single flasks and analyze them on the GC-MS with a single injection based on flask and air availability and instrument time constraints. On average, from 2008 to 2013, we analyzed 9400 flasks of all types each year on GC-MS instruments. We update these data regularly on internal GMD databases, and some are available on request.

Instrumentation modifications and upgrades

In 2009, we replaced the original HP 5971A GC-MS analyzer (M1), used since 1991, with an Agilent 5973 GC-MS (M3). This change was necessary, as the performance of the original instrument had deteriorated. The instrument upgrade notably improved precision for nearly all gases (Figure 5-2). We built a second GC-MS instrument (M2) in 2007 to handle the additional samples collected from the CCGG's tower and aircraft network. Currently all ground-based, non-tower network flasks are analyzed on the M3 GC-MS. We analyze only some of

Table 5-1a: New sites at which flask collection and analysis by GC-MS was initiated during 2004-2013 either as part of the HATS or CCGG networks. Note that previously ongoing sites are not listed.

A) Ground-based tower network (CCGG) sites with flasks analyzed by GC-MS

Site	Lat	Long	Alt. (m)	Start - End
LEF	45.93	90.27	716	Oct. 2006
INX	39.8	86.02	406	Oct. 2010
LEW	40.94	76.88	256	Jun. 2013
MBO	43.98	121.7	2742	Apr. 2010
MWO	34.22	118.1	1774	Feb. 2006
NWF	40.03	105.55	3052 or 3073	Feb. 2006 – Nov. 2009
STR	37.75	122.45	486	Oct. 2007
SCT	33.41	81.83	420	Aug. 2008
WBI	41.72	91.35	620	Jun. 2007
WGC	38.26	121.49	91 or 483	Sep. 2007
WKT	31.32	97.33	708	Aug. 2006

B) Profiling aircraft network (CCGG) sites with flasks analyzed by GC-MS

Site	Lat	Long	Start - End
AAO*	40.1	88.56	Jun. 2006 – Sep. 2009
ACG**	87 to 86	130 to 170	Apr. 2009 (no winter samples)
BGI	42.82	94.41	Sep. 2004 – Nov. 2005
BNE	40.8	97.18	Sep. 2004
CAR	40.37	104.3	Jan. 2005
CMA	38.83	74.32	Sep. 2005
CRV**	60 to 71	144 to 164	Mar. 2011
DND	48.14	97.99	Sep. 2004
ESP	49.58	126.37	Mar. 2005
ETL	54.34	104.99	Oct. 2005
FWI	44.66	90.96	Sep. 2004 – Nov. 2005
HAA	21.23	158.95	Aug. 2006 – Apr. 2008
HIL	40.07	87.91	Sep. 2004
INX	39.59	86.4	Oct. 2010
LEF*	45.93	90.27	Jun. 2005
NHA	42.95	70.63	Oct. 2005
OIL	41.28	88.94	Sep. 2004 – Nov. 2005
PFA	65.07	147.29	Apr. 2009
RIA	42.4	91.84	Sep. 2004
RTA	20.96 S	159.78	Sep. 2007
SCA	32.77	79.55	Oct. 2005
SGP*	36.8	97.5	Mar. 2006
TGC	27.73	96.86	Feb. 2005
THD	41.05	124.15	Nov. 2004
ULB*	47.4	106 E	Nov. 2004 – Nov. 2005

* maximum altitude routinely < 25000 ft

** sites where the flask sampling plan includes spatial surveys in addition to vertical profiling.

Table 5-1b: Newly added ground and aircraft sites where halocarbon measurements are made from flasks (CCGG Network). (All latitudes are °N unless indicated; All longitudes: °W)

Site	Flask Type	Frequency	Start Date	End Date
ALT	SS	1/wk	pre-1991	Ongoing
BRW	SS	1/wk	pre-1991	Ongoing
SUM	glass	0.5 to 1/wk	Jun 2004	Ongoing
MHD	SS	1/wk	Oct 1998	Ongoing
LEF	SS	1/wk	Oct 1996	Ongoing
HFM	SS	1/wk	Nov 1995	Ongoing
THD	SS	1/wk	Feb 2002	Ongoing
NWR	SS	1/wk	pre-1991	Ongoing
WLG	glass	0.5 to 1/wk	Sep 2009	Feb 2014
WIS	glass	0.5/wk	Jan 2007	Ongoing
KUM	SS	1/wk	Nov 1995	Ongoing
MLO	SS	1/wk	pre-1991	Ongoing
SMO	SS & glass	1/wk	pre-1991	Ongoing
CGO	SS & glass	1/wk	pre-1991	Ongoing
TDF	SS	1/wk	May 2004	May 2010
PSA	glass	1/wk	Dec 1997	Ongoing
SPO	SS & glass	1-2/month	pre-1991	Ongoing

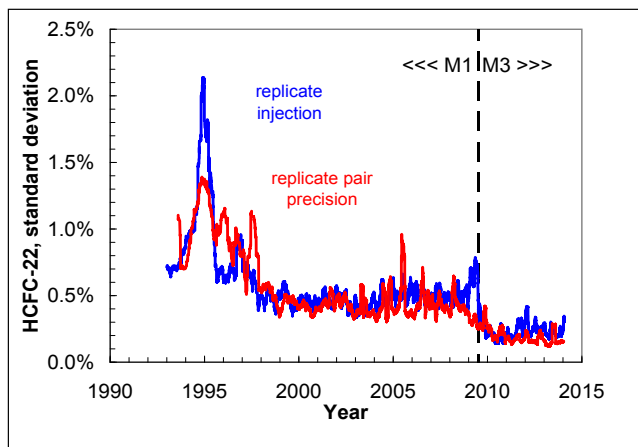


Fig. 5-2: Instrument performance in the analysis of HCFC-22 from flask air. Shown are running mean replicate injection precisions from ~18,500 flasks analyzed since 1992 as part of the HATS sampling network on M1 and on M3 (100-point running means of the individual replicate injection precisions, which aren't displayed; blue line). Also shown are the differences between the individual flasks filled simultaneously as a pair (~9000 pairs, 100-point running means of these individual pair differences are shown as red lines).

these flasks on M2 to provide global distributions of the subset of gases uniquely measured on M2 (see Table 5-2). We analyze on M2 the majority of samples collected by the CCGG group using auto-

mated flask packages from towers and aircraft

In the transition from instrument M1 to M3 in mid-2009, nearly all the plumbing for sample handling, valves, and sensors remained unchanged with one exception: we replaced the 25-year old capillary column (60-m, 0.25-mm I.D., 1-micron film DB-5) with a newer one. We made small adjustments to the oven temperature program to maintain optimal separation for chemicals of interest with the new column. An unanticipated result of this column change was the chromatographic behavior of residual water. Residual water on the new DB-5 column periodically interferes with the quantification of HCFC-142b and sample-to-sample variability for this chemical has worsened. As of late 2013, we have been looking into a solution to this problem. A 30-m, 0.32-mm I.D. PLOT column provides separation on M2. This column enables separation and quantification of a number of additional gases not readily measured on the DB-5 column used on M3. Though this instrument provides excellent results for most gases (Figure 5-3) and residual water elutes in an idle part of the chromatogram, we found that measurement precisions for some low concentration chemicals are not as tight as they are on M3, in part due to peak broadening on the more highly-retentive PLOT column. We are currently

Table 5-2: GC-MS Compounds: Chemical measured in flask air by GC-MS.

Chemical	Instrument	New Compounds Since 2004 Analysis Start Date
N ₂ O	Otto	
SF ₆	Otto	
CFC-11	M1&M2&M3 & Otto	
CFC-12	M1&M2&M3 & Otto	
CFC-113	M1&M2&M3 & Otto	
CFC-115	M2	2007
HCFC-22	M1&M2&M3	
HCFC-141b	M1&M2&M3	
HCFC-142b	M1&M2&M3	
HCFC-21***		
HFC-134a	M1&M2&M3	
HFC-152a	M1&M2&M3	
HFC-32	M2	2007
HFC-125	M2	2007
HFC-143a	M2	2007
HFC-365mfc	M2&M3	2007
HFC-227ea	M2&M3	2007
H-1211	M1&M2&M3	
H-1301	M1&M2	2004
H-2402	M1&M2&M3	2004
CCl ₄	M1&M2&M3 & Otto	
CH ₃ CCl ₃	M1&M2&M3 & Otto	
CH ₃ Br	M1&M2&M3	
CH ₃ I	M1&M2&M3	
CH ₂ Cl ₂	M1&M2&M3	
CHCl ₃	M1&M2&M3	
C ₂ Cl ₄	M1&M2&M3	
CH ₂ Br ₂	M1&M2&M3	
CHBr ₃	M1&M2&M3	
COS	M1&M2&M3	
CS ₂ **	M2&M3	2005
C ₂ H ₂	M2	2007
C ₃ H ₆	M3	2011
C ₃ H ₈	M2&M3*	2007
n-C ₄ H ₁₀	M2&M3*	2007
i-C ₄ H ₁₀	M3*	
n-C ₅ H ₁₂	M2&M3	2007
i-C ₅ H ₁₂	M2&M3*	2007
n-C ₆ H ₁₄	M2&M3	2007
C ₆ H ₆	M1&M2&M3	
CHBrCl ₂ ****	M3	2009
CFC-13****	M2	
HFC-23****	M2	

Notes:

- * Only measured on a subset of CCGG flasks analyzed on M3
- ** Only reliably measured at some sites
- *** Robust calibration scale not yet developed
- **** No longer measured regularly

M1, M2, and M3 are different GCMS instruments (see text); Otto is a GC-ECD instrument. Measurements of Halon-1211 and Halon 1301 on LEAPS are discontinued.

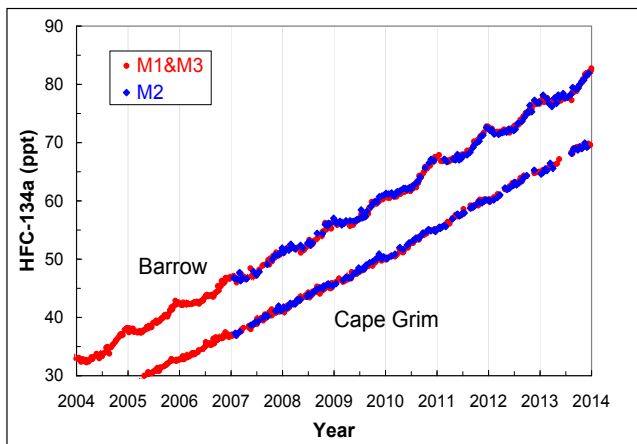


Fig. 5-3: Results for HFC-134a from flasks collected at Barrow, Alaska and Cape Grim, Tasmania since 2004. Points represent the measured mean mixing ratio in each sampled flask pair from an analysis on the different GC-MS instruments. Results from M1 and M3 (red points) are compared to the subset of flasks analyzed on M2 (blue points; ~2 flask pair/month) since 2007. The difference in mean annual mixing ratios determined from the flasks analyzed on these different instruments is $-0.1 \pm 0.2\%$ at CGO and $-0.1 \pm 0.3\%$ at BRW (± 1 s.d., $n = 7$ years).

developing an additional instrument to provide highly precise measurements of all these gases and additional chemicals in a single injection. We anticipate that this instrument will provide higher precision, accuracy, and reliability at reduced analysis costs.

Compounds analyzed

In addition to the suite of chemicals measured from flasks before 2004 on GC-ECD and GC-MS (CFC-11, CFC-12, CFC-113, N_2O , SF_6 , HCFC-22, HCFC-141b, HCFC-142b, Halon-1211, CH_3CCl_3 , CCl_4 , CH_2Cl_2 , $CHCl_3$, C_2Cl_4 , HFC-134a, HFC-152a, CH_3Br , CH_3Cl , CH_3I , CH_2Br_2 , $CHBr_3$, COS, and Benzene), we have added a number of new chemicals to the list of those regularly measured in flasks. In particular, the M2 GC-MS allows a broader suite of HFCs to be measured (Figure 5-4).

Although most trace gas measurement records have been derived from measurements on a single instrument with minimal modifications over time, there are some exceptions. We obtained results for halons (H), H-2402 and H-1301, from GC-MS during 2004 to 2006 (and a portion of 2007) with

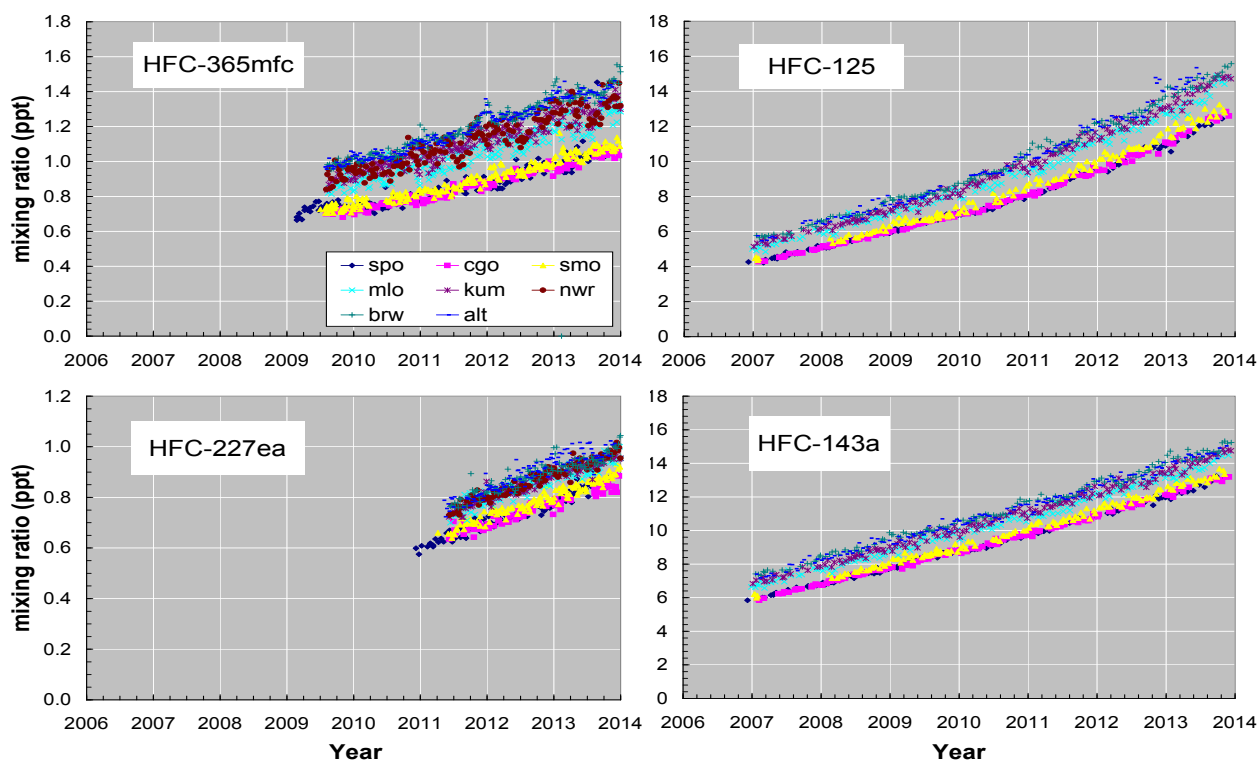


Fig. 5-4: Results for select HFC's added to the list of gases analyzed by HATS during the 2004-2013 period. Results are from HATS flasks analyzed on M3 (left-hand panels) and M2 (right-hand panels).

Ascarite scrubbing as air was transferred from the flask to the cryogenic trap. This enabled sample volumes approximately double the normal size (500 vs. 250 sccm) without peak splitting of early-eluting gases owing to co-trapping of CO₂. Results for H-1301 after 2007 are from analysis of a subset of remote-site flasks on M2, while results for H-2402 after 2007 are from analysis on M3.

We made additional improvements with the introduction of M3, including the removal of a co-eluting chemical in the analysis of H-1211. We corrected data obtained from M1 to account for this artifact, providing a consistent measurement record beginning in the early 1990s through to the present.

Flask sampling

We conduct measurements at most HATS sites solely from either stainless steel (SS) or glass flasks. Since the early 2000s, we have used both glass and SS flasks at SPO; SMO; Cape Grim, Tasmania (CGO); and Park Falls, Wisconsin (LEF). At the Southern Hemisphere sites, they fill the different flask types using the same pumping apparatus. These procedures have allowed us to identify flask artifacts associated with sampling containers for some sensitive chemicals in dry air, and they have prompted the use of glass flasks exclusively at low humidity sites associated with long storage times (e.g., Summit, Greenland (SUM), Negev Desert in Israel (WIS), Mt. Waliguan in China (WLG)).

Personnel at LEF fill samples in flask types with different pumps and pumping systems (45.9°N, 90.3°W), including HATS pumps and the automated CCGG programmable compressor packages. Results for nearly all measured gases are independent of the pumps used and flask types in which samples are collected and transported to Boulder, even fairly reactive compounds such as COS and CHBr₃ (Figure 5-5). Results from this site demonstrate good comparability with results from the different sampling apparatus and different instruments.

While flask sampling in the HATS network continues as paired samples filled in parallel or series, samples collected in the CCGG tower and aircraft network are typically single flasks. We collect only a small fraction of the CCGG samples as paired flasks, and the air in these pairs is often used for co-measurements of ¹⁴CO₂ at INSTAAR.

Flask Analysis by GC-ECD (“Otto”) DataProcessing

We use an electron-capture gas chromatograph (GC-ECD) to analyze flask samples with an instru-

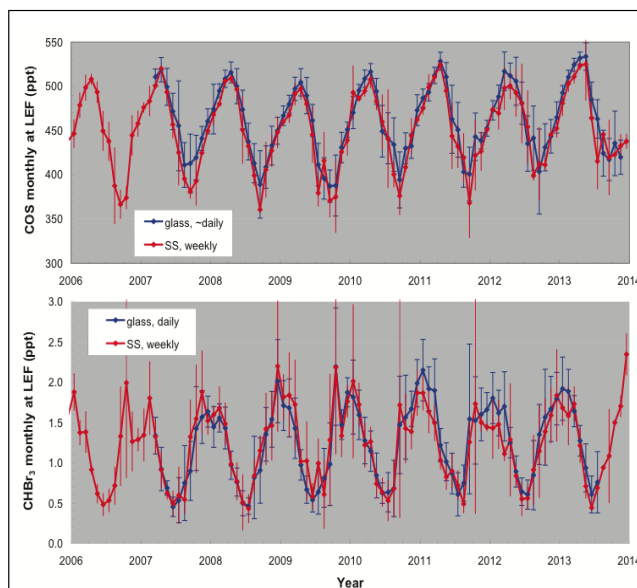


Fig. 5-5: Monthly mean mixing ratios for carbonyl sulfide (COS) and bromoform (CHBr₃) at LEF as determined from two different instruments, flask sampling apparatus, and flask types. Results from M2 (blue line) are from 10 to 50 glass flasks sampled per month with the automated CCGG programmable compressor package; results from M1&M3 (red line) are derived from paired SS flasks sampled once per week. Error bars represent one standard deviation of the results obtained during each month.

ment nicknamed “Otto”. Otto has been in operation since 1995, and is capable of measuring N₂O, SF₆, CFC-11, CFC-12, CFC-113, CH₃CCl₃ and CCl₄ in stainless steel and glass flasks. We compare flask samples to two calibration standards, one with ambient mole fractions and one diluted 10% with zero-grade air. We use a linear approximation (two-point method) to determine mole fractions. The linear approximation works well as long as the ECD response is reasonably linear and the mole fraction of the sample is within the range spanned by the calibration standards.

In practice, the sample mole fractions may be outside the range covered by the two calibrations standards, and this can lead to errors in the linear approximation. This is particularly true for compounds whose atmospheric mole fractions have changed rapidly (e.g., CH₃CCl₃). To overcome these potential errors, we introduced a new data processing method in 2008. The new method takes advantage of the fact that calibration standards used over time span a range of mole fractions (they are installed on the system within a few months of being filled, and are replaced about every three

years) and that both calibration standards used on the system are typically not changed simultaneously. Periods of overlap among existing and replacement standards provide more information about ECD non-linear response than is obtained from two standards alone. In the new method, we combine bilateral comparisons of standards over many years to estimate a non-linearity factor, which is then used to adjust the linear method to be consistent with the long-term calibration data across changes in calibration gas. This method has led to improvements in long-term consistency as mole fractions of various trace gases have changed with time. See a detailed explanation at <ftp://ftp.cmdl.noaa.gov/hats/doc/HATSflaskECDanalysis.docx>.

IN SITU MEASUREMENTS - HATS

We deployed six custom built gas chromatographs (GCs) at remote NOAA and cooperative institute facilities where continuous background air measurements are conducted nearly every hour. These instruments make up the HATS ground-based in situ program. We installed the current set of instruments (known as CATS: Chromatograph for Atmo-

spheric Trace Species) in 1998 (at BRW, MLO, SMO and SPO), 2000 (at NWR) and 2007 (at SUM) and replaced the RITS instruments. The CATS GCs are composed of four chromatographic channels, each equipped with gas sample valves, flow controllers, packed columns, and an electron capture detector (ECD). NOAA built the GCs in the 1990s and they have undergone field maintenance, repairs and upgrades. We documented many of the significant changes to each CATS instrument in Table 5-3.

The CATS instrumentation measures mole fractions of N₂O, SF₆, CFC-11, CFC-12, CFC-113, CCl₄, CH₃CCl₃, and halon-1211. CH₃Cl, HCFC-22 and HCFC-142b are also measured, but the chromatography for these gases can be affected by a whole host of problems leading to poor accuracy and/or precision. Measurement of CH₃Cl, HCFC-22 and HCFC-142b requires pre-concentrating a large air sample (80 mL) onto a cold trap (a packed column from Restek: Hayesep-D, 80/100 mesh, three inches of column material in the center of a one ft, 1.0 mm ID tube), and then flash-heating the sample onto a megabore capillary column (25 ft, Chrom-

Table 5-3: Significant events and changes to CATS instruments.

Location	Date	Comment
BRW	6/15/98	Installation of CATS instrument.
BRW	Dec 2006 - May 2007	N ₂ O/SF ₆ ECD temperature control problems.
BRW	3/13/08	WMO N ₂ O audit.
BRW	9/5/08	Installed new carrier gas flow controllers.
BRW	9/7/08	Installed Nafion dryer on sample lines.
BRW	5/30/13	Significant improvements to ECD temp controll-affecting N ₂ O/SF ₆ .
MLO	10/11/98	Installation of CATS instrument.
MLO	Nov 2001 - May 2003	Very nosy ECD affecting N ₂ O/SF ₆ precision.
MLO	9/23/03	N ₂ O/SF ₆ ECD replaced.
MLO	9/27/07	ECD replaced. CFC-11, CFC-12, and CFC-113 precision affected.
MLO	2/25/08	Installed new carrier gas flow controllers.
MLO	6/19/09	Installed Nafion dryer on sample lines.
NWR	11/9/00	Installation of CATS instrument.
NWR	7/1/06	Rainwater severely damaged GC, removed and refurbished.
NWR	10/31/07	Changed N ₂ O/SF ₆ Chromatography to use N ₂ carrier gas and CO ₂ doping.
NWR	10/31/07	CG rebuilt and reinstalled.
NWR	10/28/08	Installed Nafion dryer on sample lines.
SMO	12/2/98	Installation of CATS instrument.
SMO	6/12/09	Installed new carrier gas flow controllers.
SMO	9/11/09	Installed Nafion dryer on sample lines.
SMO	9/29/09	Observatory hit by 8.3 mag. Earthquake. GC sustained minor damage.
SPO	1/25/98	Installation of CATS instrument.
SPO	5/18/07	Replace N ₂ O/SF ₆ ECD due to poor precision.
SPO	1/24/09	Installed new carrier gas flow controllers.
SUM	6/26/07	Installation of CATS instrument.
SUM	8/19/09	Installed Nafion dryer on sample lines.
SUM	6/6/10	Installed new carrier gas flow controllers (replaced Tylan MFC).
SUM	10/5/10	Building and tower moved to a new location.
SUM	7/30/13	Raised buiding and inlets about 10 ft.

pack Poraplot Q-HT). We encountered problems in the field including sample contamination, variability in sample volume, failure of chiller or flash heating electronics, and unstable calibration cylinders. Consequently, we have experienced many data gaps and accuracy issues for the CATS CH₃Cl, HCFC-22 and HCFC-142b measurements. For these gases, we should evaluate the long-term trends and tropospheric gradients from the HATS GC-MS flask program. However, we can estimate hourly and day-to-day variability for these gases from the CATS data.

You can access regularly updated CATS data online at <http://www.esrl.noaa.gov/gmd/hats/insitu/cats/>. The data are also used in several GMD data products including the combined N₂O, SF₆, CFC-11, CFC-12, CFC-113, and CCl₄ data sets, as well as the NOAA indices, the Annual Greenhouse Gas Index (AGGI) and Ozone Depleting Gas Index (ODGI). Several national and international assessments and publications have included these data.

Improvements to all CATS instruments

The HATS group constructed all of the CATS GCs in the 1990s with some custom designed parts, as well as commercially available power supplies, sensors, and controllers. We continue routine maintenance, including repairing and replacing components, however there have also been improvements made to the GCs during the last decade. Most significantly, we replaced all six of the carrier gas digital flow controllers (custom-built) with an off-the-shelf unit (Pneucleus Technologies LLC, 100 cc/min controller). The new controllers improved the stability of the gas flows and ultimately the precision of the GC measurements.

We dry air and calibration gas samples prior to injection via a custom-packed, inline magnesium perchlorate trap. The lifetime of these traps is much shorter at humid sampling locations. From 2008 to 2009 we installed Nafion membrane dryers (Perma Pura, ¼" OD S.S. tubing) upstream to the magnesium perchlorate trap. This improvement lengthened the duration a magnesium perchlorate trap could be used, thus simplifying field maintenance.

Instrument Changes at Niwot Ridge, Colorado

During the summer of 2006, strong winds blew off the protective cover over the air inlet at Niwot Ridge, Colorado (NWR). Subsequently, rainwater was drawn into the GC, severely damaging most of

the valves, traps, columns, and flow controllers. We removed the GC from the field site and later refurbished it in Boulder. We disassembled and cleaned all of the valves, and installed new rotors. It was also an opportune time to replace the aging Tylan flow controllers with new, smaller, and more stable controllers from Pneucleus Technologies LLC. We also modified the N₂O/SF₆ chromatographic channel to improve measurement precision by changing the carrier gas, columns, and chromatography.

Installation at Summit, Greenland

We built two GCs in the mid-1990s and installed them at a pair of North American tall-tower sites (WITN in North Carolina and WLEF in Wisconsin). These GCs were very similar to the CATS instruments; custom-built, four channels equipped with electron capture detectors. Likewise, these instruments measured CFCs, N₂O, SF₆, and halon-1211; however, in place of the complicated CH₃Cl and HCFCs channel, we installed a doped ECD channel measuring H₂, CH₄ and CO. After many years of successful measurements and publications, we removed these instruments and returned them to Boulder. We refurbished one of them and deployed it at Summit, Greenland during the summer season of 2007 and incorporated it into the HATS CATS in situ program.

World Meteorological Organization N₂O audit

In March 2008 a representative of the World Meteorological Organization (WMO) World Calibration Centre (WCC) for Nitrous Oxide visited the Barrow, Alaska station. The representative conducted a site assessment and several blind audits of trace gas measurements including the CATS N₂O channel. We substituted a calibrated N₂O cylinder for an air sample on the CATS instrument. We sampled the tank eleven times over a course of 22 hours and processed the data with normal CATS algorithms as an air sample. Based on the NOAA-2006 N₂O scale, we obtained a value of 315.74 ± 0.30 ppb (1σ), which is in agreement (315.73 ppb) with the value assigned by the WCC-N₂O.

5.2 SPECIAL PROJECTS

SPECIAL HATS FLASK SAMPLING PROGRAMS

HATS-analyzed flasks associated with a number of special projects during 2004–2013 (Table 5-4). These projects focused on deriving long-term measurement histories of trace gases (firn-air

Table 5-4: Special Projects Involving Halocarbon Measurements from Flasks

Firn Air Sampling Analysis Instrument	Project
Antarctica:	
M1	Megadunes, 2004
M1	Wais Divide, 2006
M1&M2	South Pole, 2008
Greenland:	
M1	Summit shallow tubes: 2004, 2006, and 2008
M1	Summit deep hole: 2006
Other Analysis Instrument	Project
M2	HIPPO, tropospheric transect with profiles, 2009-2011
M2	CARVE, Arctic samples, 2001-ongoing
M1	ARCPAC, Arctic samples, 2008
M1	Harvard Forest Intensive, diurnal COS variability, 2006
M3	Boulder COS Intensive, comparisons in situ COS analyzer, 2011
M1	TROICA, Samples across Russia from a train, 2004
Additional Short-Term Projects in Collaboration with CCGG	
BARCA 2009 (Amazon)	
Sacramento [Turnbull et al.]	
Indianapolis	
Oil and Gas development investigations (Denver Julesberg, Utah, Texas, Pennsylvania)	

projects), characterizing the remote Pacific basin throughout the troposphere in all seasons (HIPPO), more focused regional aircraft studies particularly in the Arctic (CARVE and ARCPAC), regional studies to characterize trace gases associated with continental oil and gas drilling, and other short-term research investigations. The HIPPO deployments substantially augmented sampling coverage in the remote atmosphere during the five HIPPO deployments that we conducted in different months; NOAA flask programs provide long-term, ongoing atmospheric sampling throughout the year (Figure 5-6).

5.3 HATS STANDARDS PROJECT

The HATS Standards Project is an important part of the HATS overall program. We first developed gravimetric capabilities in the late 1980s and have progressed over the years. The HATS standards project supports the HATS and CCGG groups through preparation of gravimetric, compressed gas standards and whole air standards filled at the Niwot Ridge C-1 facility. You can find further details related to HATS standards and calibration activities in section 8.

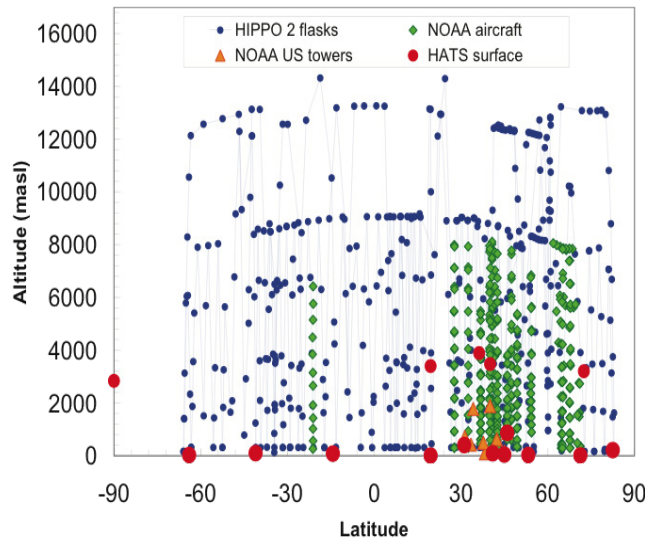


Fig. 5-6: Locations of samples collected during the month of November 2009 from HATS, CCGG, and special projects which were subsequently analyzed by GCMS: HATS paired surface flasks (red points); CCGG aircraft profiles (green points); CCGG tower network (orange points), and the second HIPPO deployment (blue points connected by lines).

5.4 AIRCRAFT

Measurements of trace gases in the free troposphere and lower stratosphere are an important part of our measurement program. We have developed several custom instruments to measure halo-

Table 5-5: Science missions involving HATS airborne instruments.

Date	Mission Name	Location	Platform	Instrument Used
2011-2014	ATTREX 1-3, Airborne Tropical Tropopause Experiment	NASA DFRC, CA; Guam	NASA Global Hawk	UCATS (O ₃ (2), H ₂ O)*
2013-2014	Sky Wisp - NOAA	Boulder, CO	Balloon, Sky Wisp	O ₃ , ground-based GC
2010	GloPac, Global Hawk Pacific	NASA DFRC, CA	NASA Global Hawk	UCATS (O ₃ , H ₂ O)
2009-2012	HIPPO 1-5, HIAPER Pole-to-Pole Observations (HIPPO) of Carbon Cycle and Greenhouse Gases	Pole-to-Pole open Pacific	NSF Gulfstream V	PANTHER (H ₂ O), UCATS (O ₃ , H ₂ O)
2008	Erie Tower	Erie, CO	Tall Tower	PANTHER
2008	START08, Stratosphere-Troposphere Analyses of Regional Transport (START) Experiment (2008)	Jeffco, North America	NSF Gulfstream V	PANTHER (H ₂ O), UCATS (O ₃ , H ₂ O)
2007	TC4, Tropical Composition, Cloud, and Climate Coupling	Costa Rica	NASA WB-57F	PANTHER
2006	NASA/USDA-Forest Service Fire Mission, Altair UAS	Gray Butte, CA	NASA Altair	UCATS (O ₃ , H ₂ O)
2005-2006	CR-AVE, Aura Validation Experiment (Costa Rica)	Costa Rica	NASA WB-57F	PANTHER
2005	The NOAA UAS Demonstration Project, Altair UAS	Gray Butte, CA	NASA Altair	UCATS (O ₃ , H ₂ O)
2005	ACE (WIIF), Aura Validation Experiment - Water Isotope Intercomparison Flights	NASA JSC, Houston, TX	NASA WB-57F	PANTHER (H ₂ O)
2005	AVE (2005), Aura Validation Experiment	NASA JSC, Houston, TX	NASA WB-57F	PANTHER
2004	Pre-AVE, Pre Aura Validation Experiment	NASA JSC, Houston, TX; Costa Rica	NASA WB-57F	PANTHER
2004	TROICA-8	Moscow to Vladivostok, Russia	Trans-Siberian Railway	ACATS-IV
2002-2004	BOS, Balloon Observations of the Stratosphere	Fort Sumner, NM	Balloon	LACE

* Second O₃ instrument added during ATTREX-2, second mission

carbons, nitrous oxide, sulfur hexafluoride, ozone, water vapor, and peroxyacetyl nitrate (PAN). We have deployed these instruments on various platforms associated with numerous campaigns (Table 5-5). The instrument PANTHER was originally designed to measure PAN, select halogenated gases, and nitrous oxide in the lower stratosphere (NASA WB-57). We then used it to determine the vertical and latitudinal distributions of a number of trace gases in the troposphere. The original design of Unmanned aircraft systems Chromatograph for Atmospheric Trace Species (UCATS) was intended for use on unmanned aerial vehicles (NASA Altair), but it has also been deployed alongside PANTHER on the NCAR Gulfstream V (GV). We developed a flask collection package called the NOAA Whole Air Sampler (NWAS) for use on larger aircraft such as the NCAR Gulfstream V. The Lightweight Airborne Chromatograph Experiment (LACE), last deployed in 2004, was designed to measure select halogenated gases and N₂O in the lower stratosphere via a balloon-borne platform. We are also developing a remotely piloted glider aircraft that could be used to collect air samples and derive vertical profiles of select trace gases. Table 5-5 lists the various platforms, instruments, and missions we have been

involved in from 2004 to 2013.

Over the period 2004 to 2013, we have transitioned our missions from those focused on understanding stratospheric ozone depletion (e.g., airborne chromatograph for atmospheric trace species (ACATS) and Lightweight Airborne Chromatograph Experiment (LACE) to missions focused on climate studies, with a coincident shift from stratospheric to tropospheric observations. This shift in focus has pushed us to expand both our instrumentation and the platforms used to obtain data.

INSTRUMENTATION

ACATS-IV

Airborne Chromatograph for Atmospheric Trace Species (ACATS-IV) is a high altitude, four-channel GC-EC capable of measuring CFC-11, CFC-12, CFC-113, CH₃CCl₃, CCl₄, CH₄, H₂, SF₆, and N₂O. It was our original airborne GC designed for stratospheric air sampled by the high-altitude aircraft, NASA ER-2, and used during this period on the Russian Trans-Siberian Railway for TROICA-8 from 19 March to 1 April 2004.

LACE

Lightweight Airborne Chromatograph Experiment (LACE) is a high-altitude, three-channel GC-EC capable of measuring halon-1211, CFCs, CCl_4 , CH_3CCl_3 , SF_6 , N_2O , CH_4 , CO , and H_2 .

PANTHER

PAN and other Trace Hydrohalocarbon Experiment (PANTHER) is a two-channel GC-MSD, 4-channel GC-EC, and water vapor TDL capable of measuring gases listed for LACE plus PAN, some HCFCs and HFCs, methyl halides, COS, and H_2O .

UCATS

Unmanned aircraft systems Chromatograph for Atmospheric Trace Species (UCATS) is a two-channel GC-EC, ozone photometer, and water vapor TDL capable of measuring SF_6 , N_2O , CH_4 , CO , H_2 , O_3 , and H_2O .

NWAS

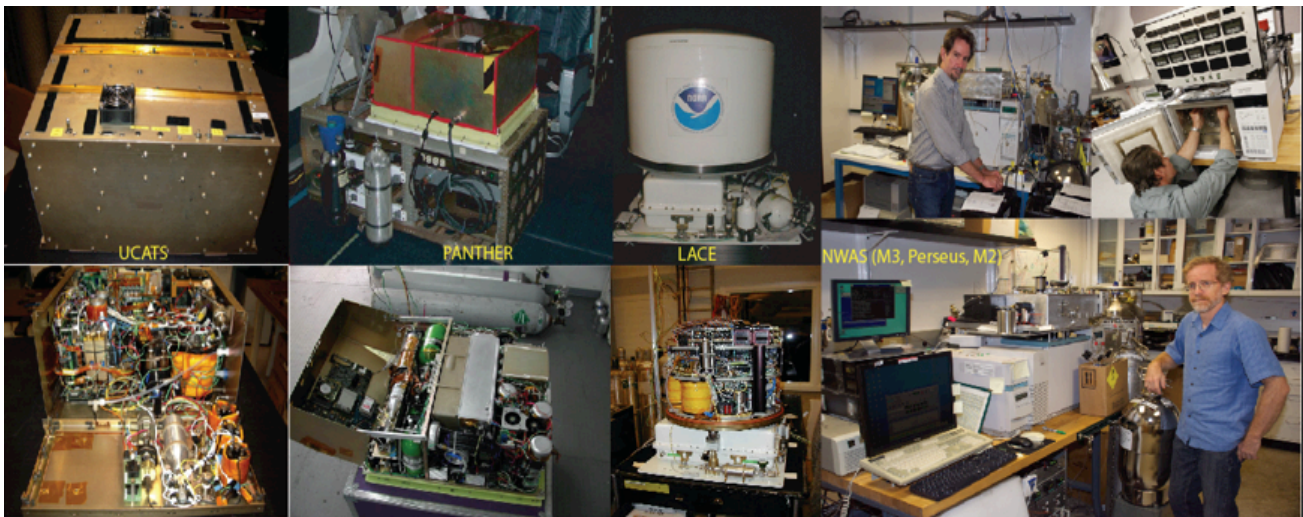
NOAA Whole Air Sampler (NWAS) is a flask-sampling system that uses the CCGG Programmable Flask Package (see section on flask special projects for more information).

StratCoreGC

This laboratory instrument is a two-channel GC-ECD capable of measuring halon-1211, CFCs, SF_6 , and N_2O from AirCores collected primarily for stratospheric air.

Science themes

Convective population of the TTL region: The tropical tropopause layer (TTL) is the gateway to the



Instruments and Platforms used to generate the Global Data sets.



Fig. 5-7: Photos of instrumentation and platforms associated with airborne and special projects. Also included are small UAS platforms, SkyWisp and the 3DR Aero, that may play a role in the future.

stratosphere, and NASA missions Aura Validation Experiment (AVE), Tropical Composition, Cloud and Climate Coupling (TC4), and Airborne Tropical Tropopause Experiment (ATTREX) all focused on improving our understanding of this important region and the convective processes that define the TTL. Many short-lived and chemically-active species reach the TTL through convection from the planetary boundary layer on timescales of hours. They remain there for weeks, isolated from the free troposphere, ultimately moving up into the stratosphere where they break down and ODS release inorganic halogens, all of which affect ozone chemistry. Intense convection in the tropics also leads to low temperatures in the TTL that control the amount of water vapor that enters the stratosphere, impacting climate and ozone. The NOAA Unmanned Aircraft Systems (UAS) Demonstration Project and the NASA GloPac missions were used to demonstrate feasibility of the Altair and Global Hawk UAS, and included some flights in the TTL. Data from AVE, TC4, GloPac, and ATTREX are available on the NASA Earth Science Project Office site at <https://espoarchive.nasa.gov>.

Tropospheric Dynamics and Chemistry: This theme involved two NSF-based programs: Stratosphere-Troposphere Analyses of Regional Transport (START-08) and HIAPER Pole-to-Pole Observations (HIPPO). START-08 was focused on stratospheric-tropospheric exchange processes. Here we targeted the phenomenon known as tropospheric-folds, a major mechanism for bringing stratospheric air into the free troposphere. These folds can be responsible for high-ozone events at the surface that have ramifications for air quality policy. This exchange is also an alternate pathway for tropospheric air entering the lowermost stratosphere, competing with the standard tropical upwelling process. START-08 was the precursor to the global survey HIPPO campaign, which acquired data in the free troposphere at altitudes from 500 ft to above the tropopause, with seasonal coverage at nearly all latitudes in the Pacific region. Models used to predict climate and the chemical composition of the atmosphere, to a large degree, are primarily constrained by the tropospheric network of surface measurements. Satellite measurements often lack the spatial resolution and/or precision to address the vertical structure and processes occurring in the troposphere. The high degree of spatial resolution and precision, coupled with the seasonal coverage of the HIPPO data set, puts a much tighter

constraint on these models, improving the accuracy of their representation of the current atmosphere. The modeling community widely requested the data set after the public release of the HIPPO data through the Carbon Dioxide Information Analysis Center (CDIAC) managed archive at <http://hippo.ornl.gov/dataaccess>. GMD personnel provided support and co-authorship on a large number of publications that resulted in peer-reviewed journals and presentations at international conferences. So far this work has quantified temporal and spatial structure in emissions of important greenhouse and ozone depleting gases, improved estimates of the tropospheric OH field that controls much of atmospheric chemistry, and led to improved estimates of tropospheric transport time scales. The data are also beneficial in process-oriented studies such as inter-hemispheric exchange, vertical transport in the tropics and extratropics, and the competition between bulk transport and mixing.

Stratospheric processing: The last LACE balloon flight to sample the lower- and middle-stratosphere occurred at the beginning of this report period. We now realize the importance of maintaining a continuous LACE-type stratospheric data set. Rapidly accumulating evidence shows climate-driven changes in stratospheric circulation which, in turn, induce strong feedbacks on tropospheric climate. There is a growing understanding that climate models will be limited if they do not incorporate a realistic representation of this changing stratospheric circulation. To this end, we have proposed an affordable and therefore sustainable long-term stratospheric circulation-monitoring program based on the new AirCore™ technology. We constructed and tested the StratCore GC, which is central to the proposed program and is now operational. In addition, we have been developing new techniques to interpret stratospheric data that provide information on age-of-air and photolytic loss. We now have the ability to detangle the distributed Brewer-Dobson circulation from tropical entrainment, quasi-biennial oscillation (QBO), and other perturbations that imprint themselves on measured tracers in a dynamically evolving stratosphere. In this stratosphere-monitoring program, the AirCore™ will be lofted to more than 30 km using a balloon. Recovery of the AirCore™ will benefit from a steerable recovery vehicle. In preparation, we have been testing lightweight, auto-piloted gliders, such as the SkyWisp, dropped from 32 km.

SECTION 8 - CALIBRATION AND QUALITY CONTROL ACTIVITIES

8.1 OVERVIEW AND WMO ACTIVITIES

The NOAA Carbon Cycle Greenhouse Gases (CCGG) and Halocarbons and other Atmospheric Trace Species (HATS) Research Groups contribute to the WMO Global Atmosphere Watch program in a number of ways. We act as the Central Calibration Laboratory for CO₂ (since 1995), CH₄ (since 2005), CO (since 1998), N₂O (since 2005), and SF₆ (since 2007). Through this role, we maintain the WMO mole fraction scales and provide to the WMO measurement community reference gas standards that are traceable to those scales. In 2010, WMO signed a Mutual Recognition Agreement (MRA) with the International Committee for Weights and Measures (CIPM), an agreement that insures compatibility among standards of the participants, mostly national metrology laboratories. Since WMO has no laboratories, it has designated NOAA/ESRL as its representative in the MRA for CO₂, CH₄, CO, N₂O, and SF₆. As WMO's representative, one major responsibility involves developing a quality system in accordance with ISO 17025 and ISO Guide 34. Development of this system continues, with NIST review conducted in January 2014.

We organized and hosted the 13th WMO/IAEA (International Atomic Energy Agency) Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, 19–22 September 2005. Members of the CCGG and HATS groups play major roles in WMO GAW meetings of measurement experts by leading discussions on measurement comparisons, data management, propagation of standards, and recording and organizing meeting recommendations (for meetings in 2011 and 2013). The recommendations define requirements for data quality, and good measurement practices to achieve those. We have ongoing comparisons of measurements with GAW participants at 16 sites. One GMD member chaired the Scientific Advisory Group (SAG) for Greenhouse Gas Measurements since 2003, another is a member of the SAG for reactive gases, and we contribute to many GAW reports, including meeting reports (Nos. 206, 194, 186, 168, and 161), measurement guidelines for CH₄ and N₂O (No. 185), CO (192), CO₂ (in preparation), and GAW Strategic Plans (Nos. 197, 172, and 156).

8.2 STANDARDS

As of 2013, in addition to the WMO scales, we continue to maintain calibration scales at various levels of maturity for 60 trace gases, see <http://www.esrl.noaa.gov/gmd/ccl/> and <http://www.esrl.noaa.gov/gmd/ccl/scales.html>. Calibration of our instrumentation is based on analysis of air from high-pressure gas cylinders with known composition. Hierarchies of reference gas standards are used to support measurement programs. For ozone-depleting gases, long-lived greenhouse gases, and related trace gases, primary standards are prepared in aluminum or stainless steel cylinders by gravimetric methods. For CO₂, primary standards consist of modified natural air in aluminum cylinders, with CO₂ mole fractions determined by a manometric method.

8.3 CALIBRATION SCALE UPDATES

Several calibration scales were updated between 2004 and 2013. We performed significant updates for N₂O, CFC-12, CH₄, CO, and CO₂ and introduced minor updates for SF₆, CCl₄, and HCFC-22, halon-1211, and halon-1301 scales. For information on current calibration scales, see <http://www.esrl.noaa.gov/gmd/ccl/> and <http://www.esrl.noaa.gov/gmd/ccl/scales.html>.

WMO N₂O SCALE UPDATE

The X2006 N₂O scale is based on 13 gravimetrically prepared standards over the range 261371 ppb, and supersedes the X2000. The X2006 scale was updated to X2006A in 2011 after a drifting secondary standard was discovered. Assignments on the 2006A scale are based on the same 13 gravimetric standards, but corrected for apparent scale drift of 0.024 ppb yr⁻¹ that occurred from 2006 to 2011 due to drift of a secondary standard. For most calibrations, differences between assignments on the X2006 and X2006A scales are less than 0.1 ppb.

WMO CFC-12 SCALE UPDATE

The update to the X2008 CFC-12 scale involved preparation of new gravimetric standards that also contained halon-1211. By including halon-1211 and better quantifying residual CFC-12 in the balance gas, the new set of primary standards is more consistent than the sets that defined the X1997 or

X2001 scales. In addition, we prepared primary standards with two different methods, using both liquid and gaseous pure CFC-12 starting material. Standards prepared by these different methods show remarkably good agreement.

WMO CH₄ SCALE UPDATE

The NOAA-2004 CH₄ scale is based on a suite of 16 gravimetrically prepared standards covering the nominal range 300–2600 nmol mol⁻¹ (ppb); five other original gravimetrically prepared standards, not used in the scale, can extend the range from 30 nmol mol⁻¹ to 20.5 μmol mol⁻¹ (ppm). Because NOAA is the WMO GAW CCL for CH₄, this scale is also the WMO CH₄ mole fraction scale used by GAW participants. We will initiate several changes in mid-2015 to meet the needs of the GAW community in analyzing air outside the narrow background range, and improve our internal consistency over a wider range of CH₄ mole fractions: New primary standards prepared with gravimetric methods covering the nominal range from 2200 to 8000 nmol mol⁻¹ were prepared in 2013 and will expand the scale at the high end. To account for potential varying non-linearity of our GC/FID system used for calibrations, we prepared a suite of 14 secondary standards covering the nominal range 390 to 5000 nmol mol⁻¹, and we are calibrating them against the primaries. We will employ the new secondary standards to define a response curve that will be used for routine calibration of tertiary standards. Response curves generated with the primary and secondary standards are now based on a power function that allows the non-linearity of the detector to change over the range of values measured.

WMO CO SCALE UPDATE

We produced new sets of CO gravimetric standards in 2006 and 2011 and compared them to the 1999/2000 gravimetric standards. These new gravimetric standards showed that the 1999/2000 gravimetric standards were biased low at the low end of the range (standards less than 200 ppb). This confirmed the suspected bias seen when the highest members of the 1999/2000 set were compared against the lower members. We revised the CO scale in 2014 to account for this bias.

WMO CO₂ SCALE UPDATE

During 2012, Brad Hall and Duane Kitzis performed

a full set of manometric measurements of the Primary cylinders that define the WMO scale. This was the first time the manometric measurements were not performed by Conglong Zhao, who had last carried out the analyses in 2009–2010. Despite several changes to the apparatus, the 2012 calibration agreed closely with previous ones. The average of all cylinders was 0.01 ppm higher than the average of previously assigned values. The assignment of mole fraction values to each of the Primaries, which takes all previous calibrations into account, did not change by more than 0.01 ppm.

8.4 INSTRUMENT CHANGES

In addition to scale updates, instruments used for calibration were also improved. We improved the precision for SF₆ analysis by adding an additional analytical column and changing the order of peak elution for N₂O and SF₆. Prior to 2006, we analyzed N₂O and SF₆ using a Porapak Q column (with SF₆ eluting after N₂O). In 2006, we installed a molecular sieve 5A column behind the Porapak Q column

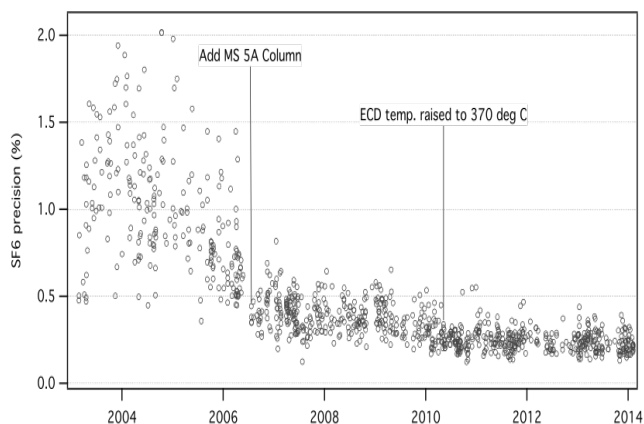


Fig. 8-1: Analytical precision (%) of SF₆ calibration measurements since 2003 for SF₆ mole fractions in the range 4–12 ppt. Note the improvement in precision in 2006 corresponding to the addition of the molecular sieve 5A column.

(SF₆ now elutes before N₂O). The effects of this and other changes are shown in Figure 8-1.

CO calibration system transfer measurements have benefited from several instruments purchased under funding by the NOAA OAR Atmospheric Chemistry, Carbon Cycle, & Climate (AC4) program (formerly ACCP). We replaced the older gas chro-

matograph in 2004 with an instrument based on resonance fluorescence in the VUV (Aero-Laser, Germany). In 2011, we replaced the Aero-Laser instrument with a new one based on off-axis spectroscopy (Los Gatos, USA). Measurement precision improved by a factor of ten from early 2004 to 2013.

8.5 NEW CAPABILITIES

In 2008, we prepared new gravimetric standards to support the measurement of HFC-23, HFC-32, HFC-125, and HFC-143a, along with CFC-13 and CFC-115 (see Section 5.2, Flask and In Situ Programs). Around that same time, we prepared gravimetric standards containing a number of hydrocarbons (acetylene, ethane, propane, n-butane, iso-butane, n-pentane, iso-pentane, n-hexane, benzene, and toluene) in support of flask measurements made by GMD and INSTAAR. The standards we prepared were in Aculife-treated aluminum cylinders, at ppb and ppt levels consistent with mole fractions found in the unpolluted troposphere. Later, in support of

work related to measurement of fugitive emissions from oil and gas production (see section 5.3, Special Projects), standards with higher mole fractions of hydrocarbons were prepared (up to 300 ppb propane). We also compared GMD scales for a number of these hydrocarbons with those established by National Metrology Institutes (NMIs) and found them to be consistent within a few percent.

8.6 COMPARISONS

In 2010, WMO signed the Mutual Recognition Arrangement (MRA) with the Comité International des Poids et Mesures (CIPM). GMD serves as a Central Calibration Laboratory with WMO/GAW. Under the CIPM MRA, GMD is required to establish a “Quality System”, and conform to international standards for calibration and measurement (ISO 17025, ISO Guide 34). We implemented this type of quality system and have also taken an active role in the Consultative Committee for Amount of Substance (CCQM) Gas Analysis Working Group.

Table 8-1: Formal and informal comparisons of gas standards

Comparison	Year Conducted	Gases	Participants
<i>Informal</i>	2005	CO ₂ in air	NIES (Japan)
<i>Informal</i>	2005	N ₂ O in air	SIO
<i>Informal</i>	2005-2007	CO in air	Five E.U. lab
<i>Informal</i>	2008-2010	CO in air	Ten E.U. labs
<i>Informal</i>	2013	CO in air	Five
<i>Informal</i>	2011	SF ₆ in air	KMA (Korea)
<i>Informal</i>	2011	N ₂ O in air	KIT (Germany)
<i>Informal</i>	2012	Hydrocarbons in air	NIST, others
<i>Informal</i>	2012	N ₂ O in air	NIST, SIO
CCQM P-41	2003	CO ₂ , CH ₄ in air	Many
CCQM K-68	2008	N ₂ O in air	Many
CCQM K-82	2012	CH ₄ in air	Many
CCQM P-151	2012	Halocarbons in air	Many
CCQM K-84	2013	CO in synthetic air	Eleven
Cucumber series	Ongoing	Whole air (CarboEurope, InGOS)	Many
IHALACE	2004-2007	Halocarbons in air	Many
CCQM K84	2008-2012	CO in air	Many
WMO RR #4	2002-2007	Whole air	Many
WMO RR #5	2009-2012	Whole air	Many
WMO RR #6	2014 -	Whole air	Many

This group consists mainly of representatives from National Metrology Institutes (such as NIST) interested in gas analysis and calibration. We have participated in a number of comparisons, both formal and informal, with NMIs and others (see Table 8-1). Comparisons are the first step in monitoring how well WMO/GAW scales are propagated to other laboratories. Comparisons with independent scales provide information on traceability to the SI, as well as scale stability and scale uncertainties.