

United States Department of Commerce (DOC)  
National Oceanic and Atmospheric Administration (NOAA)  
Environmental Research Laboratories (ESRL)  
Global Monitoring Division (GMD)  
Halocarbons and other Trace Species group (HATS)

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This area is a public access point to selected data obtained from  
NOAA/ESRL/GMD/HATS sampling sites.

##### ACCESS POINT #####

Version: 2017-12-01

Data formats: NetCDF files described below

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##### NOTICE #####

When using these data in a publication or presentation, you should acknowledge the National Oceanic and Atmospheric Administration, Global Monitoring Division, HATS Group.

The NOAA/GMD scientists would appreciate being notified of any studies involving the data. We would also like to receive drafts of presentations and publications to ensure that the quality and limitations of the NOAA/GMD data are accurately represented. Feedback from users may also help us to improve the quality of the data and the location of the sampling sites. Comments regarding the README files and the data files are encouraged. Please send comments to the e-mail addresses given above.

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### HATS Flask Sampling Program: A Brief History

HATS has been analyzing air samples collected in flasks since 1977. Originally set up under the auspices of the Geophysical Monitoring for Climatic Change (GMCC) division of NOAA's Air Resources Laboratory (NOAA/ARL), this program initially involved the analysis of flask samples

from only five remote sites in both hemispheres: Point Barrow, Alaska (BRW), Niwot Ridge, Colorado (NWR), Mauna Loa, Hawaii (MLO), American Samoa (SMO), and the South Pole (SPO). As of 2017, the flask program has expanded to include approximately weekly air sampling at 16 sites across the globe. Samples obtained in this program are collected as two flasks filled simultaneously.

Originally, air was collected weekly in pairs in 300-ml electropolished, stainless-steel flasks (from Whitey with Nupro SS-4H metal bellows valves) filled to 1.5 atm with a metal bellows pump to minimize contamination of CFC's by plastics or other elastomers. All samples were analyzed for N<sub>2</sub>O, CFC-11, and CFC-12 in the Boulder labs on a Hewlett Packard 5713A electron-capture gas chromatograph (GC-ECD) equipped with a Porasil A column (Thompson et al, 1985). This system, called "Pre-Otto" for reasons that will become apparent below, was operated in an almost entirely manual mode making data reduction a cumbersome process. In 1986, slightly larger stainless-steel flasks (850 ml, Biospherics) were circulated to sites and pressurized with ambient air to ~4 atmospheres of absolute pressure with KNF Neuberger diaphragm pumps (Model UN05SV1). This allowed for the analysis of larger quantities of air for improved measurements of trace gases present at low concentrations or trace gases that only respond weakly on the ECD. By 1991, the first of several automated instruments, a three-channel GC-ECD capable of measuring seven gases, was under development. After a few years of debugging, intercomparison and streamlining of its data processing procedures, it was put into full time service by late 1994. This system, called "Otto", analyzed flask samples for CFC-11, CFC-12, CFC-113, CH<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub>, N<sub>2</sub>O and SF<sub>6</sub>. The Pre-Otto system was retired early in 1996.

In late 1991, HATS began analyzing flask samples for hydrochlorofluorocarbons (HCFC's), hydrofluorocarbons (HFC's), and other halogenated trace gases by gas chromatography with detection by mass spectrometry (GC-MS) on the "M1" instrument. This development necessitated another size increase to 2.4 L - 3.0 L stainless steel flasks. Glass flasks were also added at a number of sites where cold, dry air is routinely sampled. This was for the purpose of dealing with a storage loss issue known to affect several trace gases, most notably CCl<sub>4</sub>, when very dry air is sampled into stainless steel flasks. GC-MS measurements were expanded in 2007 with the construction of a new "M2" instrument, and the deteriorating M1 was upgraded to the new "M3" instrument in 2009. Measurements from these GC-MS systems, while available elsewhere, are not yet available from this access point at this time. Through the Big Earth Data Initiative (BEDI), ESRL/GMD has taken their data collection formerly in ascii format and converted files into NetCDF-4, a self describing format. The netcdf-4 format is what will be archived at NCEI. Both historic record and future observations will be archived.

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HATS Flask Sampling Program: Significant Events and Changes to the Flask Program

### 1973

Interest in CFC-11 as an inert tracer especially well suited for estimating inter-hemispheric transport prompts the establishment of GMCC/ARL's halocarbons measurements program. Flask samples collected in evacuated cylinders at BRW, MLO, and SMO were shipped to a GC-ECD system at an ARL laboratory in Idaho Falls, ID for analysis.

### 1975

A New Hewlett-Packard 5713A GC-ECD system was installed at Boulder, CO. Flasks were analyzed on both systems (i.e. Boulder and Idaho Falls) for inter-comparison.

### 1976

Modifications to the HP 5713A electronics were performed to increase sensitivity. Stainless steel flasks were electropolished and fitted with stainless steel Nupro type SS-4H bellows valves to minimize wall effects and contamination of samples from outgassing elastomer parts. A new sampling site was instituted at NWR.

### 1977

Flask pressurization systems were implemented at all baseline stations (BRW, MLO, and SMO) and at the South Pole (SPO) for the commencement of flask sampling at this site. Sample pressurization was used to increase sample volume and prevent contamination by inward leakage. Unpressurized samples continued to be collected at NWR. The GC-ECD system in Boulder was modified for the analysis of two additional trace gases, CFC-12 and N<sub>2</sub>O, using two separation columns (i.e. "channels"). Production and usage of reference gases for daily calibration injections was also initiated. Several long term reference tanks and one working reference (T3072) for daily system calibrations were filled with background air at Niwot Ridge and defined against a standard scale maintained at the Oregon Graduate Center (OGC) in Beaverton, OR.

### 1979

Analyses of reference gases performed at multiple laboratories showed wide ranging calibration uncertainties for all gases and potential stability issues over time.

### 1980

A new gravimetric reference for N<sub>2</sub>O was developed to help resolve a 10% discrepancy between the GMCC reference gas values reported after analyses by two independent labs. The results favored the lower Scripps Institute of Oceanography ("SIO", R. F. Weiss) value over the higher OGC (R. A. Rasmussen) value. The CFC-11 and CFC-12 reference values continued to be defined with respect to OGC scales.

### 1983

A modified Shimadzu mini-2E chromatograph was installed at SPO for local analysis of in situ samples to minimize issues arising from lengthy storage times. Flask samples from SPO continued to be collected and analyzed.

#### 1984

The halocarbons and nitrous oxide measurements program was folded into the new Trace Gases Group of GMCC that also included programs for the measurement of ozone and water vapor.

#### 1985

Reference tank T3072 was retired and replaced by T3088 that was defined against the OGC 1985 scale for CFC-11 and CFC-12.

#### 1986

The Nitrous Oxide and Halocarbons group (“NOAH”) split off from what was formerly known as the Trace Gases Group and was placed under the leadership of a new group chief that arrived in Boulder from the National Bureau of Standards, Dr. James W. Elkins. The independent, local development of reference gases and standard scales via gravimetric techniques was formalized in response to the new Radiatively Important Trace Species (RITS) in situ sampling initiative that was developed to measure N<sub>2</sub>O, CFC-12, CFC-11, CH<sub>3</sub>CCl<sub>3</sub> and CCl<sub>4</sub> at the five baseline sites.

#### 1987

New GMCC calibration scales for CFC-11 and CFC-12 were developed for the RITS program, though, for consistency, the OGC reference scales continued to be used in the flask program.

#### 1988

Flask sampling began at Alert, Nunavut, Canada (ALT). Primary reference tank no. T3088 was replaced by aluminum cylinder 62631 that was treated with a Scott Specialty Gases proprietary treatment called “Aculife”.

#### 1989

GMCC was renamed the Climate Monitoring and Diagnostics Laboratory (CMDL). In response to increased sample volume demands from a new Low Electron Attachment Potential Species (“LEAPS”) GC-ECD that focused on measurements of HCFC-22, H-1301 and H-1211, the flask program began using larger volume flasks pumped to a higher pressure (~3 atm).

#### 1991

Cape Grim, Tasmania (CGO) was added to the list of flask sampling sites. Gravimetric calibration scales for CFC-11, CFC-12 and N<sub>2</sub>O that were independently derived by CMDL/NOAH were used to redefine the reference values for all three reference tanks used in the flask program since 1977. Historic data from the flask program referenced to other scales were recomputed and reported with reference to the new “NOAA” scales from this point onward. Cryogenic trapping and adsorbent material techniques were developed to enable chromatographic analysis of many new molecules using mass spectrometric detection (GC-MS). Flasks as large as 2.5 L were added to the flask program to accommodate the ever increasing

demand for sample volume as routine analysis by GC-MS was implemented. A new automated GC-ECD flask analysis system based on a RITS system design entered the testing and development phase.

### 1993

Development and testing of the new “Autoflask” system continued, and a new automated four-channel in situ GC-ECD system entered the testing and development phase.

### 1995

Several new flask measurement sites were added at WITN Tower, North Carolina (ITN), WLEF Tower, Wisconsin (LEF), Harvard Forest, Massachusetts (HFM), and Kumakahi, Hawaii (KUM). The HP5713A manual mode GC-ECD that had analyzed flask samples since 1977 was retired and replaced by the new Autoflask GC-ECD dubbed “OTTO” (or sometimes just “Otto”). Otto is a three-channel system built around an HP5890 GC that added CFC-113, CH<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub> and SF<sub>6</sub> to the list of trace gases measured by GC-ECD analysis of flask samples in the NOAA program.

### 1997

Flask sampling was initiated at Palmer Station, Antarctica (PSA). Meticulous comparisons of atmospheric measurements and reference standards between CMDL and the Advanced Global Atmospheric Gases Experiment (AGAGE) network were performed in what has become a continuing effort to resolve differences. There is a very extensive degree of overlap in the gases independently measured by both groups. New NOAA calibration scales were developed for CFC-12, CH<sub>3</sub>CCl<sub>3</sub> and CCl<sub>4</sub>.

### 1999

The NOAA group changed its name to the Halocarbons and Other Trace Species, or “HATS”, group. The three-channel standards calibration GC-ECD was replaced by a four-channel GC-ECD. Differences of a few tenths of a percent between the two systems for several of the flask and in situ sampled gases were noted before the old system was retired. A new hire, Dr. Bradley Hall, took over and modernized the program directed toward making and defining reference standards and calibration scales for trace gases measured by CMDL/GMD.

### 2001

New sampling sites were incorporated into the flask program at Mace Head, Ireland (MHD), Trinidad Head, CA (THD), and Ushuaia, Argentina (formerly TDF, now USH). The three-channel RITS in situ sampling systems were successively retired over the course of two years and replaced by the next generation, four-channel, Chromatograph for Atmospheric Trace Species (“CATS”) systems.

### 2003

A new ECD was installed on the N<sub>2</sub>O/SF<sub>6</sub> channel of Otto.

2005

CMDL changed its name to the Global Monitoring Division (GMD) in response to a broader reorganization that brought six separate NOAA labs under one organization called the Earth System Research Laboratory (ESRL).

2008

A new data processing method for Otto was introduced. A detailed explanation is available at <ftp://aftp.cmdl.noaa.gov/hats/doc/HATSflaskECDanalysis.pdf>.

2013

The ECD on Otto's N2O/SF6 channel quit working.

2015

Otto's CFC-12 channel began experiencing a progressively worsening degradation.

2017

Otto continues to report measurements of CFC-11, CFC-113, CH3CCI3, and CCl4.

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HATS Flask Sampling Program: Recent Calibration Scale Histories □

NOAA ESRL GMD is the World Meteorological Organization (WMO), Global Atmospheric Watch (GAW) Central Calibration Laboratory (CCL) for CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, SF<sub>6</sub>, and CO. NOAA ESRL also maintains internal scales for a number of trace gases that are not part of the set of WMO GAW CCL scales. Scales are defined by a specific set of primary standards. Mixing ratios (expressed as dry air mole fraction) are assigned to the primary standards based on the mean response observed on GC-ECD or GC-MSD instruments. The scales are tied to a specific set of primary standards and named according to the year in which they were adopted. Thus, the preparation and use of new primary standards for a particular compound results in a new scale for that compound. Additional information can be found on the National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD) Halocarbons and other Atmospheric Trace Species Group (HATS) Central Calibration Laboratory website (<https://www.esrl.noaa.gov/gmd/ccl>).

N2O

Previous Scales: 1993, 2000, 2006

Current Scale: 2006A

Number of Primary Standards: 13

Note: WMO GAW CCL scale

SF6

Previous Scales: 1994, 2000, 2006

Current Scale: 2014

Number of Primary Standards: 17

Range: 2-20 ppt

Conversion Equation:  $Y = 2.6821e-3 * X^2 + 9.7748e-1 * X + 3.5831e-2$  (where Y = value of SF6 on the 2014 scale and X is SF6 on the 2006 scale)

Note: WMO GAW CCL scale

#### CFC-11

Previous Scale: 1992

Current Scale: 2016

Number of Primary Standards: 5

Range: 100-260 ppt

Conversion Equation:  $Y = -1.7948e-6 * X^3 + 7.4134e-4 * X^2 + 0.89385 * X + 6.54$  (where Y = value of CFC-11 on the 2016 scale and X = value of CFC-11 on the 1992 scale)

#### CFC-12

Previous Scales: 1997, 2001

Current Scale: 2008

Number of Primary Standards: 15

Range: 150-650 ppt

Conversion Equation:  $Y = 1.0021 * X + 5.807$  (where Y = value of CFC-12 on the 2008 scale and X = value of CFC-12 on the 2001 (or 1997) scale)

Note: The 2008 CFC-12 scale is 1.3% higher than the 2001 scale, see scale page for more information. Update using  $Y = 1.002 * X + 5.807$  ppt.

#### CFC-113

Previous Scale: 1993

Current Scale: 2003

Number of Primary Standards: 10

Range: 20-110 ppt

#### CCI4

Previous Scale: 1996

Current Scale: 2008

Number of Primary Standards: 7

Range: 25-150 ppt

Note: Seven standards prepared from 2001-2004 are now used to define the scale. These seven standards are consistent to within 0.5%. Four standards prepared in 1996 have been removed from the scale. For ECD-based results the conversion is 0.9954 at 95 ppt. For GCMS results the conversion is 0.9853.

#### CH3CCI3

Previous Scale: 1996  
Current Scale: 2003  
Number of Primary Standards: 10  
Range: 10-180 ppt

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### HATS Flask Sampling Program: File Structure

For each of the seven trace gases measured by Otto, there is a tar file holding three netCDF files, each reporting measurements at one of three distinct reduction levels. In the discussion that follows, an “event” refers to a unique flask sample. Sampling events occurred approximately once per week - depending on the prevailing wind conditions - at each sampling site. A “valid event” refers to a unique flask sample whose measurements pass all requisite quality control criteria.

Valid events from all sampling sites represent the minimally reduced level at which the Otto data are reported. These data are then binned and averaged by month to produce monthly means from all sites, and the monthly means are subsequently binned and averaged by latitude zone to produce global-hemispheric means.

The Pre-Otto data are reported only as monthly means at the seven sites in operation during the time period of these measurements.

#### “ValidEvents” Files

These are based on the NCEI incomplete time series netcdf file template and are used to report trace gas time series measurements from a range of sampling sites. The two primary dimensions defined within these files are called “site” and “ntimeMax”. Other dimensions have names beginning with “nchar\_” and serve only to define the storage space required for certain character strings.

Each stride along the site dimension corresponds to a unique field site where flasks are filled with samples of atmosphere at ground level. The positional identity of these sites is given in the “site\_code” variable. “site\_place\_name”, “site\_classification”, “longitude”, “latitude”, and “altitude” are the other “1-D” variables that hold information describing the sampling sites.

Several 2-D variables are dimensioned as (site, ntimeMax). These are the variables that hold the actual time series data for each of the sampling sites. ntimeMax is defined by the site with the highest number of samples to report. Fill values appear at the tail end of this dimension in all 2-D variables at the site positions associated with sites reporting fewer than ntimeMax samples. The “time” variable gives the netCDF time index value (UTC) for each collected sample. The “timestring” variable is an ISO-8601 formatted character string version of the time. The variable reporting dry air mole fractions is named after the particular trace gas that is being described.



Other variables are the mole fraction uncertainty and a bitwise boolean flag that offers quality control information.

Three null, scalar variables called “platform\_variable”, “instrument\_parameter\_variable”, and “crs” are little more than standard NCEI containers for metadata attributes holding additional information about the platform, instrument, and the coordinate reference system, respectively.

### “MonthlyMeans” Files

These are structured very much like the “ValidEvents” files with a few key differences. The two primary dimensions defined within these files are called “site” and “time”. The “1-D” site dimensioned variables are no different than those in the “ValidEvents” files, but the time series for all sites in the “MonthlyMeans” files are now synchronized and tied to a common 1-D “time” dimensioned variable. This variable, also called “time”, increments in twelve regular intervals per year each landing on the half month. And because of its 1-D nature, the NCEI orthogonal time series template is used. The “timestring” variable is now a yyyy-mm formatted string giving the year and month of the reported mole fractions. And because of the monthly averaging, a new (time, 2) dimensioned “timebounds” variable defining the averaging bins has been added.

Fill values may appear at either end of the time dimension in the mole fractions array, or at any other time when a given site has no measurements to report. The bitwise boolean flag variable is no longer included, as it pertains only to individual sample events. The mole fraction data found in the “ValidEvents” files are precisely the data that are reduced to monthly means.

### “HemisphericMeans” Files

Like the “MonthlyMeans” files, these files are also built around the NCEI orthogonal time series template. But again, there are a few key differences. The two primary dimensions defined within these files are now called “region” and “time”. Owing to the fact that these data are derived from the “MonthlyMeans” data, the time dimension is laid out no differently from that within the “MonthlyMeans” files. Sites, however, have now been replaced by three regions named “Southern Hemisphere”, “Global” and “Northern Hemisphere”. These are listed in the “region\_name” variable that replaces the “site\_place\_name” variable in the “MonthlyMeans” files. The “site\_code” and “site\_classification” have simply gone away.

The coordinate variables, “longitude”, “latitude”, and “altitude”, are all now arbitrary and virtually meaningless, but they are included nonetheless in an effort to placate to the extent possible a number of online algorithmic compliance checkers. Since the measurements from baseline sites (see the “site\_classification” variable in the “MonthlyMeans” files) are considered representative over time of the latitude at which they are located, longitude is ignored in favor of latitude in the regional averaging. So, longitudes and altitudes are all set to zero, and the latitudes are set at -30, 0 and 30 degrees. A “latbounds” variable has been added to define the latitudinal averaging bins.

Southern hemispheric sites in the “MonthlyMeans” files are weighted by the cosine of their latitudes and averaged together to compute a Southern Hemispheric mean. Likewise for the Northern Hemisphere. The Global mean is simply the average of the two hemispheric means. These gases tend to be vertically well mixed throughout the troposphere, and the reported data are considered representative of the tropospheric mean time series for the regions they are associated with.