Global Monitoring Division

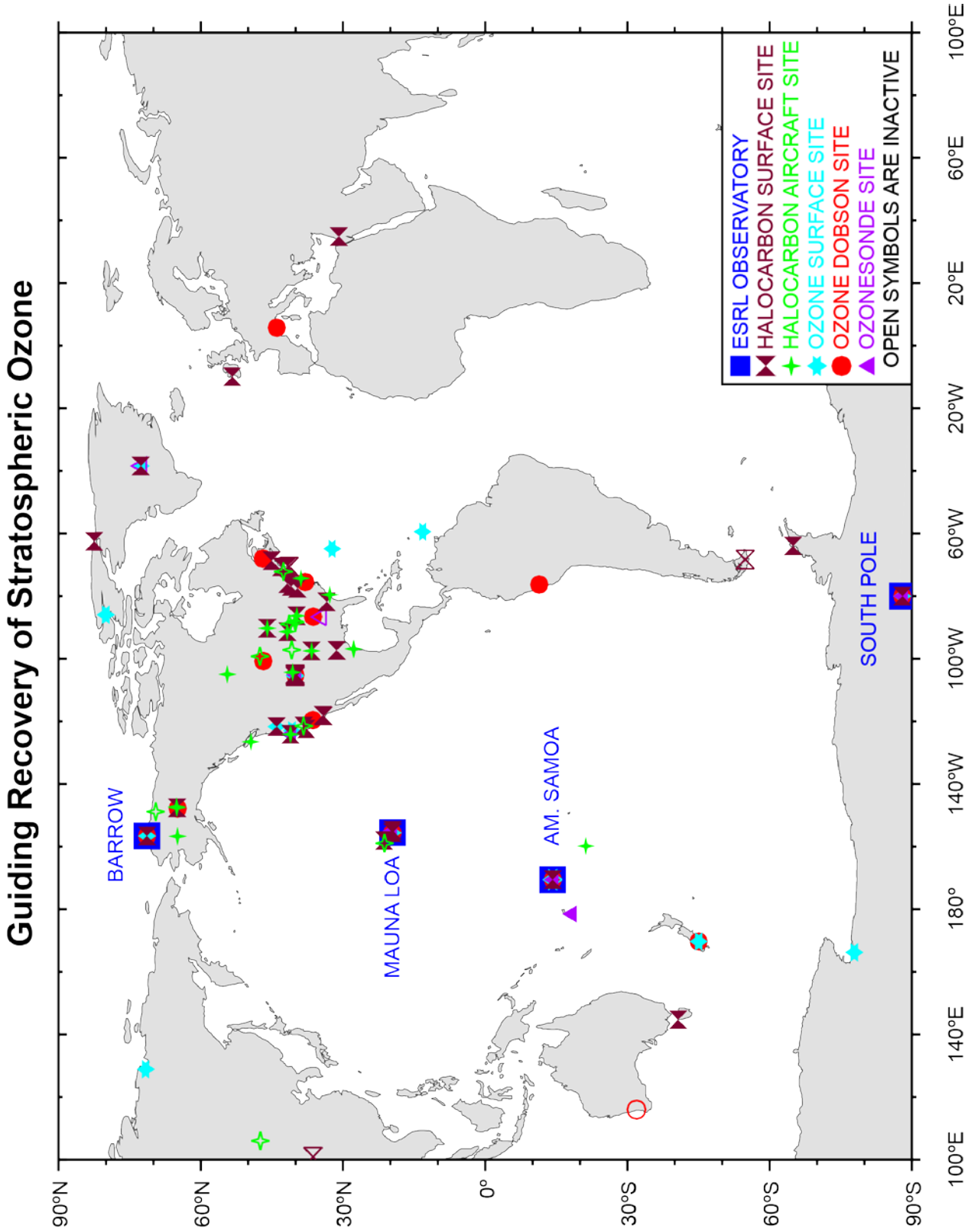
Theme 3 Networks: Guiding Recovery of Stratospheric Ozone

2013-2017 Review

May 21-24, 2018

Contents:

Page


Guiding Recovery of Stratospheric Ozone
ESRL OBSERVATORY
HALOCARBON SURFACE SITE
HALOCARBON AIRCRAFT SITE
OZONE SURFACE SITE
OZONE DOBSON SITE
OZONESONDE SITE
OPEN SYMBOLS ARE INACTIVE
BARROW
MAUNA LOA
AM. SAMOA
SOUTH POLE
90°N
60°N
30°N
0°
30°S
60°S
90°S
100°E
140°E
180°
140°W
100°W
60°W
20°W
20°E
60°E
100°E

Theme 3, Part 1: NOAA Ozone and Water Vapor (OZWV) Networks

> *"Without a protective ozone layer in the atmosphere, animals and plants could not exist, at least upon land. It is therefore of the greatest importance to understand the processes that regulate the atmosphere's ozone content."* ***(Royal Academy of Sciences, announcing the 1995 Nobel Prize for Chemistry for Paul Crutzen, Mario Molina, and F. Sherwood Rowland)***

> *"…stratospheric water vapor probably increased between 1980 and 2000, which would have enhanced the decadal rate of surface warming during the 1990s by about 30% as compared to estimates neglecting this change. These findings show that stratospheric water vapor is an important driver of decadal global surface climate change."* ***Susan Solomon, Science, 05 March, 2010***

The Global Monitoring Division addresses both of these environmental issues and has compiled the longest continuous stratospheric water vapor measurement record and some of the longest continuous global ozone records available.

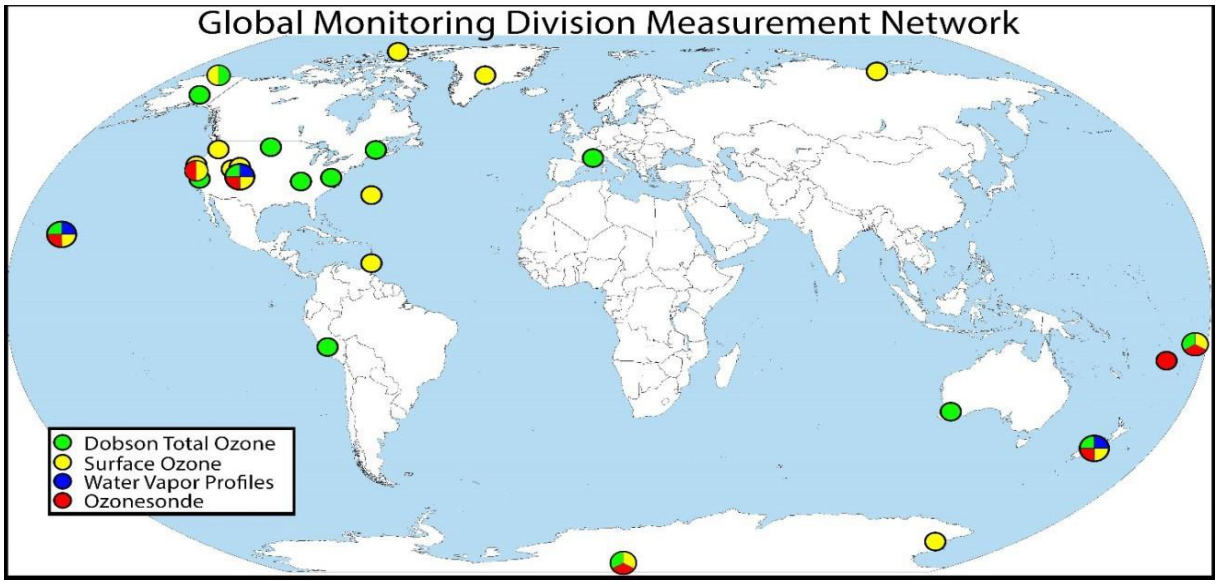
Mission Statement:

The Ozone and Water Vapor research program conducts research on the nature and causes of the depletion of the stratospheric ozone layer and the role of stratospheric and tropospheric ozone and water vapor in forcing climate change. This mission is accomplished through long-term observations and intensive field programs that measure total column ozone, ozone vertical profiles, ground level ozone, and water vapor vertical profiles in the upper troposphere and stratosphere.

Stratospheric Ozone Profile Measurements

Ozonesondes

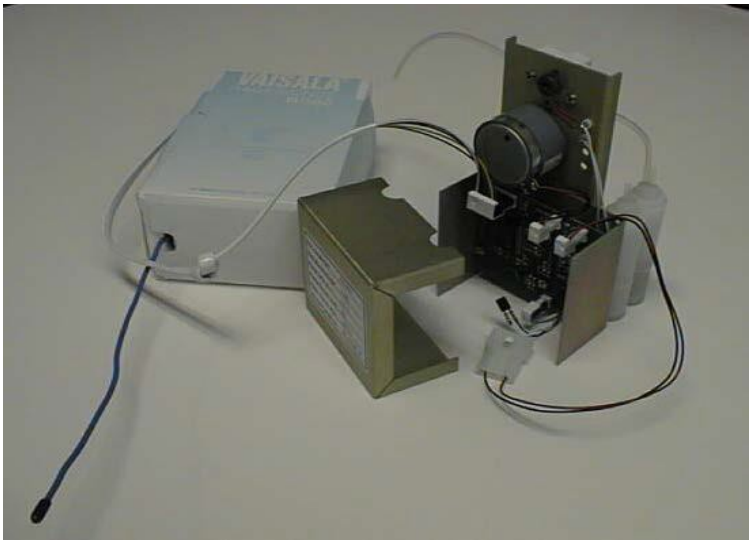
GMD measures stratospheric ozone in two ways; with balloon borne ozonesondes that transmit the data by radiosondes back to surface stations and with Dobson Ozone Spectrophotometers that look at the sun and measure the attenuation produced by the column of ozone in the atmosphere. The ozonesonde was invented by Walter Komhyr in the 1950s, a scientist in a predecessor organization of the present NOAA GMD. The ozonesonde was commercialized and is still making measurements in the same basic configuration.



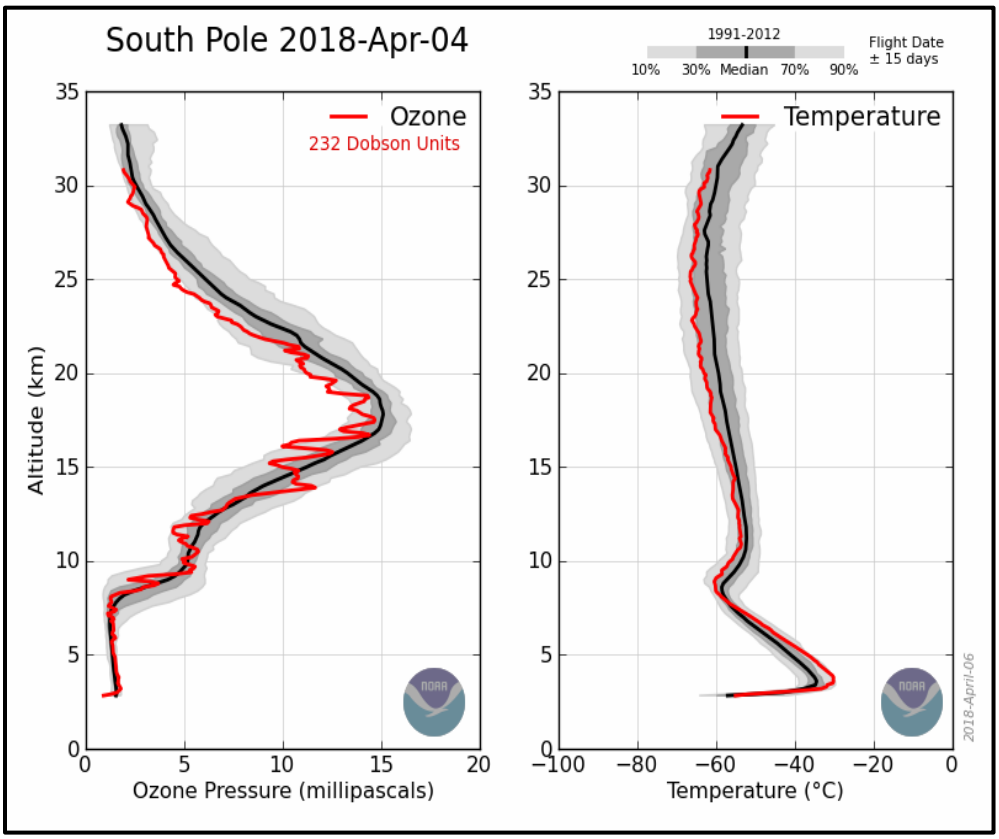
Map of the Dobson total column ozone (green), ozonesondes (red), water vapor sondes (blue) and surface ozone (yellow) GMD OZWV network.

GMD conducts about 600 ozonesonde soundings each year from eight globally distributed sites using the balloon-borne electrochemical (ECC) ozonesondes. The soundings provide vertical profiles of ozone, temperature, and humidity from the surface to approximately 32 km (~100,000 ft). Ozonesondes send back data as they rise and then descend by parachute. Some ozonesondes are recovered and reconditioned for reuse.

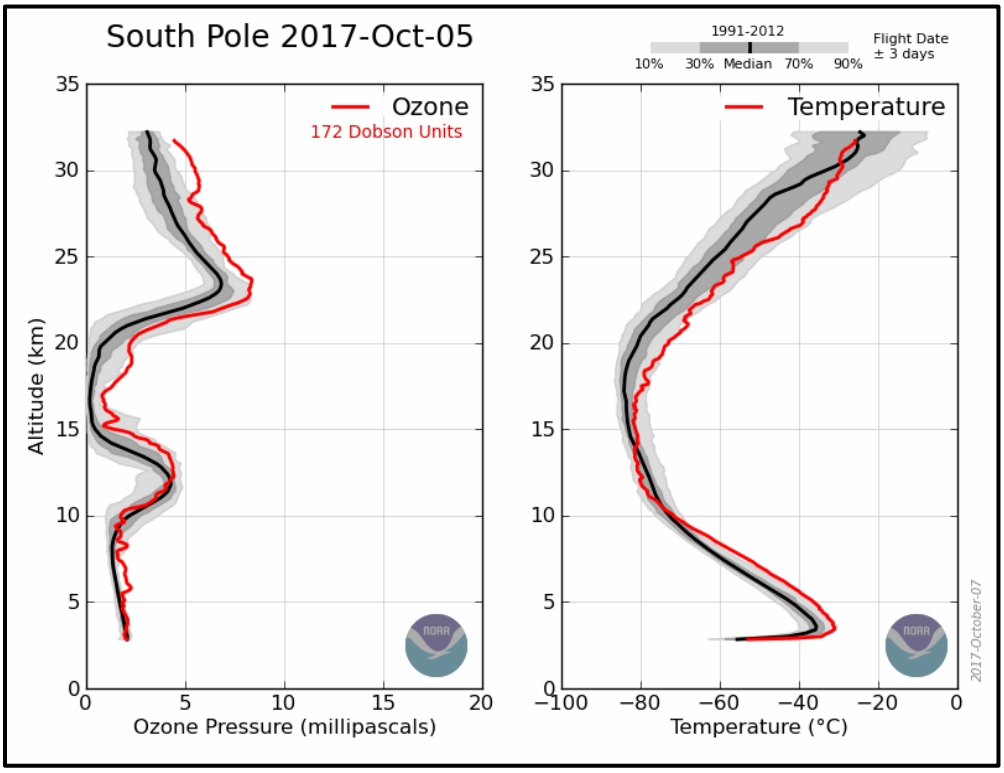
Ozonesondes are especially valuable in monitoring the annual Antarctic “Ozone Hole” as satellites are unable to measure stratospheric ozone at high southern latitudes during the six month dark season. The South Pole ozone and temperature profile for April 4, 2018 is presented on the next page along with the 1991-2012 climatology of profiles.



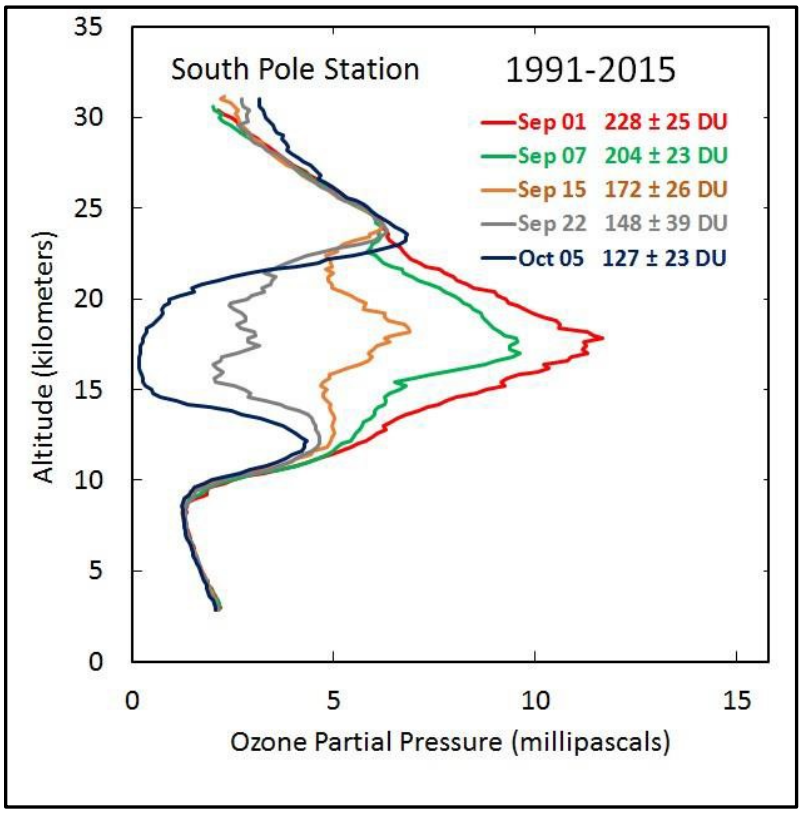
The ozonesonde is a simple and robust instrument that, over decades, has proven its ability to reliably and accurately measure in situ ozone from sea level to 32 km (100,000ft). In a profile, temperature may decrease from $+40^0$C at the surface to -85^0C at the tropopause. During descent the ozonesonde is subjected to the reverse temperature gradient.



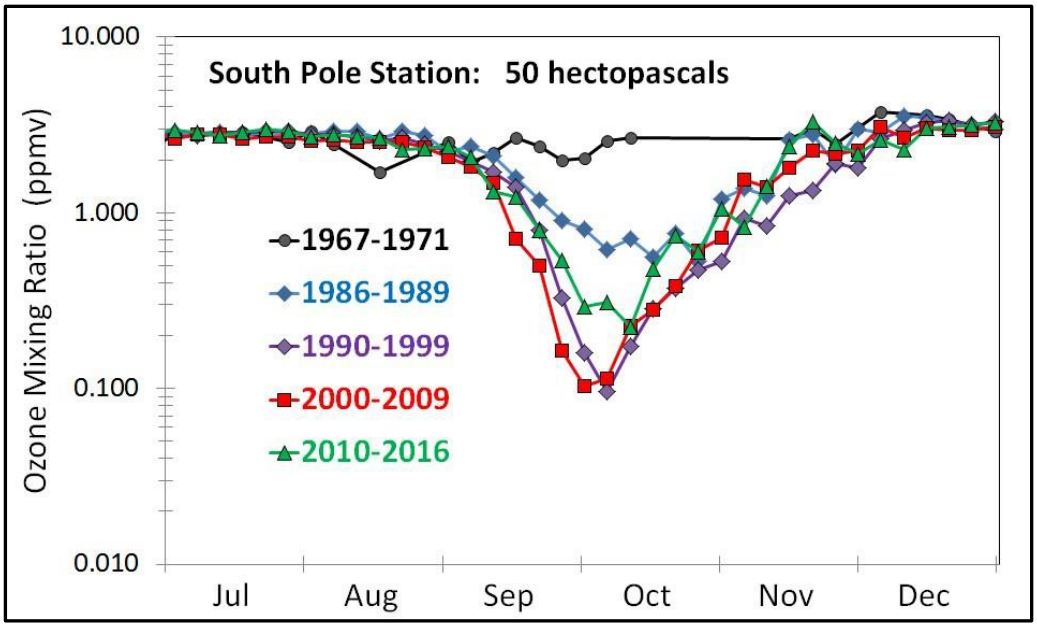
Ozonesonde and temperature profiles from the South Pole, April 4, 2018 (in red) along with long term statistics for April 4 ± 15 days over the period 1991-2012. Note the temperatures are warmer than the ~-80^{0}C temperature required to produce Polar Stratospheric Clouds that provide a base for Cl to destroy ozone in a catalytic reaction.



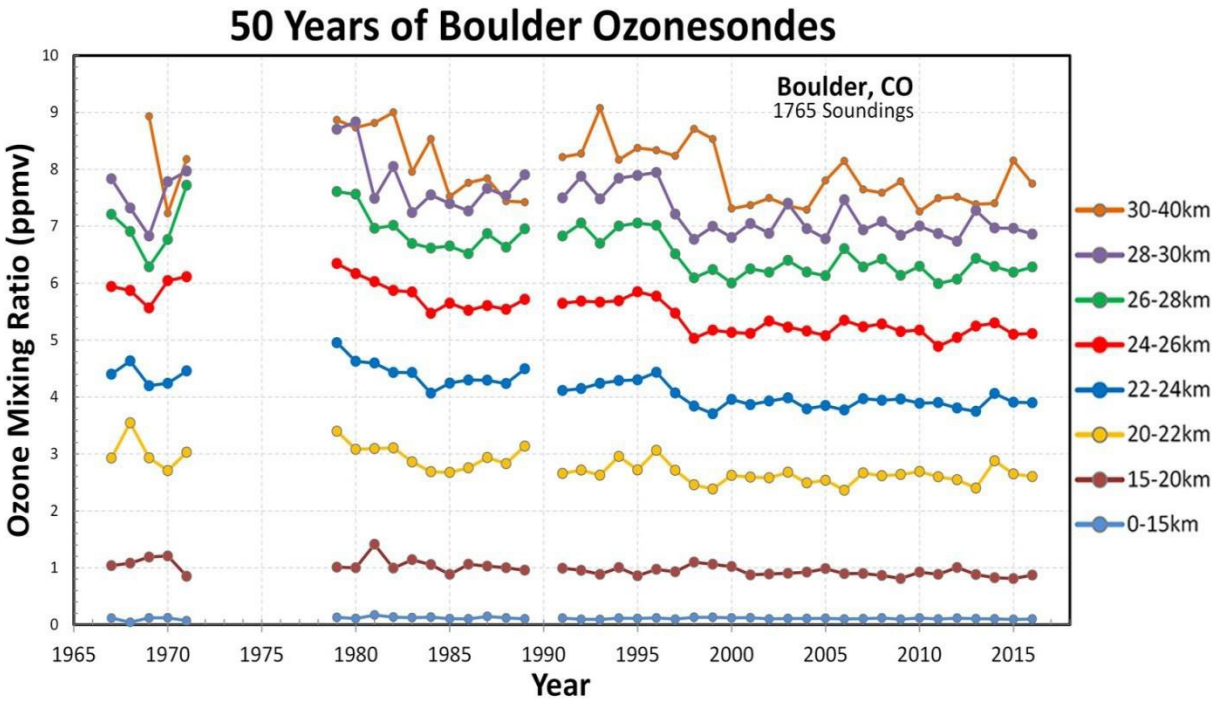
Ozonesonde and temperature profiles from the South Pole, October 5, 2017 (in red) during the 2017 ozone hole. Note the ozone depleted layer between 15 and 20 km where temperatures are ~-80^{0}C and colder which coincides with the zone of depletion.



Average ozone profiles over South Pole for specific days prior to the onset of springtime ozone depletion (September 1); in the middle of the depletion events (September 15): and at their peak (October 5).

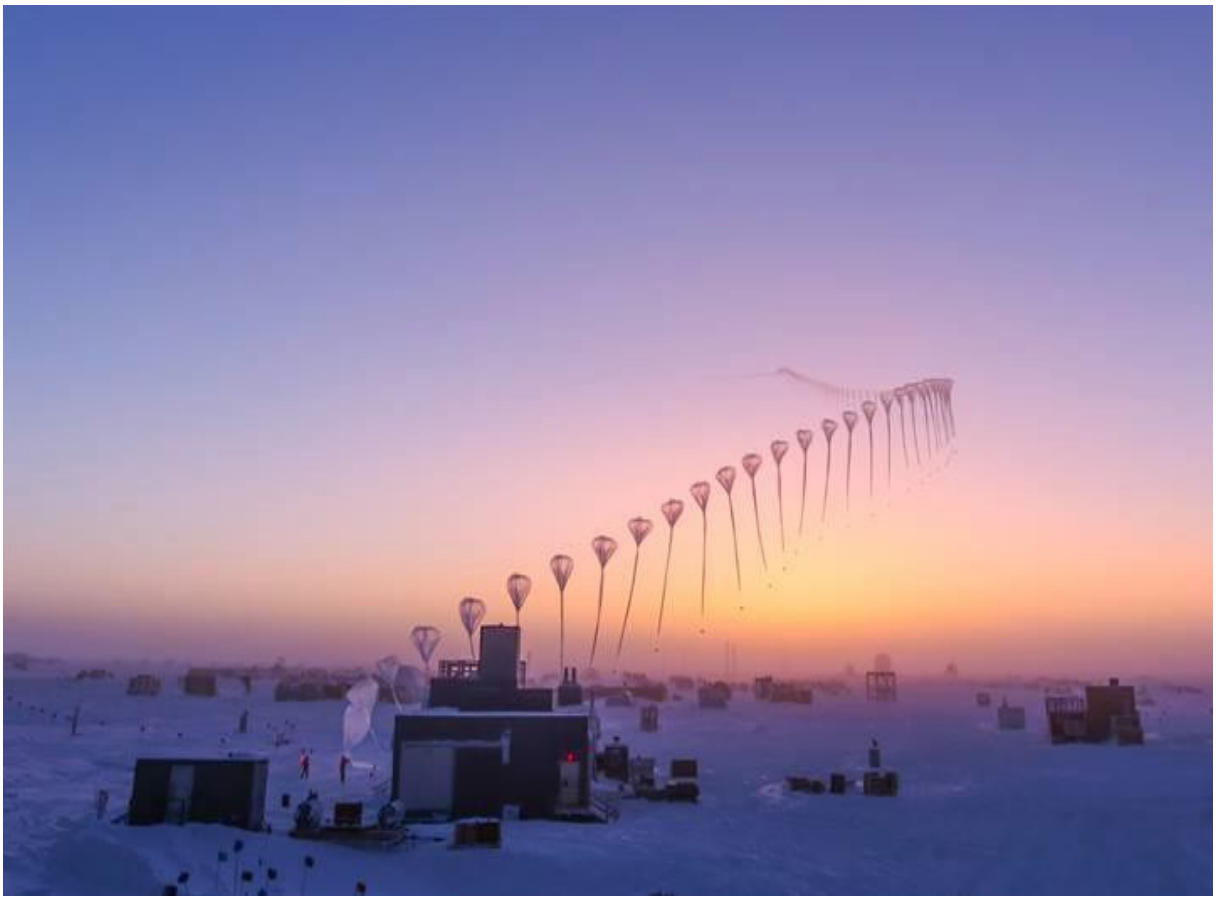


Ozonesonde measurements at South Pole at 50 hectopascals (~18 km) in the upper level of the ozone depletion zone. It appears that the annual ozone depletion at 50 hPa may be lessening.



Boulder ozonesonde data (1765 soundings) averaged over 50 profiles per year at the levels indicated on the right side of the graph. Before 2000 the trends were negative, but after 2000 trends in the upper levels change to increasing or flat.

Preparing to launch a combination ozonesonde and radiosonde package from American Samoa.

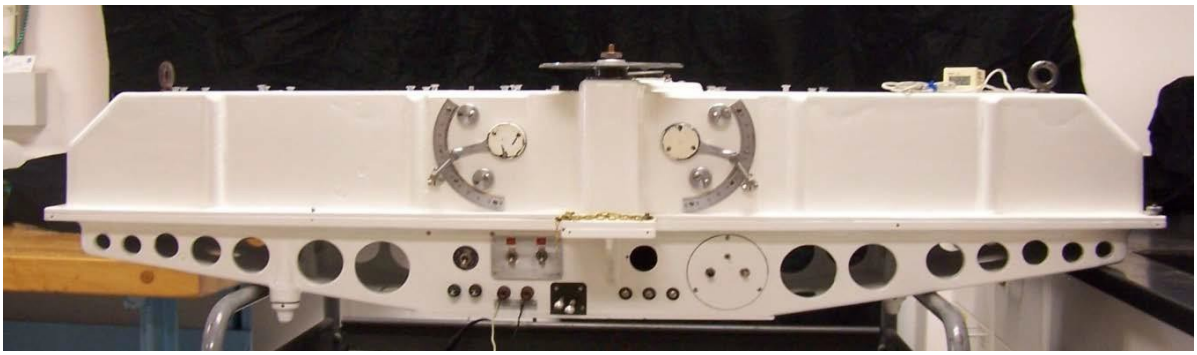


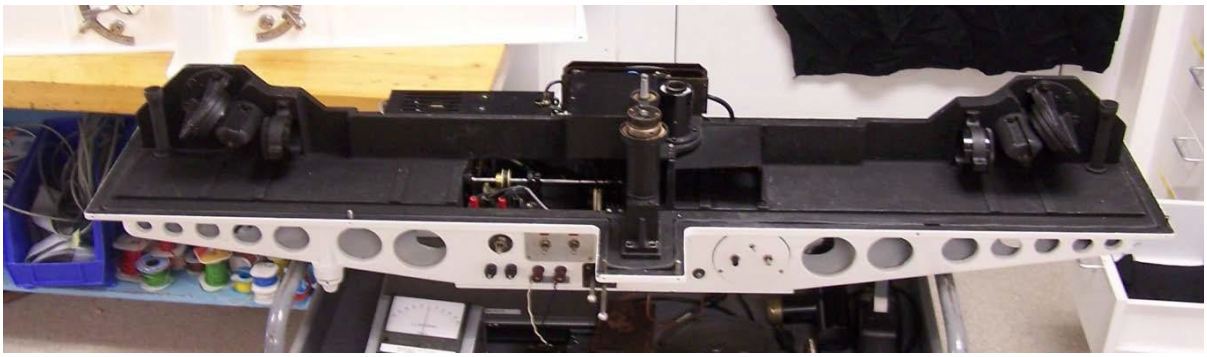
Composite time lapse image of a GMD ozonesonde balloon launched from the Amundsen-Scott South Pole Station. Multiple consecutive exposures track the path of the balloon as it rises in the pre-dawn sky over Antarctica. Photo credit: Robert Schwarz

Total Column Ozone: Dobson Spectrophotometer Measurements

The Dobson Ozone Spectrophotometer has been used to study total ozone since its development in the 1920's. The observations of total ozone, the total amount of ozone in a column from the surface to the top of the atmosphere with this instrument has produced one of the longest geophysical records of this nature in existence.

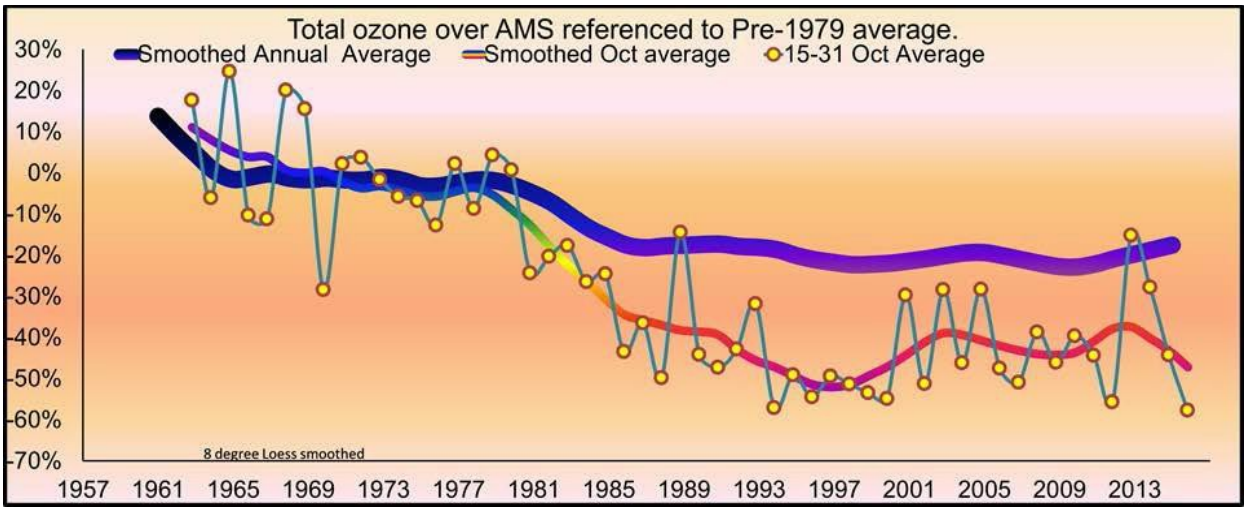
Today, the instrument is an important part of a global effort to understand the role of stratospheric ozone in atmospheric chemistry; biological and ecological effects of solar UV radiation; and climate and weather. Every two years this instrument is sent to our observatory in Mauna Loa, Hawaii for an absolute calibration using the Langley method. From this, the calibration is transferred to fifteen Dobson Ozone Spectrophotometers in the NOAA GMD global network, and to over one hundred instruments worldwide under the auspices of the WMO Global Atmosphere Watch program.



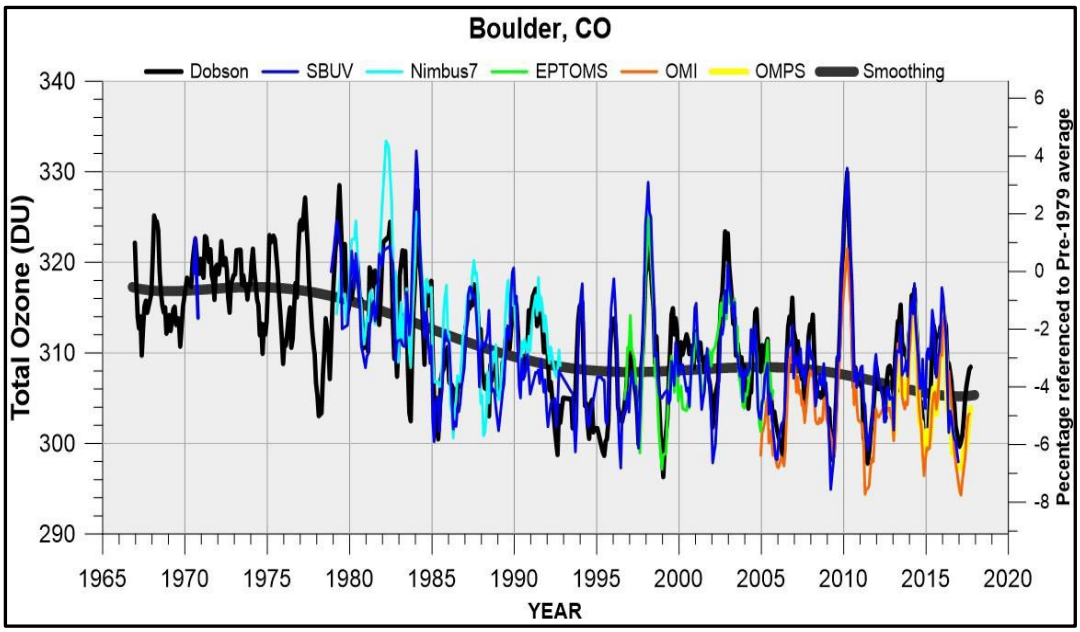


A Dobson Spectrophotometer is constructed of machined steel, is 4.5 ft long and weighs 150 lbs. The interior of the instrument is mainly mechanical hand operated prisms and mirrors. The youngest Dobson Spectrophotometers in the NOAA network were built in the 1950s.

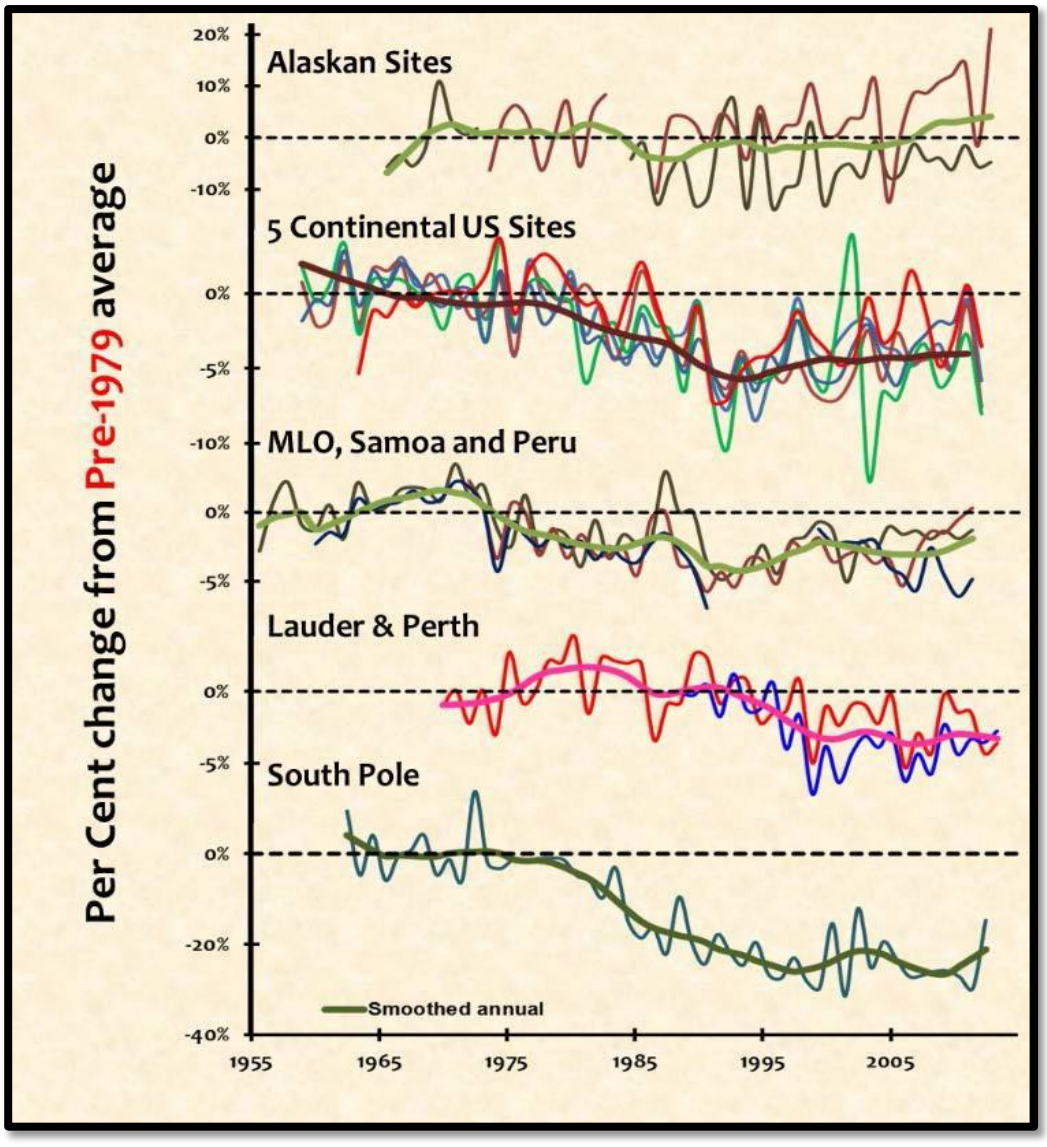
Total Column Dobson Measured Stratospheric Ozone Trends



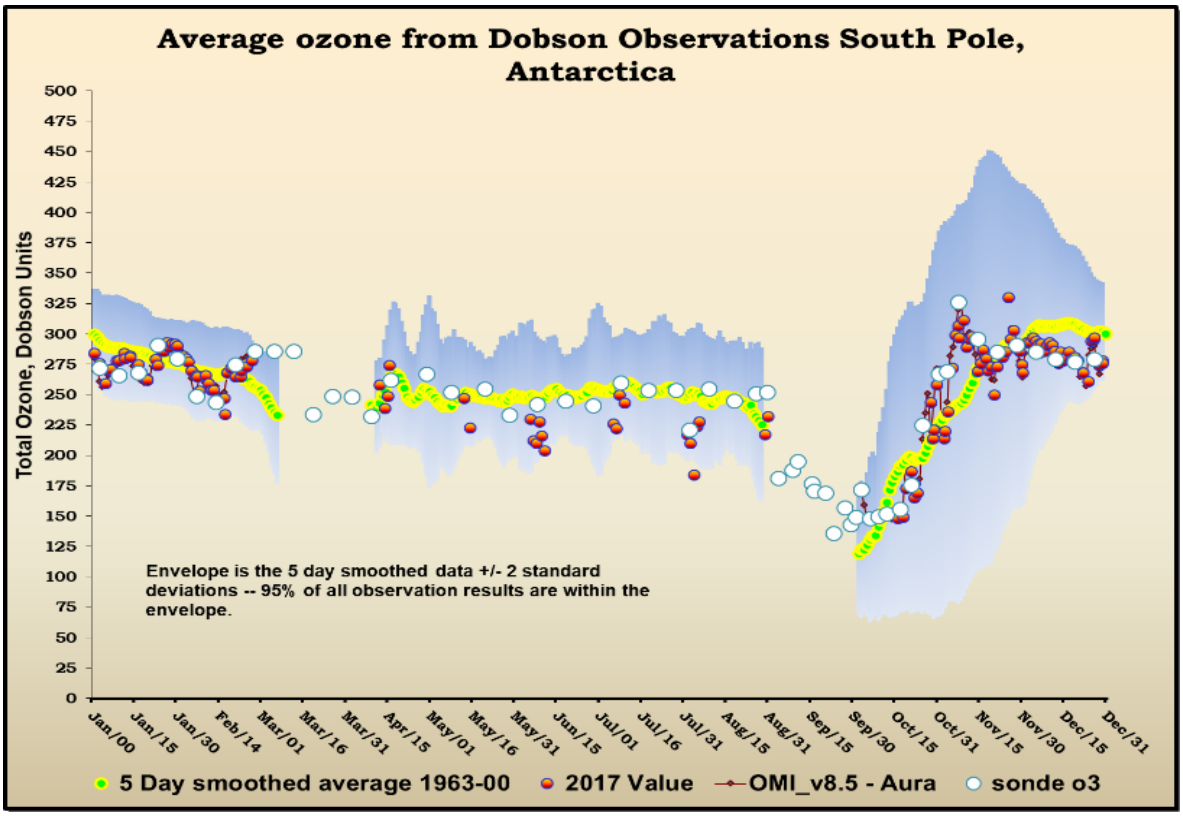
South Pole total column ozone time series. The yearly averages over the 15-31 October observation periods are shown as yellow circles. The annual average is shown with a blue line. In 2015 South Pole station observed the lowest averaged ozone (120 DU) in its 50+ year record (in 1993 ozone was at 121 DU). Stable vortex conditions in 2015 delayed ozone recovery until the end of December.



Dobson total column ozone (black line) and satellite overpass total column data over Boulder, CO. The scale on the right shows percent change in ozone records relative to pre-1978 ozone levels.



Long term ozone changes are shown (top to bottom) for the Alaska region (Barrow and Fairbanks), continental U.S. region (5 stations), tropical region (MLO, Samoa, Peru), South hemisphere middle latitudes (Perth and Lauder), and at South Pole. Data are shown as percent change in ozone column relative to the pre-1997 averaged ozone level.

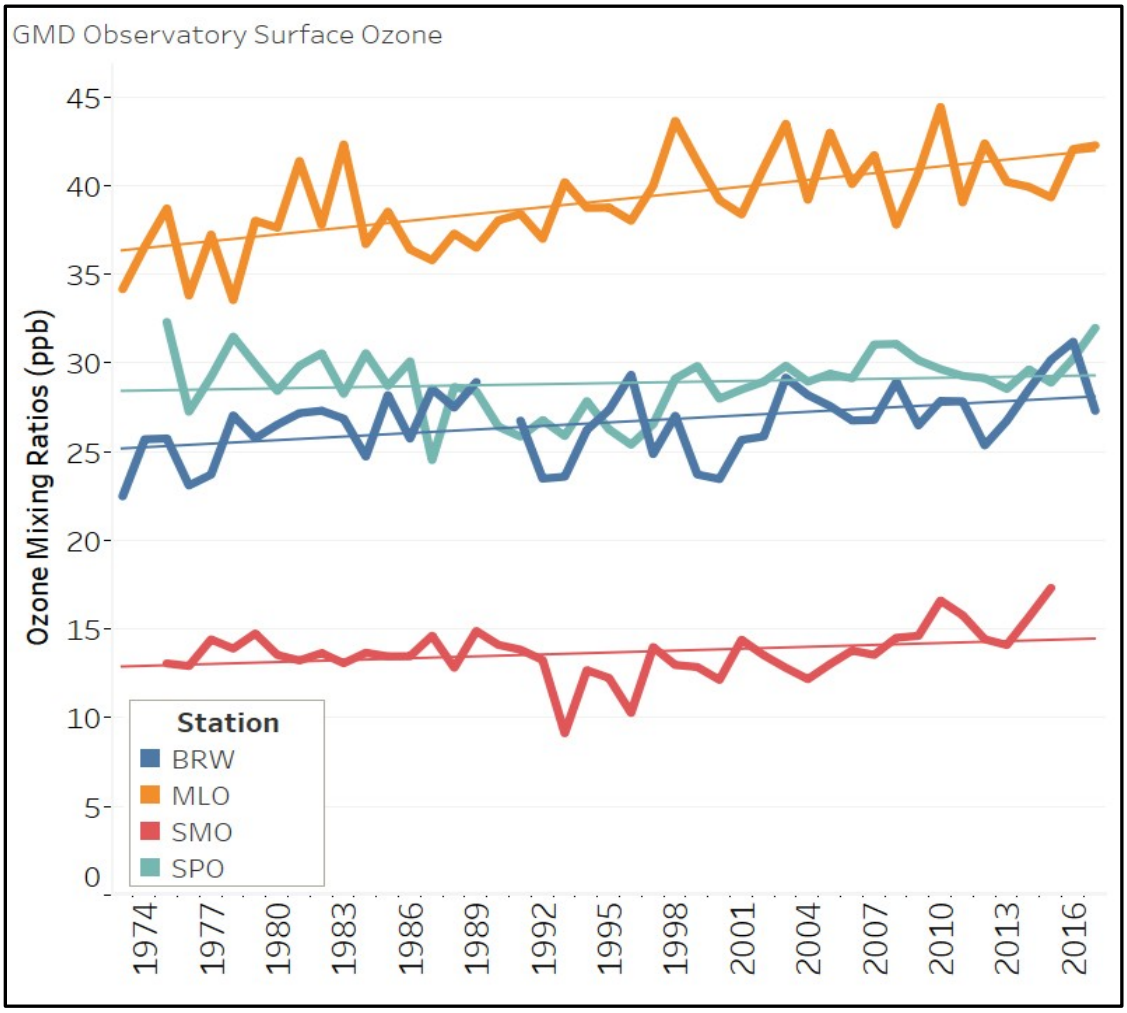


Daily South Pole total column Dobson Ozone measurements (red circles) in 2017. Green-yellow line indicates 5-day smoothing for daily averages during 1963-2000. Blue envelopes represent 2 standard deviations above and below the daily average. Red thin line September 30 to December 15 shows Aura OMI v8.5 overpass data for South Pole. Ozonesonde estimated total ozone column is shown as white circles.

Surface Baseline Ozone Monitoring

In the troposphere, ozone is a short-lived greenhouse gas with a radiative forcing comparable to halocarbons. It is an important regulator of the oxidizing capacity of the atmosphere (both itself and as the main source of hydroxyl radicals, OH), as well as being an important pollutant, with negative effects on vegetation and human health (e.g. Prather et al., 2001; UNEP, 2015). The future evolution of ozone in the troposphere is a concern for climate change and air quality during the 21st century.

The ultimate background level for tropospheric ozone existed before humans began to alter the atmosphere. Baseline O_3 is used here to describe a measurable quantity, the statistically defined lowest abundances of O_3 in the air flowing into a measurement site, which is typical of clean-air at remote marine sites. Baseline air thus includes remote upwind pollution that contributes to the diffuse, uniform increase in O_3 but not the episodic events. **Concisely stated, baseline O_3 is the lower envelope of the frequency distribution of ozone concentrations reflecting conditions of minimum pollutant source influence.**

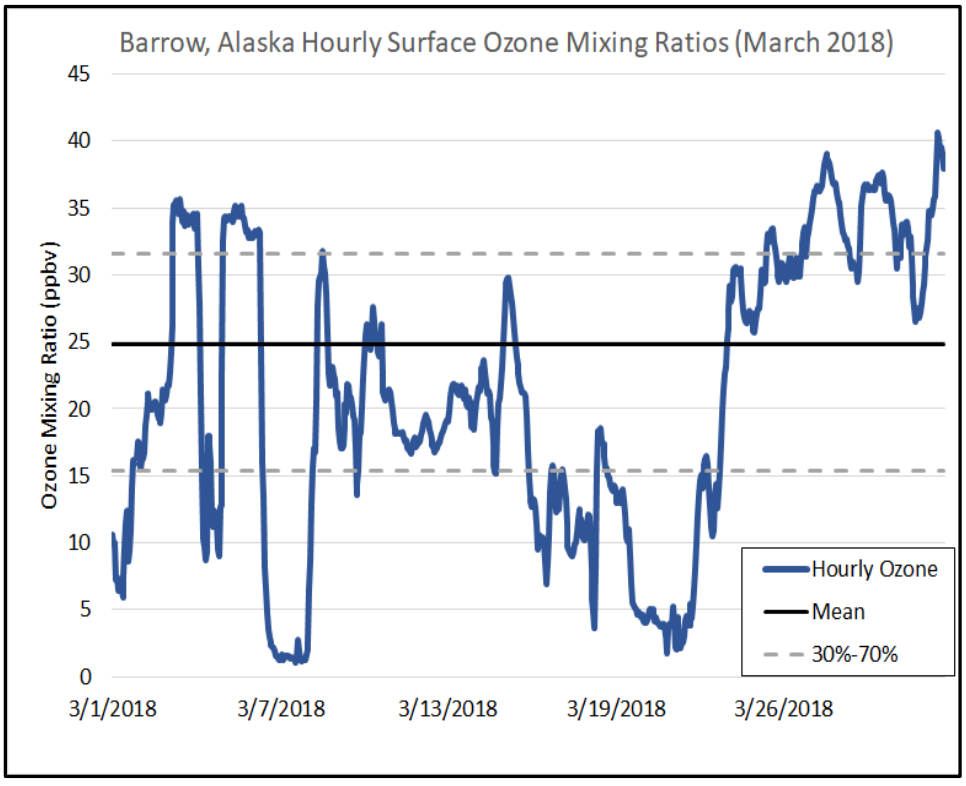


Yearly average surface ozone mixing ratios calculated from QA/QC hourly data measured from the four GMD Baseline Observatories. Mauna Loa, Samoa, and Barrow show a slight positive trend since measurements began in 1973.

NOAA GMD measures baseline ozone at 17 globally distributed sites. The longest continuous records are 45 years at South Pole and 43 years at Mauna Loa. Trends in the yearly average for the four GMD Atmospheric Baseline Observatories are shown above where it may be observed that background ozone has been increasing in the troposphere over the past 40+ years.

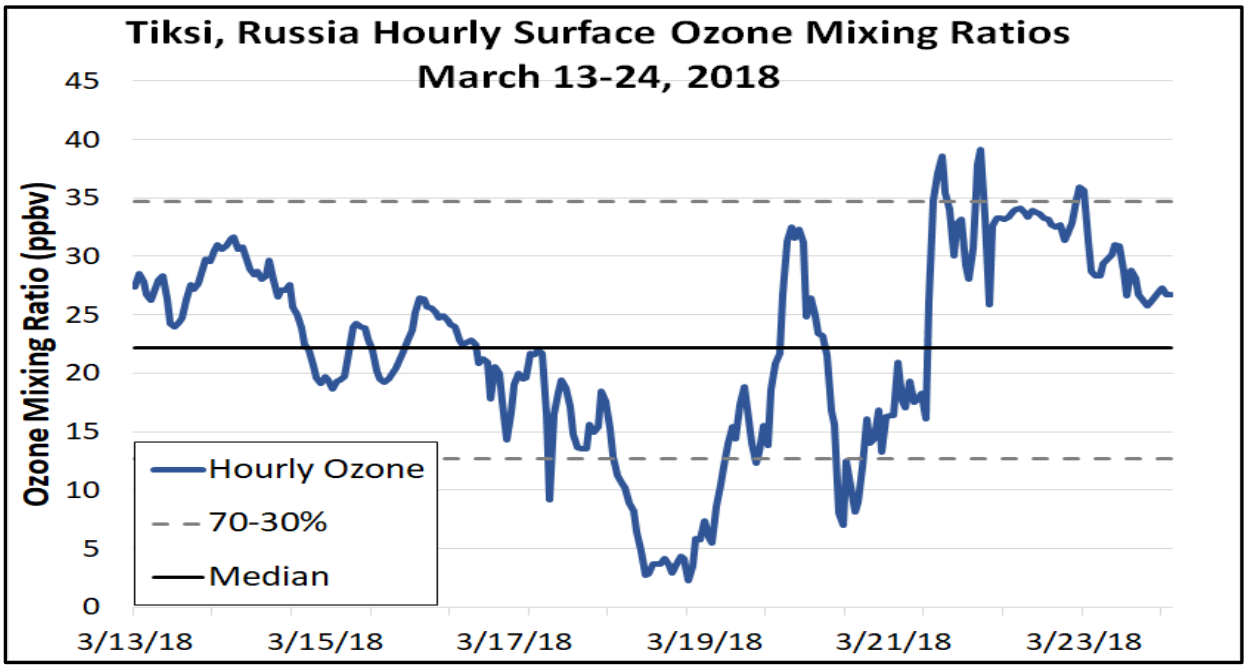
An interesting result from the surface ozone monitoring is the discovery of springtime photolytic ozone destruction in the Arctic boundary layer related to bromine chemistry. Graphs showing the destruction of baseline ozone at Barrow and Tiksi in the spring of 2018 are presented below. The Tiksi, Russia data come to GMD electronically from the station.

End of the winter dark period at the Barrow Baseline (Utqiaġvik) Observatory, Alaska. The small amount of sunlight seen in this photo is capable of destroying ozone throughout the surface boundary layer in air flowing off the frozen Arctic Ocean.



Hourly average concentrations of ozone at Barrow Observatory, spring 2018, showing two depletion events. This same phenomenon, over the same period, was observed in the Russian Arctic at the Tiksi Observatory on GMD supplied instruments.

Tiksi, Russia Atmospheric Observatory located on the Arctic Ocean where GMD has surface ozone, black carbon, solar radiation and greenhouse gas flask sampling operations. The surface ozone record at Tiksi began in 2008. The U.S. NSF paid for the construction of the Tiksi Observatory that is operated by Roshydromet.



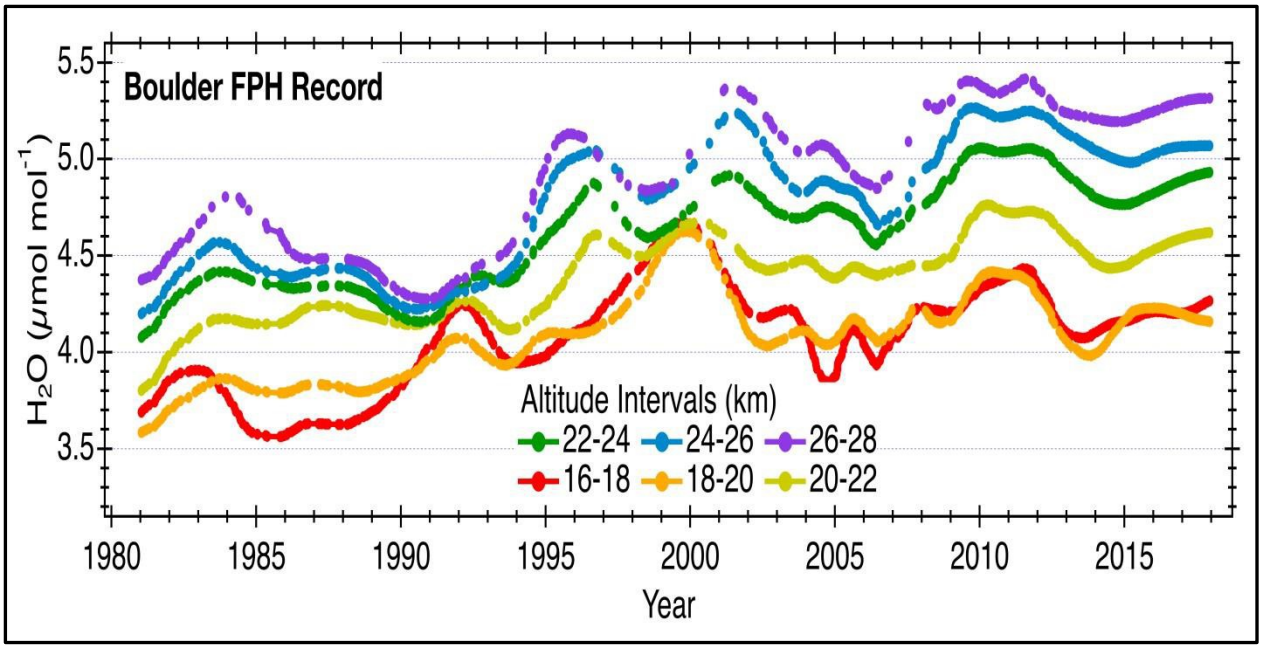
Hourly average ozone concentrations measured at the Tiksi, Russia Atmospheric Baseline Observatory showing a strong surface photolytic ozone depletion event on March 19, 2018 and a lesser event on March 21.

Stratospheric Water Vapor Monitoring

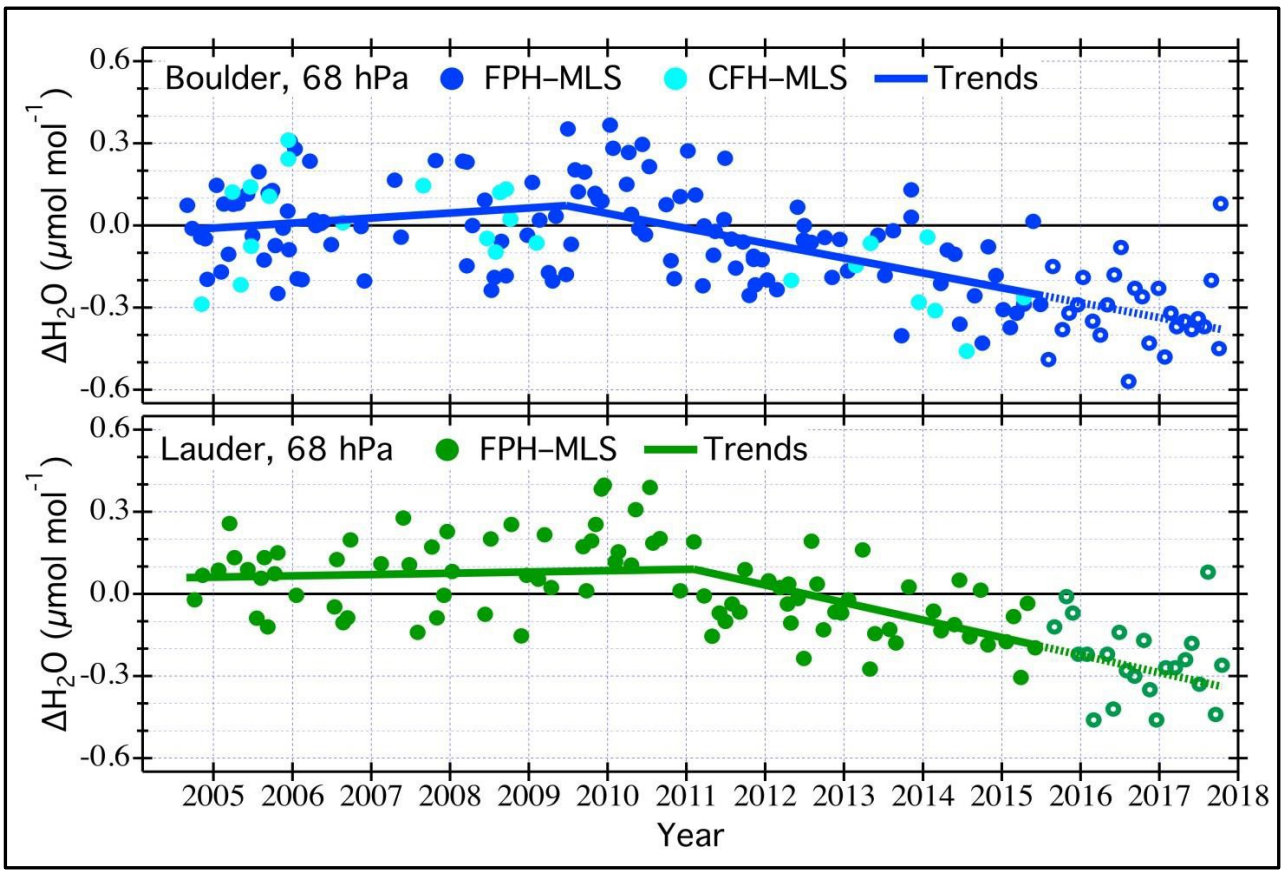
Monthly measurements of water vapor vertical profiles by balloon-borne frost point hygrometers (FPHs) at Boulder began in 1980 and continue today. In the late 1970s, Sam Oltmans of GMD developed the FPH and had the foresight to initiate the measurement program based on his realization that changes in upper tropospheric and/or lower stratospheric (UTLS) water vapor could have a strong impact on Earth's climate. Today, monthly FPH soundings are also performed at Hilo, Hawaii, and Lauder, New Zealand.

The 38-year Boulder Record is the longest continuous set of UTLS water vapor measurements in the world.

The data from the 3 FPH sounding sites are used to examine seasonal and longer-term changes in stratospheric water vapor, such as the 25% increase detected above Boulder during 1980-2010. The data sets provide reality checks for satellite-based water vapor measurements, and are used to test chemistry-climate models' simulations of upper atmospheric water vapor.



Smoothed time series of stratospheric water vapor mixing ratios in six altitude bins over Boulder, Colorado. Each data point represents a uniquely measured vertical profile by a balloon-borne frost point hygrometer. This record depicts a 25% increase in stratospheric water vapor from 1980 through 2017.



Trends in the differences between stratospheric water vapor measurements by frost point hygrometers (FPH, CFH) and the Aura Microwave Limb Sounder (MLS) over Boulder, Colorado, and Lauder, New Zealand. Solid lines depict the trends in FPH-MLS differences through mid-2015, as published in Hurst et al. (2016). Open circles show the FPH-MLS differences from mid-2015 through 2017 and dotted lines are simple extrapolations of the post-breakpoint trends. The downward trends in FPH-MLS differences since 2009-2011 imply that drifts in the MLS retrievals have produced significant and persistent biases through 2017.

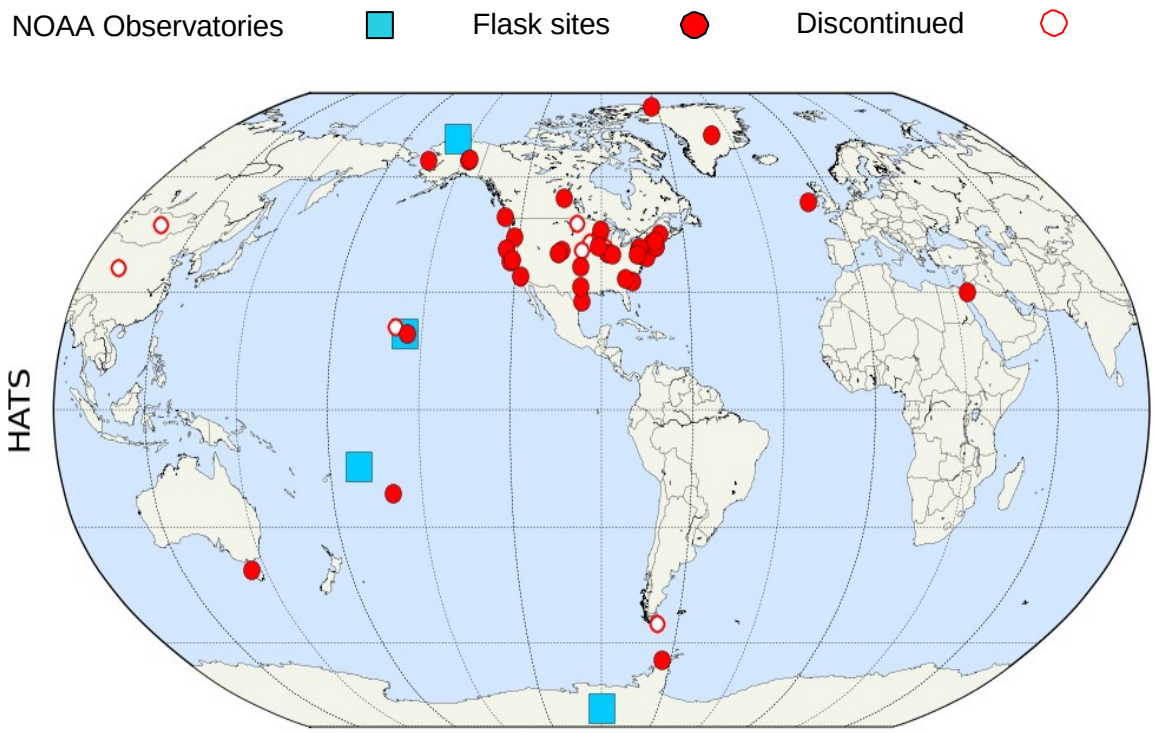
Ozone Network Data Archiving

GMD ozone data is archived on site and at a backup off-site location in electronic format and at the World Ozone and Ultraviolet Radiation Data Centre (WOUDC), Downsview, Canada; Network for Detection of Atmospheric Composition Change (NDACC), Asheville, North Carolina; and at the National Center for Environmental Data Information (NCEI) as an outcome of the NOAA Big Earth Data Initiative, Washington, DC.

Theme 3, Part 2: Halocarbons and other Atmospheric Trace Species (HATS) Network

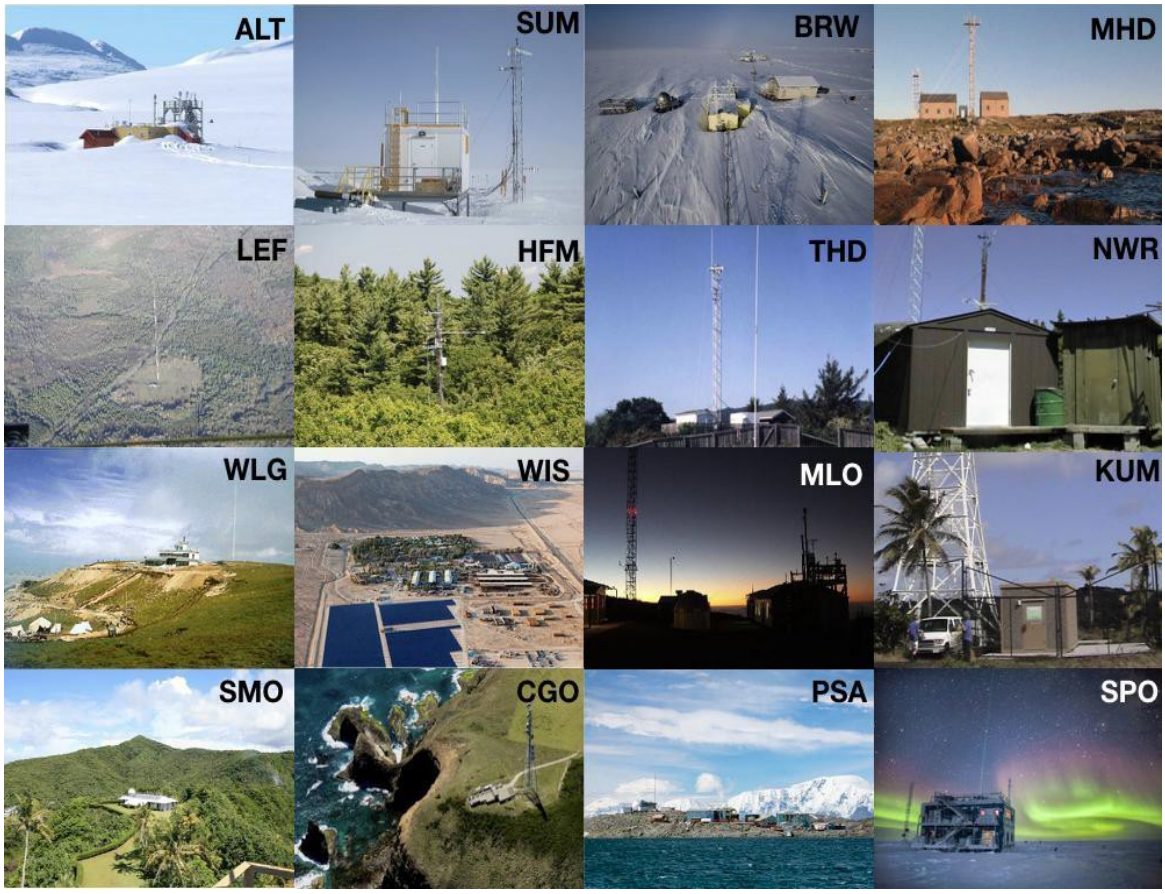
Mission, Justification, and Introduction of the HATS Network

"The Montreal Protocol is a model of cooperation. It is a product of the recognition and international consensus that ozone depletion is a global problem, both in terms of its causes and its effects" President Ronald Reagan after signing the Montreal Protocol, April 1998.



HATS ground based sites (16), tall tower sites (13) and light aircraft profiling sites (19) from ground to 8 km (tower and aircraft in collaboration with NOAA GMD CCGG).

Mission Statement: The mission of the Halocarbons and other Atmospheric Trace Species group is to quantify the distributions and magnitudes of sources and sinks for atmospheric nitrous oxide (N_2O) and halogen-containing ozone-depleting compounds. The HATS group utilizes numerous types of platforms, including ground-based stations, towers, ocean vessels, aircraft, and balloons to accomplish its mission.



HATS Network sites (above) and locations sorted by latitude (below).

HATS surface Network sites.

Label	Name	Latitude	Longitude	Elevation (m)
ALT	Alert, Canada	82.5 N	62.3 W	210 asl
SUM	Summit, Greenland	72.6 N	38.4 W	3209 asl
BRW	Barrow, AK, USA*	71.3N	156.6 W	27 asl; 16 agl
MHD	Mace Head, Ireland	53.3 N	9.9 W	42 asl
LEF	Park Falls, WI, USA	45.9 N	90.3 W	868 asl; 396 agl
HFM	Harvard Forest, MA, USA	42.5 N	72.2 W	340 asl; 29 agl
THD	Trinidad Head, CA, USA	41.0 N	124.1 W	120 asl
NWR	Niwot Ridge, CO, USA*	40.1 N	105.5 W	3476 asl (F);3048 asl*
WLG	Mt. Waliguan, China	36.3 N	100.9 E	3890 asl (discontinued)
WIS	Negev Desert, Israel	30.9 N	34.9 E	482 asl
MLO	Mauna Loa, HI, USA*	19.5 N	155.6 W	3422 asl; 36 agl
KUM	Cape Kumukahi, HI, USA	19.5 N	154.8 W	39 asl; 36 agl
SMO	American Samoa, AS, USA*	14.2 S	170.5 W	77 asl
CGO	Cape Grim, Australia	40.7 S	144.7 E	164 asl; 70 agl
PSA	Palmer Station, Antarctica	64.6 S	64.0□W	15 asl
SPO	South Pole, Antarctica*	90.0 S	----------	2837 asl

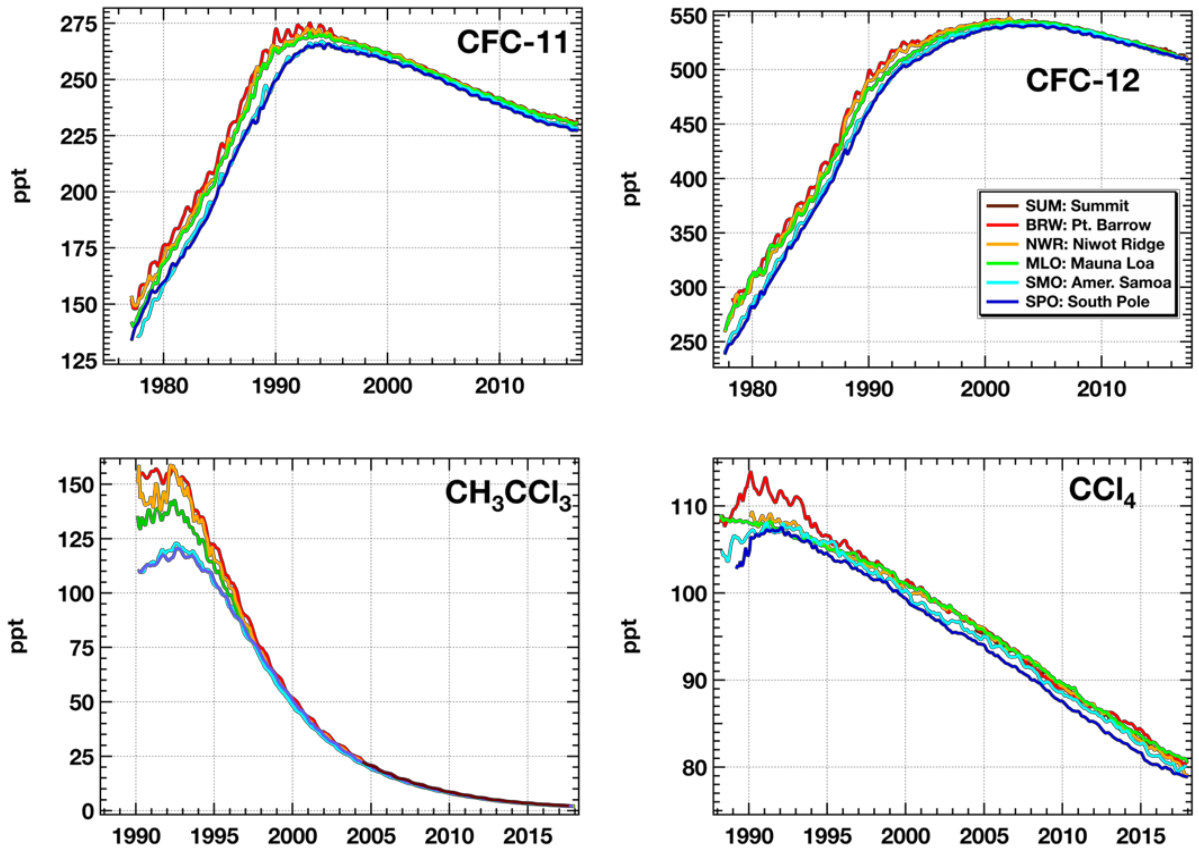
*with in situ instruments. asl = above sea level; agl = above ground level; F=flask elevation

HATS Network Gas Measurements

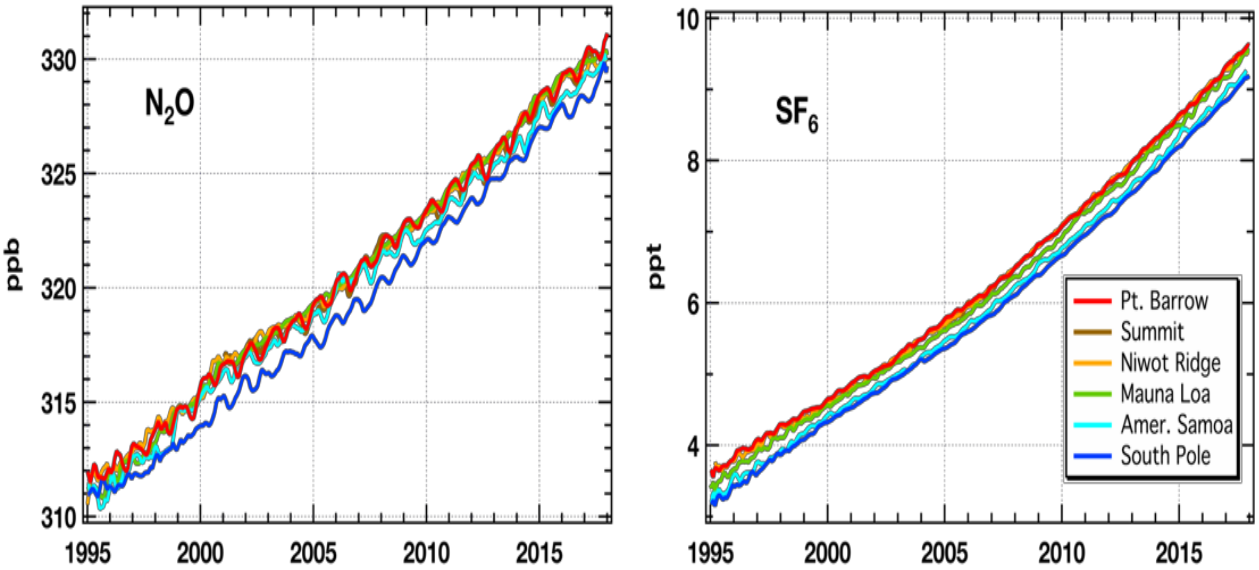
In 1977 the HATS group measured 3 gases, today over 40.

- Major greenhouse gases (GHGs, Kyoto Protocol)
  - (N_2O, SF_6, PFCs, CH_4 on airborne & Summit)
- Halocarbons (Stratospheric ozone depletion and minor GHGs)
  - Chlorofluorocarbons (CFCs,-11,-12,-113,-115)
  - Chlorinated solvents ($CHCl_3$, CH_3CCl_3, CCl_4, C_2Cl_4, CH_2Cl_2). These also affect air quality in the workplace and urban areas
  - Hydrochlorofluorocarbons (HCFCs, -22, -141b, -142b)
  - HFCs (-134a, -143a,-152a, -125, -32, -227ea, -365mfc)
  - Halons (-1211, -1301, -2402)
  - Methyl halides (CH_3Cl, CH_3Br, CH_3I)
  - Other Brominated gases ($CHBr_3$, CH_2Br_2)
- Sulfur gases (SF_6, COS) COS is a major source of sulfate to the stratospheric aerosol layer.
- Air Quality
  - Hydrocarbons (C_2H_2, C_3H_8, nC_4H_{12}, iC_5H_{10}, C_6H_6, nC_6H_{14})
  - Hydrogen (H_2), methane (CH_4), and carbon monoxide (CO) on airborne platforms & at Summit Station (SUM) until 2017
  - Water vapor (H_2O) and ozone (O_3) on airborne platforms
  - Peroxyacetyl nitrate (PAN), airborne (PANTHER only); PAN is the principal tropospheric reservoir for nitrogen oxide radical

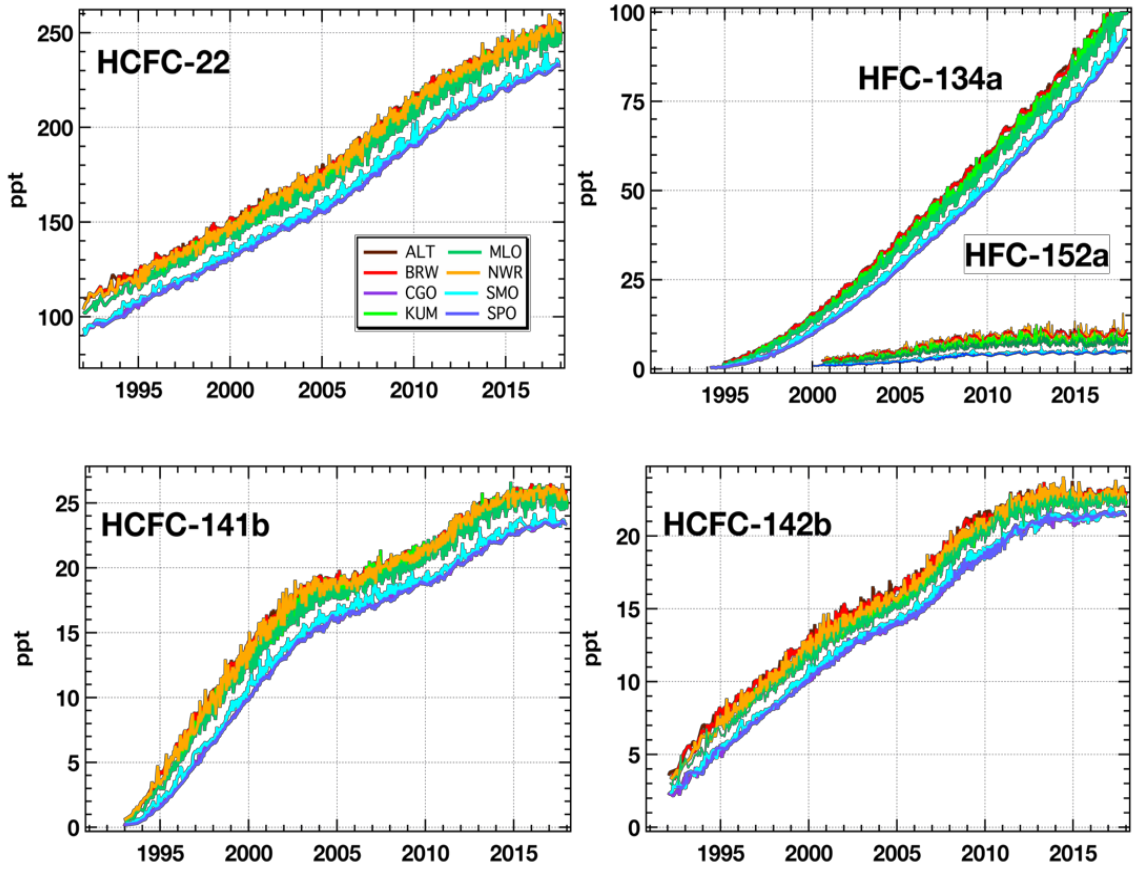
Various instruments for measuring HATS gases. GC/flasks on Otto, MLO CATS/in situ, Perseus GC-MS, CATS GC/in situ, developing standards and M3 GC-MS.



Ground-based measurements of select halocarbons controlled by the Montreal Protocol in parts-per-trillion (ppt). All are in decline, where the rate of decrease is a function of their atmospheric lifetime and emissions.



GMD ground-based measurements of nitrous oxide (N_2O) and sulfur hexafluoride (SF_6)

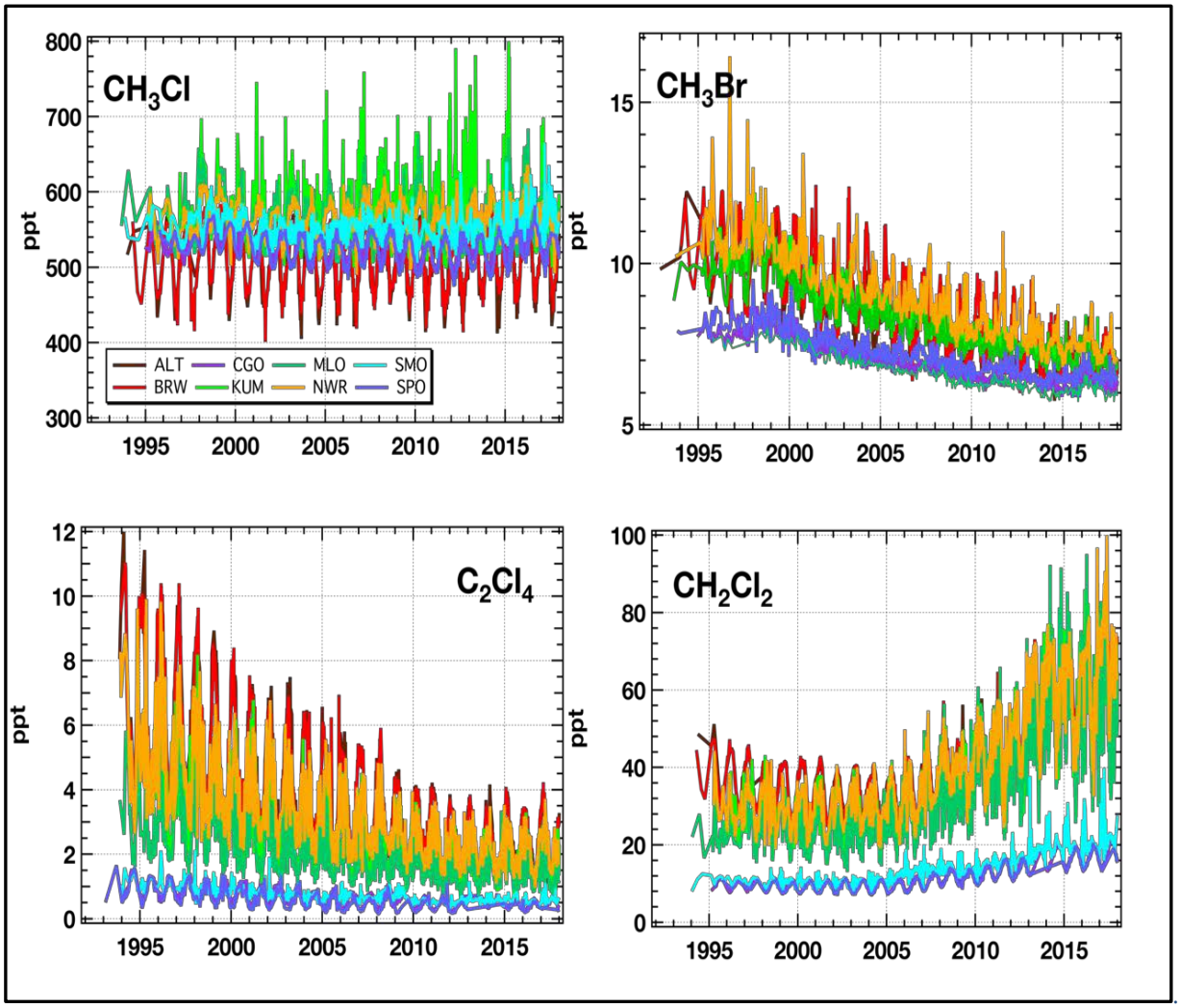


CFC Substitutes (HCFCs & HFCs). Note that the atmospheric abundances of HCFCs are leveling off because of the Montreal Protocol. HFC-134a is linearly increasing and will be subject to restrictions under the Kigali Amendment of the Montreal Protocol.

Why do we continue to measure these compounds?

We need to ensure that the Montreal Protocol is working as expected. There have been some surprises in the recent trends of some ozone-depleting gases CCl_4, CFC-11, CH_2Cl_2, and CH_3Br. N_2O also is the dominant ozone depleting gas based on current and future emissions. In addition to ozone depletion, many gases we measure are also greenhouse gases, including four of the six major greenhouse gases included in the Kyoto Protocol (N_2O, SF_6, HFCs & PFCs).

"From 1990 to 2010, the Montreal Protocol's controls on production and consumption of ODSs will have reduced GHG emissions by the equivalent of a net 135 Gt CO_2, which is equivalent to 11 Gt CO_2 per year. Considering only the direct warming effect, these actions of the Montreal Protocol delayed the increase in climate forcing from CO_2 by 7–12 years." *Mario Molina, PNAS, December 2009*



Ground-based measurements of short lived halocarbons CH_3Cl, CH_3Br, CH_2Cl_2 &, C_2Cl_4. Note a slight increase in CH_3Br after 2016 and a doubling in CH_2Cl_2 since the beginning of measurements; both a potential future threat to

"The Administrators of the National Aeronautics and Space Administration and National Oceanic and Atmospheric Administration shall monitor, and not less often than every 3 years following November 15, 1990, submit a report to Congress on the current average tropospheric concentration of chlorine and bromine and on the level of stratospheric ozone depletion. Such reports shall include updated projections of—

(A) peak chlorine loading;

(B) the rate at which the atmospheric abundance of chlorine is projected to decrease after the year 2000; and

(C)) the date by which the atmospheric abundance of chlorine is projected to return to a level of two parts per billion."

--1990 Amendments of the Clean Air Act, Title VI-Stratospheric Ozone Protection

Current Trends in Ground-based Halocarbon Measurements

- Atmospheric abundances of CFCs, methyl bromide, methyl chloroform, carbon tetrachloride, and most halons have decreased from peak values as a direct result of the Montreal Protocol.
- HCFCs -141b and -142b have leveled off and HCFC-22 is decreasing.
- HFC-134a has continued to increase, because it is still used as a CFC-replacement.
- The chlorinated solvent, tetrachloroethylene (C_2Cl_4), is used as an industrial solvent, particularly in the dry-cleaning industry. Efforts to reduce emissions have been implemented owing to its toxity.
- Recent increases in CFC-11 and CH_3Br, doubling of atmospheric dichloromethane (CH_2Cl_2) and continued increases in atmospheric N_2O are all of concern to stratospheric ozone depletion.

Role of Standards, WMO Central Calibration Lab (CCL)

NOAA GMD is the World Meteorological Organization (WMO), Global Atmosphere Watch (GAW) Central Calibration Laboratory (CCL) for CO_2, CH_4, N_2O, SF_6, and CO. GMD offers calibration services for these gases on a cost-recovery basis and also calibrates compressed gas standards to NOAA/GMD internal scales for other CFCs, HCFCs and the stable isotopes of CO_2.

The WMO has recognized GMD as an institute qualified to operate among the National Metrology Institutes (NMIs) following guidelines for calibrations conforming to ISO 17025 standards. As such, the GMD CCL meets international guidelines for “the competence of testing and calibration laboratories”.

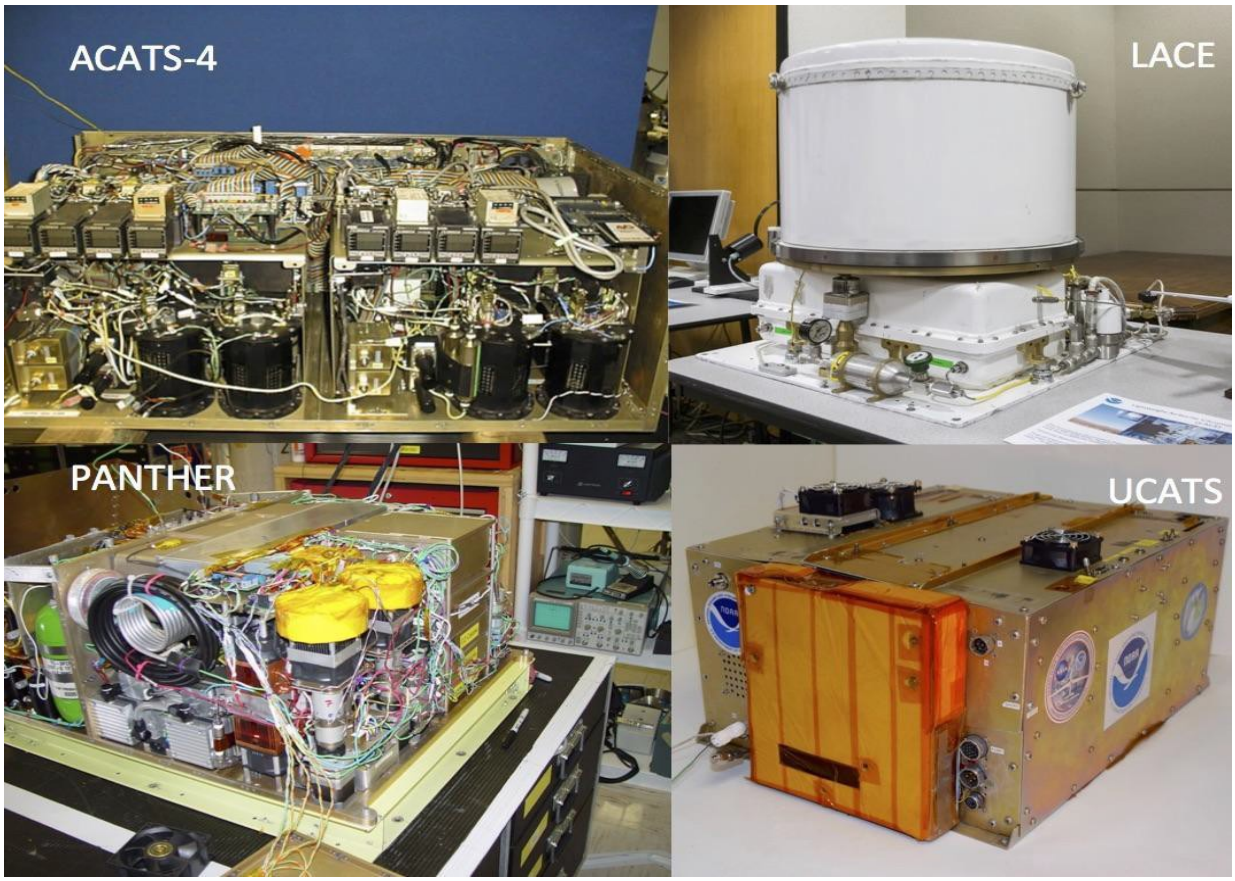
In 2016 GMD Calibration and Measurement Capabilities (CMCs) for CO_2, CH_4, and N_2O were published in the CMC database, maintained by the Bureau of International Weights and Measures (BIPM). This means that GMD’s role as a WMO/GAW Central Calibration Laboratory is internationally recognized as having measurement standards equivalent to NMIs, such as NIST (US), KRISS (Korea), and NPL (United Kingdom).

For the halocarbons and other trace gases measured by HATS and the NASA Advanced Global Atmospheric Gas Experiment (AGAGE), meetings are held every six months to discuss our measurements and calibration scales. The purpose is to resolve differences in trace gas measurements between networks and come up with an intercomparison matrix to relate the different calibration scales to each other.

High Altitude Airborne Measurements Program

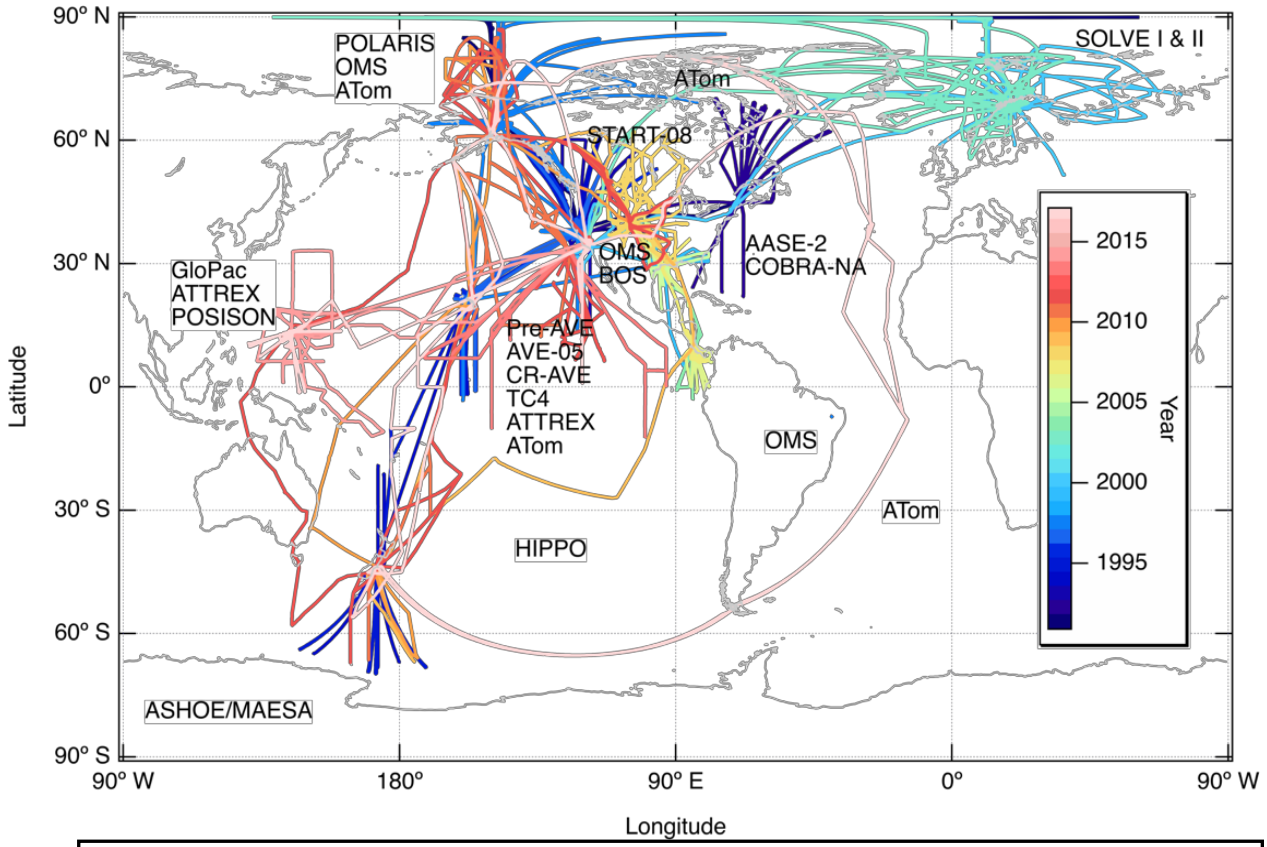
GMD scientists have developed an in situ airborne instrument that has flown many missions on a NASA ER-2 to measure ozone-depleting and climate forcing gases (N_2O, SF_6, CFC-11, -12, -113, halon-1211, CCl_4, CH_3CCl_3, CH_4, CO, and H_2). This instrument is known as the Airborne Chromatograph for Atmospheric Trace Species instrument (ACATS). These gases are also measured in profile with a balloon-borne GC developed by GMD called the Lightweight Airborne Chromatograph Experiment (LACE) that operates up to 32 km.

When CFC replacements began to take hold, GMD developed a gas chromatograph-mass spectrometer system that flies on the NASA DC-8 and WB-57F aircraft. This instrument is known as the "PAN and other Trace Hydro-halocarbon Experiment" (PANTHER). For UAV platforms, GMD built a lightweight gas chromatograph for operation on the NASA Altair and Global Hawk. These airborne measurements complement GMD ground-based measurements. Photos of GMD airborne instruments and some of the platforms they fly on are presented below and on the next page.

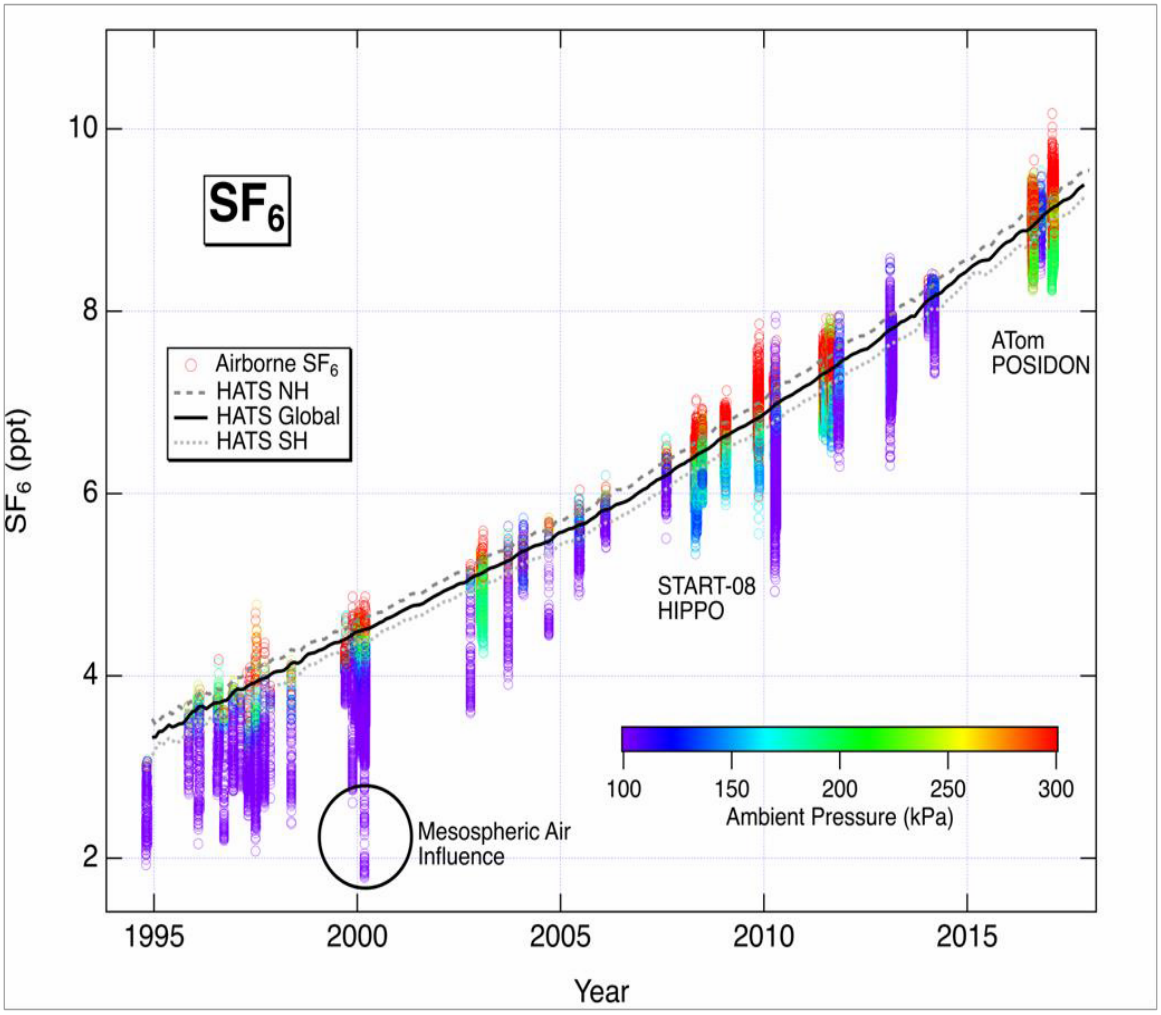


GMD HATS Airborne Instruments: ACATS, LACE, PANTHER, and UCATS.

High altitude airborne platforms used by HATS: NASA ER-2, DC-8, JPL Gondola, Altair, WB-57F and Global Hawk and the NCAR GV.



Flight paths of missions flown with GMD HATS instruments. In April and May 2018 GMD HATS instruments are being flown on the NASA DC-8 global scale ATom mission.



Time Series of airborne and ground based measurements of SF_6. These GMD data were used to calculate a reduction in the accepted atmospheric lifetime of SF_6 lowering its lifetime from 3200 to 850 years.

Collaborations with other Scientific Organizations.

The HATS Halocarbon Network is a cooperating network within the Advanced Global Atmospheric Gas Experiment (AGAGE), the World Meteorological Organization's (WMO) Global Atmospheric Watch (GAW) and the Network for the Detection of Atmospheric Composition Change (NDACC) operations.

HATS data are archived in-house, offsite, at the WMO World Greenhouse Gas Data Center in Japan once every six months, and will soon go to the NOAA NCEI data center.

HATS Scientific Highlights (2013-2017)

- **Ozone treaty taking a bite out of U.S. Greenhouse Emissions.**

  Reductions in emissions of ozone-depleting gases from 2008 to date has eliminated the equivalent of >170 million tons of carbon dioxide (CO_2) emissions each year. That's roughly the equivalent of 50 percent of the reductions achieved by the U.S. for CO_2 and other greenhouse gases over the same period.

  Hu, L., et al. (2017), Considerable contribution of the Montreal Protocol to declining greenhouse gas emissions from the United States: U.S. CFCs, HCFCs, and HFCs Emissions, Geophysical Research Letters, doi:10.1002/2017GL074388.

- **Possible new threat to Earth's ozone layer, dichloromethane**

  Dichloromethane (CH_2Cl_2) mixing ratios have doubled since GMD started measuring the gas. It is not subject to the Montreal Protocol, but the chlorine from this gas is getting into the stratosphere and represents a possible new threat to stratospheric ozone.

  Hossaini, R., M. P. Chipperfield, S. A. Montzka, A. A. Leeson, S. S. Dhomse, and J. A. Pyle (2017), The increasing threat to stratospheric ozone from dichloromethane, Nat Commun., 8 (ARTN 15962), doi:10.1038/ncomms15962.

- **NOAA's annual greenhouse gas index (AGGI) up 40% since 1990**

  Carbon dioxide is the leading contributor to the AGGI. Steadily increasing N_2O is the 3rd most important greenhouse gas and has been measured reliably by GMD since 1977.
  https://www.esrl.noaa.gov/gmd/aggi/aggi.html

- **Unexpected Increase in Ozone Depleting CFC-11 controlled by the Montreal Protocol**

  An unexplained increase in global concentrations of CFC -11 has been documented. This gas is a strong ozone-depleting gas and either some entity is producing the gas outside of the Montreal Protocol guidelines but much more likely it is a by-product of some chemical process not covered under the Montreal Protocol.

  Montzka et al., (2018), An unexpected and persistent increase in global emissions of ozone-depleting CFC-11, Nature, doi:10.1038/s41586-018-0106-2.

- **Study published on reduced lifetime for future strong greenhouse gas, sulfur hexafluoride**

  Based on measurements of SF_6 in the stratospheric polar vortex, we estimated that the atmospheric lifetime of SF_6 is 850 years, which is nearly a factor of three lower than the previous estimate of 3200 years.

  Ray, E. A., F. L. Moore, J. W. Elkins, K. Rosenlof, J. Laube, T. Röckmann, D. R. Marsh and A. E. Andrews, (2017), Quantification of the SF6 Lifetime Based on Mesospheric Loss Measured in the Stratospheric Polar Vortex , J. of Geophys Res., 10.1002/2016JD026198.

- **GMD has shown that the emission rates of carbon tetrachloride (CCl_4) are 30 to 100 times higher than emission inventories**

  The gas, CCl_4, accounts for 10-15 percent of the ozone-depleting substances in the atmosphere and is regulated by the Montreal Protocol. The source of the unexpected emissions in the U.S. appears associated with the production of chlorinated chemicals (such as those ultimately used to create things like Teflon and PVC).

  Hu, L., et al. (2016), Continued emissions of carbon tetrachloride from the United States nearly two decades after its phase-out for dispersive uses, P. Natl. Acad. Sci. USA, 113(11), 2880-2885, doi:10.1073/pnas.1522284113.

- **Long term trends of stratospheric age of the air mass deconvoluted from balloon observations of SF_6 and CO_2**

  Chemistry Climate Models (CCMs) predict that stratospheric circulation will change from the influence of increasing GHGs. Using 37 years of balloon CO_2 and SF_6 data in the stratosphere, GMD determined a more rapid exchange of air in the stratosphere consistent with CCM predictions.

  Ray et al., (2015), An idealized stratospheric model useful for understanding differences between long-lived trace gas measurements and global chemistry-climate model output, J. Geophys. Res. Atmos., 121, 5356–5367, doi:10.1002/2015JD024447.