Global Monitoring Annual Conference 2012
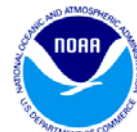
Boulder, Colorado   May 15th - 17th

PROGRAM & ABSTRACTS

Hosted by:
NOAA Earth System Research Laboratory
Global Monitoring Division

Mission of the Global Monitoring Division:

To acquire, evaluate, and make available accurate, long-term records of atmospheric gases, aerosol particles, and solar radiation in a manner that allows the causes of change to be understood.

Conference Website:

http://www.esrl.noaa.gov/gmd/annualconference/

Purpose of the Global Monitoring Annual Conference:

To bring together preeminent scientists to discuss the latest findings in climate research and how to integrate science, observations and services to better serve society.

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Cover info:

Jakobshavn Glacier near Disko Bay on the Eastern coast of Greenland; the photograph was taken during a C-130 flight from Summit Station to Kangerlussuaq, Greenland.

UNITED STATES DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
Office of Oceanic and Atmospheric Research
Earth System Research Laboratory
325 Broadway – David Skaggs Research Center
Boulder, Colorado 80303-3337

NOAA Earth System Research Laboratory
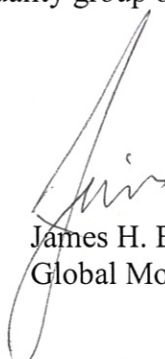# 40th Global Monitoring Annual Conference 2012

May 15-17, 2012
Boulder, Colorado

We in the Global Monitoring Division of NOAA's Earth System Research Laboratory welcome you to our 2012 Global Monitoring Annual Conference. Once again, this is a great opportunity to present the "latest and greatest" findings from on-going research efforts among a community with common goals. A phrase you often hear in these meetings is "you heard it here first . . . ". The goal of the conference is to create a forum for thoughtful and lively discussion on the research that comes from sustained measurement records and what it takes to understand them.

The theme for this year's conference is *Looking Forward to the Next 55 Years of Global Monitoring*. Long-term records have proven to be the gold standard for understanding complex climate system variables and this value will only grow with time. We anticipate that conference discussions and topics will highlight long term data sets, advances in technology, expansion of global monitoring networks, cooperation among agencies and nations, challenges that confront us, and the opportunities within them.

In addition to 2012 marking our 40th conference, this year's event is also notable for setting numerous conference records: over 240 participants, 52 foreign attendees from 18 countries on 5 continents, 60 talks and 66 posters all contribute to making this the largest and most diverse conference yet. The conference agenda and abstracts from all 126 presentations and posters to be discussed at the conference are posted at http://www.esrl.noaa.gov/gmd/annual/conference/.

Thank you for attending and we look forward to a high-quality group of presentations and vigorous interaction among colleagues.

James H. Butler, Director
Global Monitoring Division

NOAA Atmospheric Baseline Observatories

Barrow, Alaska (est. 1973), 71.32˚ North, 156.61˚ West

Trinidad Head, California (est. 2002), 41.05˚ North, 124.15˚ West

Mauna Loa, Hawaii (est. 1957), 19.53˚ North, 155.57˚ West

Cape Matatula, American Samoa (est. 1974), 14.24˚ South, 170.56˚ West

South Pole, Antarctica (est. 1957), 90.00˚ South, 24.80˚ West

Summit, Greenland (est. 2010), 72.58˚ North, 38.48˚ West

Tuesday Morning, May 15, 2012 AGENDA
(Only presenter's name is given; please refer to abstract for complete author listing.)

• *07:00*   *Registration Opens in GC-402 – lunch orders and posters collected at registration table*

• *07:30 - 08:10*   *Morning Snacks – Coffee, tea, fruit, bagels & donuts served*

                                                                                 Page No.

• *Session 1*   ***Introduction, Keynote Address, and Setting the Stage*** — *Chaired by Russ Schnell*

08:10 - 08:30	Welcome Address	-
	James H. Butler & Alexander E. MacDonald (NOAA Earth System Research Laboratory, Boulder, CO)	
08:30 - 09:00	**KEYNOTE:** Atmospheric Chemical Composition, Climate, and Societal Implications	1
	Steven Wofsy (Biosphere-Atmosphere Exchange Group, Harvard University, Cambridge, MA)	
09:00 - 09:15	Global Atmospheric Distributions of Some Short-lived Halocarbons	2
	Stephen A. Montzka (NOAA Earth System Research Laboratory, Boulder, CO)	
09:15 - 09:30	Partitioning of Terrestrial Carbon Sources Using $^{14}CO_2$: Observations and Modeling	3
	Scott Lehman (University of Colorado, Boulder, CO)	
09:30 - 09:45	Are Oceanic and Terrestrial Sinks of CO_2 Not Able to Keep Up with Emissions?	4
	Pieter Tans (NOAA Earth System Research Laboratory, Boulder, CO)	

• *09:45 - 10:15*   ***Morning Break***

• *Session 2*   ***Carbon Cycle - Methane*** — *Chaired by Pieter Tans*

10:15 - 10:30	Thirty Years of Atmospheric CH_4 Monitoring: What Have We Learned?	5
	Ed Dlugokencky (NOAA Earth System Research Laboratory, Boulder, CO)	
10:30 - 10:45	Monitoring and Detecting Arctic Greenhouse Gas Budgets: The Importance of Long-term Surface Observations and the Role of CarbonTracker-CH_4	6
	Lori Bruhwiler (NOAA Earth System Research Laboratory, Boulder, CO)	
10:45 - 11:00	Isotope Variations in Atmospheric Methane Over the Last Two Millenia	7
	Thomas Röckmann (Institute for Marine and Atmospheric Research, Utrech University, Utrecht, Netherlands)	
11:00 - 11:15	Reconstruction of 1950 – 2010 Northern Hemisphere Non-methane Hydrocarbon Histories	8
	Detlev Helmig (Institute of Arctic and Alpine Research (INSTAAR), University of Colorado, Boulder, CO)	
11:15 - 11:30	Trace Gas Images of the Alaskan Atmosphere: The First Year of Measurements from the Carbon in Arctic Reservoirs Vulnerability Experiment (CARVE)	9
	John B. Miller (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)	
11:30 - 11:45	Observation of Atmospheric CH_4 Mixing Ratios at the Three WMO/GAW Stations in China	10
	Shuangxi Fang (Centre for Atmosphere Watch and Services, Chinese Academy of Meteorological Sciences, China Meteorological Administration, Beijing, China)	

• *11:45 - 13:00*   ***Catered Lunch Service – Outreach Classroom GB-124 (pre-payment of $12.00 required at registration table)***

Tuesday Afternoon, May 15, 2012 AGENDA

(Only presenter's name is given; please refer to abstract for complete author listing.)

Page No.

• *Session 3*   ***Carbon Cycle - Quantification of Emissions*** *— Chaired by Tom Conway*

13:00 - 13:15   Estimate of CH_4 Emissions from Oil and Gas Operations in the Uintah Basin Using Airborne CH_4 Measurements and LiDAR Wind Data   11

   Anna Karion (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

13:15 - 13:30   Quantifying California's Anthropogenic Greenhouse Gas Budget   12

   Marc L. Fischer (Lawrence Berkeley National Laboratory, Berkeley, CA)

13:30 - 13:45   Urban Greenhouse Gas Emissions Monitoring in Davos, Switzerland, Before, During and After the 2012 World Economic Forum Annual Meeting   13

   Thomas Lauvaux (The Pennsylvania State University, Department of Meteorology, University Park, PA)

13:45 - 14:00   Hourly, Daily, and Seasonal Patterns of Atmospheric CO_2 Along an Urbanization Gradient   14

   Allison Dunn (Worcester State University, Worcester, MA)

14:00 - 14:15   Toward Simultaneous Multi-station Data Pre-processing for Inversions of Greenhouse Gas Emissions and Uptake in California   15

   Elena Novakovskaia (Earth Networks, Inc., Germantown, MD)

14:15 - 14:30   Two Decades of Atmospheric O_2 Measurements and Their Implications   16

   Ralph Keeling (Scripps Institution of Oceanography, University of California at San Diego, La Jolla, CA)

• *14:30 - 15:00*   *Afternoon Break*

• *Session 4*   ***Aerosols*** *— Chaired by John Ogren*

15:00 - 15:15   Long-term Trends in African Dust Transport to the Caribbean: African Sources, Changing Climate, and Future Scenarios   17

   Joseph M. Prospero (Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Miami, FL)

15:15 - 15:30   Aerosols at Mauna Loa Observatory (MLO) – Spring 2001 Versus Spring 2011   18

   Thomas A Cahill (University of California at Davis, Davis, CA)

15:30 - 15:45   Seasonal Variability in the Southeast U.S. Background Aerosol Direct Radiative Effect – An Initial Measurement-based Climatology from a Regionally-representative Location   19

   James Sherman (Department of Physics and Astronomy, Appalachian State University, Boone, NC)

15:45 - 16:00   Climatology of Aerosol Optical Properties Over the High Arctic   20

   Auromeet Saha (Université de Sherbrooke, Quebec, Canada)

16:00 - 16:15   The Cloud, Aerosol Backscatter and Polarization LiDAR at Summit, Greenland   21

   Ryan Neely (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

16:15 - 16:30   Isoprene Suppression of New Particle Formation in a Mixed Deciduous Forest   22

   Shan-Hu Lee (Kent State University, Kent, OH)

16:30 - 16:45   Investigating Potential Biases in Aerosol Light Absorption Measurements   23

   Christine Walsh (NOAA Earth System Research Laboratory, Lund University, Lund, Sweden)

• *17:00 - 20:00*   *Poster Session in DSRC Cafeteria (GC-425) with appetizers & refreshments*

KEYNOTE: Atmospheric Chemical Composition, Climate, and Societal Implications

S. Wofsy

Biosphere-Atmosphere Exchange Group, Harvard University, Cambridge, MA 02138; 6174954566, E-mail: swofsy@seas.harvard.edu

Global atmospheric concentrations of greenhouse gases and aerosols are significantly under human control, affecting climate, ecosystems, and key atmospheric chemical processes. This talk discusses global and regional measurements in two major aircraft campaigns: HIAPER Pole-to-Pole Observations program ("HIPPO", sponsored by NSF and NOAA) and CalNEX (sponsored by NOAA and CARB), and explores the synergy between ground-based, aircraft, and satellite measurements. All of these types of observations, made with exquisite quality control and constant improvements, are needed to disentangle the diverse influences on the global atmosphere. We explore some of the new information on the drivers of long-term changes in the global atmosphere that has emerged recently, emphasizing emissions and large-scale environmental change in the US and in tropical and arctic regions.

Figure 1. The equatorial Pacific Intertropical Convergence Zone (ITCZ).

Global Atmospheric Distributions of Some Short-lived Halocarbons

S.A. Montzka[1], B.R. Miller[2], C. Siso[2], F. Moore[2], B. Hall[1], J.W. Elkins[1], A. Andrews[2], C. Sweeney[2], J.H. Butler[1], E. Atlas[3] and S. Wofsy[4]

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[2]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309
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[4]Department of Earth and Planetary Sciences and the Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138

A number of short lived halocarbons (CH_3I, CH_2Br_2, $CHBr_3$) are emitted to the atmosphere in large quantities, predominantly from natural processes. Because these chemicals have short lifetimes (weeks to months) they supply reactive halogen to the troposphere and influence the tropospheric chemistry of ozone and mercury, for example. In the case of CH_2Br_2 and $CHBr_3$, their lifetimes are long enough so that these chemicals can deliver to the stratosphere significant amounts of Br that influences stratospheric ozone chemistry. The magnitudes of these contributions and the mechanisms by which most Br reaches the stratosphere from these chemicals are not well understood. Some of this uncertainty stems from the difficulties associated with interpreting observations of short-lived compounds at any point in space and time in terms of broader-scale mixing ratios and atmospheric impacts. We have measured these chemicals at a global network of surface and aircraft profiling sites for multiple years (up to 14). The results provide a unique picture of global distributions, inter-annual and seasonal variability, and vertical mixing ratio gradients at continental, marine and coastal locations. When contrasted with results from the recent HIPPO campaign over the mid-Pacific Ocean basin, consistent patterns emerge over land and sea that suggest we may be able to quantify mean mixing ratios and their variability over large spatial scales for some of these chemicals, particularly in the free troposphere. Such information will provide useful constraints on the influence these chemicals have on atmospheric chemistry in both the troposphere and stratosphere.
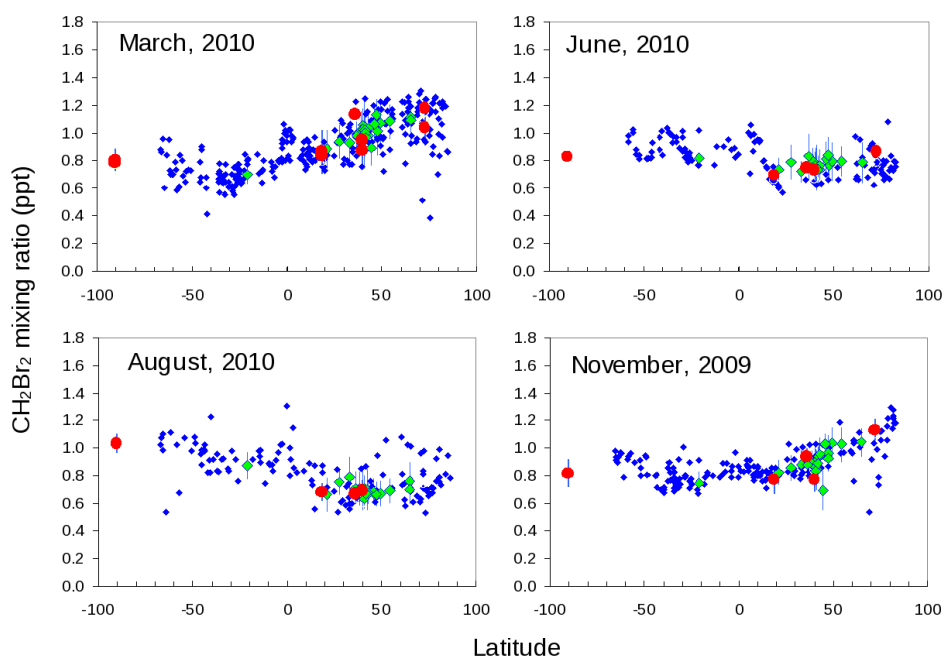
Figure 1. Monthly mean mixing ratios of CH_2Br_2 from flasks collected 1.5-8 km above sea level from surface stations across the globe (red circles) and aircraft profiles (green diamonds, predominantly over North America) during the indicated month, and from concurrent HIPPO transects (filled blue diamonds; mid-Pacific Ocean basin).

Partitioning of Terrestrial Carbon Sources Using $^{14}CO_2$: Observations and Modeling

S. Lehman[1], J.B. Miller[2], P.P. Tans[2], C. Sweeney[2], A.E. Andrews[2], J. Southon[3], B.W. LaFranchi[4], T.P. Guilderson[4] and J.C. Turnbull[5]

[1]University of Colorado, Boulder, CO 80309; 303 492 8980, E-mail: Scott.Lehman@colorado.edu
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[4]Lawrence Livermore National Laboratory, Livermore, CA 94550
[5]Rafter Radiocarbon Laboratory, Lower Hutt, New Zealand

The small radiocarbon fraction of total CO_2 (~1:10^{12} ^{14}C:C) has proven to be an ideal tracer for its fossil fuel derived component. Unlike all other significant contributions to the atmospheric CO_2 budget, the fossil fuel component is devoid of radiocarbon, so that temporal and spatial gradients in recently added fossil fuel CO_2 can be readily identified as radiocarbon gradients provided there is adequate precision in the measurements. Over large industrialized land areas such as Eurasia and North America, the use of ^{14}C to isolate the recently added fossil fuel contribution also quantifies (by difference) the change in atmospheric CO_2 due to uptake and release by the terrestrial biosphere. Simple mass balance considerations suggest that in order to apportion fossil fuel and biological components in the continental CO_2 observations to ±1 ppm, a $^{14}CO_2$ measurement repeatability of ~2 per mil (1-sigma ppt deviation from standard) is needed. Here we will report on i) our efforts to maintain the necessary measurement precision in a growing number of air craft and tall tower sampling sites around the U.S., and on ii) the ability of the TM5 transport model (as currently implemented for CO_2 and $^{14}CO_2$) to represent the $\Delta^{14}CO_2$ observations. The latter is an important step towards using $^{14}CO_2$ as an additional constraint on regional fossil fuel emissions and Net Ecosystem Exchange flux retreivals in CarbonTracker
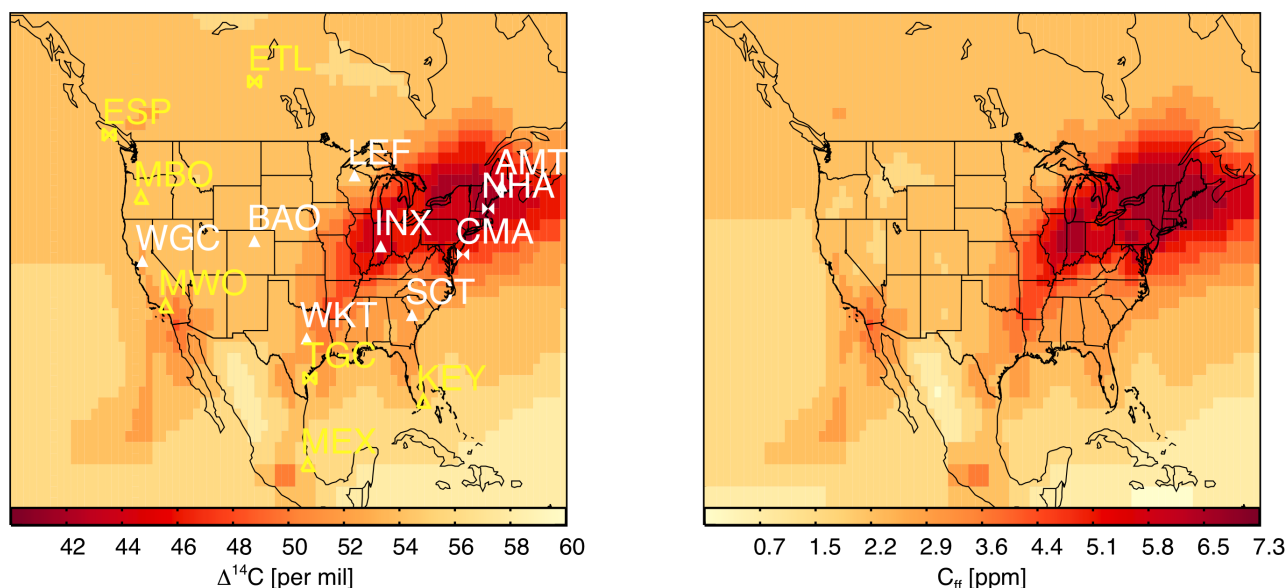
Figure 1. Model representations of a) Δ^{14}C (left panel) and b) the fossil fuel component of total CO_2 (C_{ff}; right panel) in the atmosphere near the surface over North America for a week in January of 2006. The color scales correspond to the expected mass balance relationship between Δ^{14}C and C_{ff} of -2.7 ‰/ppm. The sites labeled in white are existing ^{14}C sampling sites, as are Mount Wilson Observatory (MWO) and Niwot Ridge (NWR) (which underlays Boulder Atmospheric Observatory (BAO)).

Are Oceanic and Terrestrial Sinks of CO$_2$ Not Able to Keep Up with Emissions?

P. Tans[1], A. Ballantyne[2], C. Alden[3], J. Miller[4] and J. White[3]

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[4]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309

The CO$_2$ emitted by our society into the atmosphere is shared between the oceans, terrestrial biosphere, and atmosphere. Over the last several years an impression has been generated in the scientific literature that the capacity of the oceans and terrestrial biosphere to take up continuing emissions of CO$_2$ shows signs of weakening. We make a mass balance for the entire record of direct atmospheric measurements of CO$_2$ in the atmosphere, and published estimates of emissions from fossil fuel burning and land use change. It shows that total global sinks continue to increase, roughly in proportion to the increasing rate of emissions. An airborne fraction has been defined as the rate of atmospheric CO$_2$ increase divided by the rate of either fossil fuel emissions alone or emissions from fossil fuel burning combined with land use change. A careful statistical analysis reveals that, with the first definition, the airborne fraction has decreased somewhat over time (relatively more uptake), and with the second definition it has no measurable trend.
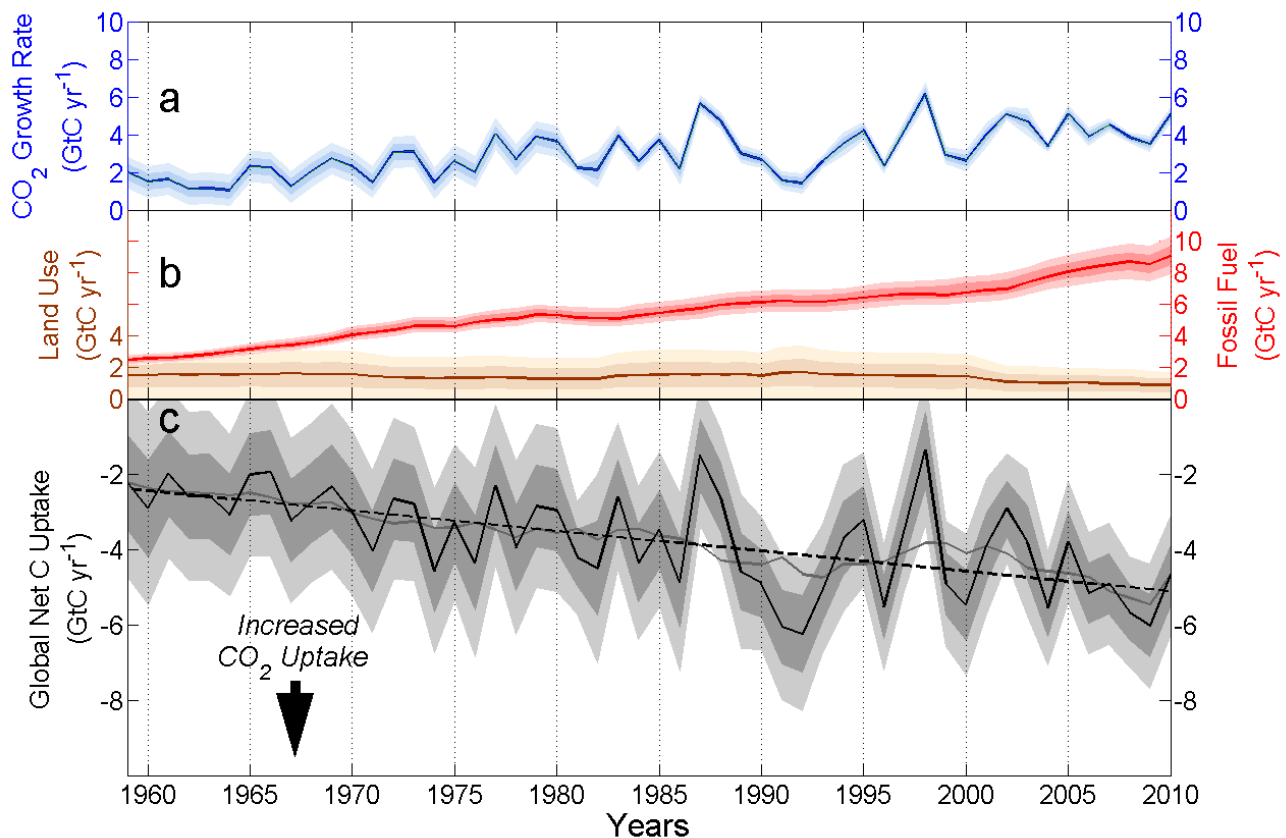
Figure 1. Panel a) observed annual mean growth rate of atmospheric CO$_2$; b) annual estimated emissions from fossil burning (red) and land use change (brown); c) observed growth rate minus total emissions. The outer lightly shaded bands represent 2-sigma uncertainty, the inner darker shade represents 1-sigma uncertainty.

Thirty Years of Atmospheric CH$_4$ Monitoring: What Have We Learned?

E. Dlugokencky[1], M. Heller[2], E.G. Nisbet[3], D. Lowry[3], P.M. Lang[1], K.A. Masarie[1], A. Crotwell[1] and L. Bruhwiler[1]

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Methane (CH$_4$) is the most important greenhouse gas influenced by human activities after CO$_2$, with 0.5 W m^{-2} radiative forcing since 1750. Its atmospheric chemistry results in additional indirect climate effects from production of tropospheric O$_3$, which also affects air quality, and stratospheric H$_2$O abundance.

ESRL Global Monitoring Divivion has measured atmospheric CH$_4$ from discrete samples collected by the carbon cycle group's Global Cooperative Air Sampling Network since 1982. The trends, seasonal cycles, and spatial distributions obtained from these measurements provide large scale constraints on the global CH$_4$ budget including the atmospheric burden, total global emissions, and the imbalance between emissions and losses. Nearly every chemical transport model study of the global CH$_4$ budget uses these NOAA CH$_4$ observations to constrain estimated emissions. It is fitting that on the 40th Anniversary of the Global Monitoring Annual Conference we look back at some of the important discoveries that are based on these measurements, and then look at current trends in CH$_4$.

From the beginning of the measurements through 2006, the rate of increase was decreasing from ~14 ppb yr^{-1} in 1984 to near zero from 1999 to 2006. Superimposed on this decreasing growth rate are significant anomalies in global growth rate. These anomalies result from variations in natural wetland and biomass burning emissions and from changes in [OH], and they allow us to test our understanding of processes that emit CH$_4$. During 2007, atmospheric CH$_4$ began increasing again, and this increase continues through 2011 (see Figure). While greater than average temperatures in the Arctic were a likely contributor to the increase in 2007, since then, continued wet conditions in the tropics, particularly in the southern hemisphere, driven by strong La Niña conditions in 4 of the past 5 years, are the likely drivers. It is clear from our data that since 2007, emissions from the Arctic are not playing a significant role in the continued CH$_4$ increase.
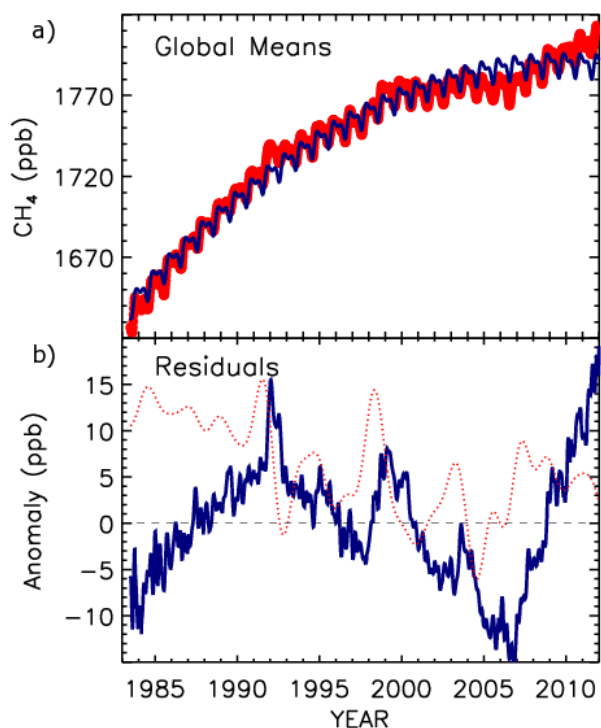
Figure 1. a) Globally averaged CH$_4$ dry air mole fractions (red). Blue line shows a function fitted to the global averages that approximates the long term trend and average seasonal cycle. b) Rate of increase in atmospheric CH$_4$ (red in ppb yr^{-1}) and residuals from function (blue).

Monitoring and Detecting Arctic Greenhouse Gas Budgets: The Importance of Long-term Surface Observations and the Role of CarbonTracker-CH$_4$

L. Bruhwiler[1], E. Dlugokencky[1], K. Masarie[1] and C. Sweeney[2]

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Vast stores of organic carbon are thought to be frozen in Arctic soils; as much as 1,700 billion tonnes of carbon, several times the amount emitted by fossil fuel use to date and about equal to known coal reserves. If mobilized to the atmosphere, this carbon would have significant impacts on global climate, especially if emitted as CH$_4$. A recent study suggests that permafrost carbon climate feedbacks have had profound impacts on past climate, possibly driving the Paleocene-Eocene Thermal Maximum 55 Million years ago. Model studies project that by the middle of the 21st Century, the Arctic will be a net source of carbon to the atmosphere.

NOAA/ESRL, Environment Canada, and other agencies have collected observations of greenhouse gases (GHG) in the Arctic and the rest of the world for at least several decades. Analysis of this data does not currently support increased Arctic emissions of CO$_2$ or CH$_4$. However, it is difficult to detect changes in Arctic emissions because of transport from lower latitudes and high inter-annual variability. Arctic surface emissions are also especially difficult to detect from space, and current satellite platforms do not provide useful information about GHG budgets in the lower Arctic troposphere. Modeling/assimilation systems, such as NOAA's new CarbonTracker-CH$_4$ system can help untangle the Arctic budget and trends of GHGs. CarbonTracker-CH$_4$ has shown success in simulating the inter-annual variability of Arctic fluxes, and it is able to distinguish Siberian fluxes from Boreal North American fluxes.

We address the plausibility of monitoring the Arctic GHG emission trends. How large would Arctic emission trends have to be before they could be identified in network observations? What spatial information could be recovered? How would the spatial density of observations affect our ability to perceive and attribute trends in Arctic emissions? Could emission have already been increasing during the close of the 20th Century? Trends in emissions need to be large before they can be discerned in network observations; our calculations show that emissions of methane must increase by at least 5TgCH$_4$/yr to be seen in a 10-year observational record. Long-term surface observations of GHGs are crucial to monitoring the fate the vast and currently frozen Arctic soil carbon reservoir.
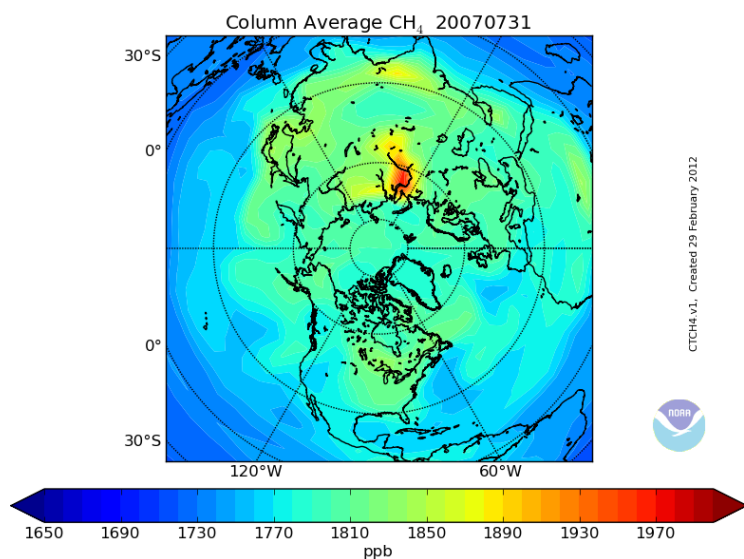
Figure 1. Daily average of the pressure-weighted mean mole fraction of methane simulated by CarbonTracker-CH$_4$. Units are nanomoles of CH$_4$ per mole of dry air (nmol mol-1), and the values are given by the color scale depicted under the graphic. Gradients in CH$_4$ concentration are due to exchange between the atmosphere and the earth surface, including fossil fuel emissions, emissions from agriculture and waste, wildfire emissions, and emissions from wetlands.

Isotope Variations in Atmospheric Methane Over the Last Two Millenia

T. Röckmann[1], C. Sapart[1], G. Monteil[1], M. Prokopiou[1], R.V.D. Wal[1], P. Sperlich[2], J. Kaplan[3], K. Krumhardt[3], C.V.D. Veen[1], S. Houweling[1], M. Krol[1], T. Blunier[2], T. Sowers[4] and P. Martinerie[5]

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[3]Ecole Polytechnique Federale de Lausanne, Route Cantonale, Switzerland
[4]Earth and Environmental Systems Institute, Geosciences, Penn State University, University Park, PA 16802
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Methane (CH_4) is an important greenhouse gas that is emitted from multiple natural and anthropogenic sources. Atmospheric levels of CH_4 have varied on various timescales in the past, but in many cases the causes of these variations are not understood. Analysis of the isotopic composition of CH_4 preserved in ice cores provides evidence for the environmental drivers of variations in CH_4 mixing ratios, because different sources and sinks affect the isotopic composition of CH_4 uniquely. We have analyzed ($\delta^{13}C$) of CH_4 in air trapped in Greenland ice cores over the last 2 millenia and find that the carbon isotopic composition underwent pronounced centennial-scale variations between 200 BC and 1600 AD without clear corresponding changes in CH_4 mixing ratios. The long-term CH_4 increase observed over this period is accompanied by a small overall $\delta^{13}C$ decrease. Two-box model calculations suggest that the long-term CH_4 increase can only be explained by an increase in emissions from biogenic sources. The centennial-scale variations in isotope ratios must be primarily due to changes in biomass burning, which are correlated with both natural climate variability including the Medieval Climate Anomaly, and with changes in human population, land-use and important events in history.
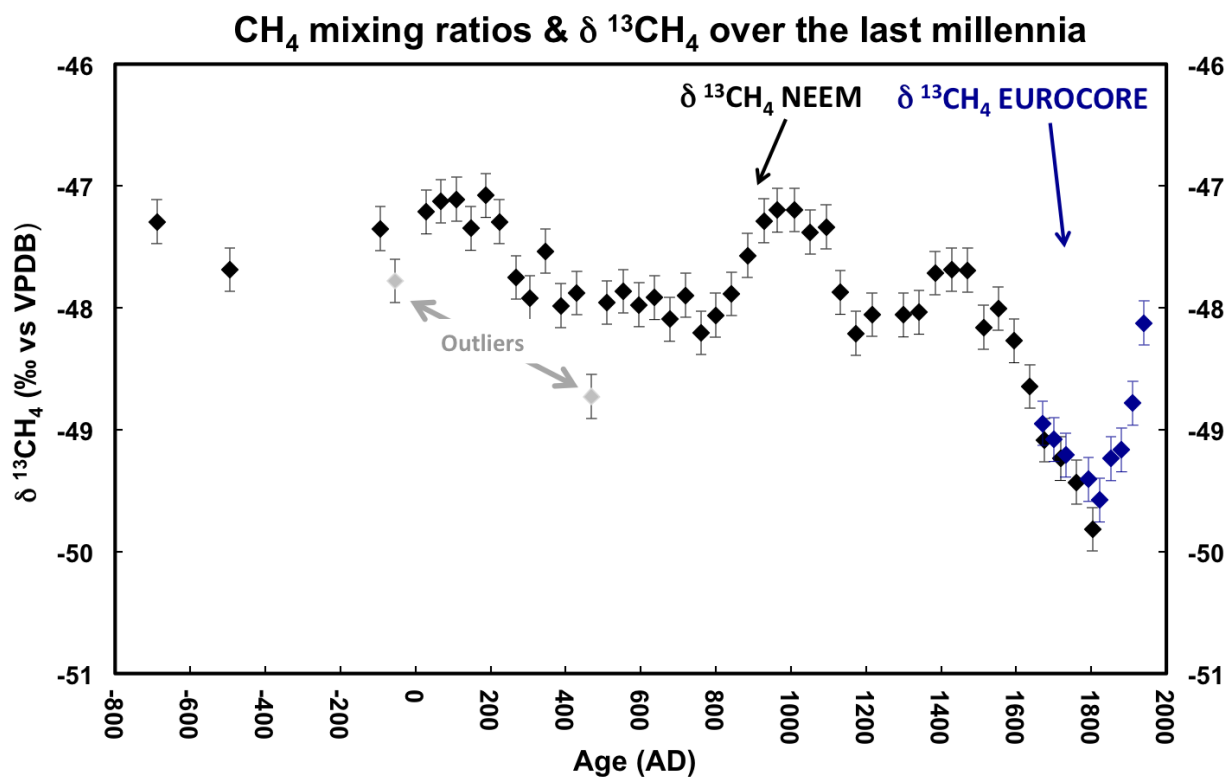
Figure 1. The $\delta^{13}C$ record of CH_4 over the last 2 millennia as determined from the NEEM (black) and EUROCORE (blue) ice cores.

Reconstruction of 1950 – 2010 Northern Hemisphere Non-methane Hydrocarbon Histories

D. Helmig[1], V. Petrenko[1], P. Martinerie[2], E. Witrant[2], J. Caramore[1], J. Hueber[1], W. Sturges[3], A. Baker[4], T. Blunier[5], T. Roeckmann[6], D. Etheridge[7], M. Rubino[7], P. Tans[8], ESRL/GMD Cooperative Air Sampling Network and NEEM Ice Core Project Members

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[2]Josef Fourier University-CNRF, Grenoble, France
[3]University of East Anglia, Norwich, Great Britain
[4]Max Planck Institute for Chemistry, Mainz, Germany
[5]Niels Bohr Institute, Copenhagen, Denmark
[6]Institute for Marine and Atmospheric Research, Utrech University, Utrecht, Netherlands
[7]Commonwealth Scientific Industrial Research Organization (CSIRO), Aspendale, Australia
[8]NOAA Earth System Research Laboratory, Boulder, CO 80305

Several recent studies, including three presentations by University of California, Irvine, scientists at previous NOAA-GMD annual meetings, have pointed out a tight linkage of non-methane hydrocarbon (NMHC) and methane emissions. Furthermore, NMHCs play a pivotal role in photochemical production of ozone in the troposphere. We reconstructed the 1950-2010 Northern Hemisphere concentrations of ethane, propane, i-butane, n-butane, i-pentane, and n-pentane using records of: 1) firn air samples extracted from three boreholes from the North Greenland Eemian Ice Drilling (NEEM) project; 2) eight years of ambient NMHC monitoring at five Arctic NOAA/GMD Cooperative Air Sampling Network sites; 3) two years of continuous NMHC monitoring at GeoSummit, Greenland; and 4) one year of atmosphere-snowpack gas exchange studies at GeoSummit. This information was incorporated in the LGGE-GIPSA model of gas transport in firn to estimate historic atmospheric NMHC concentrations and emissions. Results indicate that these C2-C5 NMHC increased by ~ 40-120% after 1950, peaked between 1965-1985, and have since declined again to be now back close to 1950 concentrations.
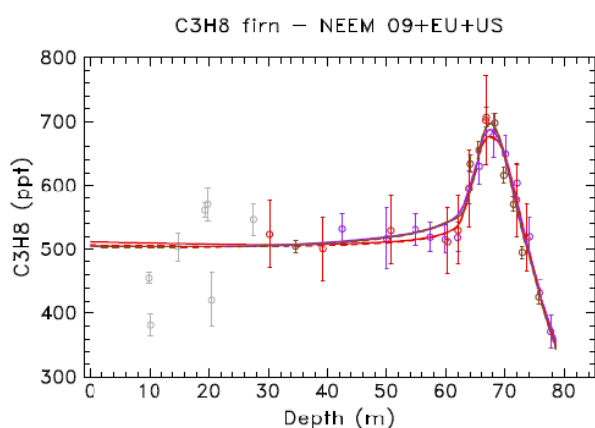
Figure 1. Mixing ratio of propane (mean with uncertainty range) from the U.S. (brown) and EU (purple) NEEM firn air samples. Red points show results from the NEEM-2009 drill hole. Grey data points were excluded from the scenario reconstruction because they were influenced by seasonal variations. Continuous lines represent runs of the reconstructed scenario through the forward firn air model.
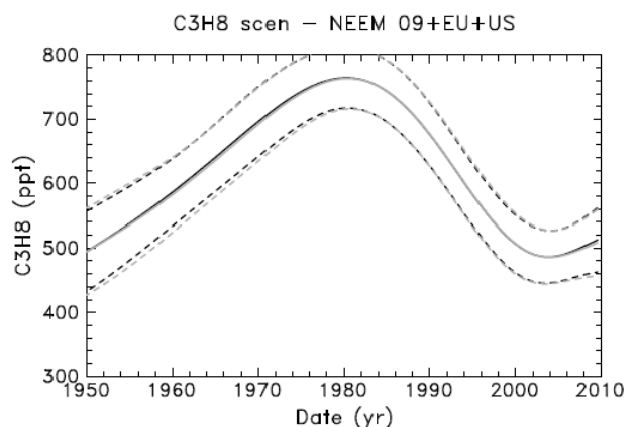
Figure 2. Reconstructed ambient propane mixing ratios over Greenland (solid line) with upper and lower limit uncertainty range (dotted lines).

Trace Gas Images of the Alaskan Atmosphere: The First Year of Measurements from the Carbon in Arctic Reservoirs Vulnerability Experiment (CARVE)

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Arctic and Boreal soils are estimated to hold more than twice the amount of carbon presently in the atmosphere. These regions are warming faster than any other region on Earth, leading to the possibility of large releases of carbon as CO_2 and/or CH_4 in the coming century. Moreover, the Arctic and Boreal carbon cycle represents a prime example of a potentially vigorous climate-carbon cycle positive feedback system, in which CO_2 and CH_4 releases will exacerbate warming and thus lead to more carbon emission, *et cetera*. Our current knowledge of the controls on CO_2 and CH_4 release from northern ecosystems, including wetlands, permafrost soils, and fires is poor, limiting our ability to assess the validity of predictive models. The object of CARVE is to link Alaskan tower and aircraft-based measurements of CO_2 and CH_4 with remotely-sensed surface hydrology and fire emissions over seasons and years.

Here, we will present analysis of trace gas data collected at a tower recently established in central Alaska by the NOAA/CIRES CARVE team. *In situ* measurements of CO_2, CH_4 and CO as well as daily air sampling for laboratory measurement of more than 50 additional mixing and isotope ratios commenced in October 2011. These measurements will form the year-round backbone for summertime CARVE aircraft missions, and will help us establish a long-term baseline for future Alaskan greenhouse gas changes. Analysis of back trajectories (Figure 1) shows that this site has sensitivity over large regions of wetlands and discontinuous permafrost, where we expect the greatest sensitivity to changing moisture and temperature. A first look at fall and winter CO_2, d[13]C and CO observations (Figure 2) suggest that CO_2 variations at the site can be influenced both by terrestrial biosphere exchange and pollution, although the broad suite of anthropogenic tracers measured should allow us to identify these events. We will additionally present examples of how the wide array of biogenic and anthropogenic tracers we measure, including stable and radio-isotope ratios of CO_2 and CH_4, will provide unique capabilities for the attribution of Arctic and Boreal greenhouse gas variations.
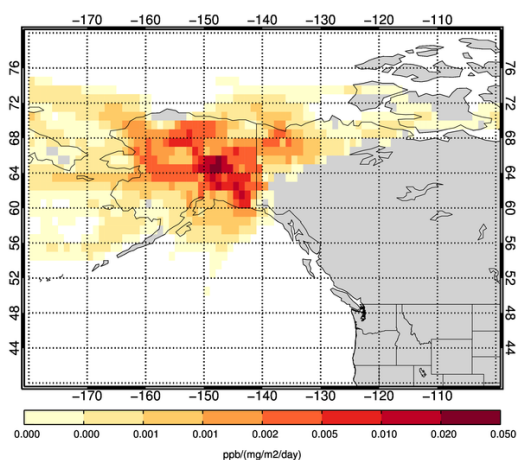
Figure 1. Average surface sensitivity (in units of mole fraction per flux; i.e. "footprint") for November, 2011 for discrete air samples collected at the CRV tower northeast of Fairbanks, AK.
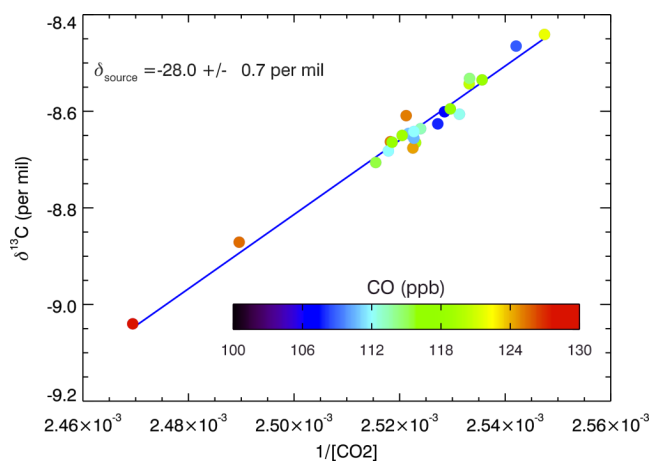
Figure 2. "Keeling" plot showing the δ^{13}C isotopic signature responsible for observed CO_2 variations. Data are color-coded according to their CO mole fraction as an indication of the degree to which combustion, as opposed to biospheric exchange has impacted CO_2.

Observation of Atmospheric CH$_4$ Mixing Ratios at the Three WMO/GAW Stations in China

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Atmospheric CH$_4$ mixing ratios were measured continuously at WLG (36°17'N, 100°54'E, 3816m asl, Waliguan in Qinghai Province), LAN (30°18'N, 119°44'E, 138.6m asl, Lin'an in Zhejiang Province) and LFS (44°44' N, 127°36'E, 330.5m asl, Longfengshan in Heilongjiang Province) by Cavity Ring Down Spectroscopy system (G1301, Picarro Inc.) from January 2009. WLG is one of the 28 WMO/GAW global stations and the observational results represent the Eurasian continent atmospheric CH$_4$ level. LAN and LFS are affiliates to WMO/GAW regional stations and the measurement could represent mixed air of Yangtze Delta and the northeastern China plain, respectively. An air inlet (80m above ground) was attached to the 89m sampling tower at WLG and shares with an *in-situ* gas chromatography system. At the beginning, an air inlet (10m above ground) was fixed at the top of wind tower at LAN and SDZ. In 2010, a new sampling tower was built at LAN (50m) and LFS (80m), respectively. An additional air inlet was attached to the top of the tower at LAN and LFS. A suite of three working standards (High, Low and Target) linked to the NOAA 04 CH$_4$ scale was used to calculate ambient CH$_4$ mixing ratios and to evaluate system performance. Preliminary results showed that the CH$_4$ mixing ratios observed from the two regional stations were obviously higher than that at WLG.
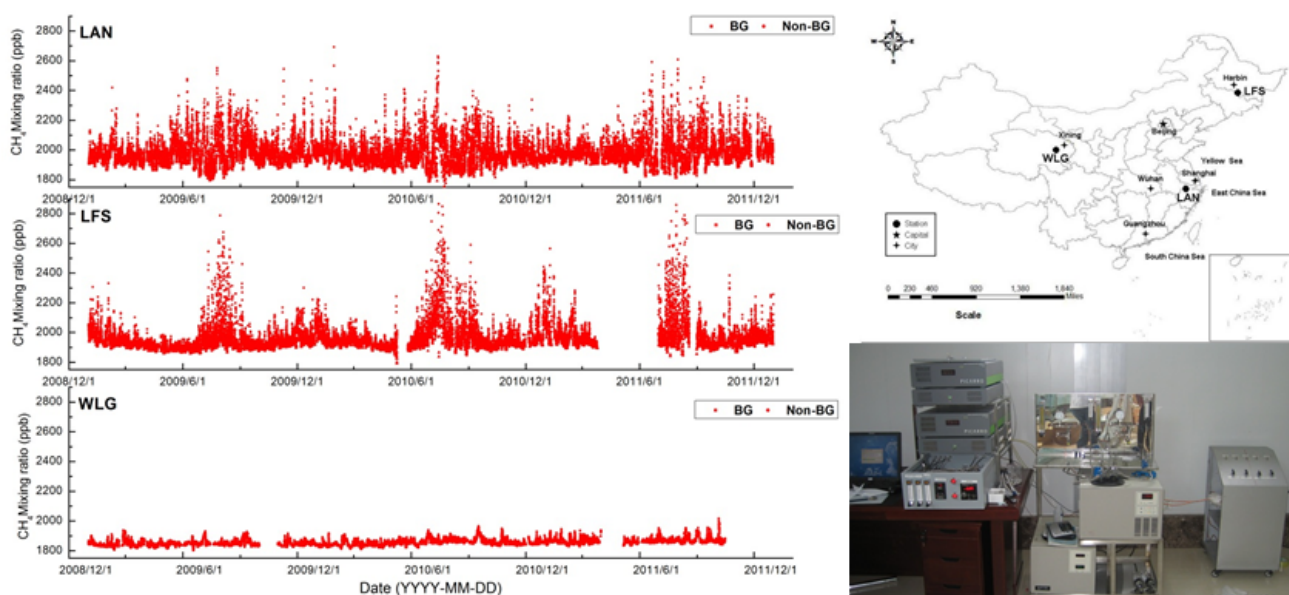
Figure 1. Left: Preliminary results of atmospheric CH$_4$ mixing ratios at the three stations. Right: Location of the stations and the Picarro system.

Estimate of CH₄ Emissions from Oil and Gas Operations in the Uintah Basin Using Airborne CH₄ Measurements and LiDAR Wind Data

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A February 2012 campaign in the Uintah oil and gas basin in Northeastern Utah was focused on studying ozone and particle precursor emissions in the natural gas and oil fields in the basin. The NOAA/ESRL Carbon Cycle Aircraft Program used this campaign as an opportunity to demonstrate the capabilities of light aircraft sampling. Flask measurements and high-resolution (0.5 Hz) observations of carbon dioxide (CO_2) and methane (CH_4) were made during flights on 13 days. We present top-down estimates of the methane flux over the region, using CH_4 measurements from the aircraft and wind measurements from the High-Resolution Doppler LiDAR deployed at a ground site. We include a detailed analysis of the errors associated with this flux estimate. We present evidence that this methane flux is associated with emissions from oil and gas production operations in the basin.
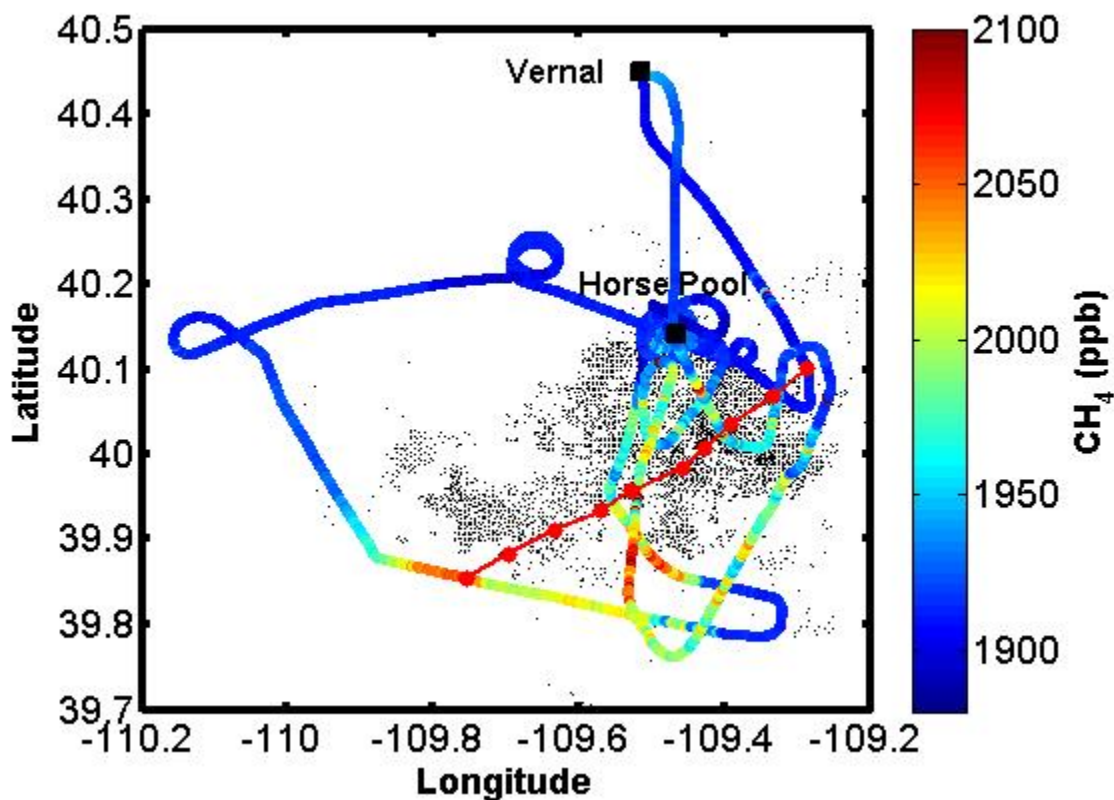
Figure 1. Flight track on 2/3/2012, colored by methane mixing ratio. The red points and line show a back trajectory of an air mass sampled downwind of the gas field, constructed using wind measurements in Horse Pool. Small black points show the locations of gas wells in the Uintah Basin.

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Quantifying California's Anthropogenic Greenhouse Gas Budget

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Sustainable environmental and energy solutions require verifiable agreements to reduce anthropogenic greenhouse gas (GHG) emissions to the atmosphere. Supporting a vision for verified emissions reductions, we are quantifying anthropogenic GHG emissions at local to regional scales in California. We estimate California's GHG emissions using a combination of atmospheric measurements and inverse models that balance prior knowledge and measured information, each weighted by their respective uncertainties. Multi-species GHG measurements made over California are compared with high-resolution transport simulations that are carefully evaluated using the combination of radar-wind and lidar-aerosol profilers.

Fossil fuel CO_2 emissions, quantified using one year of radiocarbon $^{14}CO_2$ measurements at both Central (WGC) and one month at the Southern California (CIT) site, are consistent with existing emission inventories to within ~ 10%. CH_4 emissions, quantified by a five-tower network over a one-year period, are 1.6 +/- 0.1 times higher than a California inventory estimates, with significant seasonal variation (1-3) in scaling factor. N_2O emissions, estimated using two years of flask measurements at WGC, are 2 +/- 0.4 times higher than the EDGAR emission map for Central CA, again with seasonal dependence (1.6-2.5) in scaling factor. In contrast to CH_4 and N_2O, initial evaluation of select industrial GHGs (e.g., HFC 134a) suggest emissions may be smaller than the EDGAR emissions. Taken together, these results suggest CH_4 and N_2O emissions may comprise ~ 20% of California's total GHG emission budget. We are now increasing the coverage of measurement sites across California and, in broader collaborations, expect to provide comprehensive regional GHG emissions measurements for California.
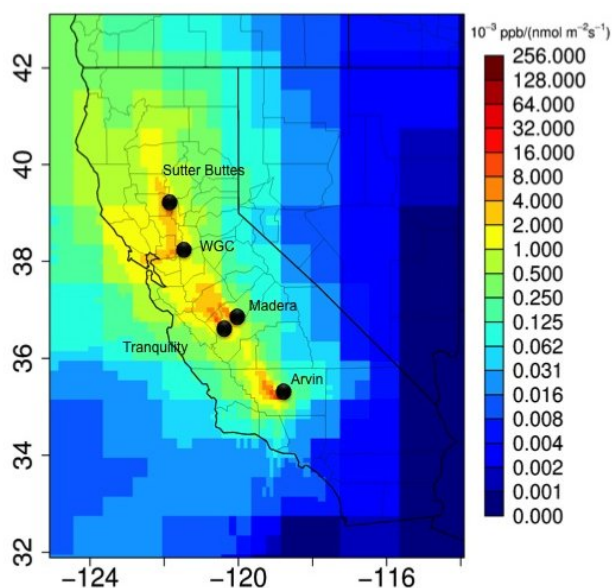
Figure 1. Footprint map showing afternoon sensitivity to surface emissions at Central Valley GHG measurement sites for May-June, 2011.

Urban Greenhouse Gas Emissions Monitoring in Davos, Switzerland, Before, During and After the 2012 World Economic Forum Annual Meeting

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Efforts to reduce anthropogenic greenhouse gas (GHG) emissions require validation. Atmospheric measurements capture all emissions, and provide a unique and powerful means of continuous validation and feedback. To demonstrate the utility of real time GHG measurements, *in situ* GHG mixing ratio instruments were deployed in Davos, Switzerland to measure emissions from the city before, during and after the World Economic Forum (WEF). Three Instruments were deployed at two separate locations over 3 months (late December 2011 to February 2012). One site was located in the middle of the Davos urban area and a second site was located out of the valley in the surrounding mountains. Carbon Dioxide (CO_2), Methane (CH_4), Carbon Monoxide (CO) and water vapor (H_2O) were measured continuously by Picarro G2401 instruments at both sites. Additionally, a Picarro flux analyzer was deployed in the city to evaluate the inverse fluxes. The mesoscale atmospheric model, WRF nudged to meteorological observations (WRF-FDDA), was used to simulate the transport of GHG over the valley of Davos at 1.3km resolution. A Mini Micro Pulse LiDAR (MiniMPL) from Sigma Space was deployed to evaluate the simulated planetary boundary layer depth from the WRF-FDDA model. The initial flux estimates for CO_2 were constructed based on inventories reported for 2005. CO_2 mixing ratio measurements prior to WEF suggest the difference between modeled (real-time) and inventory (annual) emissions to be on the order of +40%. The mismatch could be due to the increased use of heating fuel in the winter. We present here the temporal variability in the inverse fluxes, which are correlated with a cold wave severely affecting Western Europe during the past winter, as well as changes in anthropogenic activities during the week of the WEF meeting. Acknowledgments: Calibration tanks were provided by C. Sweeney, NOAA ESRL.
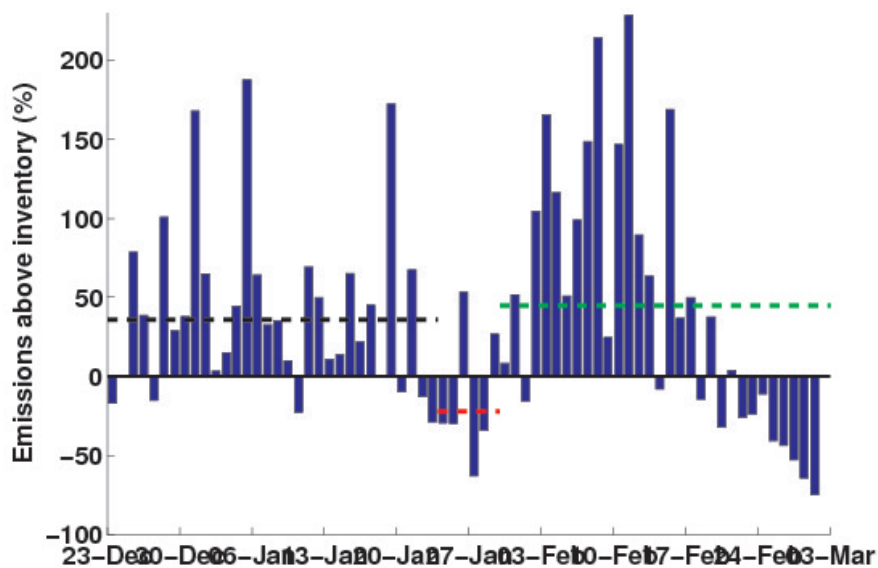
Figure 1. Emissions above inventory (3-day moving average), based on inversion modeling results, for Davos, Switzerland.

Hourly, Daily, and Seasonal Patterns of Atmospheric CO_2 Along an Urbanization Gradient

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Cities occupy less than 3% of global land area, but are estimated to produce nearly three-quarters of anthropogenic CO_2 emissions (IEA 2008). Therefore, these small geographic features exert a disproportionate influence on atmospheric CO_2 concentrations on multiple spatial scales. However, the patterns of CO_2 in urban areas are controlled not only by anthropogenic emissions, but also by biogenic and micrometeorological processes. The aggregate behavior of these diverse processes on atmospheric CO_2 concentrations represents a critical gap in our understanding of the terrestrial carbon cycle, complicating efforts to develop a framework for regulation and verification of carbon emissions.

In order to better understand these drivers of atmospheric CO_2 in an urbanized area, we analyzed measurements of atmospheric CO_2 made from towers in Boston, Worcester, and Harvard Forest (Petersham), Massachusetts. These locations span the urban-rural gradient of central and eastern Massachusetts, allowing detection of the factors contributing the atmospheric CO_2 signal in this region. Our results show significant differences between the sites on hourly, seasonal, and annual timesteps. The annual mean CO_2 mixing ratios were 408.2 ± 0.2, 401.5 ± 0.4, and 393.0 ± 0.3ppm at Boston, Worcester, and Harvard Forest, respectively. Across the gradient, peak CO_2 concentrations were observed in winter, corresponding with the timing of maximum anthropogenic emissions (Gurney *et al*. 2009) and minimum biogenic uptake. Midday CO_2 concentrations in the summer demonstrate significant drawdown (≥ 10 ppm) from the 24-hour median value across all three sites, highlighting the importance of biogenic fluxes, even at the highly urbanized Boston site.

These data represent a critical component of a model-data framework designed to make high-resolution inferences about sources and sinks of atmospheric CO_2. We will use the Stochastic Time Inverted Lagrangian Transport model to estimate surface fluxes on the basis of the time series data at our three locations. The results from this work will allow us to directly connect the influence of anthropogenic processes to observed atmospheric CO_2 for verification of future greenhouse gas agreements and treaties.
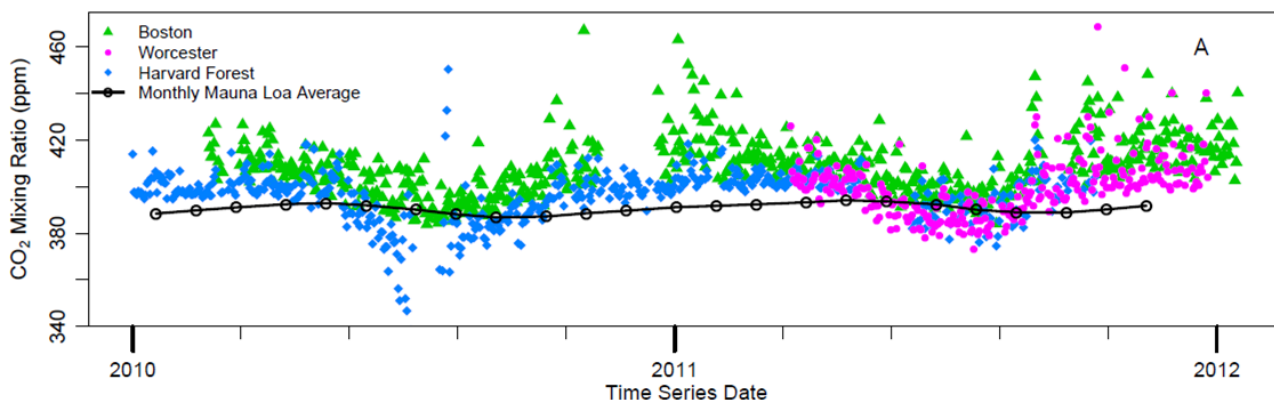
Figure 1. Time series of daily averaged CO_2 concentrations at Boston, Worcester, and Harvard Forest, Massachusetts.

Toward Simultaneous Multi-station Data Pre-processing for Inversions of Greenhouse Gas Emissions and Uptake in California

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Atmospheric observations and inverse modeling offer an objective basis to evaluate bottom-up accounting of greenhouse gas (GHG) exchange between the land surface and atmosphere, including anthropogenic emissions that may be subject to regulatory policy. Here, we describe initial progress on a project to improve atmospheric inversion estimates of California's emissions and uptake of CO_2 and CH_4 from atmospheric measurements of these gases at multiple stations. These efforts focus on development of data filtering algorithms to prepare continuous GHG observations for use with an inversion system combining mesoscale meteorology computed with the Weather Research Forecast (WRF) model with the Stochastic Time Inverted Lagrangian Transport (STILT) particle dispersion model (Lin et al., 2003). We compute variations in local GHG signals from California by subtracting estimated GHG background signals from measurements and compare them with local signals predicted with WRF-STILT footprints and EDGAR (Olivier et al. 2001) prior emission maps. We analyze the performance of the filtering algorithms for different times of day and averaging intervals. We evaluate the sensitivity of these results to the prior emissions using two versions of EDGAR (3.2 and 4.1). We expect the resulting filtering algorithms will become a useful tool for incorporating continuous GHG data streams into the WRF-STILT inversion and other GHG data assimilation systems at regional scales.
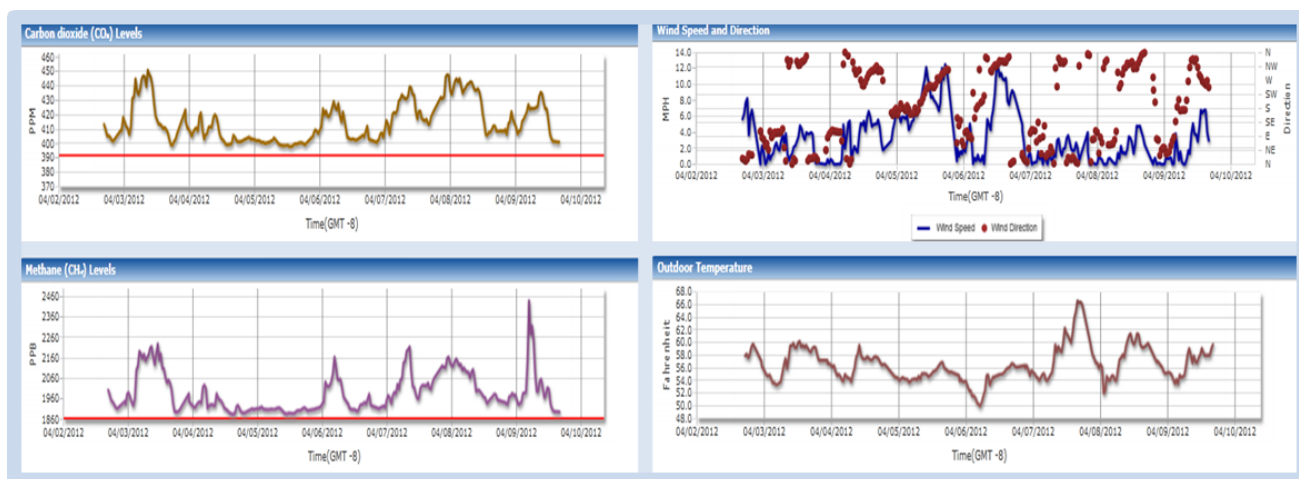
Figure 1. Observed CO_2 (top left), CH_4 (bottom left), wind speed and direction (right top), and temperature (right bottom) at La Jolla, CA site on April 4-10, 2012.

Two Decades of Atmospheric O_2 Measurements and Their Implications

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Time series of atmospheric O_2/N_2 ratio by the Scripps O2 program now span more than two decades. These measurements enable refined estimates to be made of land and ocean carbon sinks and provide benchmark tests for models depicting the response of ocean biogeochemistry to changing climate on a range of time scales, extending from seasonal, El Nino, to multi-decadal. The measurements are also relevant for quantifying the global loss of O_2 from the oceans, or "deoxygenation" and for detecting changes in ocean ventilation and production associated with warming-induced stratification that may influence future deoxygenation.

This presentation will provide highlights of several results of general interest. An updated estimate of the global land and ocean sinks of CO_2 for the decades of the 1990s and 2000s will be provided based on the O_2/N_2 data. The downward trend in O_2/N_2 has accelerated since 1999, potentially signaling an increase in the uptake rate of CO_2 by the oceans. This result will be discussed in the context of studies based on other lines of evidence that suggest, in contrast, that the ocean CO_2 sink is no longer increasing. The long-term average magnitude of the ocean sink will also be compared with studies based on the penetration of Chlorofluorocarbons into the oceans. The seasonal cycles in O_2/N_2 provide a metric of the stability of the functioning of ocean biological systems. Although some small variability in these cycles from year to year is notable, the data show little evidence of long-term trends, suggesting that ocean productivity at middle and high latitudes has not undergone major changes over the past 20 years. Interannual variability in O_2/N_2 of oceanic origin is evident on a range of additional time scales. These data provide potentially powerful constraints on the impact of changing climate or other perturbations on the ocean CO_2 sink.
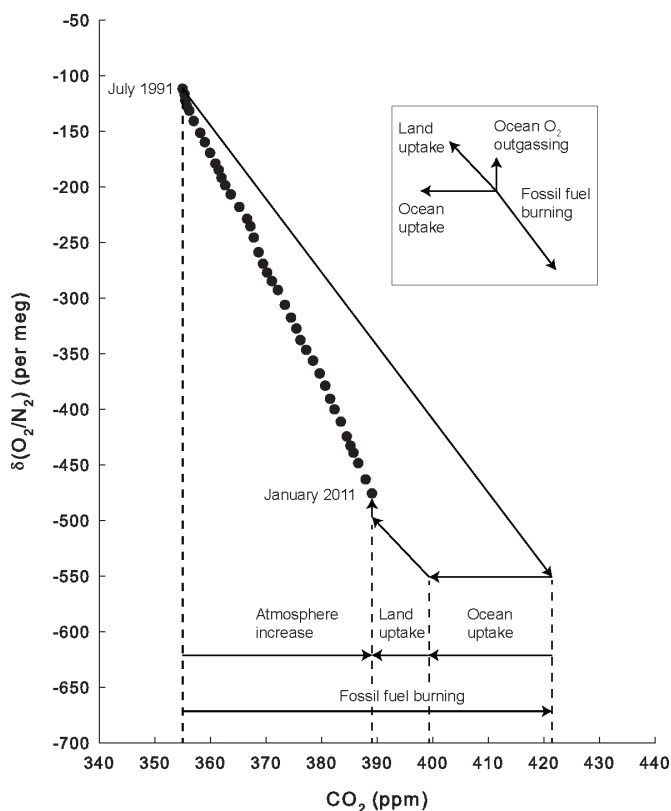
Figure 1. Land and ocean sinks from 1991 to 2011 as derived from trends in O_2/N_2 and CO_2 concentration.

Long-term Trends in African Dust Transport to the Caribbean: African Sources, Changing Climate, and Future Scenarios

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Aerosol studies were begun on Barbados in 1965 and they continue to this day at the University of Miami Atmospheric Chemistry Station [Fig. 1] situated on a promontory on the east coast at Ragged Point (13.165N; 59.432W). The monthly mean dust concentrations (based on daily filter samples) in Barbados trade winds show a strong seasonal cycle with a maximum in summer and a minimum in winter [Fig. 2]. Moreover there are great changes on interannual and decadal time scales. Over much of this record there was a strong negative correlation between dust concentrations in Barbados and rainfall in the Sahel-Soudano (SS) region of North Africa. In retrospect, this correlation was largely driven by three distinct periods in the early record: the period of high rainfall and low dust transport in the mid-to-late 1960s; the first SS drought and increased dust in the early 1970s; and the extremely intense SS drought of the early 1980s which is associated with the highest dust concentrations of the entire record. During this early period, dust transport showed promising relationships to various climate indices: e.g. ENSO, NAO, AMO. However, since the early 1990s the drought has moderated. Although there have been large year-to-year changes in SS rainfall, there is no relationship between dust on Barbados and SS rainfall or between dust and common climate indices. Furthermore, over the entire record there is a strong shift in seasonal dust transport, most notably, a great increase in winter and spring transport compared to the pre-drought and early-drought period. Over various parts of the record there are suggestions of strong relationships to various climate indices but these do not hold over the entire record. These changing relationships suggest that there have been profound long-term changes in dust emissions and transport and the driving mechanisms. A possible contributing factor could be increased population and land use in the SS region. As to the future, the Intergovernmental Panel on Climate Change 2007 multi-model projections of rainfall in Africa show drier conditions in the North but they could not reach a consensus in the SS region. The absence of a clear relationship between dust transport and African-Atlantic climate and the uncertainties in climate projections make it impossible to anticipate how transport to the Caribbean might change in the future.

Figure 1. University of Miami Atmospheric Chemistry Station.
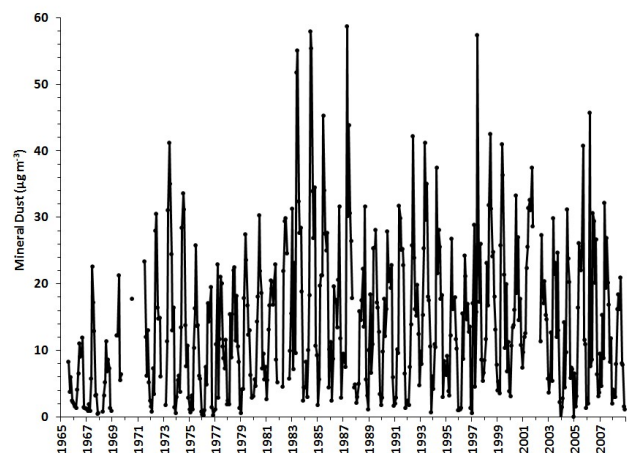
Figure 2. Barbados Monthly Mean Dust Concentration (μg m-3).

Aerosols at Mauna Loa Observatory (MLO) – Spring 2001 Versus Spring 2011

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The rapid development of Chinese industry has raised concerns about aerosol impacts and climate in the Pacific basin. This concern was addressed in the massive ACE-Asia international aerosol study of March – May, 2001. As part of a diverse multi-national program, we operated 22 aerosol sampling sites from middle China to the Arctic, the Western coast of the USA, and MLO, including a ship. The MLO site was typical of 8 other sites, where aerosols were sampled by DRUM impactors in 3 hr increments, in 8 size modes, from late March through April. Samples were analyzed for 32 elements, sodium to lead, by Synchrotron-induced X-Ray Fluorescence to picogram/m^3 sensitivity. We have duplicated the sampling and analysis of ACE-Asia at MLO in Spring 2011, and added to it new types of analysis for mass and optical properties, including a surrogate for soot. These techniques have also been applied to the 2001 samples. Transport models such as the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, satellite data, and composites of wind and sea level pressure data have been used to identify transport paths to MLO. One of the early results is the realization that Asian dust aerosols generally arrive at MLO from the East, circulating clockwise around the Pacific subtropical high, while sulfates can also meander slowly across the Pacific, especially from mid-latitudes in China. Wind circulation patterns over the Pacific Ocean were more active in the 2011 compared with 2001, with a more active jet stream. The increased wind circulation patterns in 2011 can increase the amount of dust and anthropogenic aerosols transported across the Pacific and from there to Hawaii around the Pacific subtropical high. This can help explain the increased amounts of aerosols in 2011 compared with 2001 as characterized by the optics data and for 2001, dust aerosol data. Nevertheless, there are several key dates in both 2011 and 2001 that contain very similar meteorological patterns. Comparison of aerosol data for the above dates in both 2001 and 2011 will prove useful in identifying trends in sulfate and other potential anthropogenic signatures in aerosols reaching Mauna Loa from China due to potential changes in industrial outputs between 2001 and 2011. The data will be compared to our identical site at Greenland Summit, operating since 2003.
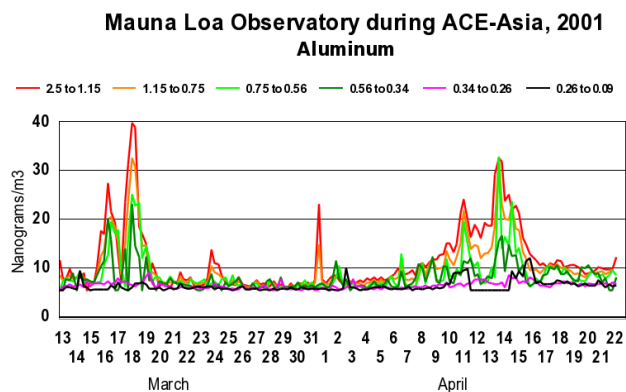
Figure 1. Fine soil aerosols transported to MLO during ACE-Asia, Spring 2001.
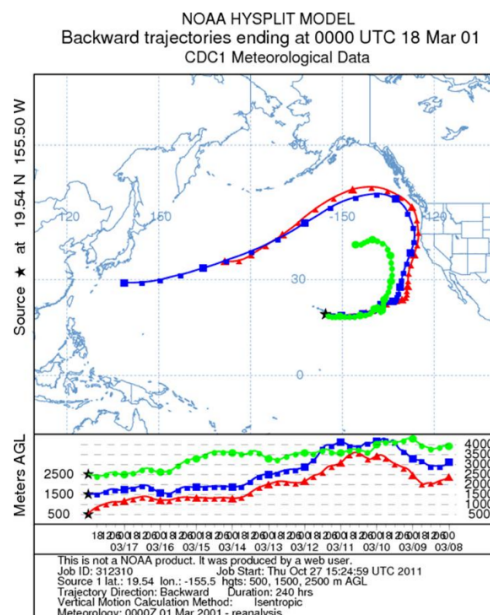
Figure 2. HYSPLIT trajectories from Asia during the March 18 episode.

Seasonal Variability in the Southeast U.S. Background Aerosol Direct Radiative Effect – An Initial Measurement-based Climatology from a Regionally-representative Location

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On a global average, the measurement-based estimates of the aerosol direct radiative effect (DRE) are 55-80% greater than the model-based estimates (Yu et al., 2009). The differences are even larger on regional scales and for the anthropogenic component. One of the high-priority tasks recommended (Kahn et al., 2009) to reduce the uncertainty in aerosol radiative effects is to "Maintain, enhance, and expand the surface observation networks measuring aerosol optical properties for satellite retrieval validation, model evaluation, and climate change assessments". The Southeastern U.S. (SE U.S.), home to large, warm-season aerosol loading, is one of only a few regions where surface temperatures did not increase in the 20th Century (Trenberth, et al., 2007). Established in 2009, the Appalachian Atmospheric Interdisciplinary Research Facility (AppalAIR) at Appalachian State University (36.21°N, 81.69°W, 1080 m) is home to the only co-located NOAA/Earth System Research Laboratory and NASA/Aerosol Robotic Network aerosol monitoring sites in the SE U.S. The recent addition of a micro-pulsed lidar, a vertically-pointing radar, and detailed instrumentation for aerosol chemical and microphysical properties and gas-phase aerosol precursor chemistry complement existing measurement capabilities and will facilitate the most comprehensive long-term study of aerosol/climate interactions in the SE U.S. Multi-year AppalAIR and Moderate-Resolution Imaging Spectroradiometer (MODIS) satellite data products will be presented to estimate the degree and geographic extent that aerosol radiative properties measured at the semi-rural, high-elevation AppalAIR facility are representative of the SE U.S. The aerosol optical depth (AOD), aerosol radiative properties, and top-of-atmosphere (TOA) and bottom-of-atmosphere (BOA) aerosol DRE exhibit large seasonal variability, with a significant summer-time aerosol cooling effect at both the TOA and the surface. The difference between TOA and BOA DRE is less than that quoted in other published studies conducted in the region. The regionally-representative aerosol optical properties, as evidenced by a statistical cluster analysis of backward air trajectories, and the fact that AOD and surface properties are fairly homogeneous over the region suggest that the long-term aerosol DRE climatology being developed at AppalAIR likely is a good measure of the background DRE in the SE U.S.
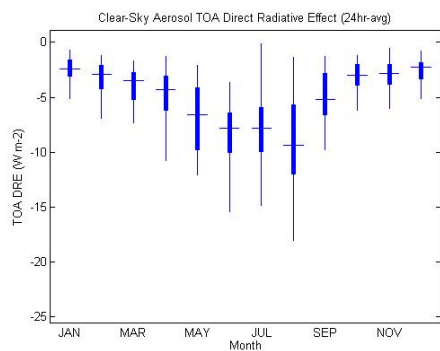
Figure 1. Monthly TOA daily-averaged clear-sky DRE for the period June 2009-May 2011, using hourly-averaged aerosol intensive optical properties from AppalAIR and MODIS-retrieved AOD and surface albedo. The whiskers correspond to 50th percentile. The box extends from 25th to 75th percentile and the line extends from 5th to 95th percentile.
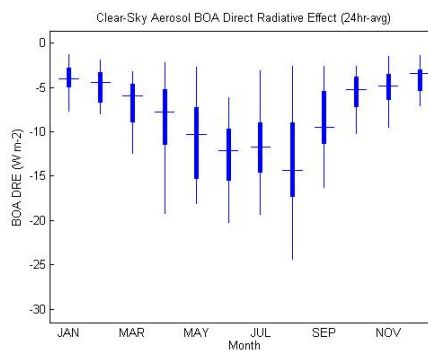
Figure 2. Monthly BOA daily-averaged clear-sky DRE for the period June 2009-May 2011, in the same context as the TOA plot shown in Figure 1.

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Climatology of Aerosol Optical Properties Over the High Arctic

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Sunphotometer/sky radiometer measurements have been acquired at the high Arctic Observatory in Eureka [Nunavut, Canada] since the spring of 2007. These (CIMEL) sunphotometers belong to the AEROCAN/Aerosol Robotic Network (AERONET) network and are part of CAnadian Network for the Detection of Atmospheric Change (CANDAC). They are located at the Polar Environmental Atmospheric Research Laboratory (PEARL) Ridge lab and Zero Altitude PEARL Auxiliary Laboratory (ØPAL) sites in Eureka. ØPAL is located about 15 km southeast of the PEARL ridge lab, which is at an elevation of 610 m. This dual placement was designed to study the layer between the two sites, as well as provide an element of redundancy for the Aerosol Optical Depth (AOD) measurements.

Based on five years of continuous, spring/summer observations (2007-2011), we report results on the seasonal and inter-annual variations of AOD at Eureka (Figure 1). The AOD data were further resolved into fine (sub-micron) and coarse (super-micron) particle modes. The results are analyzed in the context of fine mode biomass burning events that occur typically during spring, known fine mode volcanic (sulphate) events (e.g., the Kasatochi eruption of August 2008 and the Sarychev eruption of June 2009), and coarse mode events. The AOD variations over Eureka are compared with measurements made at other Arctic sites, including Barrow [Alaska, USA] and Alert [Nunavut, Canada], acquired using NOAA Sunphotometers and the AEROCAN/AERONET sites in Resolute Bay [Nunavut, Canada], Thule and Kangerlussuaq [Greenland, Denmark], and Hornsund [Spitsbergen, Norway].
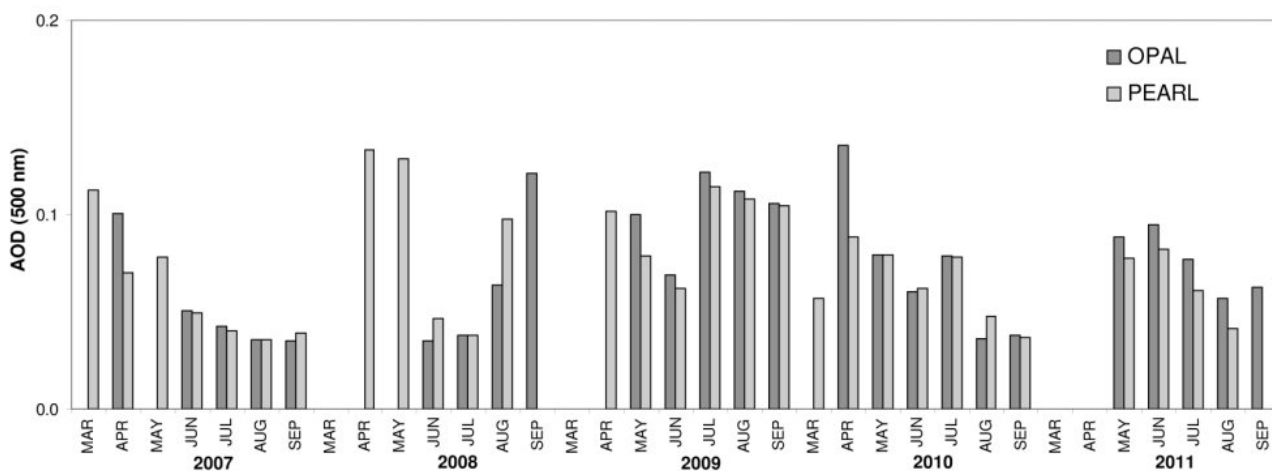
Figure 1. Monthly mean temporal variation of Aerosol Optical Depth (500 nm) at Eureka.

The Cloud, Aerosol Backscatter and Polarization LiDAR at Summit, Greenland

R. Neely[1], M. Hayman[2], J.P. Thayer[3], R.M. Hardesty[4], M. O'Neill[1], M. Shupe[4], R. Stillwell[3] and C. Alvarez[4]

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Precise measurements of cloud properties over Greenland are necessary to document the full range of cloud conditions and characteristics throughout the Arctic. The Cloud, Aerosol Polarization and Backscatter LiDAR (CAPABL) has been developed to address this need by measuring depolarization, particle orientation and backscatter of clouds and aerosols in the troposphere and lower stratosphere. CAPABL uses recent developments in optical methods to detect horizonatally oriented ice crystals (HOIC) by quantifying the diattenuation of the returned signal. The LiDAR is located at Summit, Greenland (72.6° N, 38.5° W; 3200 m.a.s.l) as part of the Integrated Characterization of Energy, Clouds, Atmospheric State, and Precipitation at Summit project and NOAA's Global Monitoring Division's LiDAR network. Here the instrument is described with particular emphasis placed upon the implementation of the new polarization methods developed as part of this instrument. Initial results of the LiDAR are also shown to demonstrate the ability of the LiDAR to observe cloud properties.
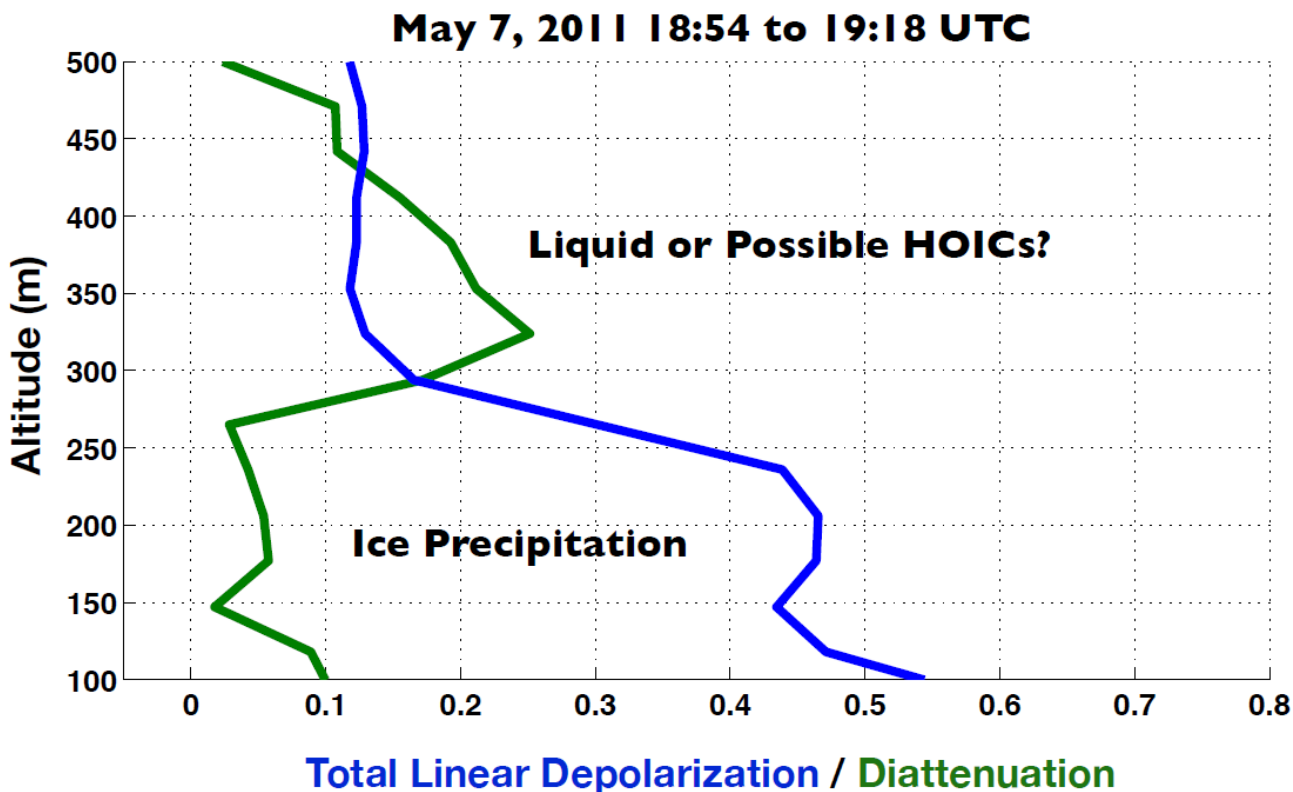
Figure 1. On May 7, 2011, CAPABL observed a diattenuation signature that appeared to coincide with a cloud at an altitude of 400 to 500 m. During that same time, a higher altitude cloud with low depolarization, strong backscatter and no diattenuation (liquid water cloud) was also observed. This observation suggests that CAPABL can detect horizontally oriented ice crystals while simultaneously determining cloud phase using their unique polarization signature.

Isoprene Suppression of New Particle Formation in a Mixed Deciduous Forest

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Production of new particles over forests is an important source of cloud condensation nuclei that can affect climate. While such particle formation events have been widely observed, their formation mechanisms over forests are poorly understood. Our observations made in a mixed deciduous Michigan forest, with large isoprene emissions during the summer, show surprisingly rare occurrence of new particle formation (NPF). No NPF events were observed during the 5 weeks of measurements, except two early evening ultrafine particle events as opposed to the typically observed noontime NPF elsewhere (Figure 1). Sulfuric acid concentrations were in the 10^6 cm^{-3} ranges with very low preexisting aerosol particles, a favorable condition for NPF to occur even during the summer. The ratio of emitted isoprene carbon to monoterpene carbon at this site was similar to that in Amazon rainforests (ratio larger than 10), where NPF is also very rare, compared with a ratio smaller than 0.5 in Finland boreal forests, where NPF events are frequent. The two evening ultrafine particle events were associated with the transported anthropogenic sulfur plumes and the ultrafine particles likely formed via ion induced nucleation. It has been suggested that isoprene emissions may suppress NPF formation in forests and our results are consistent with this conclusion although the underlying mechanism for the suppression is unclear and future studies are needed to reveal the mechanism. Changes in land cover and environmental conditions could modify the isoprene suppression of NPF in some forest regions resulting in a radiative forcing that could influence climate. In this presentation, we will also discuss aerosol number concentrations of particles in the size range from 1-3 nm, recently measured in another two locations (Long Island, New York and Kent, Ohio).
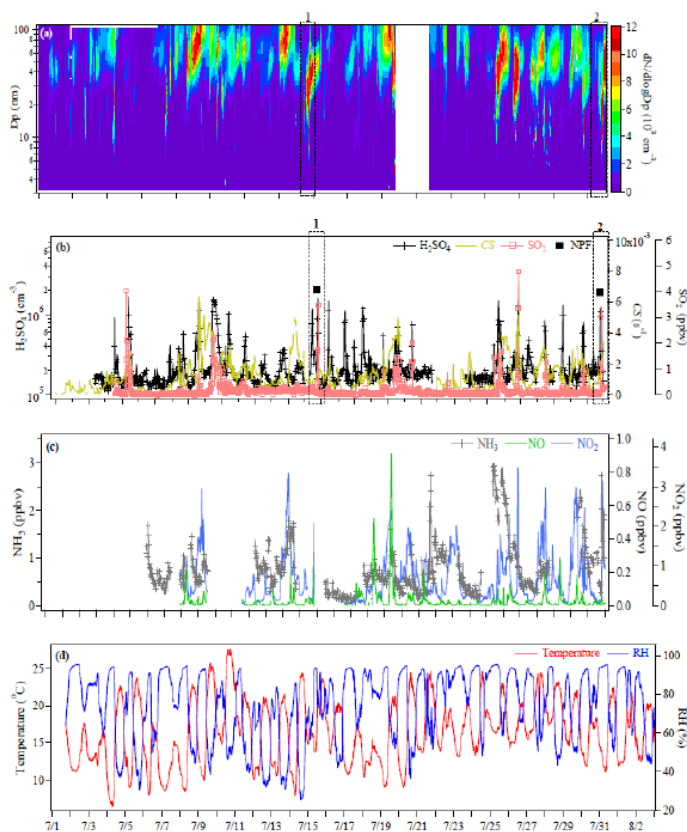
Figure 1. (a) Particle size distributions in the size range from 3-109 nm measured during July 1-August 3, 2009 in the Michigan forest. There were no Nitrosodimethylamine (NDMA) measurements from July 22-24. (b) The measured H_2SO_4 (line with black plus signs), SO_2 (light red open squares), and CS (yellow solid line) during July 1-August 3, 2009 at the same site. The two filled black squares show the observed early evening NPF events (Box 1 and 2 for July 16 and August 2 events, respectively). As mentioned in the main text, there were no conventional NPF events at noontime at all during the summer of 2009. Sharp spikes in particle number size distributions were seen at noontime (e.g. July 8), but these particles did not grow enough to show aerosol size distributions with a typical "banana shape". (c) The measured NH_3 (line connected by grey plus signs), NO (green solid line) and NO_2 (light blue solid line), and (d) the measured temperature (red line) and RH (blue line) during July 1-August 3, 2009 at the same site.

Investigating Potential Biases in Aerosol Light Absorption Measurements

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Currently, there is no single instrument for quantifying the aerosol light absorption coefficient (σ_{ap}) that offers accurate measurements, simplicity in use, and reasonable cost. Filter-based techniques, which combine simplicity and low cost, can result in measurement biases under some conditions. Possible discrepancies in the filter-based measurement of σ_{ap} were investigated utilizing a subset of measurements from two field campaigns: 1) aircraft data from 8 flights over California during the CalNex field campaign of April- May 2010, and 2) data obtained at Storm Peak Laboratory in Steamboat Springs, Colorado, between January- June 2011 during the STORMVEX campaign. Each study differed in aim and instrumentation, but both provided opportunities for addressing uncertainties in determining σ_{ap}. Here, the potential for biases in the filter-based measurement of σ_{ap} are considered.

Filter-based measurements of σ_{ap} are obtained in both of these campaigns with the Particle Soot Absorption Photometer (PSAP). This method has potential measurement biases including interference from scattering particles, which can be corrected for after the measurements are obtained, and from liquid organic aerosols which is not yet well understood or quantified. Reference measurements of σ_{ap} were provided directly with a Photo-Acoustic Spectrometer (PAS) during the CalNex campaign, and as the difference between aerosol extinction and scattering coefficients, $\sigma_{ap} = \sigma_{ext} - \sigma_{sp}$, in the STORMVEX campaign; a Cavity Attenuated Phase Shift extinction monitor measured σ_{ext} and an integrating nephelometer measured σ_{sp}.

Data are then analyzed for consistencies (e.g., closure), potential biases, and relationships to other aerosol properties. The PSAP measurements from CalNex and STORMVEX do not appear to be subject to a bias caused by organic carbon that has been suggested by other experiments. This could be due to differences in the aerosol composition, and/or loading, and should be the focus of further research efforts. Both campaigns provide further insight on the potential for variations and uncertainties that occur during measurements of aerosol σ_{ap}.
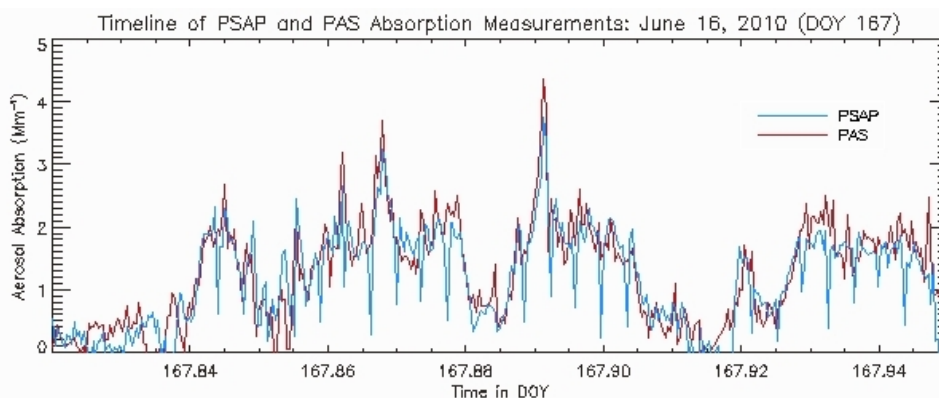
Figure 1. Timeline for the PSAP and PAS absorption measurements for June 16, 2010 (DOY 167) during a research flight on the CalNex field campaign. The flight depicted in figure 1 was where substantial time was spent flying over the agricultural fields of the San Joaquin Valley, over the cities of Fresno and Bakersfield, as well as over the Pacific ocean. It is clear that the σ_{ap} from both instruments follow closely in measure and magnitude, which was typical for all of the CalNex campaign.

NOTES:

Wednesday Morning, May 16, 2012 AGENDA

(Only presenter's name is given; please refer to abstract for complete author listing.)

• *07:00*　　　　*Registration Opens in GC-402 – lunch orders collected at registration table*
• *07:30 - 08:15*　*Morning Snacks – Coffee, tea, fruit, bagels & donuts served*

Page No.

• *Session 5*　　*Keynote Address and Carbon Cycle - Networks* — *Chaired by Arlyn Andrews*

08:15 - 08:45　**KEYNOTE:** National Emissions Verification by Merging Earth System Measurements, Global Social Data　24
and Earth System Models
　　　　　　Ronald G. Prinn (Massachusetts Institute of Technology (MIT), Cambridge, MA)

08:45 - 09:00　Earth Networks Update on Global Greenhouse Gas (GHG) Monitoring Network　25
　　　　　　Bob Marshall (Earth Networks, Inc., Germantown, MD)

09:00 - 09:15　Comparison of Primary Standards/Scales of Key Greenhouse Gases Between NOAA and NIST　26
　　　　　　Jerry Rhoderick (National Institute of Standards and Technology (NIST), Gaithersburg, MD)

09:15 - 09:30　The Value of On-site Comparisons During WCC Audits for Methane, Carbon Dioxide and Carbon Monoxide　27
　　　　　　Christoph Zellweger (EMPA, Laboratory for Air Pollution/Environmental Technology, Duebendorf, Switzerland)

09:30 - 09:45　*In Situ* CO_2 Monitoring Network Evaluation and Design: A Criterion Based on Atmospheric CO_2 Variability　28
　　　　　　Yoichi Shiga (Department of Civil and Environmental Engineering, Stanford University, Stanford, CA)

• *09:45 - 10:15*　*Morning Break*

• *Session 6*　　*Carbon Cycle - Large Scale Observations* — *Chaired by John Miller*

10:15 - 10:30　Variation of CO_2 Mole Fraction in the Lower Free Troposphere, in the Boundary Layer and at the Surface　29
　　　　　　Laszlo Haszpra (Hungarian Meteorological Service, Budapest, Hungary)

10:30 - 10:45　The ODIAC - The Second Fossil Fuel CO_2 Emission Dataset for CarbonTracker　30
　　　　　　Tomohiro Oda (Cooperative Institute for Research in Atmospheres, Colorado State University, Fort Collins, CO)

10:45 - 11:00　Global Monitoring: CARIBIC Aircraft Data for CO, Greenhouse Gases (GHGs), and Non-methane　31
Hydrocarbons
　　　　　　Carl Brenninkmeijer (Max Planck Institute for Chemistry, Mainz, Germany)

11:00 - 11:15　The Evolution of Atmospheric CO_2 Variations in a Coupled Carbon-climate Model　32
　　　　　　Gretchen Keppel-Aleks (University of California, Department of Earth System Science, Irvine, CA)

11:15 - 11:30　Estimating North America Carbon Fluxes Through Lagrangian Inverse Modeling for CO_2 and OCS　33
　　　　　　Huilin Chen (NOAA Earth System Research Laboratory, Boulder, CO)

11:30 - 11:45　AirCore: The Gold Standard for Satellite Evaluation　34
　　　　　　Colm Sweeney (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

• *11:45 - 13:00*　*Catered Lunch Service – Outreach Classroom GB-124 (pre-payment of $12.00 required at registration table)*

Wednesday Afternoon, May 16, 2012 AGENDA

(Only presenter's name is given; please refer to abstract for complete author listing.)

KEYNOTE: National Emissions Verification by Merging Earth System Measurements, Global Social Data and Earth System Models

R.G. Prinn

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With the risks of climate change becoming increasingly evident, there is growing discussion regarding international treaties and national regulations to lower greenhouse gas (GHG) emissions. Enforcement of such agreements is likely to depend formally upon national and sectoral emission reporting procedures ("bottom-up" methods). However, for these procedures to be credible and effective, it is essential that these reports or claims be independently verified. In particular, any disagreements between these "bottom-up" emission estimates, and independent emission estimates inferred from global GHG measurements and related data ("top-down" methods) need to be resolved. Because emissions control legislation is national or regional in nature, not global, it is also essential that "top-down" emission estimates be determined at these same geographic scales. The current "top down" methods are reviewed, but these are not accurate enough at present for such verification purposes. A comprehensive strategy is described for quantifying and reducing uncertainties in GHG emissions, based on a synthesis of global observations of various types with models (and their adjoints) of the global cycles of carbon dioxide and other GHGs that include both the natural and human influences on these cycles. The overall goal is to establish a global observing and estimation system that incorporates all relevant available knowledge (chemical, physical, biogeochemical, technological and economic) in order to verify GHG emissions, as a key component of any global GHG treaty. Ref: R. G. Prinn, P. Heimbach, M. Rigby, S. Dutkiewicz, J. M. Melillo, J. M. Reilly, D. W. Kicklighter and C. J. Waugh, Report 200, MIT Joint Program on the Science and Policy of Global Change, http://globalchange.mit.edu/files/document/MITJPSPGC_Rpt200.pdf/.
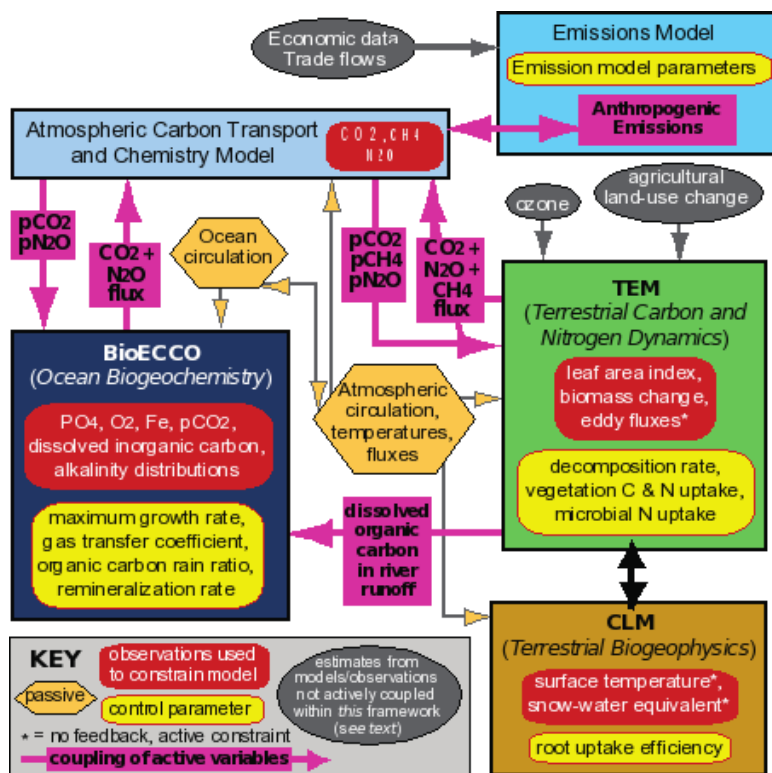

Figure 1. Coupled framework for estimating the rates of cycling of GHGs that have significant natural sources and sinks (e.g. CO_2, CH_4 and N_2O). There are four sub-models (names based on those used at MIT). The two linked terrestrial models form one sub-model in this framework. The four sub-models are linked by the fluxes of the GHGs (purple boxes and arrows). The best possible oceanic and atmospheric circulation data (orange hexagons) are treated as "passive" (not estimated) in the system along with other data (grey ovals). Red boxes give examples of the observations to be used for each sub-model (these are also "state variables" that each sub-model will estimate). The models have multiple uncertain parameters (examples in yellow boxes) treated as "control" parameters that are optimized so that the model system will be brought closer to the observed system.

Earth Networks Update on Global Greenhouse Gas (GHG) Monitoring Network

B. Marshall

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Earth Networks is collaborating with partner organizations to deploy GHG measuring instruments on a global scale for providing key science data behind carbon emissions and environmental patterns utilizing a top-down methodology for measurement, reporting and verification. Since the launch in January 2011, Earth Networks has begun deployment of the 100 sensor global network and has partnered with key institutions to develop the measurement science and tools necessary for informing the research community, policy-makers and private industry with more precise environmental intelligence of GHG levels and emissions. The following updates on the network deployment and partner activities will be discussed in this presentation:

- **NETWORK DEPLOYMENT:** Current deployment of 20 sensors in the U.S. and plans for future global site installations,
- **NOAA/ESRL:** Partnership between Earth Networks and NOAA/ESRL provides a framework for joint research and future cooperative ventures involving the use of Earth Networks GHG. NOAA/ESRL will use the GHG data collected from this network to complement the data from its existing observation and analysis network to support the environmental research missions of the ESRL Global Monitoring Division. Further, Earth Networks will use gas calibration standards from NOAA/ESRL that ensure compatibility with the World Meteorological Organization scales for GHGs,
- **NIST/INDIANAPOLIS FLUX EXPERIMENT**: Working with the National Institutes of Standards and Technology (NIST) and leading university researchers as part of an ongoing project to develop regional-level and urban-scale top-down methodologies based on extensive measurements of atmospheric GHG for emissions quantification and removals in and around the city of Indianapolis, Indiana (INFLUX),
- **CALIFORNIA MEASUREMENTS:** Collaboration with the State of California and leading atmospheric scientists from Scripps Institution of Oceanography, UC San Diego, and Lawrence Berkeley National Laboratory (Berkeley Lab) to deploy an advanced network of GHG monitoring stations for measuring concentrations of atmospheric carbon dioxide (CO_2) and methane (CH_4) throughout California, which has committed to reducing GHG emissions to 1990 levels by the year 2020. California policy-makers will directly benefit from the findings of this study, which will be applicable to any U.S. state and nationwide,
- **ICOS:** Partnering with ICOS, a European consortium of national climate research institutes from 17 countries, to work closely with ICOS' extensive network of climate scientists to increase the size of Europe's GHG monitoring network and collaborate on data management standards for the measurement, storage, and exchange of atmospheric GHG data,
- **SCRIPPS INSTITUTION OF OCEANOGRAPHY:** Earth Networks and Scripps Institution of Oceanography are working in close collaboration for the deployment of the largest global GHG observation network. Scripps scientists are playing a vital role in advising Earth Networks regarding the network design, methods to ensure data quality, and linking the network data to atmospheric modeling experts at research institutions around the world.
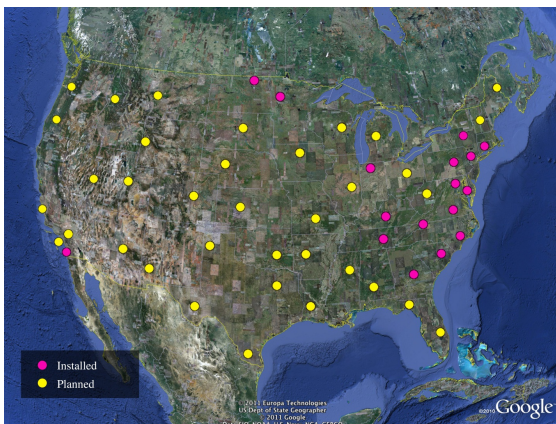

Figure 1. Earth Networks U.S. GHG Monitoring Network.

25

Comparison of Primary Standards/Scales of Key Greenhouse Gases Between NOAA and NIST

J. Rhoderick[1], M. Kelley[2], W. Miller[2], G. Mitchell[2], J. Carney[2], F. Guenther[2], B. Hall[3], E. Dlugokencky[3], D. Kitzis[3] and P. Lang[3]

[1]National Institute of Standards and Technology (NIST), 100 Bureau Drive, Gaithersburg, MD 20899; 301-975-3937, E-mail: george.rhoderick@nist.gov
[2]National Institute of Standards and Technology (NIST), Boulder, CO 80305
[3]NOAA Earth System Research Laboratory, Boulder, CO 80305

The Gas Metrology Group of the Analytical Chemistry Division at NIST and the Global Monitoring Division of NOAA/ESRL have been collaborating on comparison of standards for key greenhouse gases: CH_4, N_2O, CO and CO_2. These collaborations help to support NOAA as well as providing a solid link to the Gas Analysis Working Group of the Consultative Committee on the Quantity of Material (CCQM) – Metrology in Chemistry consisting of National Metrology Institutes worldwide, with NOAA being the World Meteorological Organization representative laboratory to the CCQM. Data on recent comparisons of current standards/scales indicate agreement to within 2.5 ppb (0.14 % relative) for CH_4 and 0.07 ppb (0.02 %) for N_2O. Based on the current NOAA 2005 CH_4 scale and applying a correction to previous comparisons (1998), the agreement between NIST/NOAA has been consistent for years. NISTs historical CH_4 analytical data set demonstrates 40 years of consistency for CH_4 in their primary standards and Standard Reference Materials (SRM). The current (2011) NIST N_2O primary standards suite has led to hard evidence as the reason for a 1.2 % disagreement between NIST/NOAA reported in 2004. Differences in N_2O values obtained by NIST using different analytical instrumentation will be discussed. Data for comparison of CO and CO_2 standards will hopefully be available for discussion. NOAA has also provided cylinders of Niwot Ridge dry air which has been analyzed for these species by both laboratories and will eventually be dual-certified as a NIST SRM. The CH_4 and N_2O data for these cylinders show very good cylinder-to-cylinder consistency between NIST and NOAA.
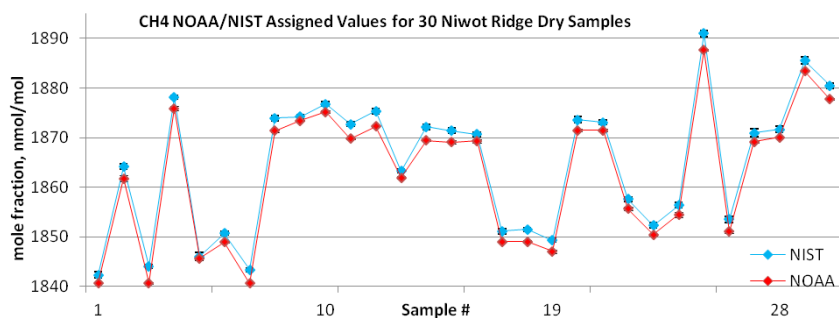

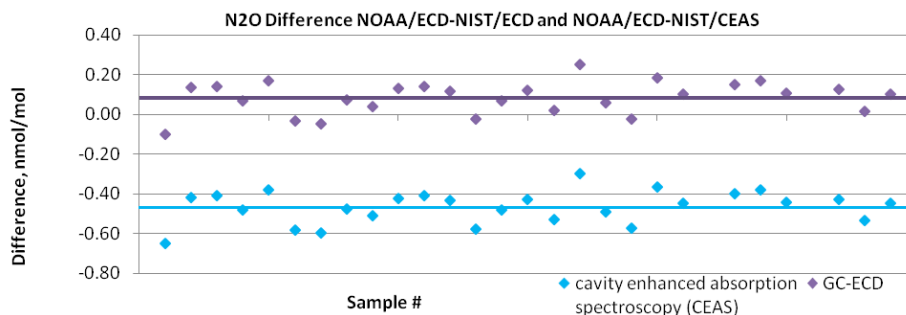**Figure 1.** CH_4 NOAA/NIST assigned values for 30 Niwot Ridge dry samples.

Figure 2. N_2O difference NOAA/ECD-NIST/ECD and NOAA/ECD-NIST/CEAS.

The Value of On-site Comparisons During WCC Audits for Methane, Carbon Dioxide and Carbon Monoxide

C. Zellweger[1], J. Hatakka[2], M. Steinbacher[1] and B. Buchmann[1]

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The Swiss Federal Laboratories for Materials Science and Technology (or Empa) operates the World Calibration Centre (WCC) for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide (WCC-Empa) within the Global Atmosphere Watch (GAW) Program. It was recognized that parallel measurements in addition to the comparison of a limited number of compressed gases during on-site audits provide valuable information about data quality and data compatibility within a network. For this purpose, WCC-Empa is using a Picarro G2401 travelling instrument. During comparisons, the measurement set-up is made as independent as possible, and the WCC instrument is using its own calibration standards and inlet system (next to the existing inlet).

A first comparison was made in 2011 at the GAW station Cape Point, which resulted in valuable findings concerning the drying system for CH_4 and CO_2. However, it was also recognized that the Picarro G2401 instrument was biased especially at low CO mole fractions due to imperfect compensation of the H_2O and CO_2 cross sensitivities (Figure 1, left panel). In the meantime, better correction functions were implemented (Figure 1, right panel), which should allow more accurate CO measurements over the entire mole fraction range.

This presentation will focus on technical advances in the water vapor correction, and first preliminary results of an on-site comparison at the GAW station Pallas (PAL) (starting in April 2012) will be presented. PAL is also operating a Picarro G2401 instrument, which is in contrast to the WCC-Empa analyzer drying the sample air by a Nafion dryer. In addition, CO_2 is also measured with an NDIR system (Licor-7000), and CO with a GC with mercuric oxide detector (Peak Performer 1 RCP).
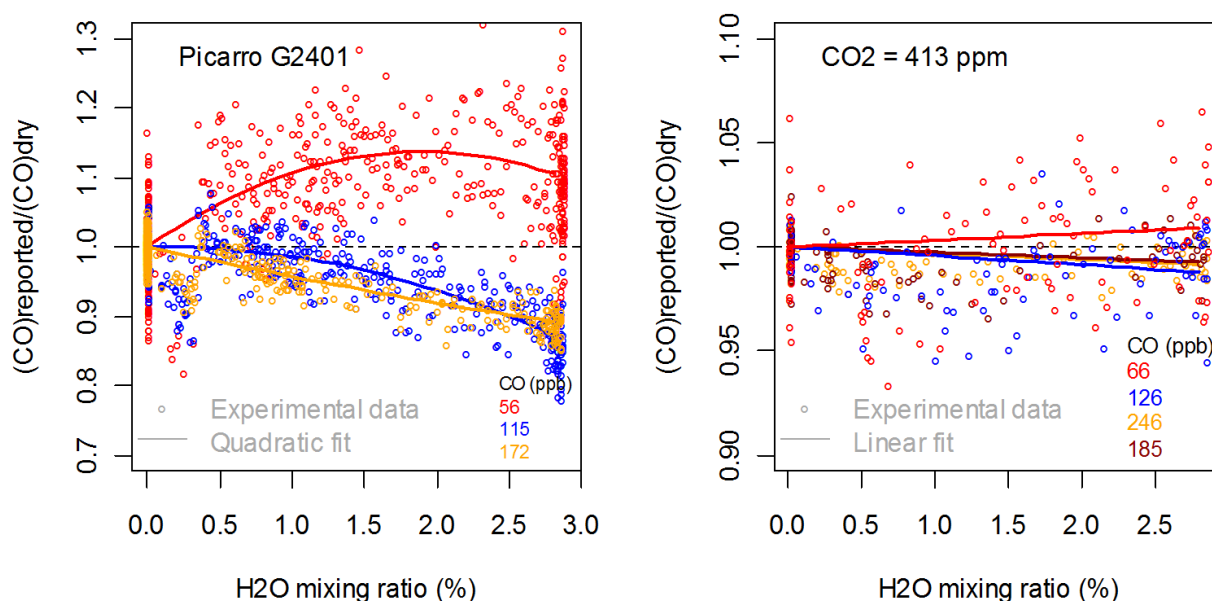

Figure 1. Ratios of COreported/COdry mole fractions vs. the water vapor mixing ratios of a Picarro G2401 instrument for different CO levels. Left: before optimization of the water vapor correction function (individual 1-min measurement points and quadratic fits). Right: after optimization (linear fits).

In Situ CO$_2$ Monitoring Network Evaluation and Design: A Criterion Based on Atmospheric CO$_2$ Variability

Y. Shiga[1], A.M. Michalak[2], A. Chatterjee[3], D. Hammerling[3], K.L. Mueller[4], S.M. Gourdji[5], V. Yadav[2], S.R. Kawa[6] and R.J. Engelen[7]

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Inverse modeling methods for estimating fluxes of carbon dioxide (CO$_2$) rely on networks of atmospheric CO$_2$ measurements. The network of continuous observations in North America grew from 9 continuous CO$_2$ monitoring towers in 2004 to approximately 39 in 2008. Despite its growth, the sparseness of the network has been cited as a limiting factor in the effort to constrain CO$_2$ fluxes at sub-continental scales. Current methods to assess the number and optimal locations for additional monitoring sites either rely heavily on expert opinion, which can be subjective, or on observational system simulation experiments, which are computationally expensive and are sensitive to specific inverse model assumptions. To bridge the gap between these methods we propose a flexible and computationally inexpensive quantitative tool to examine current and future atmospheric CO$_2$ monitoring network configurations. This tool has been developed to inform the expansion of continuous CO$_2$ monitoring stations based upon an understanding of the variability in the atmospheric CO$_2$ signal as represented in modeled CO$_2$ fields. The spatial variability is quantified through a geostatistical analysis that yields information about the spatial scales over which the CO$_2$ concentrations are correlated. This information is then used to assess the coverage provided by an existing network and to inform the optimal placement of towers for network expansions. The approach places towers using knowledge of both the location of pre-existing towers, as well as the local variability in the atmospheric CO$_2$ signal.

Two sample hypothetical networks are created to cover North America with varying degrees of coverage. The less strict coverage regime yields an additional 8 towers relative to the 2008 North American network, while the more stringent regime requires an additional 43 towers. The additional constraint provided by the two hypothetical networks is evaluated relative to the 2008 network using a synthetic data inversion. Overall, the hypothetical networks show marked improvement over the pre-existing 2008 network, and offer insights into addressing the limitations of the current network.
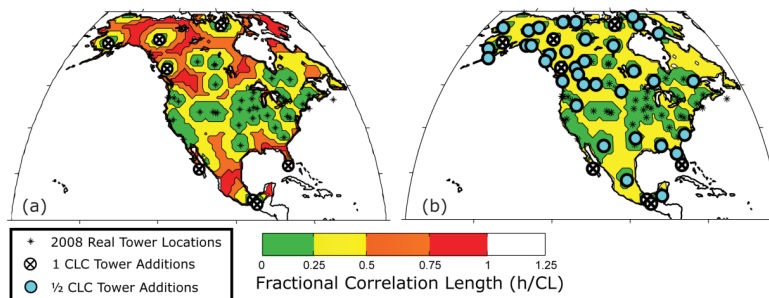
Figure 1. Hypothetical network expansion based on a criterion that a tower must be available within a) one (1 CLC) and b) a half (1/2 CLC) correlation length of CO$_2$ variability at each location. As per the requirement, the entire continent is covered in red for 1 CLC network and yellow for ½ CLC network.

Variation of CO_2 Mole Fraction in the Lower Free Troposphere, in the Boundary Layer and at the Surface

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Eight years of occasional flask air sampling and 3 years of frequent *in situ* measurements of carbon dioxide (CO_2) vertical profiles on board of a small aircraft, over a tall tower greenhouse gases monitoring site in Hungary, are used for the analysis of the variations of vertical profile of CO_2 mole fraction. Using the airborne vertical profiles and the measurements along the 115 m tall tower it is shown that the measurements at the top of the tower estimate the mean boundary layer CO_2 mole fraction during the mid-afternoon fairly well, with an underestimation of 0.27 - 0.85 µmol mol^{-1} in summer, and an overestimation of 0.66 - 1.83 µmol mol^{-1} in winter. The seasonal cycle of CO_2 mole fraction is damped with elevation. While the amplitude of the seasonal cycle is 28.5 µmol mol^{-1} at 10 m above the ground, it is only 10.7 µmol mol^{-1} in the layer of 2500 - 3000 m corresponding to the lower free atmosphere above the well-mixed boundary layer. The maximum mole fraction in the layer of 2500 - 3000 m can be observed around 25 March on average, two weeks ahead of that of the marine boundary layer reference (GLOBALVIEW). By contrast, close to the ground, the maximum CO_2 mole fraction is observed late December, early January. The specific seasonal behavior is attributed to the climatology of vertical mixing of the atmosphere in the Carpathian Basin.
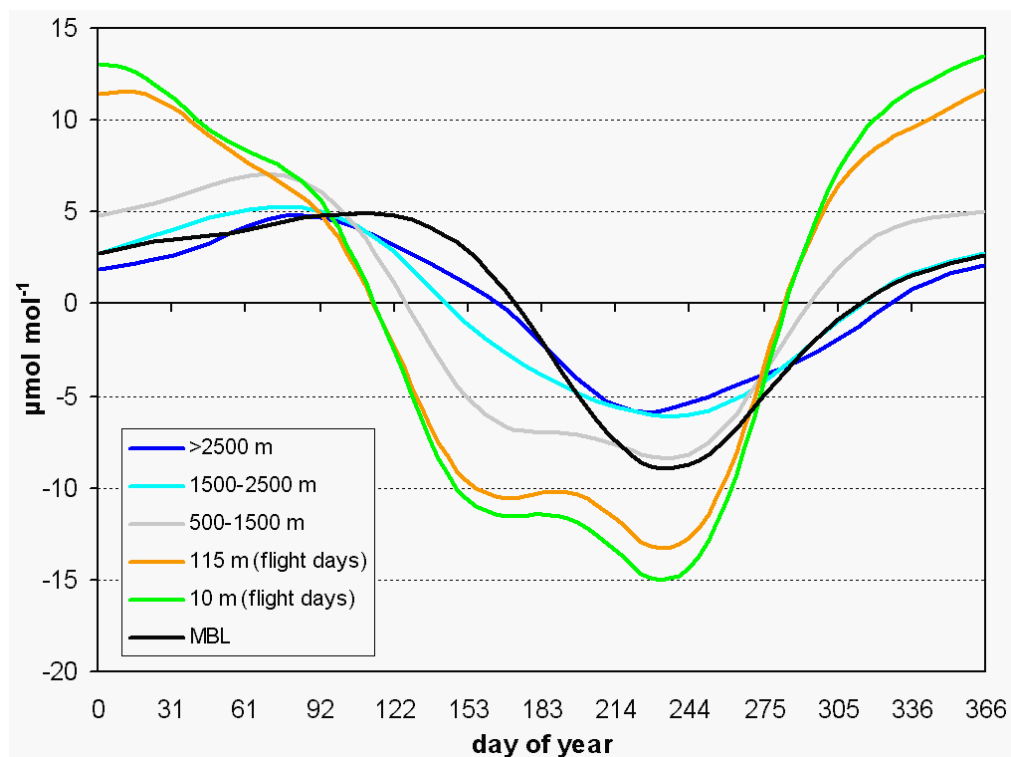

Figure 1. Mean seasonal cycle of atmospheric carbon dioxide mole fraction (relative to the corresponding annual average) at different elevations above the ground (aircraft and tower) and in the modeled marine boundary layer (MBL – GLOBALVIEW-CO_2).

The ODIAC - The Second Fossil Fuel CO_2 Emission Dataset for CarbonTracker

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Fossil fuel CO_2 emission (FFCO2) is a critical component in conventional inverse estimations of surface CO_2 sources and sinks. Unlike biospheric fluxes and oceanic exchanges, FFCO2 is often assumed to be a perfect quantity and is then never optimized. Thus, FFCO2 needs to be prescribed accurately in atmospheric CO_2 simulations. Here, we present version 3.0 of the global gridded FFCO2 dataset ODIAC (Open-source Data Inventory for Anthropogenic CO_2, hereafter ODIAC ver. 3.0). ODIAC ver. 3.0 dataset (currently available for 2000-2010) differs from the previous products in several points: 1) national emission estimates, 2) spatial proxy data, and 3) inclusion of montly variations. National emission estimates used for ODIAC ver. 3.0 are based on data published by Carbon Dioxide Information Analysis Center (CDIAC). Emission estimates for 2000-2007 are based on CDIAC data. Those over the last three years (2008-2010) were projected using BP's fuel consumption statistics. Spatial distributions of emissions in earlier versions of ODIAC were determined/estimated using power plant emissions and geographic locations in addition to satellite-observed nightlights. In ODIAC ver. 3.0, we also employed other available proxy data according to emission type, such as a nightlight data for gas flaring, and aircraft and ship tracks adopted from EDGAR and AERO2k emission inventories. Temporal variations of emissions are modeled on monthly basis using CDIAC's monthly global FFCO2 dataset for land and AERO2k for aviation. The ODIAC ver.3.0 is being used for prepartion of the next release of CarbonTracker as the second fossil fuel FFCO2 dataset.
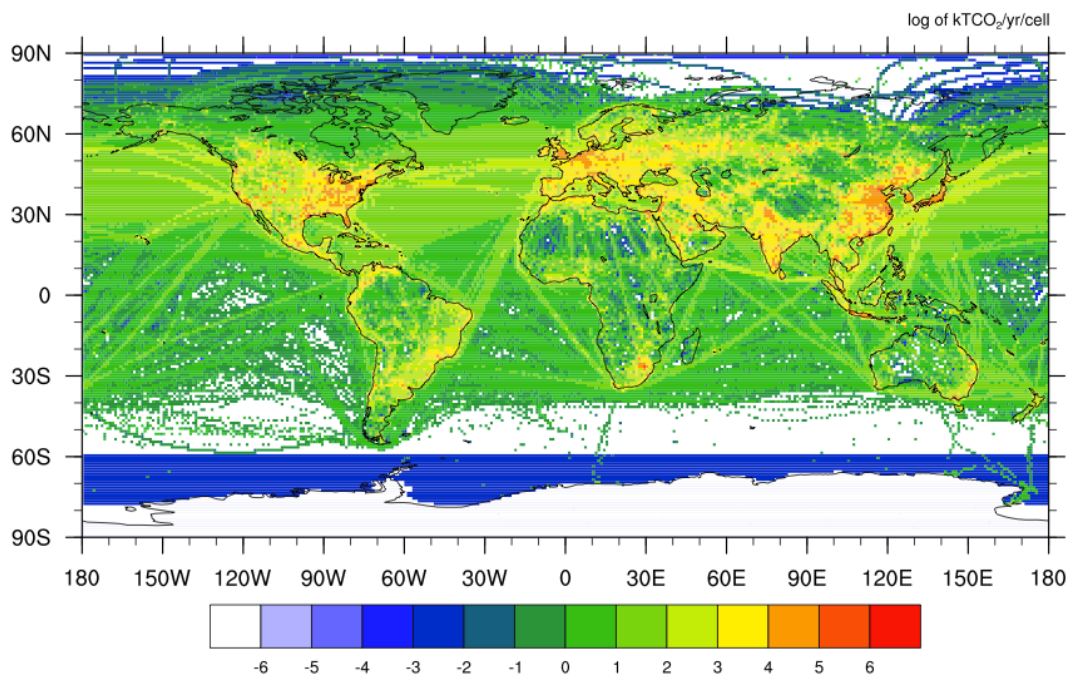

Figure 1. The spatial distribution of fossil fuel CO_2 emissions for year 2010 ($1° \times 1°$ resolution). The values are given in the units of the log (base 10) of kiloton CO_2 year^{-1} cell^{-1} to show details in emission spatial distribution.

Global Monitoring: CARIBIC Aircraft Data for CO, Greenhouse Gases (GHGs), and Non-methane Hydrocarbons

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The current Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC) measurement container has been in operation since 2005 with a steadily increasing performance. Installed in the cargo bay of a Lufthansa Airbus A340-600 for 4 long distance flights each month we have covered over 2 million miles (www.caribic-atmospheric.com). Presently we are adding CH_4 to our suite of *in situ* measurements, which already included gases such as CO_2, O_3, CO and water vapor. However, the most information is gained from analysis of monthly whole air samples; comprising 28 glass flasks each month, plus 88 stainless steel flasks since May 2010. In many cases it is an advantage to sample remotely from sources and sinks, which was also a philosophy of the early monitoring sites. In this respect the CARIBIC dataset, and the one from the sister project CONTRAIL (http://www.cger.nies.go.jp/contrail/contrail.html), offer perhaps the largest *in situ* datasets of GHGs in upper tropospheric and free tropospheric air. On the other hand, whenever flight routes pass over regions of strong convection, e.g. tropical Africa (Figure 1), more direct information about sources and sinks is obtained. The clearest example we know in this respect is the Indian monsoon, where a large scale waxing and waning distribution of trace gases is formed spanning thousands of kilometers. With the support of transport models the CARIBIC data can be used to constrain the uptake and release of CO_2 and the production of CH_4. Additionally, using tracer-tracer correlations, for instance between CH_4, CO and C_2H_6, one can even make estimates about sources without calling the help of a model. In addition to GHGs, CARIBIC data show the distribution of non methane hydrocarbons over Europe. For these gases, even in Europe upper trosheric measurements are sparse. From the examples shown, it is evident that passenger aircraft-based systems have a great potential. In Europe, this is leading to the formation of a measurement infrastructure based on equipment in a number of aircraft giving daily measurements, and in the future to be transmitted partly in near real-time. This infrastructure IAGOS will thus encompass the MOZAIC and CONTRAIL approach, namely a number of aircraft in continuous operation, and the CARIBIC system having fewer flights but more species.
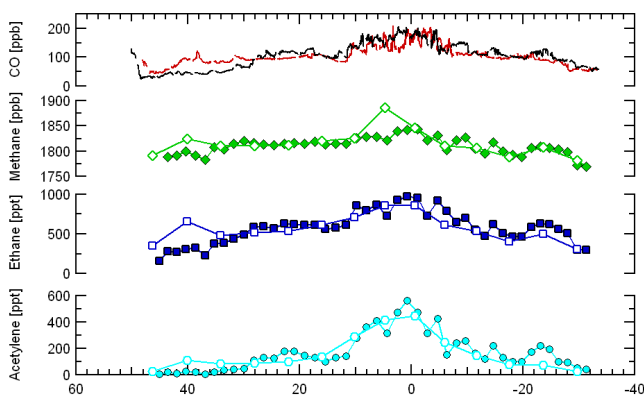

Figure 1. CO, CH_4, C_2H_6 and C_2H_2 at cruise altitude for flights in December 2010 from Frankfurt to Cape Town and back. For CO the flight data to Cape Town are color coded red, and sampling took place with the glass flask system (open symbols). The data for the return flight (closed symbols, many samples) are based on the stainless steel canisters. The profiles show elevated concentrations in the tropics over a large distance. Back-trajectories point to surface air masses that very slowly rose to flight level over a period of 7 days. The profiles for the 2 flights are fairly identical, however the return flight shows low mixing ratios for 30-40 degrees north as the aircraft flew in the lowermost stratosphere.

The Evolution of Atmospheric CO_2 Variations in a Coupled Carbon-climate Model

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We compare patterns in atmospheric CO_2 in the Community Earth System Model (CESM), a coupled carbon-climate model, against several types of atmospheric CO_2 observations characterized by different measurement footprints. We use NOAA/GMD surface and aircraft flask measurements, Total Carbon Column Observing Network total column observations, and HIAPER Pole-to-Pole Observation aircraft transects to evaluate the skill of the coupled model in predicting variations in CO_2 on seasonal, annual, and decadal timescales. We show that the interannual variability in the model responds to climatic drivers and that annual mean spatial gradients are consistent with those seen in observations, but that seasonal variations and horizontal gradients in atmospheric CO_2 are underestimated relative to observations (Fig. 1), suggesting that net ecosystem exchange in the land component of CESM is too weak. Using aircraft data, we show that CO_2 is vertically redistributed too efficiently in the CESM atmosphere, particularly during northern hemisphere summer, which impacts both the spatial and temporal patterns in the model. Despite these limitations in the current realization of CESM, coupled carbon-climate models will become an important tool in constraining the sensitivity of carbon fluxes to future climate change, and therefore in constraining the sensitivity of climatic change to these carbon fluxes. We present a preliminary analysis of changes in atmospheric CO_2 in response to two emission trajectories. These results will be useful in developing future monitoring strategies to resolve changes both in natural carbon fluxes and in anthropogenic emissions of CO_2.
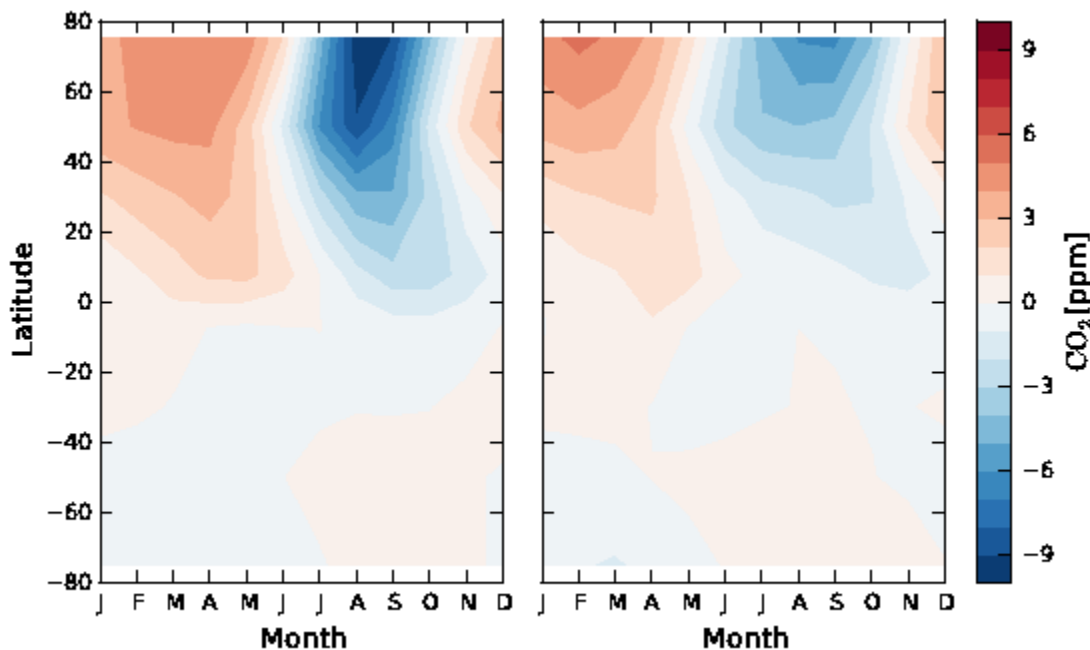

Figure 1. Hovmöller diagram showing seasonal patterns in surface CO_2 in observations (left) and CESM (right). Growing season uptake of CO_2 is weak in the coupled model, resulting on smaller meridional gradients and shallower seasonal cycles in the northern hemisphere.

Estimating North America Carbon Fluxes Through Lagrangian Inverse Modeling for CO_2 and OCS

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Understanding biospheric CO_2 fluxes is paramount if climate studies are to be able to analyze the response of terrestrial ecosystems to climate change and monitor fossil fuel emissions reductions. Carbonyl sulfide (OCS) may be a useful tracer to provide a constraint on Gross Primary Production (GPP). Here we simulate both OCS and CO_2 using the Stochastic Time-Inverted Lagrangian Transport (STILT) model coupled with various biospheric fluxes, such as fluxes estimated from the Simple Biosphere (SiB) model, CarbonTracker, and from the Carnegie-Ames-Stanford Approach (CASA) model. The STILT model is driven by Weather Research and Forecast meteorological fields. This study uses measurements of OCS and CO_2 in 2008 from the NOAA/ESRL tall tower and aircraft air sampling networks, with ~ 6,000 observations in total. Biospheric OCS fluxes are estimated from a GPP-based model coupled with the GPP estimates from above mentioned biosphere models. The Soil uptakes of OCS from SiB and *Kettle et al 2002* are assessed in the Lagrangian data assimilation framework, and are optimized using atmospheric observations of OCS and molecular H_2. Empirical boundary curtains are built based on observations at the NOAA/ESRL marine boundary layer stations and from aircraft vertical profiles, and are utilized as the lateral boundary conditions for OCS and CO_2 for North America. Comparison of the simulations for both OCS and CO_2 using different biospheric fluxes provides an opportunity to assess the performance of both the biospheric models and the representation of atmospheric transport. In addition, we will estimate the carbon fluxes for North America from a joint inversion for OCS and CO_2 in a Bayesian synthesis framework, in which the GPP and Respiration are separately optimized for each vegetation type.
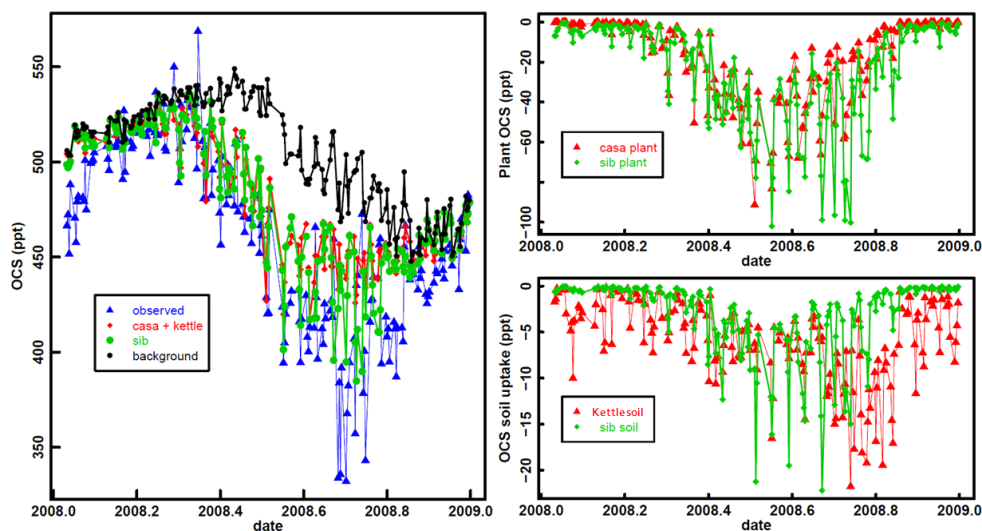
Figure 1. Modeled and observed tall tower OCS concentrations at LEF (left), and simulated OCS components: plant and soil uptake (right).

AirCore: The Gold Standard for Satellite Evaluation

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Satellite retrievals of CO_2 offer an unprecedented opportunity to measure the column mean CO_2 dry mole fractions globally. By monitoring changes in gradients of the column mean over time and space, contributions to atmospheric CO_2 from land and ocean can be estimated to better understand and quantify both anthropogenic and natural sources of CO_2. However, it is critical to modeling and interpreting the column mean that: 1) the CO_2 column mean measured by satellites be directly tied to the World Meteorological Organization (WMO) dry mole fraction scale and 2) the vertical gradients of the column be accurately modeled.

The NOAA/ESRL Carbon Cycle Aircraft Program continues to collect data and develop new instrumentation to directly tie satellite measurements to WMO column mean and better resolve the vertical gradients from the boundary layer through the stratosphere. The most recent advance is the AirCore sampling system which enables profiles from 0 to 30 km, or 99% of the total CO_2 column, to provide a primary standard directly tied to the WMO with an accuracy of better than 0.1 ppm (~ 0.025%), a significant improvement when compared to an uncertainty of 0.4-0.5 ppm of column mean CO_2 from aircraft extrapolated to the full column. The column mean derived from these profiles can be directly compared to Fourier transform spectrometers that make up the Total Carbon Column Observing Network and will serve as transfer standards for satellite retrievals.
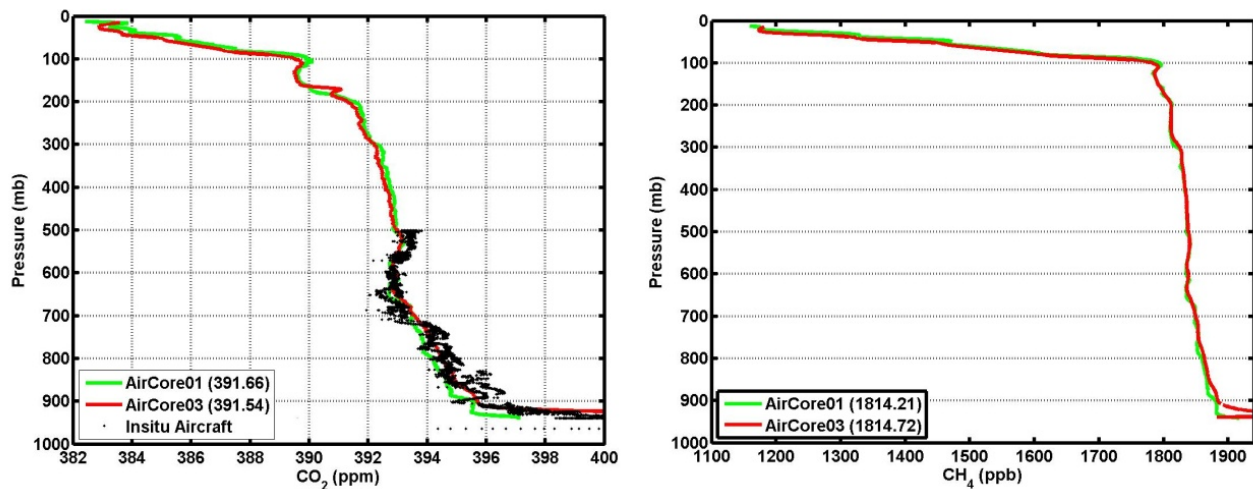

Figure 1. Side by side launches of AirCore at Lamont, OK, on January 15, 2012. This launch shows the replicate profiles demonstrating the reproducibility of the AirCore. Red line shows results from the lightweight AirCore that can be launched without a Federal Aviation Administration certificate of authorization. The column mean for CO_2 between large and small AirCores differed by 0.12 ppm and for CH_4 the column mean differed by 0.5 ppb.

CO$_2$ Measurements from Space: The Japanese GOSAT and NASA OCO-2 Missions

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The Japanese Greenhouse Gases Observing SATellite (GOSAT) and the NASA Orbiting Carbon Observatory (OCO) were the first two satellites designed specifically to collect high resolution spectra of reflected sunlight in shortwave infrared CO$_2$ and O$_2$ bands. These observations can be analyzed to retrieve surface-weighted estimates of the column averaged CO$_2$ dry air mole fraction, X$_{CO2}$. Once validated against surface *in situ* and remote sensing measurements, these X$_{CO2}$ estimates can be combined with the ground based CO$_2$ measurements and assimilated by chemical tracer transport models to quantify CO$_2$ surface fluxes on regional scales over the globe. GOSAT was successfully launched in January 2009 and has been routinely collecting CO$_2$ and CH$_4$ observations over the sunlit hemisphere since April 2009. OCO was lost in February 2009 when its launch vehicle malfunctioned and failed to reach orbit. A replacement, called OCO-2, is under development, in preparation for a late 2014 launch.

Soon after the loss of OCO, its science team began working with the GOSAT Project Team to analyze the observations collected by the GOSAT Thermal and Near-infrared Sensor for carbon Observations-Fourier Transform Spectrometer (TANSO-FTS). Recent X$_{CO2}$ products from this collaboration show little or no bias and random errors that are typically less than 0.5% on regional scales over much of the Earth. Global maps of X$_{CO2}$ for July 2009, October 2009, January 2010, and April 2010 are shown in Fig. 1. These results have been screened for clouds and optically-thick aerosols, and have passed a series of additional data quality filters. The spatial coverage each month is limited by low-solar illumination, persistent cloud cover, and the low reflectance of ocean- and ice-covered surfaces. These GOSAT data products are now being distributed by the NASA Goddard Earth Sciences Data and Information Services Center and tested in flux inversion models.

The OCO-2 instrument and spacecraft development are proceeding rapidly. Once it is successfully launched and inserted into orbit, its data are expected to complement the GOSAT X$_{CO2}$ measurements by providing improvements in coverage, resolution, and sensitivity.
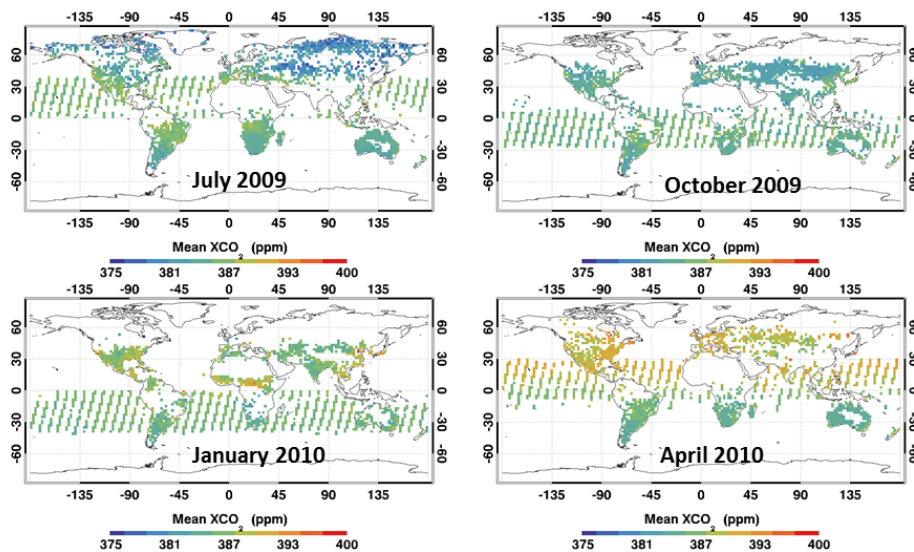

Figure 1. Monthly maps of X$_{CO2}$ retrieved from GOSAT observations by the OCO-2 team. Each data point shows the average value for a 2° by 2° box for the month.

Assessing the Utility of Atmospheric CO_2 Observations from Space (ACOS) V2.10 Greenhouse Gases Observing Satellite (GOSAT) Column CO_2 Retrievals by Comparing to Independent CO_2 Measurements

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Here we evaluate the constraint provided by ACOS v2.10 GOSAT column CO_2 retrievals on sources and sinks of CO_2 at weekly to seasonal time scales by comparing it to the constraint provided by other CO_2 measurement types, such as surface and aircraft profile data from NOAA's *in situ* measurement program, as well as column CO_2 measurements from the Total Carbon Column Observing Network (TCCON). The metric used is the fit to independent CO_2 measurements – those same data sources above that were not included in each inversion.

For our prior, we use both optimized and projected fluxes for 2009-2010 from CarbonTracker (2010 release) run forward through the Parameterized Chemistry Transport Model at 0.5°x0.67° resolution (lat/lon) on 40 vertical layers. We then assimilate the different data products individually (i.e. GOSAT-only, TCCON-only, etc.) to solve for weekly CO_2 flux corrections on a 4.5°x6° grid, using our variational data assimilation approach. Before assimilating the GOSAT data, we apply a bias correction consisting of a 3-parameter fit for each of three data types: ocean glint, high-gain land, and medium-gain land.

We assess each data type by comparing the modeled measurements given by the optimized concentration fields obtained with that type to both: a) those given by the prior fluxes and b) the measurements left out of the inversion. Using the fit to the TCCON column CO_2 measurements as a metric, for example, the bias-corrected GOSAT data improve the fit compared to that given by the prior, as well as that given by the surface *in situ* NOAA data. This suggests that the GOSAT retrievals have utility, at least for constraining the short-term flux variability.
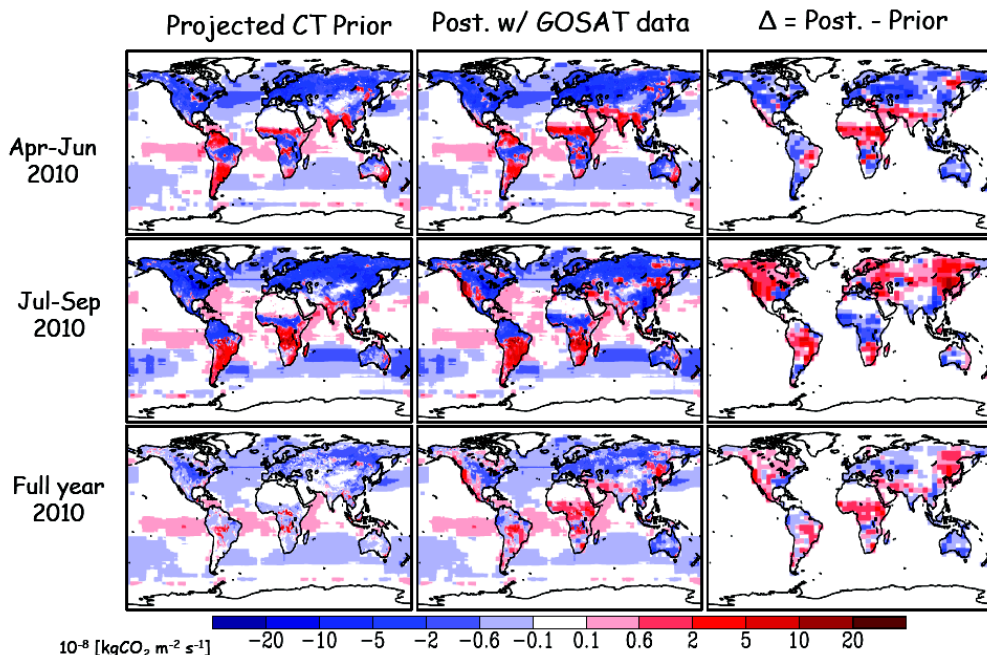

Figure 1. Flux correction obtained by inverting ACOS v2.9 GOSAT column CO_2 measurements in our variational carbon data assimilation system (right column), along with the projected CarbonTracker prior (left) and the a posteriori (center) fluxes. Weekly fluxes were estimated on a 4.5 x 6 deg (lat/lon) grid.

Ultraviolet (UV) Index Climatology of Nepal Himalaya Using Ozone Monitoring Instrument (OMI) Data

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This paper presents the UV index climatology of six stations of Nepal Himalaya using AURA/OMI satellite data. The OMI UV index is first validated with ground data using NILU UV multi-band filter radiometer (MBFR). Ground data from the year 2008 to 2010 covering altitude ranges from 70 m to 2850 m were used to validate the OMI data. The station overpass data of OMI and coincidently measured one-minute resolution ground data were used for the validation. The OMI UV index data are first separated for clear-sky and cloudy-sky condition using Lambert Equivalent Reflectivity (LER) as a proxy. It was found that the relative difference (bias) on OMI UV index varied from 34.5% to 47.9% for cloud free condition and from 106.4% to 286.4% for cloudy condition. More deviation was found on those high altitude stations due to satellite's poor performance on resolving cloud factor. High altitude stations have very high UV index values above 15 during the summer months. The satellite data was then empirically corrected to study the UV index climatology of Nepal Himalaya. A UV index more than 3 in the winter months (e.g. December) and more than 9 during the summer months (e.g. June) are common at most of the stations. High altitude stations have more extreme values (>11) during the summer months.
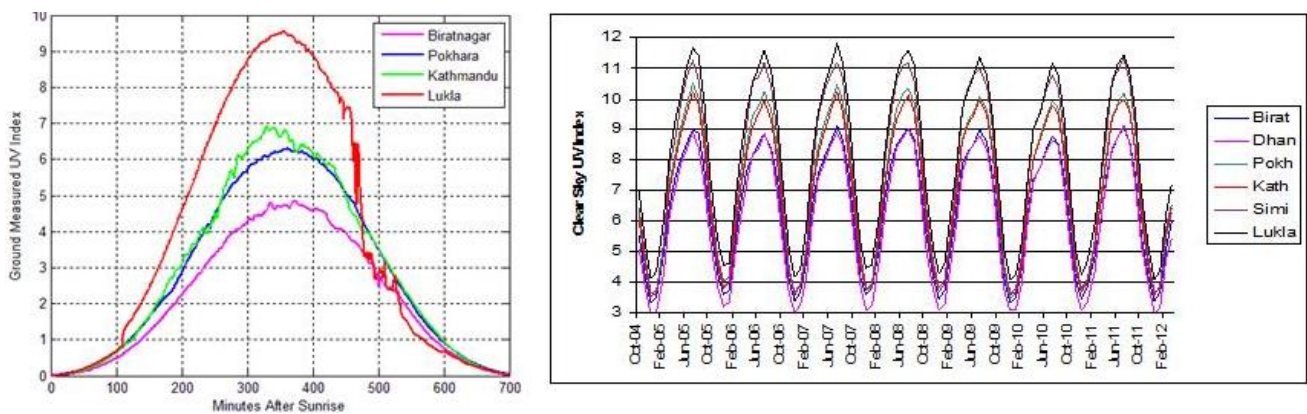
Figure 1. A typical diurnal pattern of ground measured UV index for week 3rd of March 2010 for four stations; Biratnagar (72 m, magenta), Pokhara (850 m, blue), Kathmandu (1350 m, green), and Lukla (2850 m, red) as shown in the left and OMI UV index climatology for six stations at Nepal Himalaya from October 2004 to March 2012.

Spectral and Broadband Albedos - Not an Easy Measurement

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[2]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309

Albedo is usually measured using radiometers with a near-cosine response that respond over a 180º field of view. One is oriented horizontally to measure surface reflected irradiance and the other is oriented horizontally to measure the downwelling solar irradiance. On a clear day the ratio of these two measurements, the measured albedo, varies as a function of the angle between the sun and the zenith direction. The response is also a function of wavelength. In this talk we discuss briefly the normalized difference vegetative index (NDVI), which is defined here as $(A_{870} - A_{673})/(A_{870} + A_{673})$, where the subscripts refer to wavelengths in nanometers and A is the albedo at those wavelengths. Figure 1 shows the behavior of NDVI over a four-year period. Most of the talk will focus on the wavelength and solar zenith angle dependence of snow albedos. These measurements, taken at Table Mountain north of Boulder and at the Sioux Falls SURFRAD site, will be, mostly unfavorably, compared to models and other measurements of snow albedo.

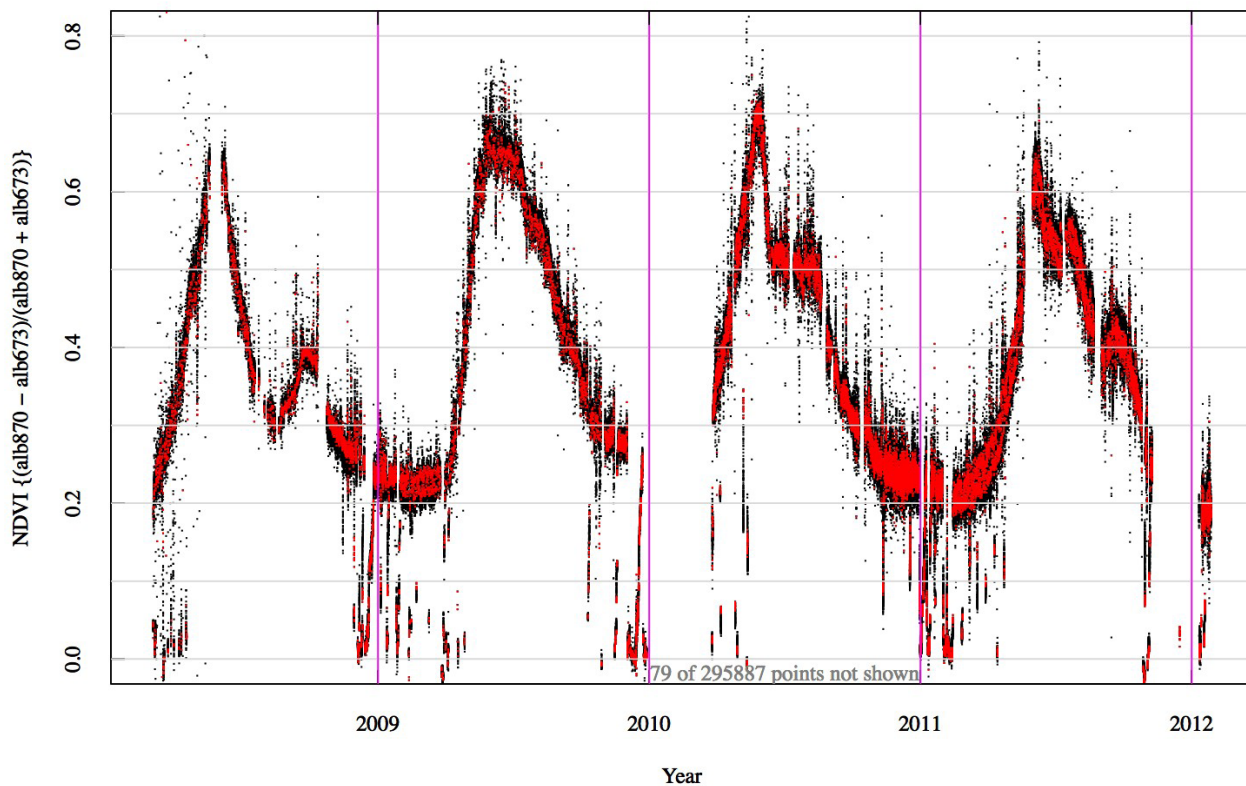**Table Mtn Test Facility (40.1249 N; 105.2368 W)**

Figure 1. The normalized difference vegetative index for Table Mountain, 16 km north of Boulder, Colorado. Note the steep increase with a consistent peak in late May with a minimum in mid winter. After the May peak the path toward the winter minimum depends primarily on precipitation, and has a different character in each of the four years of this measurement history.

Possible Extraterrestrial Solar Radiation (ETR) Spectral Variations in the Ultraviolet and Visible: A Test for Ground-based Instrumentation

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There have been recent (2009/10) suggestions, based on satellite observations and certain theoretical estimates, that the magnitude of spectral variations of the ETR over the course of the last (and presumably other) sunspot cycle(s) could be considerably larger than previously known. These variations, when incorporated into global atmospheric models, have indicated a profound impact on both stratospheric ozone and the global heat budget with subsequent substantial effects on atmospheric circulations and hence decadal-scale climate. Although not intended to monitor the ETR but rather ozone-induced changes, near continuous spectral solar irradiance observations (300 nm to < 450 nm) at the earth's surface were begun by GMD and others in the mid 1990s and continue to date. It is proposed that with careful selection of these observations, the solar cycle ETR spectral variations can be further investigated. The selection of data is based on the availability of clear pristine days and use of an appropriate spectral range where no significant spectral variations are introduced by atmospheric constituents. This proposition is further based on the rather large magnitude and distinctive spectral signature of the recently suggested variations. This presentation will report on a preliminary effort to identify a subset of the proposed spectral ETR changes using surface observations from Mauna Loa Observatory (MLO). The spectrometer used at MLO was designed and built by the New Zealand National Institute for Water and Atmospheric Research (NIWA) and has been operated jointly by NIWA and GMD. The measurements are routinely calibrated with both internal and external standard lamps traceable to NIST and the instrumentation has proven to be remarkably stable and robust over the course of its near continual deployment at MLO. Our preliminary results (Fig. 1) suggest that many of the spectral features are similar between model-provided results and the observations. The intent of the ongoing investigation is to provide independent constraints for the recently suggested ETR spectral variations from satellite observations and various models. Similar observations have been made at other higher altitude GMD sites at the South Pole and Boulder that will be incorporated into this work. Further work will also include extending the useful wavelength range of the surface observations by accounting for ozone and atmospheric pressure variability. A near continuous, several-days-per-week, time series of these results over the past 16 years can be obtained from the MLO observations.
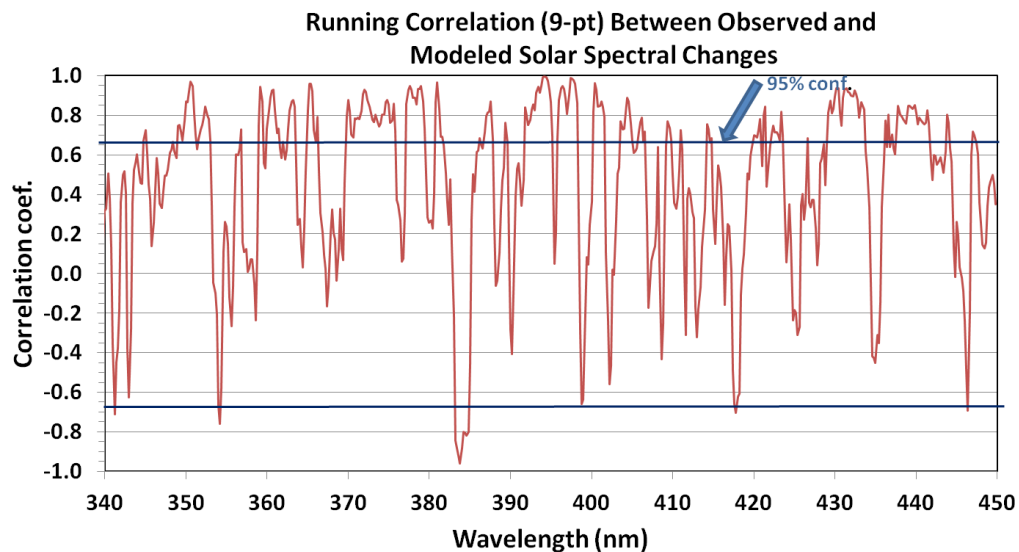

Figure 1. Correlation between the MLO surface-observed and modeled ETR solar spectra differences between high and low solar activity, (April. 2004 and Nov. 2007 respectively).

Radiative Forcing Efficiency of a Forest Fire Smoke Plume at the Surface and Top Of the Atmosphere (TOA)

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On 6 Sept. 2010, at about 10:00 AM LST a forest fire developed northwest of Boulder, Colorado. The smoke plume was carried eastward through a dry cloudless sky and drifted over several sets of instruments that were ideal for computing the surface radiative forcing efficiency (RFE) of the aerosol [*Stone et al*. 2011]. Persistent clear skies permitted unrestrained Aerosol Optical Depth (AOD) calculations throughout the day. Surface-measured AOD_{500nm} ranged from background values (0.045 prior to the event) to a peak of ~3.5. Surface RFE was documented over a wide range of solar zenith angles (SZA) for a surface albedo of 0.15. Surface RFE_{sw} varied from -194±10 at high sun (35° SZA) to -81±9 $Wm^{-2}AOD_{500}^{-1}$ at low sun (73° SZA), while RFE_{lw} was stable at +10±7 $Wm^{-2}AOD_{500}^{-1}$ throughout the day and night. Diurnally averaged RFE for Shortwave (SW), Longwave (LW) and all-wave net radiation at the surface were -61.5, +10.0, and -51.5 $Wm^2AOD_{500}^{-1}$, respectively. Computation of the plume's radiative effect at the TOA and the subsequently inferred total atmospheric heating induced by the plume requires space-borne measurements of outgoing SW and LW irradiance. NASA/CERES broadband measurements aboard its EOS satellites would be best for this task, but the plume was too small compared to the CERES footprint. The higher resolution (500 m) MODIS satellite imager did sample the smoke plume about three hours after the fire started at about 1300 LST. However, MODIS does not provide a broadband TOA irradiance product but samples spectrally at several solar wavelengths. We will estimate the total broadband SW radiative effect of the smoke plume at TOA using MODIS data and the Fu-Liou radiative transfer model. First, we will convert the MODIS spectral sampling to broadband SW using empirical methods, and then analyze the MODIS-derived broadband irradiance from the plume and clear areas outside of the plume to infer the RFE_{sw} at TOA. Our empirical results will be compared to radiative transfer model calculations.

R. S. Stone, J. A. Augustine, E. G. Dutton, N. T. O'Neill, and A. Saha (2011), Empirical determinations of the longwave and shortwave radiative forcing efficiencies of wildfire smoke, *J. Geophys. Res.*, 116, D12207, doi:10.1029/2010JD015471.
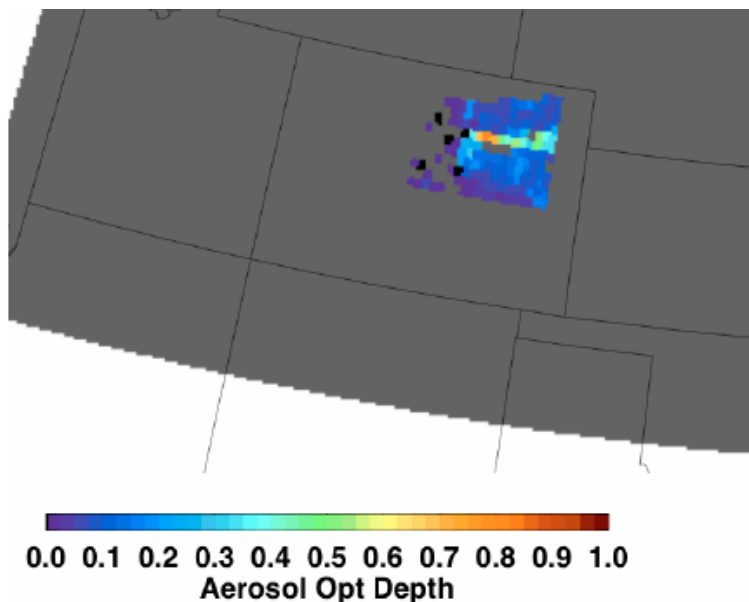

Figure 1. NASA MODIS processed AOD image of the Fourmile Canyon wildfire smoke plume at 1300 LST, 6 Sept. 2010.

Oxygenated Volatile Organic Compounds (OVOCs) in the Remote Marine Troposphere: Results from the Cape Verde Atmospheric Observatory (CVAO)

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OVOCs in the atmosphere are precursors to peroxy acetyl nitrate (PAN), affect the tropospheric ozone budget, and in the remote marine environment represent a significant sink of the hydroxyl radical (OH). The sparse observational database for these compounds, particularly in the tropics, contributes to a high uncertainty in their emissions and atmospheric significance. Here we show multi-annual measurements of acetone, methanol and acetaldehyde in the remote marine boundary layer made between October 2006 and September 2010 at the CVAO (16,848°N, 24.871°W), a subtropical marine boundary layer global Global Atmosphere Watch Station situated on the island of São Vicente. All three OVOCs show similar seasonal cycles with higher values observed in March and September and lowest in December and January. Simulations of OVOCs at Cape Verde using the CAM-Chem global chemical transport model show reasonable agreement with acetone concentrations (mean observed:model ratio of 1.23) but large discrepancies with acetaldehyde (model underestimation of a factor of 25) and methanol (model underestimation of a factor of 3). The model predicts a strong summer minimum in acetaldehyde and a broad summer maximum in methanol, whereas the observations showed much less pronounced seasonal cycles although with spring and autumn peaks. The standard CAM-Chem model was adapted to include a two-way sea-air flux parameterisation based on seawater measurements made in the Atlantic Ocean and these measurements suggest that the tropical Atlantic region is a net sink for acetone but a net source for methanol (contrary to many previous assessments) and acetaldehyde. The "ocean model" resulted in improved simulations of atmospheric methanol and acetaldehyde, although still with a four-fold underestimation in acetaldehyde concentrations. However, these simulations produced a poorer agreement with acetone (new observed:model ratio of 1.88) and no improvement in the predicted seasonal variability of the OVOCs. We suggest that terrestrial biogenic African and North American primary and/or secondary OVOC sources are also underestimated by the model, and that this may explain the very pronounced model underestimation of OVOC concentrations in autumn and spring, respectively. The secondary production of OVOCs from higher alkanes produced biogenically from plants or from the ocean may also play an important part in model uncertainties.
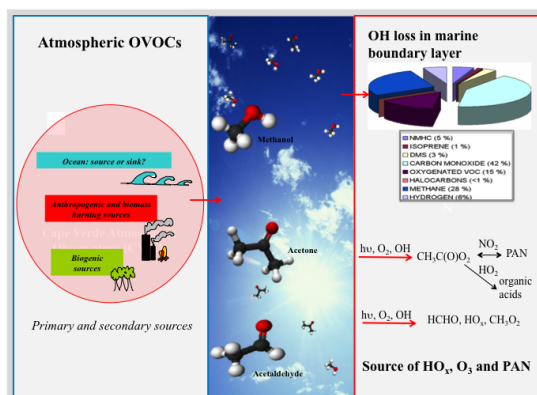
Figure 1. Atmospheric OVOCs.

Observations of Springtime Surface Ozone Depletion at Toolik Lake, Alaska (AK)

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Surface O_3 concentrations were measured at Toolik Lake, AK (68.63° N, 149.59° W; 720 m elevation) during Sept 2010 – Sept 2011 as part of a larger study investigating the role of snow over tundra and snow over a frozen lake on the chemistry of the near-surface atmosphere. Episodic springtime depletion of O_3 and gaseous elemental mercury (GEM) were observed at this inland site, which sits approximately 225 km from the coast at the northern border of the foothills of the Brooks Range. These observations were compared with surface O_3 data from Barrow, AK provided by the NOAA/ESRL Global Monitoring Division. In certain cases, especially during early spring, depletion events were observed at the coastal Barrow site, yet not at Toolik Lake. Throughout April and early May 2011, O_3 and GEM depletion were observed at both locations (Figure 1). In all cases when depleted air masses were observed at Toolik Lake, similar events were also recorded at Barrow. In this study, back-trajectory analyses and locally measured turbulence and meteorological parameters are implemented in order to interpret the observed depletion events.
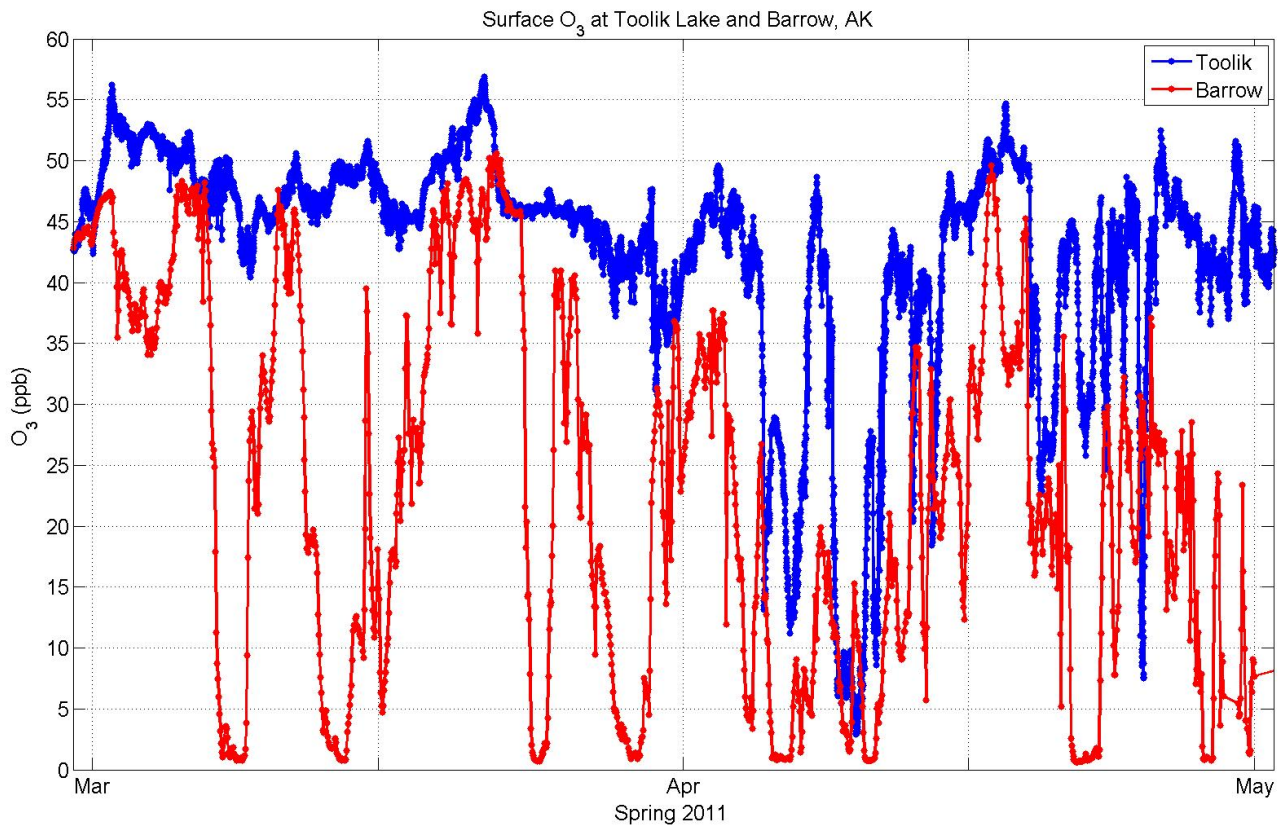

Figure 1. Shown are surface O_3 observations measured by Ultraviolet photometric O_3 analyzers. The red line shows data from Barrow, AK, and the blue line indicates data from Toolik Lake, AK, approximately 400 km to the south-east. As shown by the rapid decreases to near-zero O_3 values, O_3 depletion events were observed at both locations through the spring of 2011.

Comparison of Continuous Surface Ozone Measurements from Two Arctic Observatories

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The Hydrometeorological Observatory of Tiksi and NOAA's Barrow, Alaska Observatory are equipped with Thermo Scientific Model 49 Ozone Analyzers and have been continuously measuring surface ozone levels since October 2010. The two observatories are in the Arctic Circle at similar latitudes of 71.6°N and 71.3°N, respectively. Their locations provide a unique opportunity for measurement comparison due to minimization of solar zenith angle differences. Instrumentation at the site, data collection and quality assurance are discussed. General seasonal trends are presented and we quantify mean surface ozone levels. Both stations show surface ozone depletion events during 2011, likely due to high bromine originating in nearby ice leads. The events were investigated using back trajectories from the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) Model. At both observatories, back trajectories during depletion events indicate winds passed over the ice leads prior to reaching the stations. However, due to differences of seasonal ice lead longevity at the two sites, the depletion events were found in different months. In addition to study conclusions, recommendations for further study are also discussed.
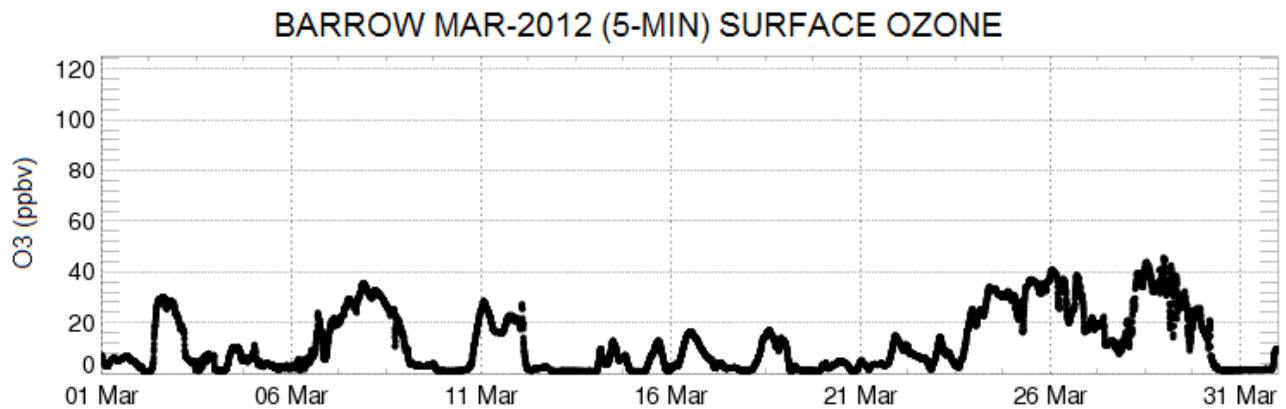
Figure 1. Five-minute averaged surface ozone recorded at Barrow Observatory for March, 2012 shows frequent depletion events during spring, lowering typical O3 mixing ratios of ~40 ppbv close to 0 ppbv.

Longstanding Discrepancies in Stratospheric Water Vapor Measurements Revisited During the 2011 Mid-latitude Airborne Cirrus Properties Experiment (MACPEX)

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For two decades, significant (15 to 60%) differences have persisted between the *in situ* stratospheric water vapor measurements by several well-established aircraft- and balloon-borne instruments. Attempts to reproduce and understand the measurement discrepancies in the laboratory have been largely ineffective.

The Mid-latitude Airborne Cirrus Properties Experiment (MACPEX) in April 2011 provided a fresh opportunity to reexamine existing measurement disparities and to compare measurements by new aircraft-based instrumentation. Here we compare water vapor measurements in the lower stratosphere by five different instruments during MACPEX. Three instruments (Harvard water, FISH, and NOAA CIMS) were aboard the NASA WB-57 aircraft, while two frost point hygrometers (CFH and NOAA FPH) were launched on balloons. Balloons were launched during six WB-57 flights for the purpose of comparing the *in situ* water vapor measurements. Aircraft and balloon flight paths were coordinated in space and time to maximize measurement coincidences. In most cases, the aircraft performed spiral descent maneuvers near balloons as they slowly descended (~5 m s^{-1}) through the stratosphere.

Water vapor mixing ratios measured by these five instruments during MACPEX generally fall into three groups. Those from the CFH, NOAA FPH and FISH are in good agreement, while Harvard water and NOAA CIMS were consistently 0.3 ppmv (8%) and 0.7 ppmv (18%) higher, respectively. Though these discrepancies appear to be large, they are considerably smaller than most of the longstanding differences between Harvard water and the frost point hygrometers, which during previous aircraft campaigns were as large as 60%.
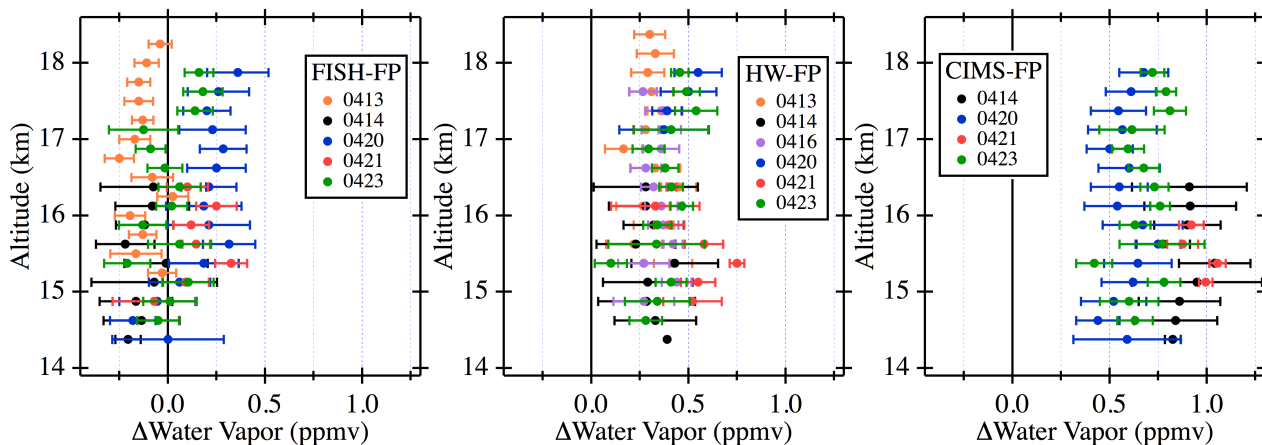

Figure 1. Measurement differences from the balloon-borne frost point hygrometers for (a) FISH, (b) Harvard water and (c) NOAA CIMS in 250-m altitude bins for each of six MACPEX flights. Error bars portray one standard deviation of the bin means for individual flights.

How the Global Climate Observing System (GCOS) Reference Upper Air Network (GRUAN) Contributes to Upper Air Climate Records

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Long-term changes of temperature, water vapor, and other essential climate variables within the free atmosphere are still questionable despite decades of observations. A key shortcoming of past observations is the lack of recognized references, against which to validate larger scale observing systems, leaving in doubt the quality of existing data. The GCOS Reference Upper Air Network (GRUAN) is now providing reference observations of temperature and humidity in the troposphere and stratosphere and is expanding to other essential climate variables, such as ozone, as the network continues to grow. To be called a reference, observations within GRUAN require traceable calibration, transparent processing and a detailed analysis of the uncertainty of all input parameters. Aspects of the observations such as proprietary methods, black box software or disregarded systematic effects are not acceptable in reference observations for GRUAN. Ongoing redundant measurements are essential to continuously test GRUAN observations for deficiencies, as is the storage of raw data and complete metadata, to allow reprocessing of the observations if necessitated by new knowledge. This approach may require new processing techniques and new observational procedures to assure the long-term stability of the observations, despite changes in instrumentation. These processing techniques are currently being developed within GRUAN in close cooperation with existing networks, utilizing capabilities found in other working groups and task teams. GRUAN is part of the World Meteorological Organization (WMO) Integrated Global Observing System, providing the essential support to continue to grow. Although not globally comprehensive, the network serves as reference to constrain and adjust data from more spatially comprehensive global observing systems, including the larger WMO radiosonde network, but also satellite systems.
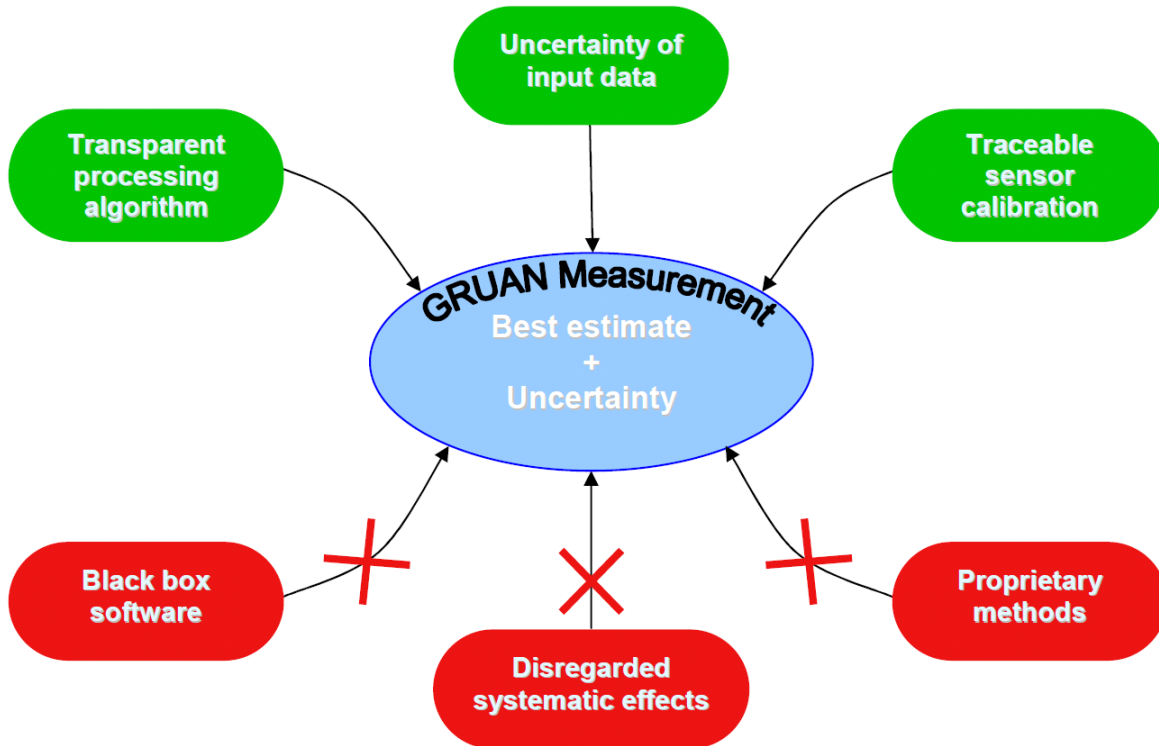

Figure 1. Do's and don'ts in establishing reference quality observations for GRUAN.

The Role of the Network for the Detection of Atmosphric Composition Change (NDACC) Measurements in Assessing Past Changes in the Vertical Distribution of Ozone

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[3]Jet Propulsion Laboratory, California Institute of Technology, Table Mountain Facility, Wrightwood, CA 92397

The evolution of atmospheric ozone throughout the 21st Century falls into two main focus areas: (1) long-term ozone changes associated with declining concentrations of ozone depleting substances and with increasing concentrations of greenhouse gases; and (2) short-term ozone changes associated with events such as volcanic eruptions, QuasiBiennial Oscillation, or El Niño/Southern Oscillation, each of which can moderate the longer-term changes.

Long-term changes have both scientific and policy relevance, whereas interest in shorter-term ozone changes is primarily scientific in nature and associated with improving our understanding of atmospheric processes. For both, accurate knowledge of the altitude, latitude, and seasonal structure of the ozone changes is required. The address of long-term questions requires a stable suite of measurements extending over decades. Addressing the short-term questions requires measurements with good spatial and temporal coverage. Critical to both issues are measurements of known high quality so that unequivocal documentation of the changes can be made and an understanding of the forcings associated with them can evolve.

During the 1990s, ozone profile trends deduced from satellite and ground-based instruments showed substantial discrepancies. Thus, a SPARC/IO3C/Global Atmosphere Watch Assessment of Trends in the Vertical Distribution of Ozone was organized and its findings were published in 1998. Since then, the end of certain satellite records has limited our observations of global changes in the vertical distribution of ozone. In an effort to improve our knowledge and understanding of the past changes in the vertical distribution of ozone, a new SPARC/IO3C/IGACO/NDACC (SI2N) initiative has been organized. Under this initiative satellite, ground-based, and airborne measurements are being critically analyzed, as are methods of preparing combined data sets. This presentation will highlight the role of two decades of ground-based measurements under the NDACC in determining recent trends in the vertical distribution of ozone.
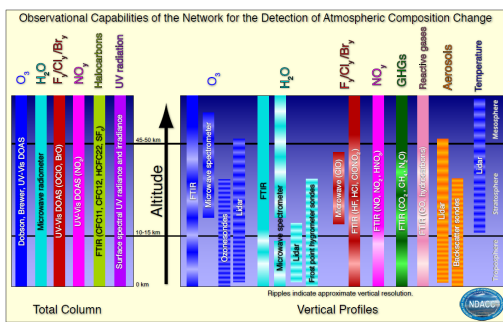

Figure 1. NDACC Observational Capabilities Chart. The Chart shows how different classes of atmospheric constituents and parameters are measured with different measurement techniques. The left panel shows total column measurements and the right panel shows vertically resolved measurements.
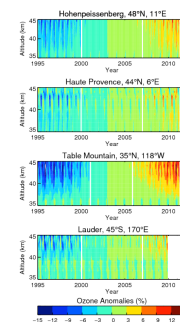
Figure 2. Lidar ozone response to the Ozone Depleting Gas Index over mid-latitude sites. The increase of ozone in the upper stratosphere as a direct response of the Montreal Protocol is observed over mid-latitude sites. Different steps are observed: 1) Ozone decrease slow down stop earlier at higher latitude than lower latitude. 2) Ozone recovery started later at higher latitude compared to lower latitude. From Kirgis et al.

Ozone Data for Climate Models: A Comparison of Three Datasets and Their Radiative Forcing

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Climate models that do not calculate their own ozone concentrations require an ozone boundary condition data set. In this study, three different ozone data sets are compared: one described by *Randel & Wu* (2007), one described by *Cionni et al.* (2011) (SPARC), and one based on the Binary Database of Profiles (BDBP) (*Hassler et al*., 2008). All consist of monthly and zonal mean multiple-linear regression fits to vertically resolved ozone observations, resulting in ozone data continuous in space and time (at least 1979 to 2005). The main differences between the data sets arise from the use of different observations, and the inclusion of different basis functions for the regression fits.

The datasets were compared against observations from ozonesondes and satellite ozone measurements, to establish the ability of a given dataset to match concentrations as well as capture interannual variability. The 1979-2005 ozone change was estimated by fitting a piecewise linear trend to the deseasonalized monthly means of specific latitude bands and pressure levels. These changes were then used to calculate the ozone radiative forcing, with the results indicating that the BDBP-based data has the largest radiative forcing.
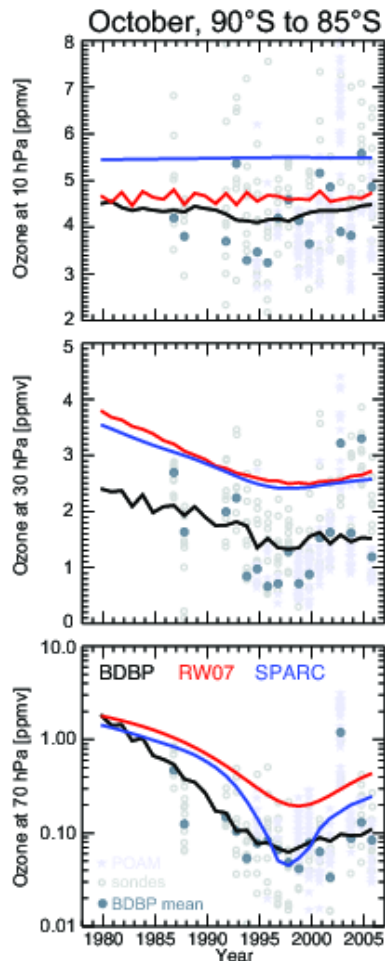

Figure 1. Time series of October mean ozone for the latitude band 90°S to 85°S, derived from the three different data sets, Randel & Wu (red line), SPARC (blue line) and BDBP (black line), for three different pressure levels. Symbols in the plots represent individual measurements on those levels from ozonesondes (gray circles) and Polar Ozone and Aerosol Measurement (light violet stars). Filled gray circles represent the raw monthly means calculated from the BDBP.

40th NOAA ESRL GLOBAL MONITORING ANNUAL CONFERENCE 2012
David Skaggs Research Center, Room GC-402
325 Broadway, Boulder, Colorado 80305 USA

Thursday Morning, May 17, 2012 AGENDA
(Only presenter's name is given; please refer to abstract for complete author listing.)

• *07:00*　　　　*Registration Opens in GC-402*
• *07:30 - 08:15*　*Morning Snacks – Coffee, tea, fruit, bagels & donuts served*

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　　　　Paul Fraser (Commonwealth Scientific & Industrial Research Organization (CSIRO), Marine and Atmospheric Research, Aspendale, VIC, Australia)

08:45 - 09:00　Global and Regional Emissions Estimates for HCFC-22　　　　50
　　　　Eri Saikawa (Center for Global Change Science, Massachusetts Institute of Technology, Cambridge, MA)

09:00 - 09:15　The Ocean in Near Equilibrium with Respect to Atmospheric CH_3Br　　　51
　　　　Shari Yvon-Lewis (Texas A&M University, College Station, TX)

09:15 - 09:30　A Revised Look at the Oceanic Sink for Atmospheric CCl_4　　　52
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09:30 - 09:45　Emissions of Tetrafluoromethane and Hexafluoroethane: Balancing Anthropogenic Budgets from Atmospheric Measurements　53
　　　　Jooil Kim (Seoul National University, Seoul, South Korea)

• *09:45 - 10:15*　*Morning Break*

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　　　　Tim Arnold (Scripps Institution of Oceanography, University of California at San Diego, La Jolla, CA)

10:30 - 10:45　Co-located Halocarbon Measurements by GC-ECDs and Medusa-GC/MS at the Shangdianzi GAW Regional Background Station, China　55
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10:45 - 11:00　Ambient Mixing Ratios and Emissions of Chlorofluorocarbons (CFCs), Hydrochlorofluorocarbons (HCFCs) and Hydrofluorocarbons (HFCs) in the Pearl River Delta Region, China　56
　　　　Wu Jing (Peking University, College of Environmental Sciences and Engineering, Bejing, China)

11:00 - 11:15　Carbonyl Sulfide Measurements in Antarctic Ice Cores: COS Loss to Hydrolysis Within the Ice Matrix and Implications for Developing Atmospheric Histories　57
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11:15 - 11:30　Ozone Depletion in Filaments of the Arctic Polar Vortex, Observed During the First Global Hawk UAS Science Mission　58
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11:30 - 11:45　A Viable Stratospheric Transport Monitoring Program; Tracking & Improving Our Understanding of Climate Change　59
　　　　Fred L. Moore (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

• *11:45*　　　　*Closing Remarks - James H. Butler (NOAA/ESRL)*

NOTES:

Re-evaluation of the Lifetimes of Ozone-depleting Substances

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Estimating the average lifetime of a molecule in the atmosphere is crucial to understanding the atmospheric concentrations of ozone depleting substances (ODSs). Predicting the concentration is the first step in obtaining estimates for ozone depletion and greenhouse forcing. Because the lifetimes of ODSs are also used to predict how the future concentrations change with emissions, they also have implications on policy decisions for limiting future release of Hydrochlorfluorocarbons (HCFCs) and other replacement compounds under the Montreal Protocol.

During the last 25 years, various methods have been used to derive lifetimes. Within the last several years evidence is growing that the lifetimes of certain ODSs are possibly somewhat longer than published values. The "Lifetime of halogen source gases" activity under the World Climate Research Programme (WCRP)/Stratospheric Processes And their Role in Climate (SPARC) project has convened a working group to re-evaluate these ODS lifetimes. The goal is to estimate the numerical values for lifetimes and their uncertainties, and to quantify how the values may depend on factors such as the use of different lifetime definitions (e.g. steady-state/instantaneous lifetimes) and changing climate.
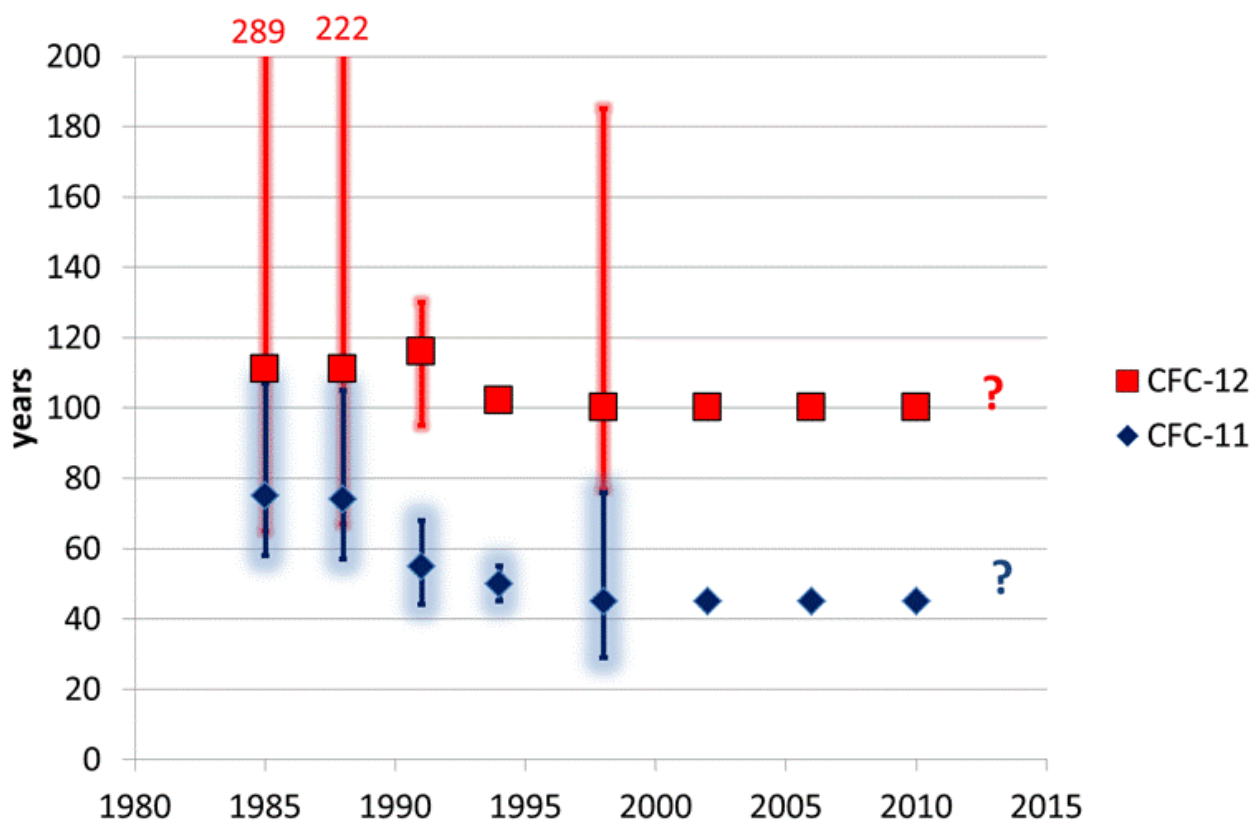

Figure 1. Estimated average lifetimes for Chlorfluorocarbons CFC-11 and CFC-12 in the course of the last 25 years.

Australian Carbon Tetrachloride Emissions: A Paradigm for a Missing Global CCl$_4$ Source?

P. Fraser[1], B. Dunse[1], P. Krummel[1], P. Steele[1] and A. Manning[2]

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Australian production of carbon tetrachloride (CCl$_4$) ceased in the late 1980s and Australian consumption of CCl$_4$ effectively ceased in the early 1990s, when imports were severely restricted. However the long-term Advanced Global Atmospheric Gases Experiment (AGAGE) CCl$_4$ record at Cape Grim (1978-2012; Simmonds *et al*., Krummel et al.) shows significant, but relatively small, CCl$_4$ emissions from Southeastern (SE) Australian urban and industrial centres (Dunse *et a*l.).

In Chapter 1 of the *Scientific Assessment of Ozone Depletion: 2010* (Montzka and Reimann, 2011) 'bottom-up' estimates of global CCl$_4$ emissions, based on fugitive emissions from the production, use and destruction of CCl$_4$, as recorded by United Nations Environment Programme (with some adjustments and additions), fall well short (currently by about 50 Gg/yr) of 'top-down' estimates of global emissions derived from AGAGE and NOAA global atmospheric observations.

Australia's contribution to the fugitive emissions described above is essentially zero, so where do the Australian emissions come from? This paper will report an update of current CCl$_4$ emissions from the Melbourne/Port Phillip/Latrobe Valley region of SE Australia, based on Cape Grim CCl$_4$ data, and attempt to identify the location and nature of these sources within the Melbourne/Port Phillip region, using *in situ* measurements of CCl$_4$ at CSIRO, Aspendale. The possible global significance of these emissions will be discussed.
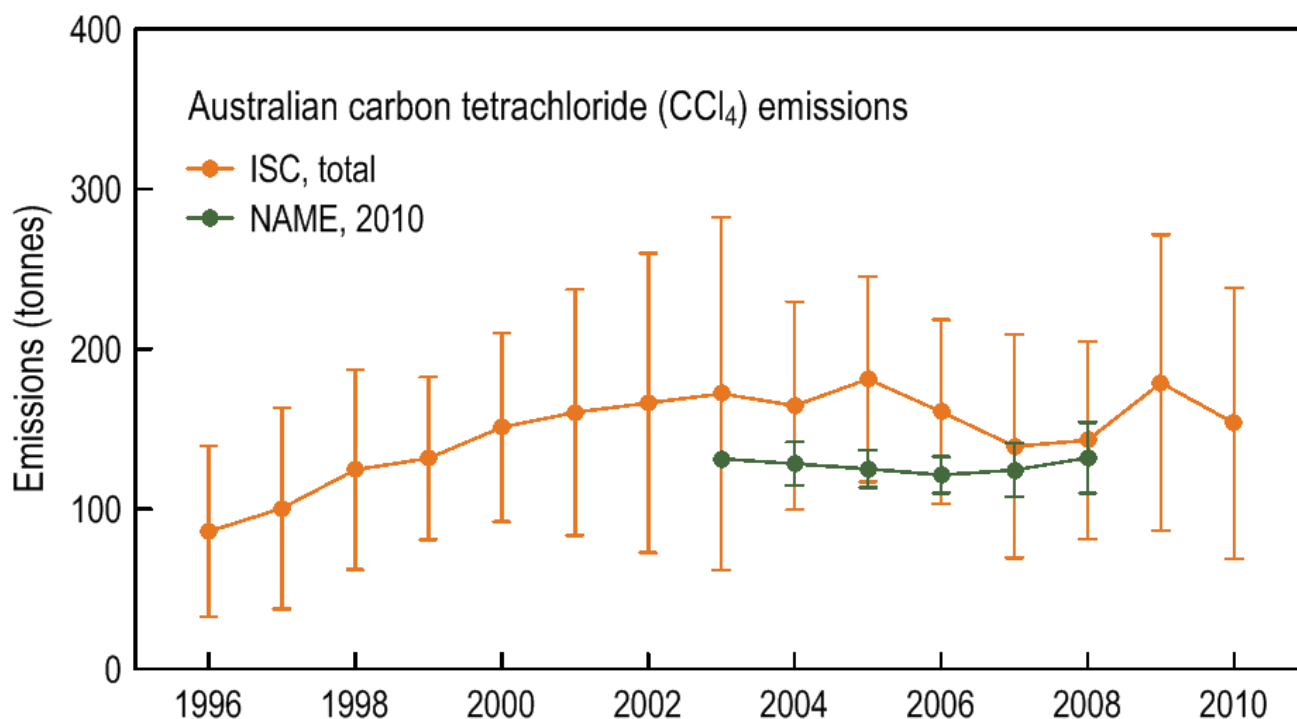

Figure 1. Australian CCl$_4$ emissions obtained from AGAGE observations at Cape Grim, Tasmania (1995-2011), using interspecies correlation (ISC, Dunse et al., 2005) and inverse modeling via the Lagrangian particle dispersion model NAME (Manning et al., 2011).

Global and Regional Emissions Estimates for HCFC-22

E. Saikawa[1], M. Rigby[2], R.G. Prinn[1], S. Montzka[3], B. Miller[3], L. Kuijpers[4], P. Fraser[5], M. Vollmer[6], B. Yao[7], L. Zhou[7], T. Saito[8], Y. Yokouchi[8], J. Kim[9], S. Park[9], D. Young[2], S. ODoherty[2], P. Simmonds[2], C. Harth[10], J. Muhle[10], R. Weiss[10], P. Krummel[5], M. Maione[11], C. Lunder[12], C. Sweeney[13], A. Andrews[3] and P. Tans[3]

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[12]Norwegian Institute for Air Research, Kjeller, Norway
[13]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309

HCFC-22 ($CHClF_2$) is a major greenhouse gas as well as an ozone depleting substance. A low frequency record of HCFC-22 in air since the late 1970s is available through measurements of the Northern Hemisphere Air Samples and the Southern Hemisphere Cape Grim Air Archives. More recently, measurements have been collected using the high-precision high-frequency instruments at the Advanced Global Atmospheric Gases Experiment (AGAGE) stations since the 1990s. NOAA Carbon Cycle Greenhouse Gases Group has also taken measurements from towers since 2006 in addition to the Halocarbon Flask Network measurements since the early 1990s. Using the United Nations Environment Programme data on consumption, as well as an existing bottom-up emissions estimate, we first create gridded a priori HCFC-22 emissions over the 15 years since 1995. We then use the three-dimensional chemical transport model (MOZART v4) and a Bayesian inverse method to estimate global, as well as regional, annual emissions. Our inversion indicates that the global HCFC-22 emissions significantly increased from 1999 to 2001and 2003 to 2006. We further find surge in HCFC-22 emissions in 2009 from Africa and the Middle East. On the other hand, emissions from the Article 5 Asia - the largest emitting region including China and India - show a large decrease in 2008 after the continuous increase from 2005 to 2007, most likely as a result of the Montreal Protocol.
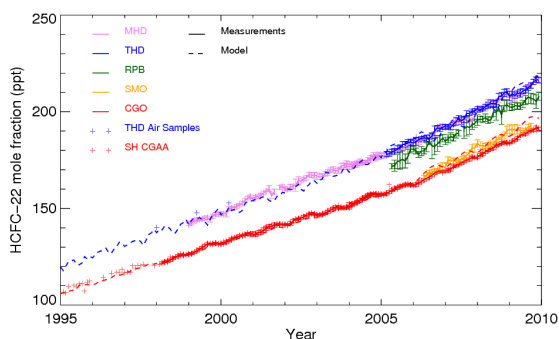

Figure 1. AGAGE archived air samples and model simulations at Cape Grim, Tasmania and Trinidad Head, California, and *in situ* measurements at Cape Grim, Tasmania; Cape Matatula, Samoa; RaggedPoint, Barbados; Trinidad Head, California; and Mace Head, Ireland.
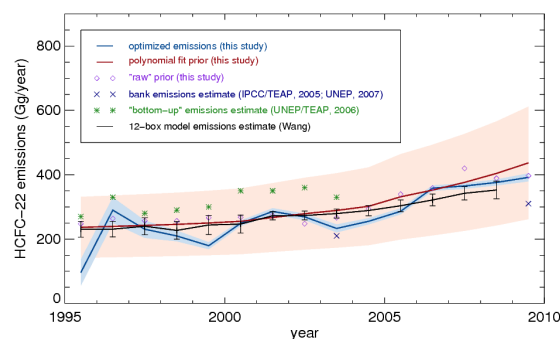

Figure 2. Global total HCFC-22 emissions from this study and published studies. Prior emissions estimates are shown in diamonds. Polynomial fit of these "raw" values that we used in our global inversion are shown in red line with shaded 40% uncertainty range. Optimized emissions from this study are shown in blue with our calculated posterior uncertainty.

The Ocean in Near Equilibrium with Respect to Atmospheric CH$_3$Br

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During the Halocarbon Air Sea Transect (HalocAST) cruises in the Pacific (3/30 – 4/27, 2010) and the Eastern Atlantic (10/25 – 11/26, 2010), we measured the saturation anomaly of CH$_3$Br to assess changes in the oceanic saturation state as the phaseout of non-Quarantine and Pre-Shipment (non-QPS) uses of CH$_3$Br nears completion and atmospheric concentrations continue to decline. These cruises occurred 16 years after the Bromine Latitudinal Air-Sea Transect (BLAST) cruises, which were conducted in the same regions and first established a global oceanic net sink of -12.6 Gg yr^{-1} for atmospheric CH$_3$Br in 1994. Results from this study suggest saturation anomalies of CH$_3$Br have become less negative than those observed 16 years ago as the atmospheric burden has declined over the past decade. The global net sea-to-air flux was estimated at -1 to 4 Gg yr^{-1} in 2010, suggesting the ocean may be nearly in equilibrium with atmospheric CH$_3$Br. There are no significant differences for determined biological loss rate constants and the calculated production rates between this study and previous studies, suggesting that production rates and oceanic degradation rate constants remained relatively constant over the past 16 years.
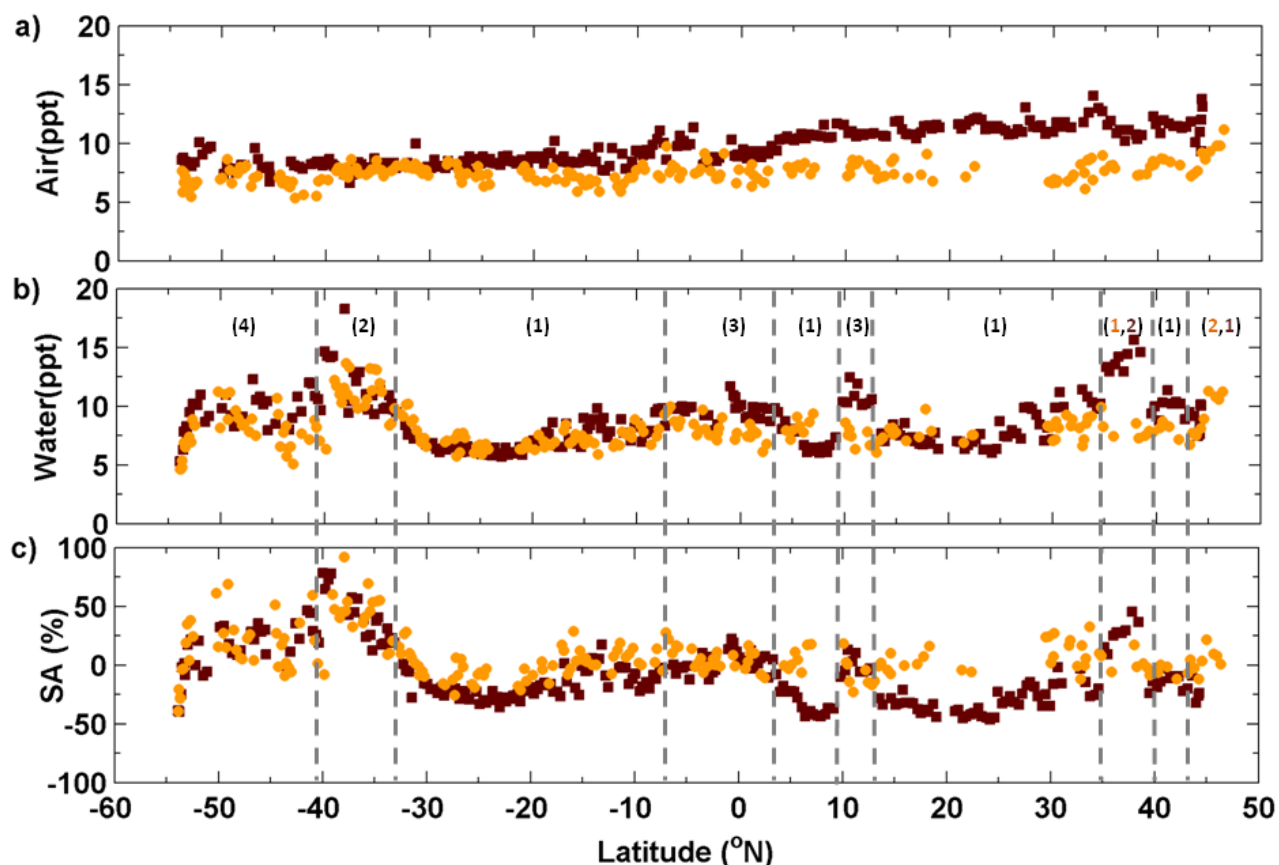

Figure 1. (a) CH$_3$Br atmospheric mixing ratios; (b) CH$_3$Br equilibrium partial pressures in surface seawater and (c) saturation anomalies for BLAST I (■) and HalocAST-P (●). The numbers between the dashed vertical lines indicate different oceanic regions with 1 = open ocean, 2 = coastal and nearshore, 3 = upwelling and 4 = coastal.

A Revised Look at the Oceanic Sink for Atmospheric CCl$_4$

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Extensive negative saturation anomalies for carbon tetrachloride (CCl$_4$) from 16 cruises in the Pacific, Atlantic, and Southern Oceans from 1987 through 2010 confirm that atmospheric CCl$_4$ is consumed in large amounts by the ocean. Data support findings previously reported from four research cruises, all in the Pacific Ocean [JH Butler et al, EOS 78 (46):F105, 1997; SA Yvon-Lewis and JH Butler JGR 107 (D20):4414, 2002], with only slight quantitative change. All seasons in both hemispheres are captured in this record and some cruises are repeat transects separated by over a decade. Nearly continuous, in situ measurements were made by gas chromatography with electron capture and/or mass spectrometer detection on air and surface water samples. Surface water was equilibrated with a continuous flow equilibrator. Grab samples of air were collected to confirm in situ measurements with independent instruments on land and, on some cruises, supporting grab samples of surface water were analyzed on board ship. Net CCl$_4$ saturation anomalies, corrected for physical effects associated with radiative heat flux, mixing, and air injection, were commonly on the order of -5% to -10%. The atmospheric flux required to sustain these anomalies still implies that the ocean accounts for about 1/4-1/3 of the total sink of atmospheric CCl$_4$. Although CCl$_4$ hydrolyzes in seawater, currently published hydrolysis rates for this gas cannot support such large saturation anomalies and inferred losses, given our current understanding of air-sea exchange rates. Explanation of the measured, surface-water undersaturations requires higher hydrolysis rates, additional sink mechanisms, such as biological consumption in surface waters or at depth, lower rates of air-sea exchange, or some combination of these processes.
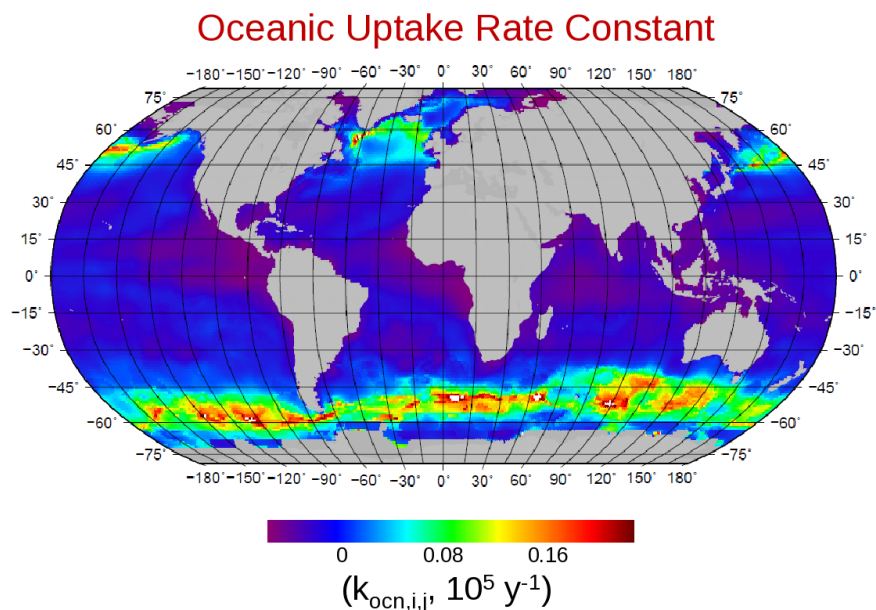
Figure 1. The distribution of oceanic uptake of atmospheric CCl$_4$ is a function of wind speed, sea-surface temperature, solubility, and aquatic removal rate.

Emissions of Tetrafluoromethane and Hexafluoroethane: Balancing Anthropogenic Budgets from Atmospheric Measurements

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The perfluorocarbons, tetrafluoromethane (CF_4, PFC-14), and hexafluoroethane (C_2F_6, PFC-116) are powerful, long-lived greenhouse gases emitted mainly from aluminum production and semiconductor manufacture. While both industries report significant reductions in PFC emissions during the past two decades, more than half of the recent emissions derived from atmospheric PFC observations ("top-down" emissions) remain unaccounted-for in the emissions reported by industry ("bottom-up" emissions, based on statistical analysis/emission factors). Here we present industry-specific top-down emissions, based on industry-specific emission "signatures" derived from *in situ* measurements of the Advanced Global Atmospheric Gases Experiment program. We also performed regional inversions for East Asia, where both of the major emitting industries are heavily concentrated, using two independent inversion schemes.

Our results from the analysis of historical emissions show that about 75% of the unaccounted-for accumulated emissions of CF_4 during 1990-2009 can be attributed to the semiconductor industry, representing the major source of underestimation in previous studies. Most of the underestimated emissions in the aluminum industry occur after 2001 and are centered in China, where the emissions from this fast-growing sector remain poorly quantified. These results are supported by our regional emission inversion results for East Asia, where China's top-down emissions (3.9 ± 0.7 Gg/yr, for 2007-2010) significantly exceed bottom-up estimates (e.g. 1.3 Gg/yr for 2009).
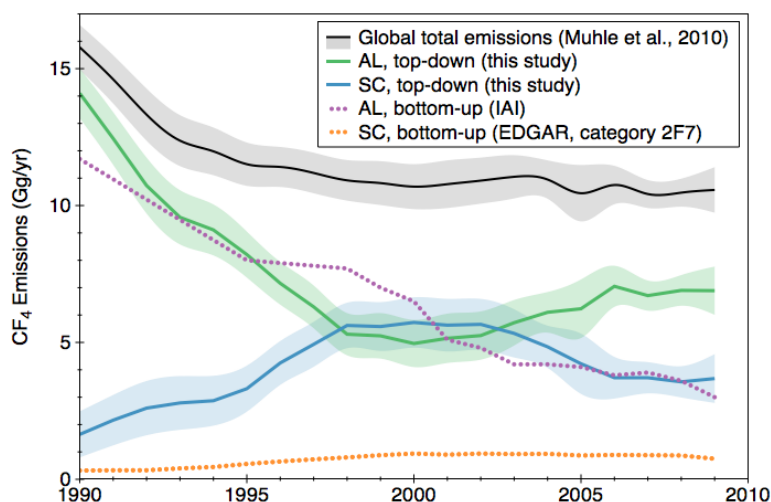

Figure 1. Top-down aluminum (AL) and semiconductor (SC) emissions of CF_4 derived in this study, compared with the bottom-up AL emissions from the International Aluminum Institute (IAI), and the SC emissions from the Emissions Database for Global Atmospheric Research (EDGAR), within context of the global total top-down emissions.

Nitrogen Trifluoride Global Emissions and Emission Factors Estimated from Atmospheric Observations

T. Arnold[1], C.M. Harth[1], J. Mühle[1], P.K. Salameh[1], A.J. Manning[2], J. Kim[1] and R.F. Weiss[1]

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Nitrogen trifluoride (NF_3), an anthropogenic greenhouse gas with a 100-yr Global Warming Potential (GWP) of over 16,000, has an increasing atmospheric abundance due to its emission from a growing number of manufacturing processes and an expanding end-use market. We present an updated historical record for atmospheric NF_3 based on a new and rigorous calibration (SIO-2012 scale), and show the latest analyses using our automated analytical method (an adapted Medusa GC-MS), including *in situ* measurements at La Jolla, California (32.87° N, 117.25° W).

We used a 2D atmospheric chemical transport model and inverse method together with our atmospheric data to optimally calculate global emissions over the last three decades. CO_2-equivalent NF_3 emissions (based on a 100-yr GWP) in 2011 totaled around 20 Mt, which equates to ~0.06% of global CO_2 emissions due to fossil fuel combustion and cement production. Our results suggest that the global emission factor has recently stabilized after many years of efficiency gains. Longer-term market trends for NF_3 are difficult to predict, however, production is expected to continue rising significantly in the foreseeable future. Given our latest findings, we expect a similar relative rise in both production and emissions over the coming years. This would lead to an accelerating rise in atmospheric NF_3 and a significant increase in the contribution of NF_3 to total radiative forcing. Although the emission factors we calculate are higher than "bottom-up" estimates from industry, from a climate perspective NF_3 continues to be preferred to C_2F_6 as source of fluorine plasma in industrial processes.
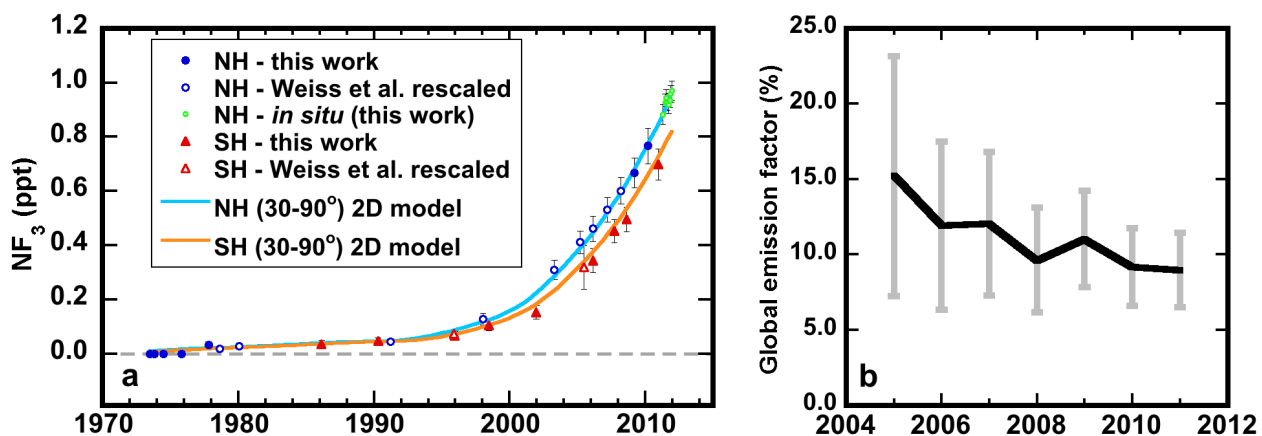

Figure 1. a) Nitrogen trifluoride abundances given in ppt (parts-per-trillion, dry air mole fraction) from Northern Hemisphere (NH) and Southern Hemisphere (SH) archived air sample measurements and *in situ* analyses at La Jolla, California in 2011. b) Emissions calculated from the atmospheric measurements were compared with industry production figures to estimate the global emission factor over recent years. Error bars represent a 1-σ uncertainty from the model-inversion emissions calculation. Uncertainties in the production figures were not available and are not included here.

Co-located Halocarbon Measurements by GC-ECDs and Medusa-GC/MS at the Shangdianzi GAW Regional Background Station, China

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In October 2006, an *in-situ* Gas Chromatography-Electron Capture Detector *(*GC-ECD) system was installed at the Shangdianzi Global Atmosphere Watch (GAW) regional station in China. The system can measure SF_6, CFC-11, CFC-12, CFC-113, HCFC-22, HCFC-142b, H-1211, H-1311, CH_3Br, $CHCCl_3$, CH_3CCl_3, CCl_4, PCE and TCE with a 40 minute time resolution. In May 2010, an *in-situ* Medusa-Gas Chromatograph/Mass Spectrometer (GC/MS) system was installed to allow co-located measurement of many compounds and to add capabilities of HFC and PFC measurements with a 60 minute time resolution. The two systems share a common sampling line and the inlet was attached to the top of a sampling tower. The measurements are closely tied to the Advanced Global Atmospheric Gases Experiment (AGAGE), on the calibration scales developed at the Scripps Institution of Oceanography (SIO), and the University of Bristol (UB). The common species measured by both systems from May 2010 to May 2011 were carefully compared. Taking SF_6 for example, we set a time window for 4 hours for the two systems with different time resolutions. The differences between average mixing ratios of the two systems in the same time windows were statistically analyzed. The differences between the SIO-05 scale and the NOAA-2006 scale of SF_6 was also compared and discussed.
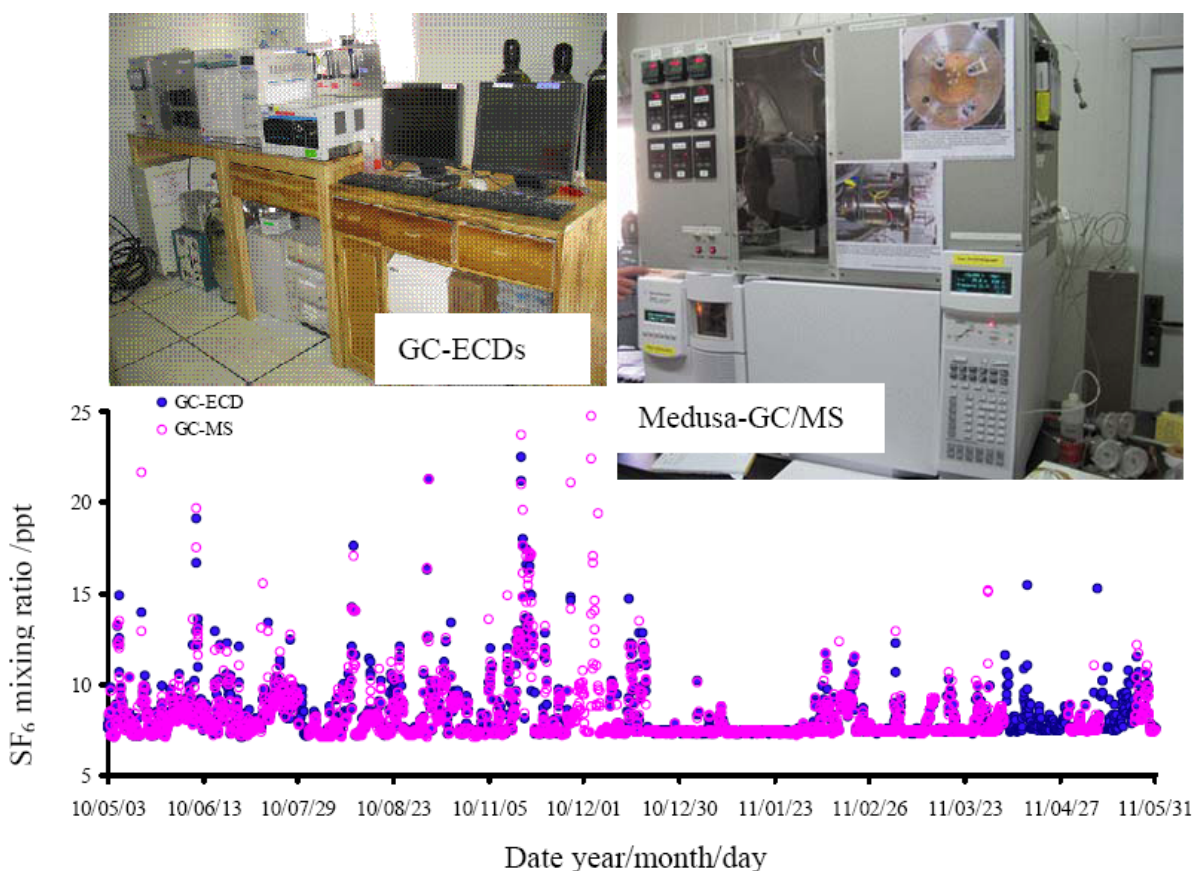

Figure 1. Time series of SF_6 measured by GC-ECDs and Medusa-GC/MS systems.

Ambient Mixing Ratios and Emissions of Chlorofluorocarbons (CFCs), Hydrochlorofluorocarbons (HCFCs) and Hydrofluorocarbons (HFCs) in the Pearl River Delta Region, China

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By using a Gas Chromatography-Mass Spectrometry system, the ambient mixing ratios of seven halocarbon species, including CFC-11,-12,-113, HCFC-22, -141b, -142b and HFC-134a, were analyzed from 167 air samples collected in 2010 from the Pearl River Delta (PRD) region of southern China. Results indicate that, compared with the observations in 2004, the CFC concentrations in PRD have declined, similar to the corresponding Northern Hemisphere (NH) background levels (enhancement from 10-11%), suggesting small local emissions of CFCs existing in PRD. Though the concentration variations of the three CFCs are relatively low (Relative Standard Deviation (RSD) from 10–18%), they still exceed the variability of the remote atmosphere in China (RSD from 0.48–0.78%). Therefore, CFC concentrations in PRD were still being influenced by some bank emissions in 2010. In contrast to the CFC levels, the concentrations of HCFC-22, -141b, -142b and HFC-134a have increased rapidly in the past few years, rising far above the NH background levels (enhancement from 40-336%). Their temporal variations are also evident (RSD from 32–69%), suggesting significant regional emissions. Correlations between the mixing ratio of each species and HCFC-22 were examined, and then the emissions of seven halocarbons in PRD were quantified, respectively, based on the interspecies correlation between other species and HCFC-22. Results reveal that the mass of HCFC-22(9.72Gg) accounts for about 43% of total emissions, followed by CFC-12(1.50 Gg), HFC-134a(1.19Gg) and HCFC-141b(1.08 Gg), while the emissions of CFC-11(0.84Gg) and HCFC-142b(0.55Gg) are relatively low. The interspecies correlation method may be a useful tool for assessing regional halocarbon emissions.
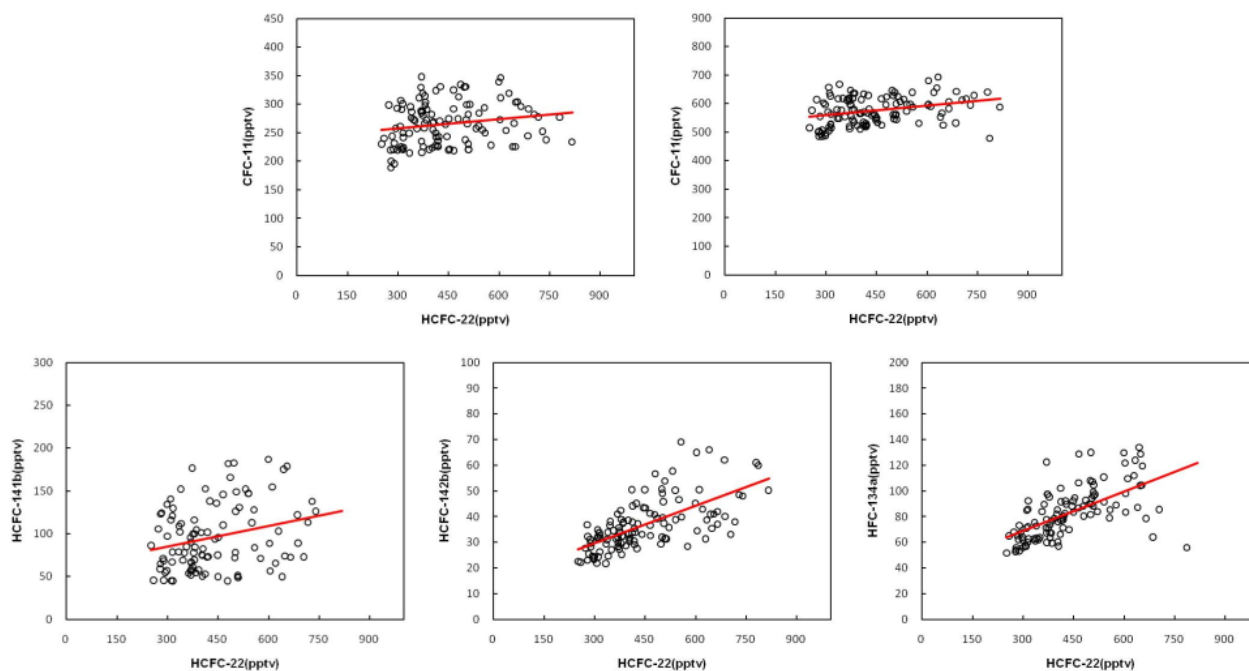
Figure 1. Other species and HCFC-22 relationship of the data set. Regression lines are indicated by the red solid lines. Statistical outliers were removed prior to performing the regressions.

Carbonyl Sulfide Measurements in Antarctic Ice Cores: COS Loss to Hydrolysis Within the Ice Matrix and Implications for Developing Atmospheric Histories

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We measured carbonyl sulfide (COS) in ice cores from Siple Dome and Taylor Dome sites in Antarctica (Fig. 1). Siple Dome measurements are mostly from the Holocene, while the Taylor Dome record covers the last 50 ky (thousand years) before present. Previous ice core data were combined with the firn air and instrumental measurements to provide a continuous and self-consistent COS record for the last 2,000 years. The new measurements expand this existing record considerably, allowing us to explore the stability of COS in ice cores over much longer time scales. At Taylor Dome, where ice temperatures are much colder, the Holocene COS levels are higher than the contemporaneous measurements from Siple Dome, providing strong evidence for COS loss to hydrolysis within the ice core matrix over multi-millennial time scales. Ice core COS measurements cannot be directly interpreted as atmospheric mixing ratios without accounting for the *in situ* loss. We developed Lagrangian temperature histories for the ice core samples from all three sites, using 1-dimensional ice flow and thermal models. The temperature histories are used to correct the COS measurements, assuming the COS hydrolysis in ice cores is described by pseudo first order kinetics. The preliminary corrections to the Taylor Dome data suggest that COS mixing ratios were 10-30 % lower during the last glacial period than they were during the Holocene. The results do not implicate any changes to the existing 2,000-year COS record, which was based largely on measurements in a shallow South Pole ice core (Fig. 1) where mean annual surface temperature is about -51°C, and consequently the COS hydrolysis is negligibly slow. Ice cores from thick ice sheets with cold surface temperatures are ideal for COS measurements, as they may require little or no correction for *in situ* loss to hydrolysis.
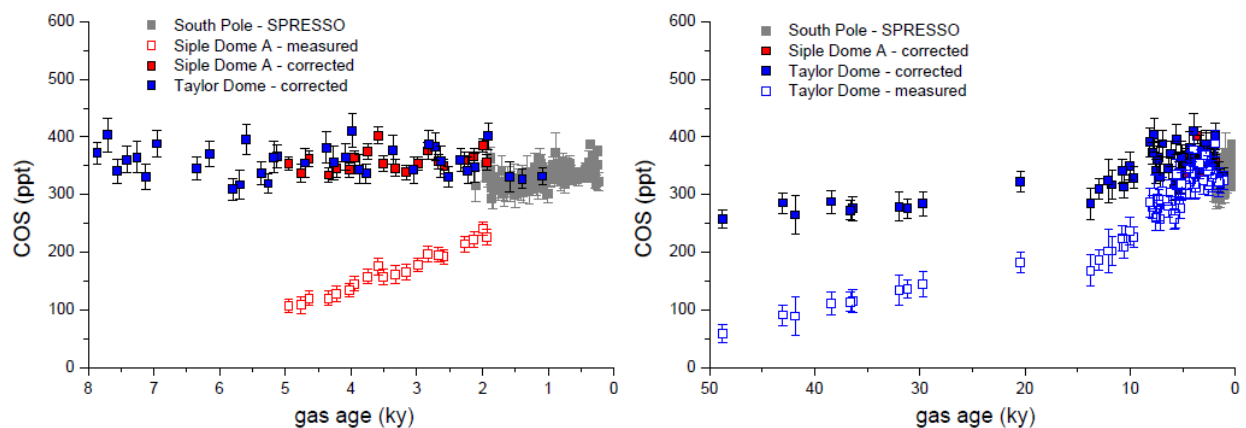

Figure 1. Left panel – New ice core data from Taylor Dome (blue) and Siple Dome (red) corrected for the *in situ* loss are compared with the existing South Pole record (gray). Actual measurements from Siple Dome (open red squares) are also shown. No correction has been applied to the South Pole record. Right panel – Same data sets as in the left panel on a 50 ky time scale, except the measured values from Taylor Dome (open blue squares) are shown instead of measured values from Siple Dome. Note that the correction for Taylor Dome is relatively small for the most recent 5 ky.

Ozone Depletion in Filaments of the Arctic Polar Vortex, Observed During the First Global Hawk UAS Science Mission

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One of the important potential uses of the NASA Global Hawk Unmanned Aircraft System (UAS) in scientific research is to study stratospheric ozone depletion in polar regions. Manned flights involve remote and hazardous duty, which pose great risks to pilots, crew, and scientists. Arctic ozone depletion observed in the Spring of 2010 by satellites, manned aircraft campaigns and ground stations was less severe than that observed in 2011. The Global Hawk UAS flight on 7 April 2010 was the first to observe ozone-depleted air with a UAS platform. Temperatures in the polar vortex were cold enough for Type II Polar Stratospheric Clouds (PSC) to form for a short period (days) at 50 hPa in 2010, and cold temperatures that were sufficiently low for almost 2 months for Type I PSC formation. Based on the NOAA Global Monitoring Division's Unmanned aircraft systems Chromatograph for Atmospheric Trace Species ozone versus nitrous oxide tracer correlation plot (below), there is 25% less ozone in air from a polar filament sampled on 7 April 2010, compared to the Arctic air sampled later on 23 April 2010. The NOAA Chemical Science Division UAS Fast Ozone Instrument showed a similar pattern with respect to N_2O. The low value of on-board SF_6 observations indicate air inside the polar vortex rather than in midlatitude air. The results from the Global Hawk are compared to those from the manned GV aircraft during HIPPO/3, MLS on the Aura satellite, and ozone loss from models. The Global Hawk UAS flights were part of the Global Hawk Pacific Experiment (GloPac), which demonstrated flights up to 28.6 hr duration, altitudes as high as 19.8 km and a maximum range of 9200 nm while carrying a payload of *in situ* and remote instrumentation for atmospheric chemical and aerosol tracers.
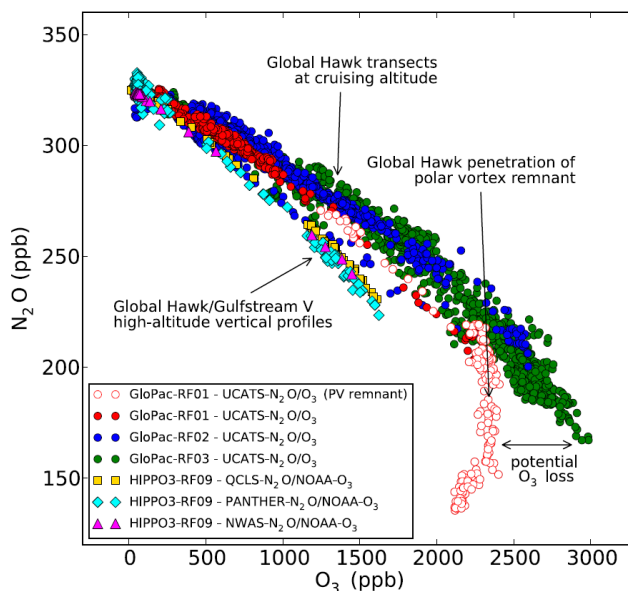

Figure 1. The NASA Global Hawk UAS.

Figure 2. N_2O vs. O_3 showing O_3 loss in 2010.

A Viable Stratospheric Transport Monitoring Program; Tracking & Improving Our Understanding of Climate Change

F.L. Moore[1], E. Ray[1], J.W. Elkins[2], P.P. Tans[2], A. Karion[1] and C. Sweeney[1]

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Climate change drives change in tropospheric weather. This in turn modifies the generation of wave activity, the major driver of stratospheric circulation. Coupled chemistry-climate models predict that stratospheric circulation will increase in strength with increased greenhouse gases [e.g. *Butchart et al.*, 2010]. Knowledge of change in stratospheric circulation is of significant importance. This was highlighted in a recent model study (*Scaife et al.*, 2011) that shows how changes in stratospheric circulation can play a significant role in predictions of future climate change. These stratospheric changes "induce change in the baroclinic eddy growth rate across the depth of the troposphere," altering predictions of regional rainfall, mean winds, and troposphere storm tracks. Other related examples are the recovery of ozone [*Butchart, et al.*, 2010], the concentration of stratospheric water vapor [Solomon *et al*., 2010], and tropopause height. Climate-monitoring programs will benefit substantially by having a stratospheric circulation-monitoring component to track the coupling of these two regimes.

To validate model predictions of change in stratospheric circulation requires high quality, long-term measurements. The trace gases SF_6, N_2O, CFC-12, CFC-113, CFC-11, and halon-1211 are uniquely influenced by stratospheric circulation time scales, through changes in the "age" of stratospheric air [*Waugh and Hall*, 2002], and stratospheric path and recirculation which manifests in both age distributions, and the "maximum path height" distributions [*Hall*, 2000] through photolytic loss. A recent study by *Engel et al.* [2009] and extended by *Ray et al.* [2010] pieced together available balloon based SF_6 and CO_2 measurements over the past three decades to show that the mean age of stratospheric air has increased, in apparent opposition to the decreased mean age predicted by models that show stratospheric circulation strengthening. This study highlighted the role long-lived trace gas measurements can play in helping to understand model predictions, but also clearly reveals the limitations of the currently available stratospheric measurements. Recent laboratory studies have proven the feasibility of using the low cost AirCore techniques of *Tans* [2009] coupled with our fast chromatograph, *Moore et al.* [2003], to acquire such stratospheric data. We outline a series of technically feasible measurements that would substantially improve our ability to monitor most of the relevant aspects of stratospheric circulation change.
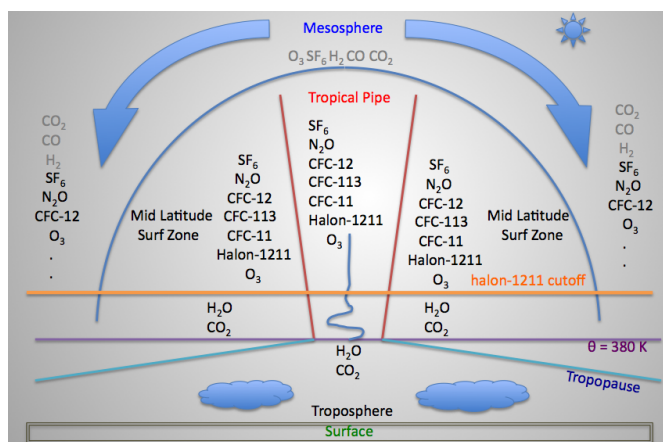

Figure 1. A monitoring program based on technically and financially feasible trace gas measurements, with the seasonal data acquired using inexpensive hand launched balloons descending from 30 km.

Tuesday, May 15, 2012 17:00 - 20:00 POSTER SESSION AGENDA
(Only presenter's name is given; please refer to abstract for complete author listing.)

• *Ozone & Water Vapor*

P-1 Adoption of a New Data Processing Scheme for Dobson Data

Robert Evans (NOAA Earth System Research Laboratory, Boulder, CO)

P-2 Highlights of the New Multi-spectral Brewer Umkehr Ozone Profile Retrieval

Irena Petropavlovskikh (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-3 Another Step Toward Stratospheric Ozone Recovery as Observed by Multiple Network for the Detection of Atmospheric Composition Change (NDACC) LiDARs and Satellite Instruments

Guillaume G. Kirgis (Jet Propulsion Laboratory, California Institute of Technology, Table Mountain Facility, Wrightwood, CA)

P-4 Experimental Validation of a New Balloon-Borne Supercooled Liquid Sensor

Emrys Hall (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-5 SkySonde, a Weather Balloon Telemetry and Data Processing System

Allen Jordan (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-6 New Tether Ozonesonde System Developed for Uintah Basin Ozone Study in February, 2012

Bryan J. Johnson (NOAA Earth System Research Laboratory, Boulder, CO)

P-7 Changes in Arctic Atmospheric Chemistry Linked to Ocean Sea Ice Changes

Samuel J. Oltmans (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-8 Ozone Tropospheric and Stratospheric Trends (1995-2011) at Six Ground-based FTIR Stations (28°N to 79°N)

James Hannigan (National Center for Atmospheric Research, Boulder, CO)

• *Halocarbons & Other Trace Species*

P-9 Atmospheric Chemistry of Replacement Compounds: OH Reactivity of the (*E*)- and (*Z*)- $CF_3CH=CHCF_3$

Munkhbayar Baasandorj (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-10 Three Decades of Continuous Monitoring of Long-lived Halocarbons

Geoff Dutton (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-11 New High-frequency Measurements of CH_4, N_2O and SF_6 from a High-altitude Station in Darjeeling, Eastern Himalayas, India

Anita L. Ganesan (Center for Global Change Science, Massachusetts Institute of Technology, Cambridge, MA)

P-12 Revision of the NOAA 2006 N_2O Scale

Brad Hall (NOAA Earth System Research Laboratory, Boulder, CO)

P-13 Polyhalogenated Very Short Lived Substances (VSLS) in the Atlantic Ocean, and Their Linkages with Ocean Primary Production

Yina Liu (Texas A&M University, College Station, TX)

P-14 The Atmospheric Distribution of Molecular Hydrogen (H_2) and Related Species Observed During the HIPPO Project

Eric Hintsa (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-15 Snapshot of Atmospheric Trace Gases "Pole to Pole" – Highlights from the HIPPO Whole Air Sampler

Benjamin R. Miller (NOAA Earth System Research Laboratory, Boulder, CO)

P-16 Improving Our Understanding of Ozone-depleting Substances in the Upper Atmosphere

David J. Nance (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-17 A Study of the Behavior of $Mg(ClO_4)_2$ Drying Traps Used in Gas Chromatography-Mass Spectrometry (MS) Analysis of Flasks

Carolina Siso (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

Tuesday, May 15, 2012 17:00 - 20:00 POSTER SESSION AGENDA

(Only presenter's name is given; please refer to abstract for complete author listing.)

• *Carbon Cycle & Greenhouse Gases*

P-18 Atmospheric Network Design in Europe
  Elena Novakovskaia (Earth Networks, Inc., Germantown, MD)

P-19 Monitoring Patterns and Anomalies Using the Dense GHG Network in the Northeastern U.S.
  Elena Novakovskaia (Earth Networks, Inc., Germantown, MD)

P-20 Emissions from Oil and Natural Gas Operations in Northeastern Utah
  Gabrielle Pétron (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-21 NOAA Mobile Laboratory Measures Oil and Gas Emmissions
  Jonathan Kofler (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-22 Evaluating New High-frequency, High-precision Measurements of δ^{13}C-CH$_4$ and δD-CH$_4$ for Top-down Emissions Estimation
  Matthew Rigby (School of Chemistry, University of Bristol, Bristol, United Kingdom)

P-23 The Identification and Quantification of Greenhouse Gas Point Source Emissions Using Cavity Ring-down Spectroscopy, Complementary to Other Techniques
  Graham Leggett (Tiger Optics LLC, Warrington, PA)

P-24 Interannual Variability of Carbon Monoxide Emission Estimates Over South America from 2006 to 2010
  T. Röckmann (Institute for Marine and Atmospheric Research, Utrech University, Utrecht, Netherlands)

P-25 Temporal and Spatial Variability of the Stable Isotopic Composition of Atmospheric Molecular Hydrogen
  Thomas Röckmann (Institute for Marine and Atmospheric Research, Utrech University, Utrecht, Netherlands)

P-26 Decadal Trends in ^{18}O of Atmospheric CO$_2$
  Bruce H. Vaughn (Institute of Arctic and Alpine Research (INSTAAR), University of Colorado, Boulder, CO)

P-27 The Monitoring Network of the MPI for Biogeochemistry, Jena for Atmospheric Greenhouse Gases, Oxygen and Their Isotopic Signatures
  Martin Heimann (Max Planck Institute (MPI) for Biogeochemistry, Jena, Germany)

P-28 Stable Isotopic Measurements of Carbon Monoxide in Air: Work In Progress
  Isaac Vimont (Institute of Arctic and Alpine Research (INSTAAR), University of Colorado, Boulder, CO)

P-29 Twenty Years Measuring CO in the Troposphere: What Have We Learned and Where Do We Go?
  Paul Novelli (NOAA Earth System Research Laboratory, Boulder, CO)

P-30 Linking Carbon Isotopes of Methane to International Standards – Can We Close the Loop on Calibration?
  Jason P. Winokur (Institute of Arctic and Alpine Research (INSTAAR), University of Colorado, Boulder, CO)

P-31 Methane Fluxes to the Atmosphere from Deepwater Hydrocarbon Sources
  Lei Hu (Texas A&M University, College Station, TX)

P-32 Toward a Combined Data-fusion Atmospheric Inversion System at Continental Scale: Structure of Flux Errors and Atmospheric Regional Variability Over North America
  Thomas Lauvaux (The Pennsylvania State University, Department of Meteorology, University Park, PA)

P-33 Seasonal Variation of the Global Carbon Fluxes Using CarbonTracker
  Kyungna Kim (National Institute of Meteorological Research / Korea Meteorological Administration, Seoul, Korea)

P-34 Studies of Carbon Isotopic Ratios in Atmospheric Methane and Some of It's Sources in India
  D.Kameswara Rao (Physical Research Laboratory, Ahmedabad, India)

P-35 INFLUX: Model-data Comparison and the Detection Limit of the Observational Network
  Laura McGowan (The Pennsylvania State University, Department of Meteorology, University Park, PA)

P-36 Isoflux Inversion Progress Report: Towards Building a Regional Bayesian Inversion for δ^{13}C of Terrestrial CO$_2$ Fluxes
  Caroline Alden (Institute of Arctic and Alpine Research (INSTAAR), University of Colorado, Boulder, CO)

Tuesday, May 15, 2012 17:00 - 20:00 POSTER SESSION AGENDA

(Only presenter's name is given; please refer to abstract for complete author listing.)

• *Carbon Cycle & Greenhouse Gases (continued)*

P-37   Single-Photon LiDAR for Measuring & Monitoring Forest Carbon Fluxes
  Phil DeCola (Sigma Space Corporation, Lanham, MD)

P-38   ICOS-ATC Lab Test for GHG Instrumentation: Presentation and First Results
  Benoit Wastine (Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Orme des Merisiers, France)

P-39   Improving and Extending a CO_2 Observation Network in the Pacific Northwest
  Andres Schmidt (Oregon State University, Corvallis, OR)

P-40   University of Washington (UW)-NOAA Cooperation at the Mt. Bachelor Observatory (MBO)
  Dan Jaffe (University of Washington, Department of Atmospheric Sciences, Seattle, WA)

P-41   Synoptic Process and Higher Values of CO_2
  Oyunchimeg Dugerjav (Institute of Meteorology and Hydrology, Ulaanbaatar, Mongolia)

• *Aerosols*

P-42   Impact of Aerosols on Climate Changes in the 20th Century
  Sungbo Shim (National Institute of Meteorological Research / Korea Meteorological Administration, Seoul, Korea)

P-43   Developing Useable Black Carbon Information – Case Studies from the IASOA Network
  Sandy Starkweather (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-44   Soot Surveys in the Air and Snow During PAMARCMIP 2011 and DOSA Campaigns
  Sangeeta Sharma (Environment Canada, Toronto, Ontario, Canada)

P-45   Seasonal & Annual Variations in Aerosol Elemental Carbon (EC) Observations Over Canada: Constraints on Changes of Fossil Fuel Emissions
  Lin Huang (Atmospheric Science Technology Directorate/ STB, Environment Canada, Toronto, Ontario, Canada)

P-46   Aerosol Optical and Radiative Properties Measured at Mt. Lulin During Biomass Burning Seasons
  Neng-Huei Lin (Department of Atmospheric Sciences, National Central University, Chung-Li, Taiwan)

P-47   Aerosol Optical Properties from the Himalayan Foothills Site During Ganges Valley Aerosol Experiment (GVAX)
  Anne Jefferson (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-48   An Inexpensive Method for Estimating Particle Pollution
  Michael M Seltzer (Fairview High School, Boulder, CO,)

P-49   A Field-deployable Polar Nephelometer
  John E. Barnes (NOAA Earth System Research Laboratory, Mauna Loa Observatory, Hilo, HI)

P-50   Assessing the Importance of Contact Ice Nucleation
  Yi-wen Huang (Massachusetts Institute of Technology (MIT), Cambridge, MA)

P-51   How Does the Nature of Rain Affect the Climate? Black Carbon – Rain Interaction Over Eastern Himalaya, India
  Abhijit Chatterjee (Bose Institute, Department of Science and Technology, West Bengal, India)

Tuesday, May 15, 2012 17:00 - 20:00 POSTER SESSION AGENDA

(Only presenter's name is given; please refer to abstract for complete author listing.)

• *Observatories, Global Cooperative Measurements, & Instrumentation*

P-52   Recent Science from the Cape Verde Atmopsheric Observatory (CVAO)

   James Lee (National Centre for Atmospheric Science, University of York, York, United Kingdom)

P-53   Ten Years of Observations of Ozone-depleting Substances at Monte Cimone (Italy) for Deriving Trends and Regional Emissions.

   Michela Maione (University of Urbino, Departement of Basic Sciences and Foundations, Urbino, Italy)

P-54   Comparison of Surface Measurements of Equivalent Black Carbon at Four Arctic Stations

   Taneil Uttal (NOAA Earth System Research Laboratory, Boulder, CO)

P-55   The Tiksi, Russia Hydrometeorological International Facility for Atmospheric, Terrestrial and Ocean Observations: First Measurements and Future Plans

   Alexander Makshtas (Arctic and Antarctic Research Institute, St. Petersburg, Russian Federation)

P-56   Atmospheric Data Management at ICOS Atmospheric Thematic Center: Collection, Processing, Archiving and Access

   Lynn Hazan (Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Orme des Merisiers, France)

P-57   The ICOS Atmospheric Network and Atmospheric Thematic Center (ATC)

   Michel Ramonet (Laboratoire des Sciences du Climat et de l'Environnement (LSCE), Orme des Merisiers, France)

P-58   Measurements of Trace Gases at Lulin Atmospheric Background Station (LABS) and Dongsha Island (DSI), Taiwan

   Chang-Feng Ou Yang (Department of Chemistry, National Central University, Chung-Li, Taiwan)

• *Atmospheric Radiation (Solar)*

P-59   Atmospheric Radiation Measurement Program Data Quality Office Overview

   Kenneth Kehoe (University of Oklahoma, Norman, OK)

P-60   Nocturnal Aerosol Optical Depth Measurements Using a Lunar Photometer

   Robert S. Stone (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-61   Surface Fluxes and Boundary-layer Measurements in Arctic at the Eureka (Canada) and Tiksi (Russia) Climate Observatories

   Andrey Grachev (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-62   Maps of Isolines of Ultraviolet (UV)-B Dose at the Republic of Panama

   Alfonso Pino Graell (Laboratory of Atmospheric Physics of the University of Panama, El Cangrejo, Republic of Panama)

P-63   High Arctic Ultraviolet (UV) Radiation Levels in the Spring of 2011 Caused by Unprecedented Chemical Ozone Loss

   Germar Bernhard (Biospherical Instruments, San Diego, CA,)

P-64   The Antarctic, Boulder, and Mauna Loa Ultraviolet (UV) Monitoring Program Update

   Patrick Disterhoft (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-65   NEUBrew - The NOAA/Environmental Protection Agency (EPA) Brewer Spectrophotometer Ultraviolet (UV)-Ozone Monitoring Network Update

   Patrick Disterhoft (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

P-66   NOAA/GMD Participation in the Eleventh International Pyrheliometer Comparison (IPC-XI) September 26-October 15 2010 World Radiation Center (WRC) Davos, Switzerland

   Don Nelson (NOAA Earth System Research Laboratory, Boulder, CO)

Adoption of a New Data Processing Scheme for Dobson Data

R. Evans[1], G. McConville[2], I. Petropavlovskikh[2] and D. Quincy[2]

[1]NOAA Earth System Research Laboratory, 325 Broadway, Boulder, CO 80305; 303-497-6679, E-mail: robert.d.evans@noaa.gov
[2]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309

NOAA and its predecessors have operated a network of Dobson ozone spectrophotometers beginning with measurements made at Mauna Loa observatory in 1957. As of today this network consists of 15 stations. A complete list of the stations and the operational status of each is displayed in Table 1. Several of these station have have been automated using a software package
designed and maintained by the Japanese Meteorological Agency (JMA). This package (WINDOBSON) features data processing and enhanced data analysis tools in addition to functions needed for data collection. The current computer and operating systems used to process data from the NOAA Dobson network are antiquated and increasingly difficult to maintain. This situation has forced a decision to adopt (WINDOBSON) for future processing of data collected by all stations within its network; not just those automated with the JMA system. Data collected from the station in Lauder New Zealand between 1992 and 2010 was reprocessed using the JMA software and compared to results from our contemporary system in order to investigate any potential systematic bias.

The comparison of the Select (NOAA) and Representative (JMA) value of the Day has an average 0.3 DU difference. The JMA Representative is chosen automatically, the NOAA is selected Semi-Automatically with manual over-ride. Ten days were removed from the NOAA record, these days were also removed from the JMA record. There is no trend in the difference.
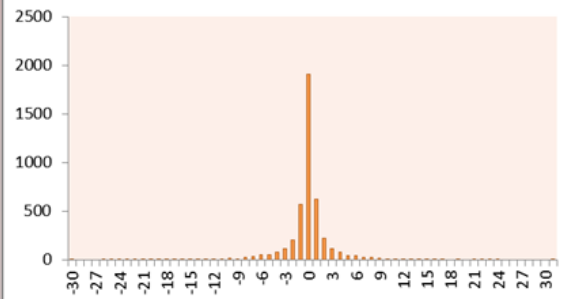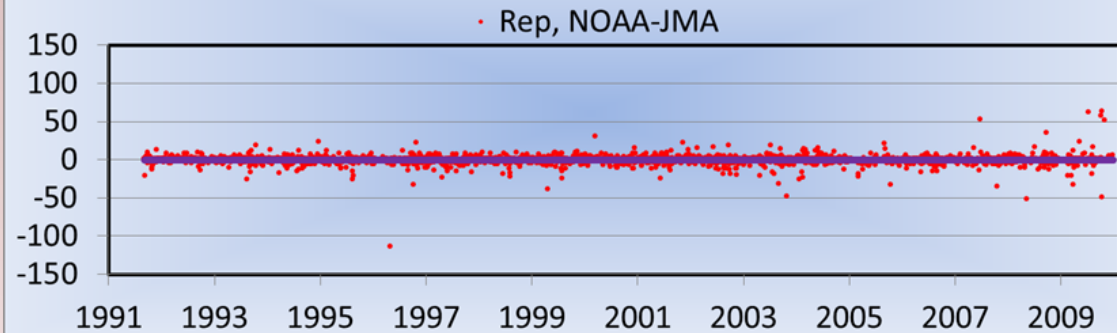
Figure 1.

Highlights of the New Multi-spectral Brewer Umkehr Ozone Profile Retrieval

I. Petropavlovskikh[1], P. Disterhoft[1], B. Evans[2], G. McConvile[1], B. Johnson[2], L. Flynn[3], R. McPeters[4] and M. Stanek[5]

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[5]IOS, Canada and Czech Republic Meteorological Institute

The Dobson Umkehr network has been a key data set for stratospheric ozone trend calculations and has earned its place as a benchmark network for stratospheric ozone profile observations. The Umkehr data has also been used to provide a long-term reference to the merging of the satellite ozone records, estimate the seasonal influence of an 11-year solar signal in the vertical distribution of stratospheric ozone, and to assess the ability of several remote and *in situ* sensing systems in capturing ozone variability. It was found that Dobson Umkehr measurement errors were often comparable to errors derived for satellite and ozone-sounding methods. In 2005, the Dobson Umkehr algorithm (UMK04) was modified to retrieve ozone profile data from Brewer Umkehr measurements taken at two spectral channels [Petropavlovskikh et al, 2011]. The PC version of the Brewer algorithm was implemented at the NEUBrew network for operational processing of Umkehr data (http://www.esrl.noaa.gov/gmd/grad/neubrew/). The most recently developed Brewer ozone retrieval algorithm (MSBU) utilizes Umkehr measurements at multiple wavelength channels (similar to the satellite BUV method) and significantly reduced range of solar zenith angles. Intercomparisons against ozone climatology, sounding, satellite overpasses and Dobson ozone datasets for NASA/Goddard, Boulder, CO and Mauna Loa Observatory, HI sites show reduction in ozone profile retrieval noise by as much as 30% in stratosphere and by about 50% in troposphere as compared to the single pair ozone retrieval. Tropospheric ozone retrievals also appear to be very promising. The intra-annual tropospheric ozone variability captured by the MSBU algorithm is comparable to variability found in collocated ozone sonde data.
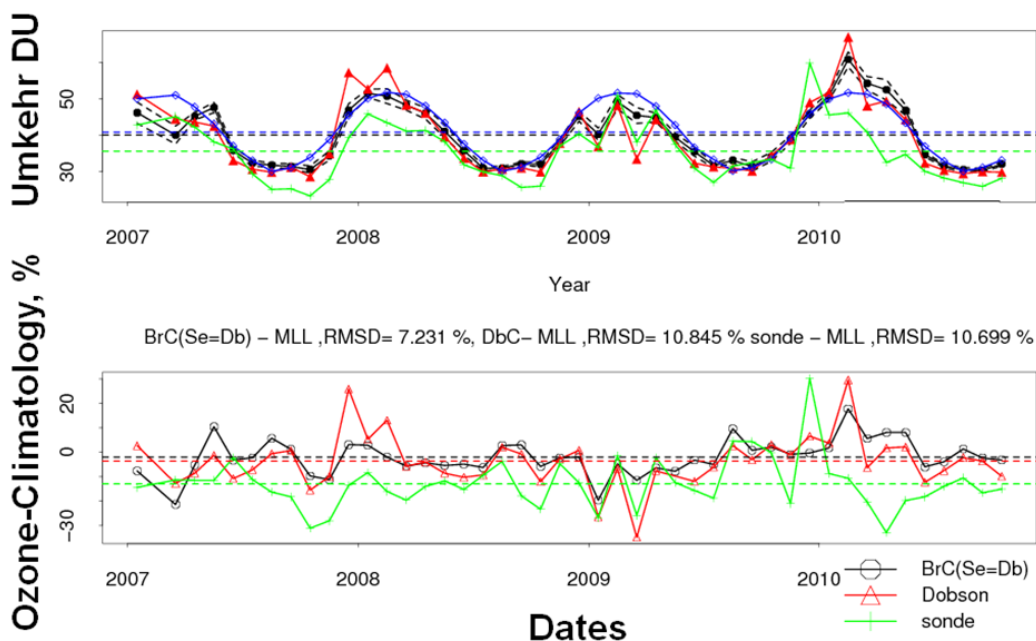

Figure 1. Ozone at 63-250 hPa (~10-15 km) measured by Brewer in Boulder, CO. Dobson (red), ozone sounding (green) and climatology (blue) data are shown for comparisons. Limited (once a week) temporal sampling in sounding data can instigate apparent differences in month-to-month variability when compared to Dobson or Brewer monthly averaged data.

Another Step Toward Stratospheric Ozone Recovery as Observed by Multiple Network for the Detection of Atmospheric Composition Change (NDACC) LiDARs and Satellite Instruments

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Jet Propulsion Laboratory, California Institute of Technology, Table Mountain Facility, 24490 Table Mountain Rd, Wrightwood, CA 92397; 760-249-4829, E-mail: kirgis@tmf.jpl.nasa.gov

Long-term variability in stratospheric ozone at Mauna Loa Observatory (MLO), Hawaii, Table Mountain Facility, California, Hohenpeissenberg, Germany, Observatoire de Haute-Provence, France, and Lauder, New Zealand, was investigated using various observational records. The analysis comprises a comparison of collocated ozone measurements from several NDACC LiDARs and a long-term time series merged from different satellite instruments. Regression analysis was performed on the deseasonalized monthly mean ozone time series for each 1 km-altitude bin between 20 and 40 km from January 1995 to April 2011 (a period of low volcanic aerosol loading). Among others interannual and annual components, the mid-latitude Ozone Depleting Gas Index (ODGI) was found to significantly improve the regression model. A strong positive response to the ODGI was observed over mid-latitude sites in the upper stratosphere since 2005 as well as a negative response at MLO in the lower stratosphere. Clear signatures of the 11 year Solar Cycle and El Niño-Southern Oscillation (ENSO) were also identified above MLO showing negative response in the lower stratosphere. These responses were already identified by models as a change in tropical upwelling which leads to the strengthening of the Brewer-Dobson circulation and thus to accelerate the process of ozone recovery above mid-latitudes.
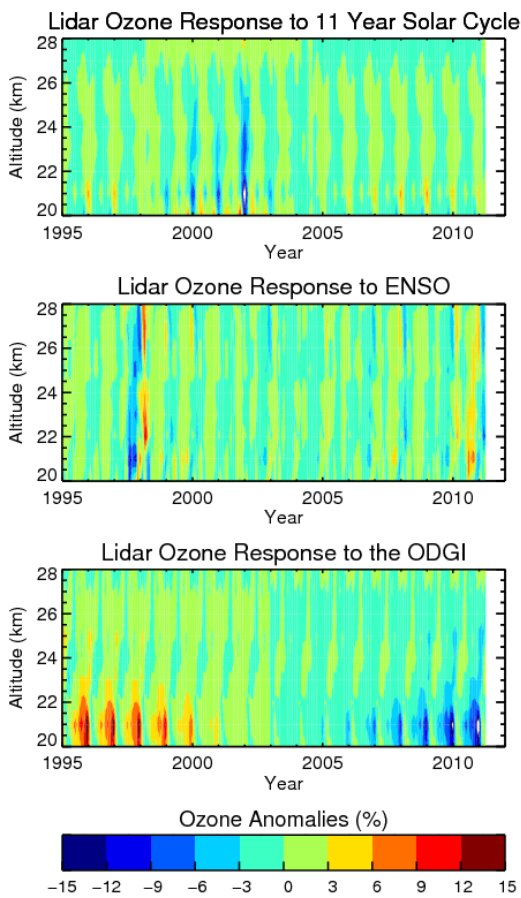
Figure 1. MLO LiDAR ozone response to 11 year Solar Cycle (top), ENSO (middle) and ODGI (bottom).
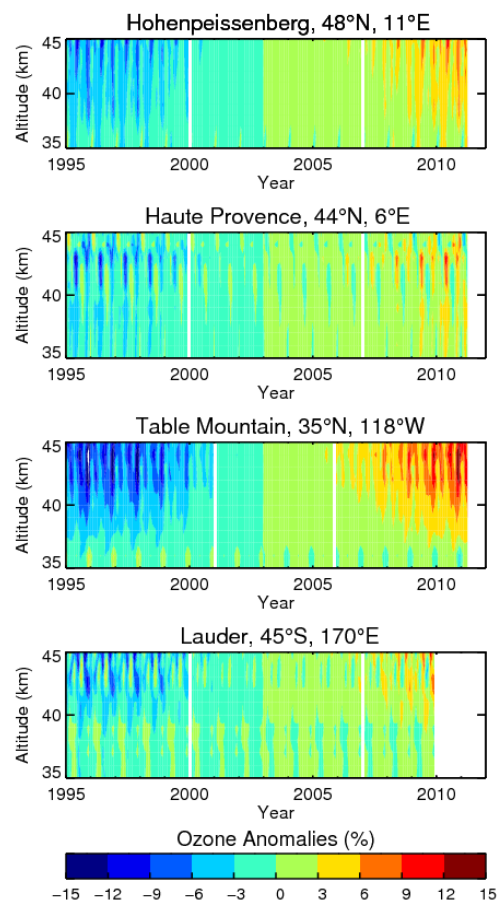
Figure 2. LiDAR ozone responses to the ODGI above four mid-latitudes Network for Detection of Stratospheric Change sites. White lines mark the two steps of ozone recovery (stop of the ozone decrease and start of recovery).

Experimental Validation of a New Balloon-Borne Supercooled Liquid Sensor

E. Hall[1], A. Jordan[1], D. Serke[2], F. McDonough[2], J. Bognar[3], S. Abdo[3], K. Baker[3], T. Seitel[3], R. Ware[4], M. Nelson[4] and A. Reehorst[5]

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[2]National Center for Atmospheric Research, Research Applications Laboratory, Boulder, CO 80301
[3]Anasphere Inc., Bozeman, MT 59718
[4]Radiometrics Corporation, Boulder, CO 80301
[5]NASA Glenn Research Center, Cleveland, OH 44135

An improved version of the ATEK Corporation vibrating wire sensor, used to measure supercooled cloud liquid water content (LWC), has been developed by Anasphere, Inc. This updated sensor reduces the weight of the instrument while improving performance when compared to the preceding balloon-borne sensor that was developed in the 1980's by Hill and Woffinden. Results from recent laboratory testing show that data collected from the Anasphere sensor compares well to data reported during similar icing tunnel testing in 1989 at Eglin Air Force Base with the ATEK Corporation instrument. Balloon-borne test flights were performed from Boulder, Colorado during February and March of 2012 providing comparisons to integrated liquid water and profiles of liquid water content derived from a collocated multichannel profiling radiometer built and operated by Radiometrics Corporation. Inter-comparison data such as these are invaluable for calibration, verification, and validation of remote-sensing instruments. The data gathered from this sensor is important in the detection of icing hazards to aircraft and for truthing of microphysical output from numerical models. The disposable Anasphere vibrating wire sensor interfaces with an InterMet Systems iMet radiosonde measuring pressure, temperature, humidity, wind speed, and wind direction.
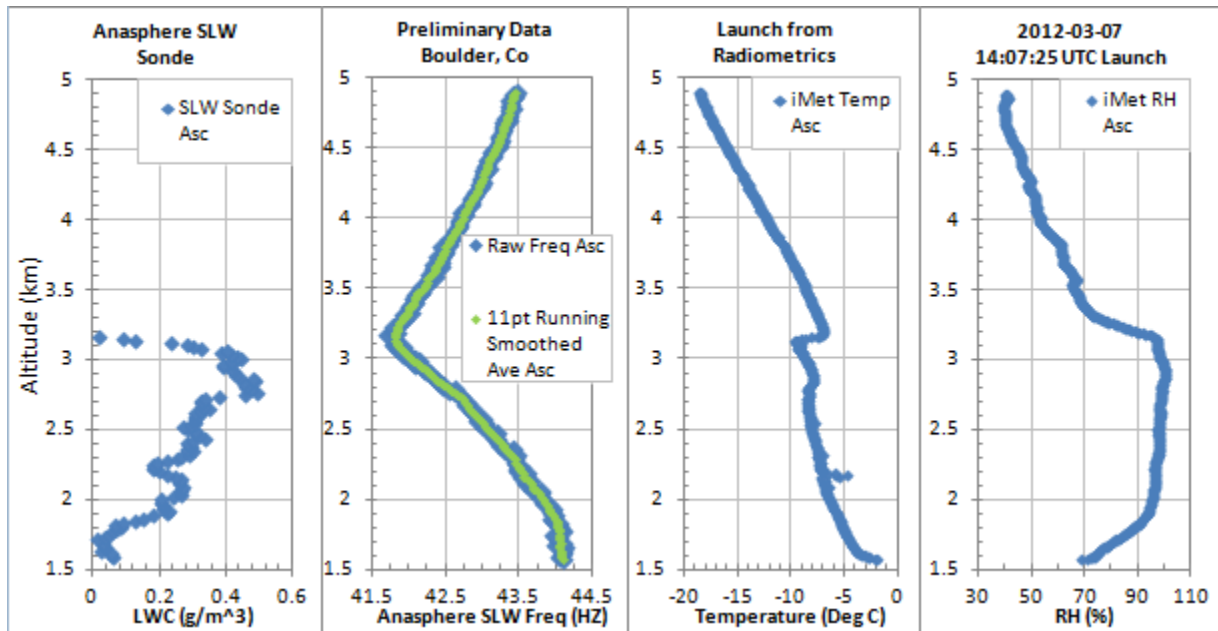

Figure 1. Anasphere SLW Sonde ascent data from March 7, 2012.

SkySonde, a Weather Balloon Telemetry and Data Processing System

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SkySonde is a suite of weather balloon telemetry and data processing software recently created in NOAA's Ozone and Water Vapor Group. It was designed to work with the Intermet iMet-1 radiosonde that measures pressure/temperature/humidity/GPS, along with several external instruments (the EN-SCI ECC Ozonesonde and the NOAA Frostpoint Hygrometer, mainly) when they are launched on the balloons. SkySonde Server collects raw balloon data from a radio receiver, and makes it available locally or through the network to SkySonde Client that plots, processes, and outputs the data. SkySonde Processor can load data files after a flight to do any post-processing calculations, data editing, and final archive-quality file outputs. These programs have greatly simplified the balloon data collection and processing system while providing many useful new features.
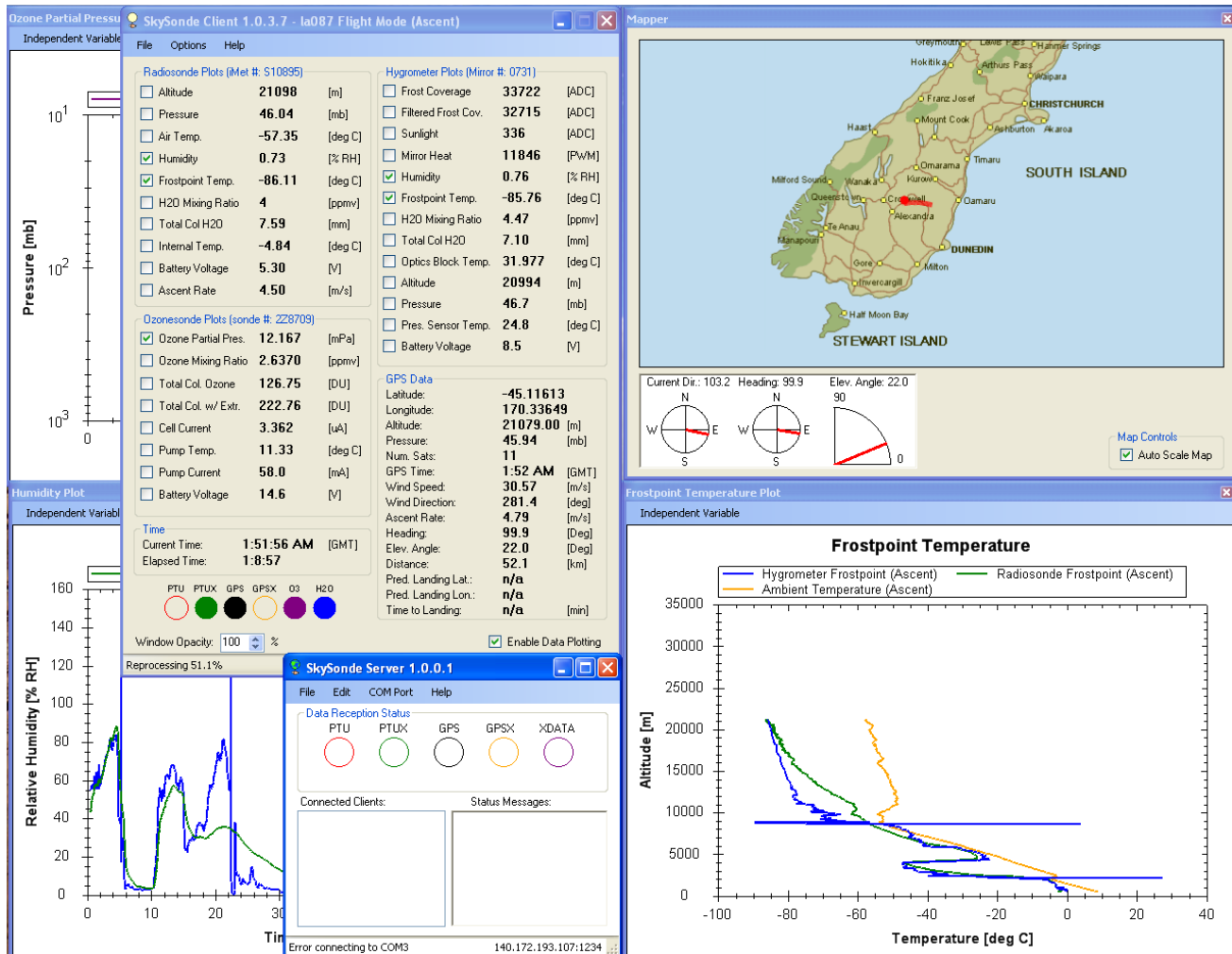

Figure 1. A screenshot of SkySonde Server and SkySonde Client with balloon data from a Lauder, New Zealand flight.

New Tether Ozonesonde System Developed for Uintah Basin Ozone Study in February, 2012

B.J. Johnson[1], J. Wendell[1], P. Cullis[2], E. Hall[2], A. Jordan[2], R. Albee[3] and R. Schnell[1]

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NOAA/ESRL/GMD participated in the February, 2012 UINTAH basin air quality campaign to measure ozone concentrations from surface to 300 meters above ground level. The study region, southwest of Vernal, Utah, is an active oil and gas production and exploration area. During the previous winter in 2011, an air quality study led by state and local agencies and Utah State University measured very high ozone at several sites, exceeding 140 ppbv centered near Ouray, Utah under shallow boundary layer with surface snow-cover conditions. The high ozone conditions never developed during the 2012 campaign due to dry and warm weather remaining in the 20 to 60 ppbv range. In order to provide near continuous ozone profiles without consuming a balloon and ozonesonde for each sounding, a tether system was developed by the Global Monitoring Division based upon a motorized deep sea fishing rod and reel with 50 pound line. The lightweight system was shown to be rugged and reliable and capable of conducting an ascending and descending profile to 300 m within 90 minutes. Communication software and data loggers continuously monitor the radiosonde pressure to control the ascent/descent rates and altitude. The system can operate unmanned as it will ascend, descend and hold an altitude as controlled from a laptop computer located up to 30 m distant. Four systems operating on 12 volt vehicle batteries are available for future campaigns.

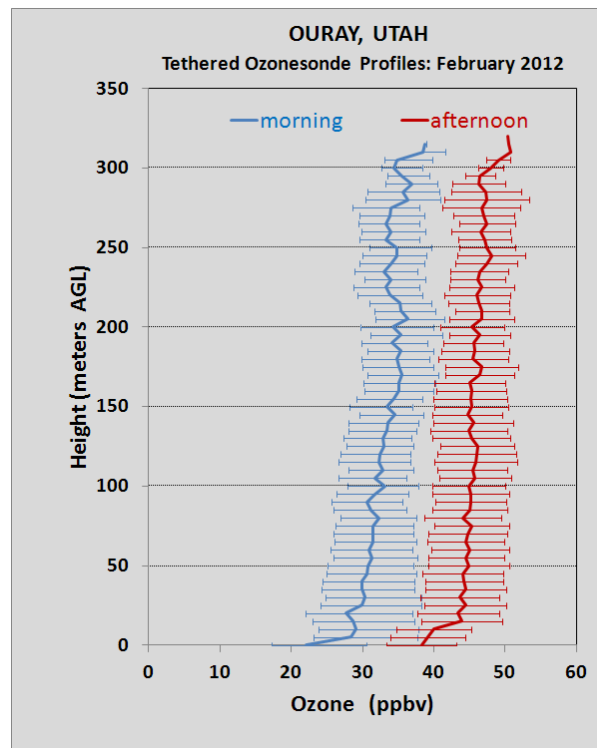

Figure 1. Tethered ozonesonde at Ouray, Utah.

Figure 2. Ozone mixing ratio averages during the Uintah campaign.

Changes in Arctic Atmospheric Chemistry Linked to Ocean Sea Ice Changes

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A forty-year record of ozone measurements at the NOAA Barrow, Alaska Observatory reveals a dramatic change in the annually reoccurring spring depletion of boundary layer ozone (Oltmans et al., 2012). This naturally occurring phenomenon has been greatly enhanced during March over the last two decades due to the changing character of Arctic sea ice. The frequency of the depletion events (defined as ozone mixing ratios <10 ppb) in March has increased by 85% in the second half of the 40-year record compared to the first half. The ozone loss is closely tied to the photochemical reaction with halogens, primarily bromine, whose source are ocean sea water. The activation of bromine takes place through the influence of reactions on snow and ice crystals over the vast Arctic sea ice. In the past, spring ice was primarily ice that had survived the previous or multiple summers (multiyear ice). Now spring ice is dominated by ice that formed during the previous winter (annual ice), which with its more numerous leads is much more conducive than the sturdier multiyear ice for promoting the production of the reactive bromine species implicated in boundary layer ozone depletion. This change in the oxidizing characteristics of the atmosphere may have important implications for the closely related chemical cycle involving mercury. Coincident with the ozone depletion events are events that deplete atmospheric gaseous elemental mercury (GEM) and convert it into a form of mercury that can be deposited to the sea ice surface and the surrounding snow covered tundra regions. It is this converted form of mercury that can be incorporated into the Arctic food chain involving both sea life and terrestrial animals.
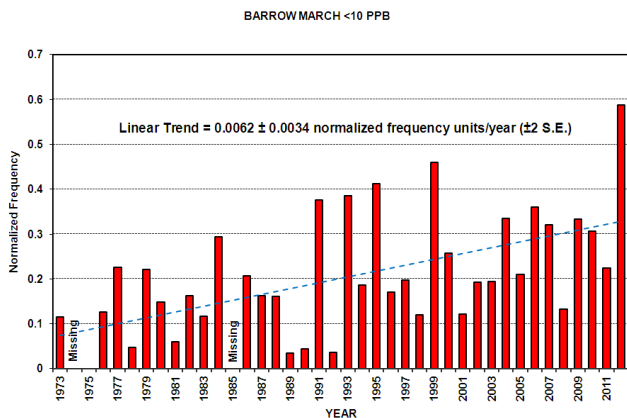

Figure 1. The normalized frequency of hourly average ozone values <10 ppb for the month of March of each year from 1973-2012. The linear trend and two standard error limits for the normalized frequency are 0.0062 ± 0.0034.
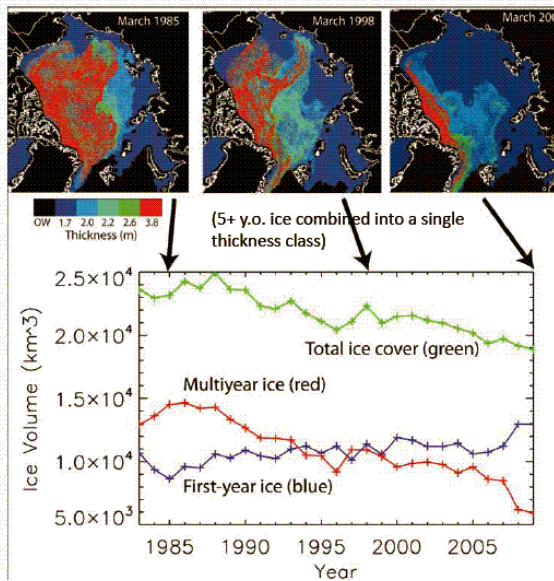

Figure 2. Changes in Arctic sea ice characteristics from M. Tschudi et al.,"Trends and Patterns in Sea Ice Age Distributions within the Arctic Basin and Their Implications for Changes in Ice Thickness and Albedo" presented at the State of the Arctic Conference, March 2010, Miami, Florida.

Ozone Tropospheric and Stratospheric Trends (1995-2011) at Six Ground-based FTIR Stations (28°N to 79°N)

C. Vigouroux[1], M.D. Mazière[1], P. Demoulin[2], C. Servais[2], F. Hase[3], T. Blumenstock[3], M. Schneider[3], R. Kohlhepp[3], S. Barthlott[3], J. Klyft[4], G. Personn[4], M. Palm[5], J. Notholt[5], J. Hannigan[6] and M. Coffey[6]

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[2]Institut dAstrophysique et de Géophysique, University of Liège ULg, Liège, Belgium
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[4]Chalmers University of Technology, Göteborg, Sweden
[5]Institute of Environmental Physics, University of Bremen, Bremen, Germany
[6]National Center for Atmospheric Research, Boulder, CO 80307

As part of the Network for the Detection of Atmospheric Composition Change (NDACC), the retrieved ozone profiles from Fourier transform infrared (FTIR) solar absorption spectra from five stations in Western Europe, from 79°N to 28°N, have been analyzed in Vigouroux et al. (2008)[1]. Using the optimal estimation method, vertical information is obtained for the total column and in four distinct layers: ground-10, 10-18, 18-27 and 27-42km. A bootstrap resampling method was used to determine the trends of the total and partial columns, over the 1995-2004 period. Updated trends for the 1995-2009 have been published in the World Meteorological Organization 2010 Report. Here, we present further updates to mid-2011for the five European stations plus the station at Thule, Greenland (77°N). The trends obtained by bootstrap resampling are discussed for each layer and the total column. A major result is the significant positive trend in the upper stratosphere at the Jungfraujoch Station (47°N), which indicates a sign of mid-latitude ozone recovery.
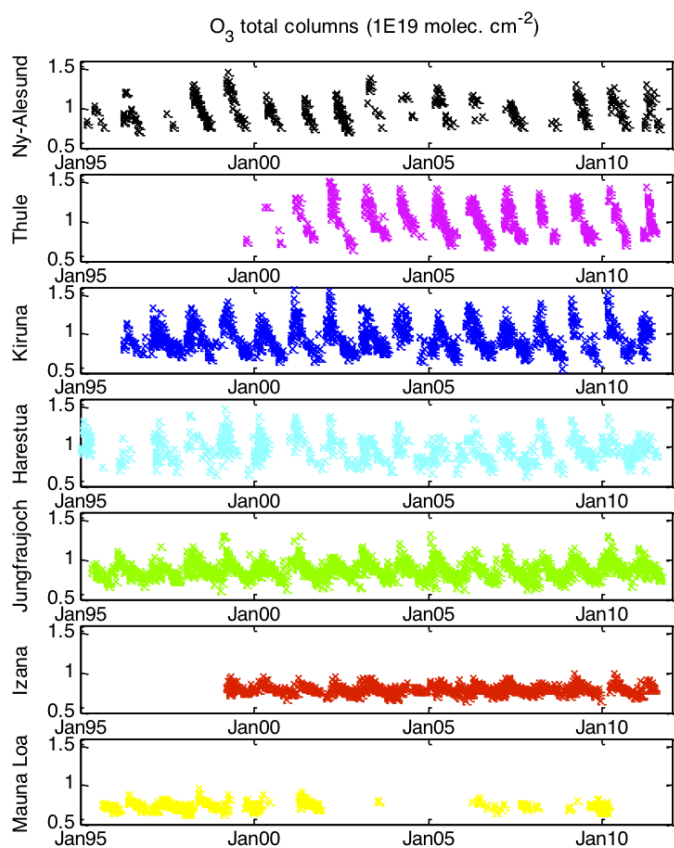

Figure 1. Total column time series for 1995 to mid 2011 from seven NDACC FTIR stations covering Europe, Greenland and Mauna Loa, HI by latitude from 19° to 78° N.

Atmospheric Chemistry of Replacement Compounds: OH Reactivity of the (*E*)- and (*Z*)- CF$_3$CH=CHCF$_3$

M. Baasandorj[1], A.R. Ravishankara[2] and J.B. Burkholder[2]

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[2]NOAA Earth System Research Laboratory, Boulder, CO 80305

Unsaturated hydrofluorocarbons (hydrofluoroolefins, HFO) are currently being considered as potential replacements for hydrochlorofluorocarbons and saturated-hydrofluorocarbons in various commercial applications. (*E*)- and (*Z*)- CF$_3$CH=CHCF$_3$ are replacement candidates, but before used commercially their atmospheric fate and potential impacts on the environment need to be fully assessed. A significant atmospheric loss process for these compounds is expected to be their gas-phase reaction with the Hydroxyl Radical (OH).

In this work, rate coefficients, *k*, for the reaction of the OH radical with (*E*)- and (*Z*)- CF$_3$CH=CHCF$_3$ were measured using two complementary experimental techniques (for this molecule (*E*) is equivalent to *trans*- and (*Z*) is equivalent to the *cis*- isomer). Rate coefficients were measured over a range of temperature (212 – 373) K and total pressure (20 – 600 Torr; He, N$_2$). The temperature dependences of the rate coefficients were, therefore, determined in the temperature regime most relevant to atmospheric chemistry. The rate coefficients were found to be independent of pressure. The (*E*)- and (*Z*)- isomer reactions have significantly different reactivity and temperature dependent behavior over the temperature range of our study as shown in Figure 1. The differences and possible explanations will be discussed. The atmospheric lifetimes of the (*E*)- and (*Z*)-isomers with respect to loss by reaction with the OH radical are estimated to be ~89 and ~20 days, respectively. As part of this work, infrared absorption spectra of (*E*)- and (*Z*)- isomers were measured and combined with the estimated OH reaction lifetimes to estimate the global warming potentials of 32 and 9.4, respectively, for the 100-year time horizon.
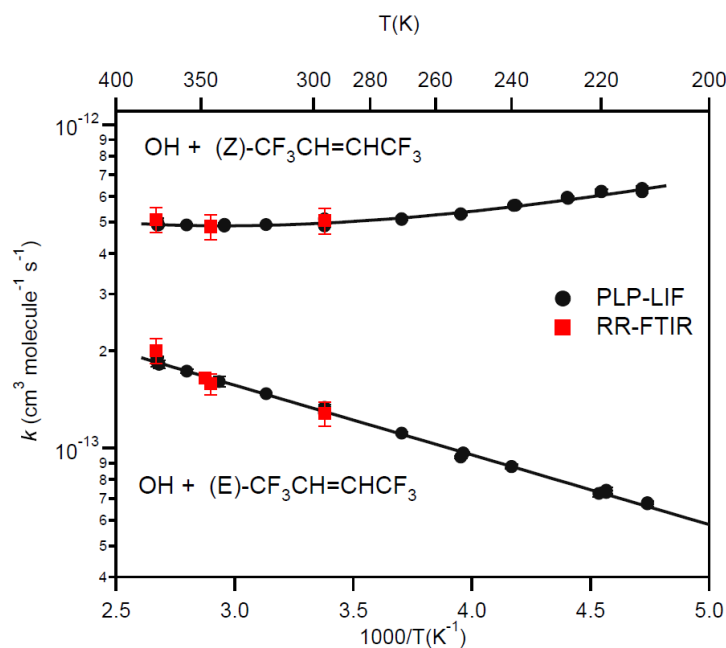

Figure 1. The temperature dependence of the rate coefficients measured for the OH reaction with (*E*)- and (*Z*)- CF$_3$CH=CHCF$_3$. PLP-LIF: Pulsed Laser Photolysis – Laser Induced Fluorescence; RR-FTIR: Relative Rate technique combined with Fourier transform infrared detection.

Three Decades of Continuous Monitoring of Long-lived Halocarbons

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In the mid-1970s, the National Oceanic and Atmospheric Administration's (NOAA) Geophysical Monitoring for Climate Change (GMCC) program made a commitment to measure and monitor trace gases including carbon dioxide, methane, nitrous oxide (N_2O) and chlorofluorocarbons (CFCs). Over the next three decades GMCC grew into a division of NOAA/ESRL, and many trace gas measurement programs evolved into separate projects with different instrumentation. Multiple measurements of the same gases at identical locations (e.g., using both *in situ* instruments and grab samples) can sometimes lead to confusion when determining what measurement to use for analysis. We present a statistical method developed to combine measurements from independent NOAA measurement programs to construct continuous long-term global records for the following ozone-depleting substances: CFC-11, CFC-12, CFC-113, methyl chloroform (CH_3CCl_3) and CCl_4. The combining technique takes advantage of co-located measurements and accounts for systematic differences between measurement programs. We also use two different statistical approaches to characterize uncertainties in hemispheric and global means. The combined data sets and uncertainties can be used in global growth rate and top down emission estimates of these important gases.
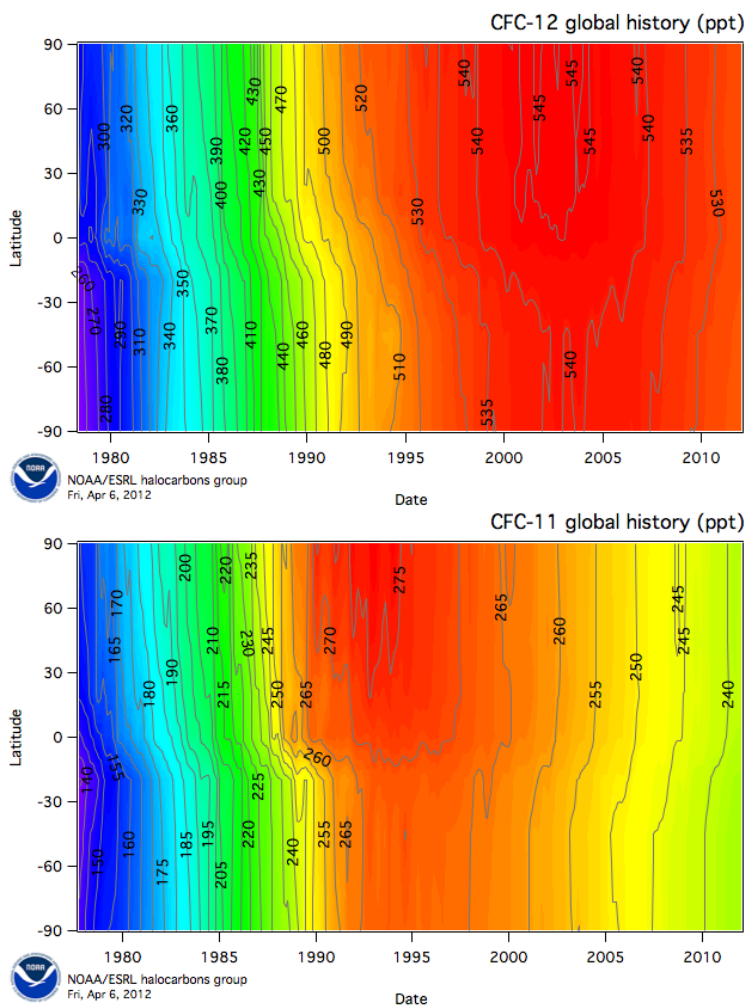

Figure 1. Contour maps of CFC-12 and CFC-11 global histories show the predominate sources in the northern hemisphere. As the mixing ratios were growing in the 1970s to 90s the southern hemisphere lagged behind the north. As the gases have been phased out the growth rates are now in decline.

New High-frequency Measurements of CH$_4$, N$_2$O and SF$_6$ from a High-altitude Station in Darjeeling, Eastern Himalayas, India

A.L. Ganesan[1], A. Chatterjee[2], P.K. Salameh[3], C.M. Harth[3], A.J. Manning[4], B.D. Hall[5], S.K. Ghosh[2], J. Muhle[3], L.K. Meredith[1], T.K. Mandal[6], R.F. Weiss[3] and R.G. Prinn[1]

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We present new *in situ* measurements from a station in Darjeeling, India (27.03°N, 88.26°E, 2300 m above sea level). These measurements comprise the first high-frequency dataset of methane (CH$_4$), nitrous oxide (N$_2$O) and sulfur hexafluoride (SF$_6$) collected in India. Measurements are made with a gas chromatographic system, using a flame ionization detector (GC-FID) for CH$_4$ and electron capture detector (GC-ECD) for N$_2$O and SF$_6$. Measurements have been linked to calibration scales used in the Advanced Global Atmospheric Gases Experiment (Tohoku University for CH$_4$ and Scripps Institution of Oceanography, 1998 and 2005, for N$_2$O and SF$_6$ respectively). Preliminary results show a significant diurnal cycle for CH$_4$, consistent with upslope flows bringing local emissions from the town and valley to the site during the day and downslope flows bringing cleaner air at night. This nighttime decrease could be attributed to a variety of factors including reduced local emissions or sampling of cleaner, free tropospheric air. This local signal is added to a much larger regional influence, which is driven by the large-scale meteorology that governs which regions contribute to the measured mole fractions at the site. We also investigate local influences on N$_2$O and SF$_6$, which are expected to be much smaller or negligible, due to the less significant nearby sources as compared to CH$_4$. Local and regional meteorology and air histories generated using the United Kingdom Meteorological Office NAME model reveal that the site regularly intercepts air from vitally important rice-growing and biomass burning regions of Northern India. This unique dataset should therefore allow further constraints to be placed on "top-down" estimates of emissions from these methane sources. Further constraints will also be possible for regional agricultural sources of N$_2$O and South Asian SF$_6$, both of which are under-sampled and poorly understood at present.
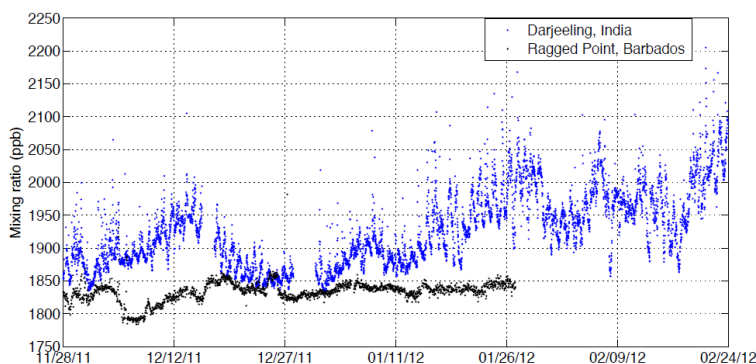

Figure 1. CH$_4$ mixing ratio (ppb) from Darjeeling, India (blue) and Ragged Point, Barbados (black) for comparison. Darjeeling typically receives polluted continental air but on occasion samples nighttime air at levels close to the background values sampled at Ragged Point, a tropical site at 13°N, 59°W. A strong diurnal cycle is present, indicative of upslope and downslope flows bringing to the site local emissions during the day and cleaner air at night.

Revision of the NOAA 2006 N₂O Scale

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NOAA/ESRL/GMD serves as the World Meteorological Organization/Global Atmosphere Watch Central Calibration Laboratory for five trace gases (CO_2, CH_4, CO, N_2O, and SF_6). Traceable, stable calibration scales are critically important for the atmospheric science community. From 2004-2009 the NOAA 2006 N_2O scale showed an apparent upward drift of 0.03 ppb yr⁻¹. The cause of the drift was determined to be downward drift in a secondary standard used for routine calibration. This secondary standard is drifting at a rate of -0.051 ± 0.014 ppb yr⁻¹. All secondary standards have been replaced and the N_2O 2006 scale was recently revised. The updated scale, NOAA 2006A, appears to be stable since 2006. The average difference between the 2006 and 2006A scales is -0.09 ppb. Actual differences are time-dependent. While the conventional wisdom holds that N_2O drift in compressed gas cylinders is rare, these and other results suggest that N_2O drift (at low rates) may be more common than previously thought.
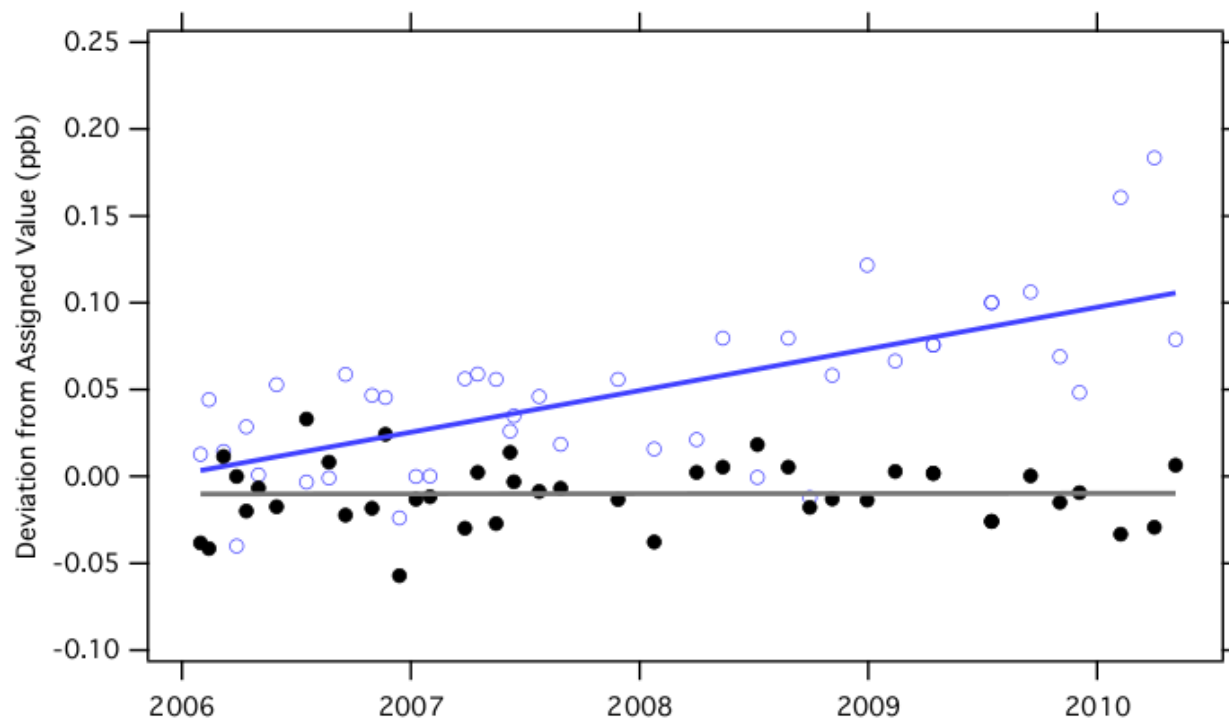

Figure 1. Apparent drift of the NOAA 2006 N_2O scale before (open symbols) and after (filled symbols) a drifting secondary standard was discovered and excluded from the calibration procedure. The downward drift in the secondary standard induced an upward drift in the N_2O scale of 0.03 ppb yr⁻¹. The scale has been updated and drift is no longer apparent.

Polyhalogenated Very Short Lived Substances (VSLS) in the Atlantic Ocean, and Their Linkages with Ocean Primary Production

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Bromoform ($CHBr_3$), dibromomethane (CH_2Br_2) and other VSLS were measured during 5 cruises from 1998 to 2010. These cruises were conducted over a large meridional (62° N - 60° S) and zonal transect (11° W – 86° W) in the Atlantic Ocean. Elevated atmospheric mixing ratio and seawater concentrations of $CHBr_3$ were observed coincident with regions of elevated chlorophyll *a*, such as the equatorial region, upwelling zones and coastally influenced / shelf waters, indicating ocean primary production is related to $CHBr_3$ production. While CH_2Br_2 seawater concentrations exhibit similar trends with $CHBr_3$, it is better mixed in the atmosphere, due to its longer atmospheric lifetime. The sea-to-air flux maxima for $CHBr_3$ and CH_2Br_2 were observed in coastally influenced / shelf waters. Assuming fluxes measured in the Atlantic open ocean are globally representative, the resulting extrapolated $CHBr_3$ global open ocean annual net sea-to-air flux is 0.13 - 3.6 Gmol Br yr^{-1}.

During one of the cruises conducted in 2010 (HalocAST – A), we also measured pigment biomarkers, flow cytometeric picoplankton counts, and other biochemical parameters to better understand the possible linkages between the production of the VSLS and different phytoplankton groups. However, none of the pigment biomarkers yield significant correlations with $CHBr_3$ and CH_2Br_2. While zeaxanthin does not distinguish between *Synechococcus* sp. and *Prochlorococcus* sp, flow cytometeric cell counts do allow for their separation and determination of their individual abundances, as well as providing cell abundance information for other picoeukaryotes and heterotrophic bacteria. Seawater concentrations of $CHBr_3$ were significantly correlated with *Synechococcus* sp. near the Northwestern African upwelling zone but not anywhere else during the HalocAST – A cruise. These findings indicate that more specific parameters are needed for assessing biogenic sources of the VSLS during large oceanographic transects due to changing biomes during the course of the cruise.
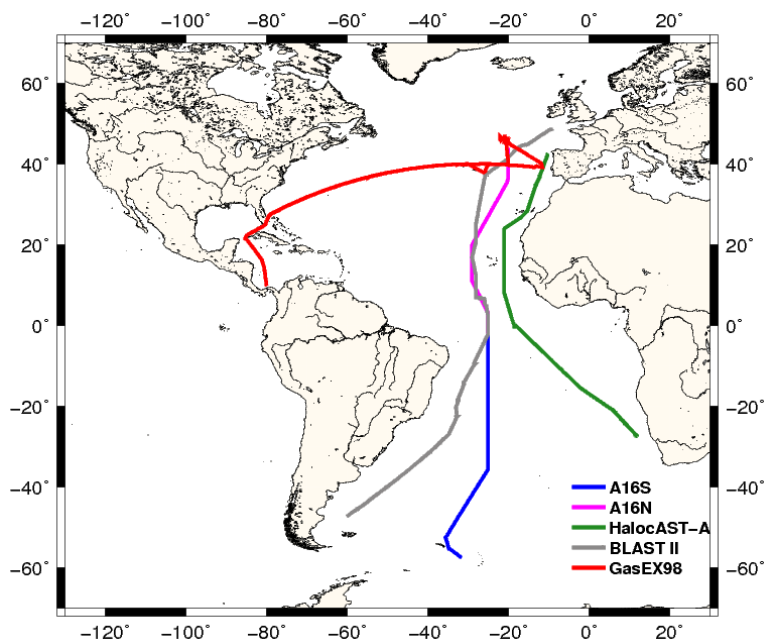

Figure 1. Ship tracks of where data were collected for cruises A16N (magenta line), A16S (blue line), HalocAST-A (green line), BLAST-II (grey line) and GasEX-98 (red line).

The Atmospheric Distribution of Molecular Hydrogen (H_2) and Related Species Observed During the HIPPO Project

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The goal of the HIAPER Pole-to-Pole Observations (HIPPO) of Carbon Cycle and Greenhouse Gases project was to measure a large set of trace gases and black carbon aerosols as a function of altitude and latitude in different seasons in order to better understand their sources, sinks, and atmospheric transport, and to use these measurements to compare with a variety of chemical transport models. This should ultimately lead to improvements in the models. The National Science Foundation/National Center for Atmospheric Research Gulfstream V (GV) aircraft (formerly known as HIAPER) was equipped with a suite of instruments for carbon cycle and greenhouse gases, ozone and a few other reactive gases, aerosols, and meteorological parameters. The GV flew a set of five transects in 2009-2011 from Colorado to Anchorage, AK, to near the north pole, then south to Christchurch, NZ, toward the edge of Antarctica, and back to the northern hemisphere high latitudes, with intermediate stops at different locations in the Pacific Ocean. On each leg of the journey, the GV carried out a series of profiles from the marine (or continental) boundary layer to the stratosphere, generating a set of altitude/latitude slices of the atmosphere in different seasons (January 2009, October-November 2009, March-April 2010, June-July 2011, and August-September 2011).

In this presentation, results are shown that were obtained from the UAS Chromatograph for Atmospheric Trace Species (UCATS) instrument and other sensors on board the GV, and from whole air samples analyzed in the laboratory post-flight. UCATS was configured to measure N_2O, SF_6, H_2, CH_4, CO, water, and ozone during HIPPO. The focus here is on the distribution of molecular hydrogen (H_2), which has a diverse set of atmospheric and terrestrial sources, and a sink term that is dominated by soil uptake. Results are broadly consistent with previous studies, showing a slight maximum in the southern hemisphere, much greater variability with altitude in the northern hemisphere, and overall stability in the global average mixing ratio in recent years. Tracer-tracer correlation plots of H_2 with methane and CO allow details of the distribution of hydrogen to be elucidated. There appears to be a local maximum in H_2 at northern hemisphere midlatitudes in spring and early summer. Low values of hydrogen persist at high northern latitudes long after the soil sink should have decreased with the onset of winter.
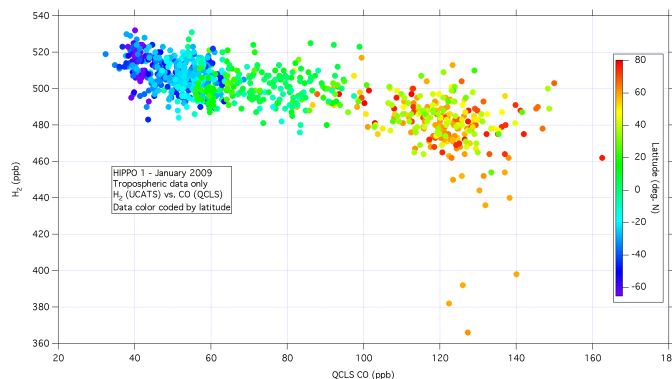

Figure 1. Tracer-tracer correlation plot of tropospheric H_2 vs. CO color-coded by latitude in January 2009, at the time of the maximum in the southern hemisphere H_2 seasonal cycle.

Snapshot of Atmospheric Trace Gases "Pole to Pole" – Highlights from the HIPPO Whole Air Sampler

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__HI__aper __P__ole to __P__ole __O__bservations (HIPPO) mission: "To measure cross sections of atmospheric concentrations approximately pole-to-pole, from the surface to the tropopause, five times during different seasons over a three year period…"

Results from the NOAA/RSMAS whole air flask sampler taken during the HIPPO missions provide an unprecedented snapshot view of ~80 atmospheric trace gas distributions throughout much of the troposphere. A custom air sampling module aboard the Gulf Stream V aircraft was used to sample whole air into stainless steel flasks and glass flask packages. Observed trace gas distributions reflect the combination of transport, chemistry and/or source/sink distributions and are evident across hemispheric scales and through atmospheric regimes that include the open Pacific Ocean and North America and from near-surface (200 m) up to regions of stratospheric influence (14,400 m). The multitude of measured atmospheric compounds, spanning a wide range of lifetimes, growth rates and source/sink distributions, provide insight into chemistry and transport processes.
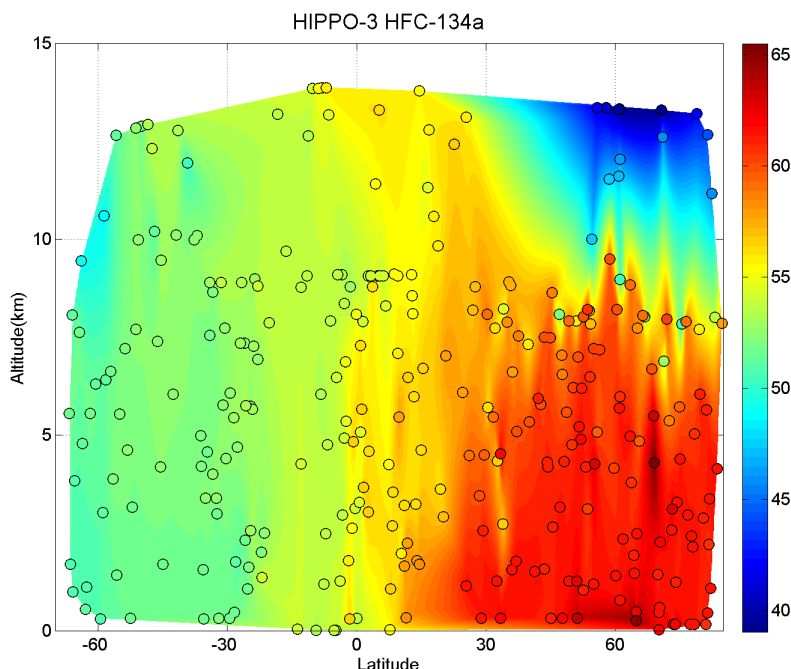

Figure 1. HFC-134a mole fractions (colorbar in parts per trillion) from the Pacific Ocean North-South transect. Circles represent coordinates of samples collected in NOAA's Carbon Cycle Greenhouse Gases Group's glass flask packages.

Improving Our Understanding of Ozone-depleting Substances in the Upper Atmosphere

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The Montreal Protocol on Substances that Deplete the Ozone Layer and its subsequent amendments has been successful in decreasing the atmospheric burden of total equivalent chlorine from man-made halocarbons by ~13% since its peak in 1994-5. The National Oceanic and Atmospheric Administration, Earth System Research Laboratory (NOAA/ESRL) maintains a global, ground-based *in situ* and flask sampling network for the measurement and analysis of halocarbons and other atmospheric trace gases. Through collaborations with the National Aeronautics and Space Administration (NASA) and the National Science Foundation (NSF), NOAA/ESRL also operates a number of *in situ* and flask sampling systems from manned and unmanned (drone) aircraft up to 21 km, and from balloon platforms up to 32 km. We measure over 40 trace gases in the atmosphere including nitrous oxide, chlorofluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons, methyl halides, numerous halocarbons, sulfur gases (COS, SF_6, CS_2), and selected hydrocarbons. We will present an overview of our ground-based and airborne measurements while highlighting some of our recent observations of halocarbons and other trace gases from the NSF and NOAA sponsored HIAPER Pole-to-Pole Observations airborne campaign over Network for the Detection of Atmospheric Composition Change and NOAA stations from 2009 to 2011, and the NASA and NOAA sponsored Unmanned Aerial Systems Missions.
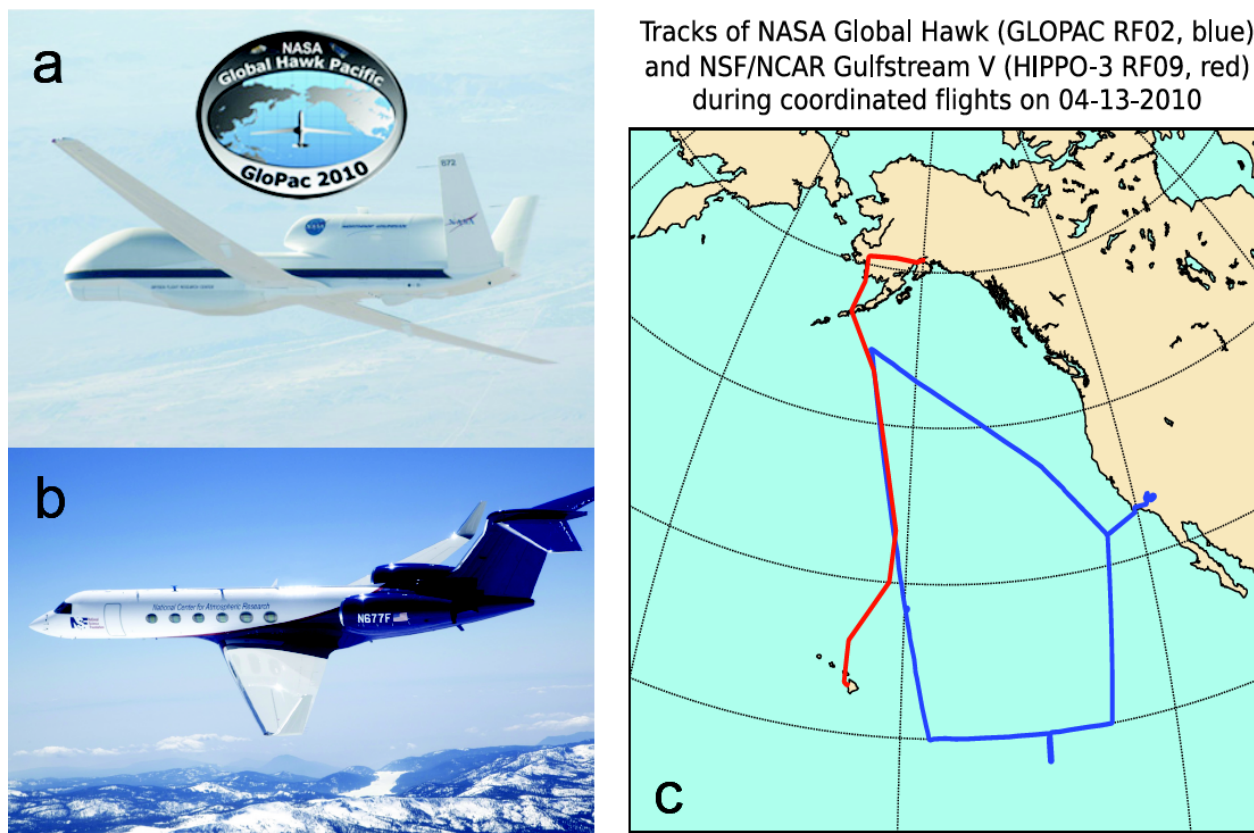

Figure 1. NASA Global Hawk (a) and NSF/National Center for Atmospheric Research (NCAR) Gulfstream V (b) with flight tracks shown for coordinated GloPac-HIPPO flights over the Pacific Ocean on April 13, 2010 (c).

A Study of the Behavior of Mg(ClO$_4$)$_2$ Drying Traps Used in Gas Chromatography-Mass Spectrometry (MS) Analysis of Flasks

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Instrumentation used during chromatographic analysis of air samples often requires drying of an air stream. We dry flask air during its analysis by passing it over short ¼" traps filled with Mg(ClO$_4$)$_2$. The reason for this study was an increasing frequency of chromatographic problems affecting the results of a group of compounds that we believed were caused by water. Water causes blockage of cold zones prohibiting sampling; water also appears to interfere with the ionization process and adversely affects the sensitivity of the mass spectrometer. While driers had behaved predictably for many years, it seemed that the capacity of a drier to remove water had become highly variable. At times dry air appeared anomalously wet while humidified samples appeared well dried. Given the universality of a mass spectrometer for detecting many different chemicals including water, we began studying the variables influencing the efficiency of our driers. By analyzing dry zero air with the MS detector in "SCAN" mode, to explicitly monitor the water passing through the Mg(ClO$_4$)$_2$ trap, we were able to confirm that high water levels were indeed interfering with the results. These tests allowed us to realize that the pressure over the drier during the analysis of different types of samples (flasks vs. cylinders) influenced the water concentration downstream of the trap (drying is more efficient at higher pressures). These tests also demonstrated that reversed flow of humid room air temporarily over the trap made it essentially unusable once flow was restored in the proper direction; it appeared as if water absorption by Mg(ClO$_4$)$_2$ was surprisingly reversible. Regular analyses of zero air for water in the "SCAN" mode are now performed and allow us to accurately track the performance of the drier. As a result, we replace the Mg(ClO$_4$)$_2$ on an as-needed basis only, and this leads to significant improvements in instrument performance and consistency, and, equally important, happier analysts.
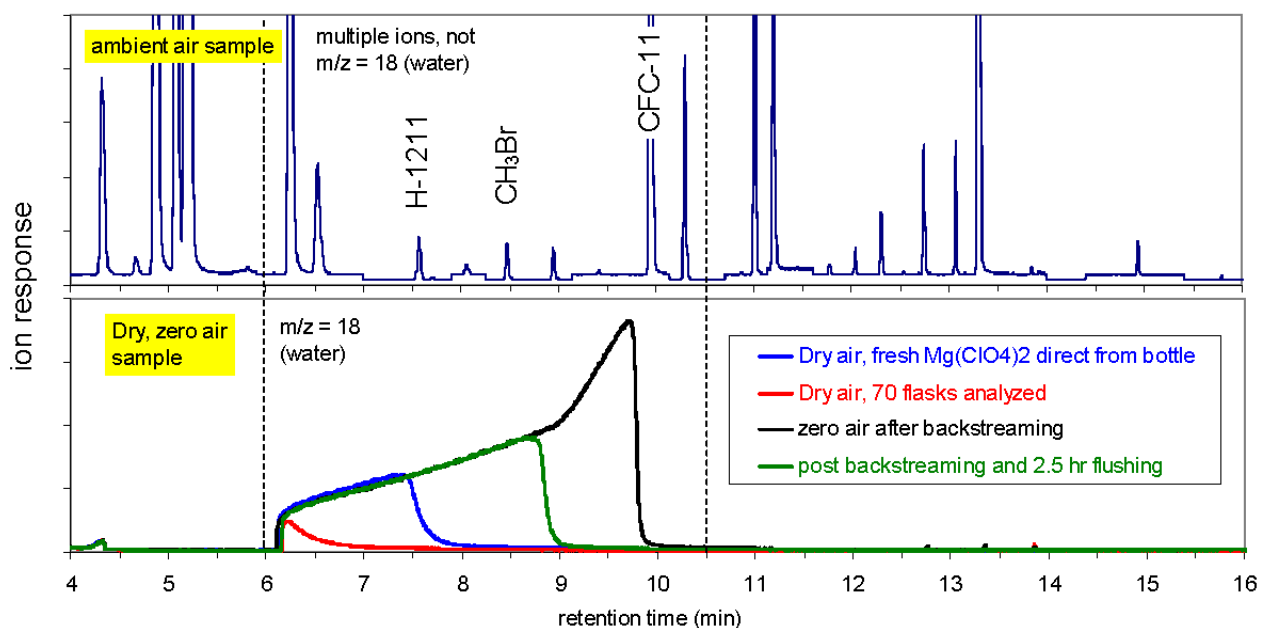

Figure 1. ion chromatograms showing the retention time of analytes (upper panel) and the elution of water as a function of past history of the Mg(ClO$_4$)$_2$ drying trap.

Atmospheric Network Design in Europe

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To improve our understanding of Greenhouse Gas (GHG) sources and sinks, as well as their rebalancing due to changes in climate and human impacts, long-term observations of atmospheric GHG made at representative locations over the continent will be an essential source of information. Atmospheric inverse systems provide the link between observed spatiotemporal patterns of atmospheric concentrations to surface fluxes based on the use of atmospheric transport models. As surface-atmosphere exchange fluxes of CO_2 and CH_4 exhibit significant variability in time and space, and as atmospheric mixing is not a reversible process, a priori information is required to regularize the inversion. This information is provided in the form of gridded inventories for anthropogenic emissions, and in the form of diagnostic or prognostic models for biospheric fluxes. Within the upcoming years ICOS and Earth Networks will largely increase the density of the atmospheric network in Europe. Coordinated efforts on planning, model aided network design, as well as data and instruments quality control have already been started. To assist decision-making with respect to the location and density of observing stations to be deployed, a quantitative network design is focused on optimizing the atmospheric constraint on specific targeted quantities given a fixed number of sites. The assessment uses multiple inversion modelling systems with different transport models and different definitions of the flux space to account for the uncertainties. In this paper an overview of the network design efforts and recommendations for synergetic deployment of stations in Europe is discussed.
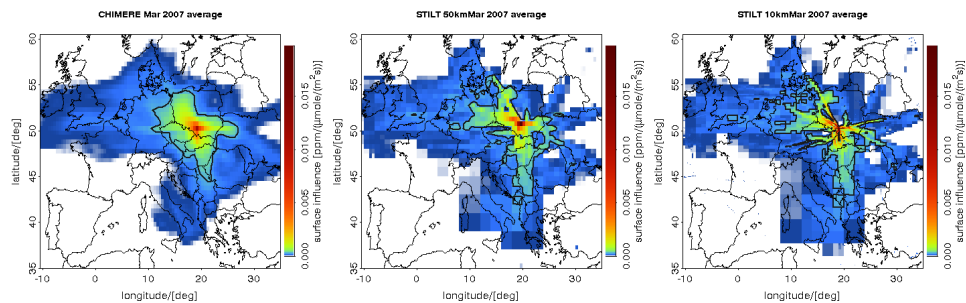

Figure 1. Sensitivities of monthly mean observations at 15:00 to surface fluxes (day and night) for the month of March 2007 for a tall tower in Poland calculated with ECMWF-CHIMERE (left), ECMWF-STILT with 0.5x0.5 deg (middle) and STILT with 1/12 x 1/8 deg resolution (right). Note: the values for the high resolution STILT case were scaled down by the grid area ratio. The black contour line indicates the 50% largest sensitivities.
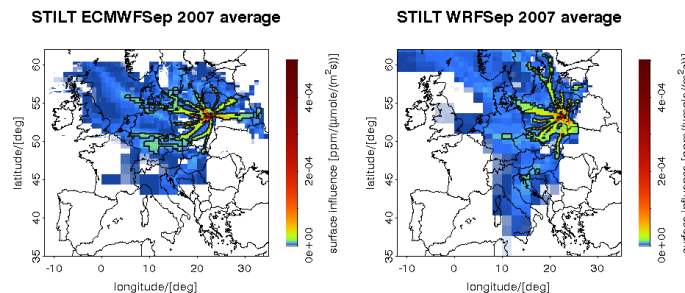

Figure 2. Sensitivities of monthly mean observations to surface fluxes for a tall tower in Poland for the month of September 2007 calculated with ECMWF-STILT (left) and WRF-STILT(right). Notation as in Figure 1.

Monitoring Patterns and Anomalies Using the Dense GHG Network in the Northeastern U.S.

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Last year Earth Networks began the five year deployment of 100 cavity ring-down spectrometers for continuously measuring CO_2 and CH_4. It is planned to place sensors at 50 tall towers in the United States, 25 in Europe, and 25 around the world. Data from this network will be used for monitoring and verification, and for inverse modeling to estimate natural and anthropogenic sources and sinks of greenhouse gases (GHGs). Instruments are calibrated daily using a standard gas mixture from NOAA. Sampling rate of the raw data from spectrometers is at the sub-minute range and higher than in flask networks previously used for regional inversions. Currently, 20 instruments are already deployed in the U.S., and most of the sites are in the northeast. Using these real-time continuous *in situ* GHG observations, patterns and anomalies in the data are analyzed to relate GHG measurements at towers to specific sources. To compute footprints and to carry out the inversions, a coupled system of the Weather Research and Forecasting and the Stochastic Time-Inverted Lagrangian Transport models is used. Observations from numerous surface weather stations are also utilized in this study. High sampling rate and the density of the sites in the region, which have diverse GHG sources, terrain and coastal line complexity, and dynamic weather patterns, are important for gaining a scientific insight into multi-scale processes both at the surface and in the atmosphere. Dense coverage of the sites in the region allows analyzing the data both for site-to-site comparison and for area-averaged estimates of GHG levels. In this talk, we provide several examples of the features revealed through the observations in the recently deployed network in the northeastern U.S. network, as well as our preliminary findings.
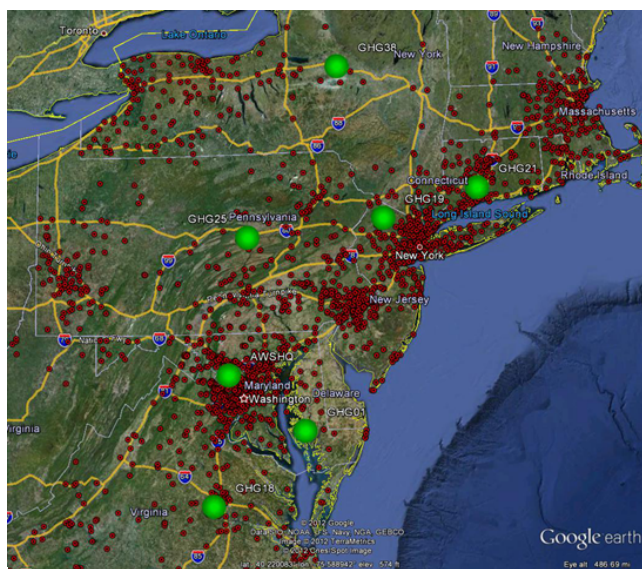

Figure 1. Earth Networks' sites in the Northeastern U.S. (green markers = GHG sites, dark red = weather stations).
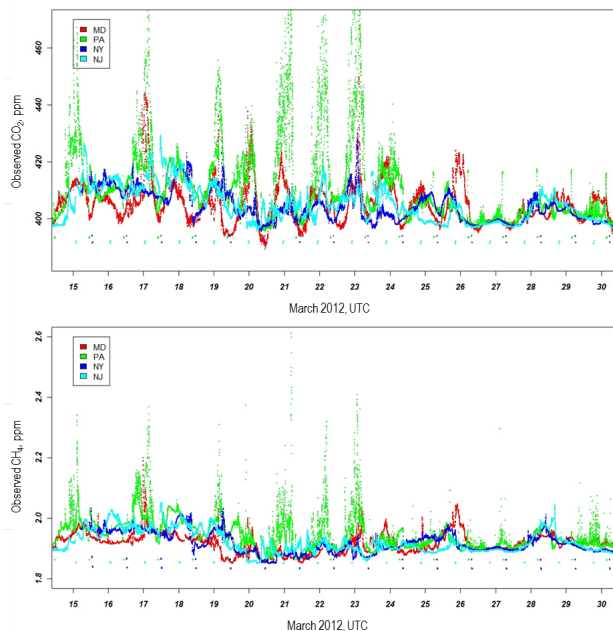

Figure 2. Observations of CO_2 (top) and CH_4 (bottom) at Earth Networks' site in the second half of March 2012.

Emissions from Oil and Natural Gas Operations in Northeastern Utah

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The Uintah oil and natural gas Basin in Northeastern Utah experienced several days of high ozone levels in early 2011 during cold temperature inversions. To study the chemical and meteorological processes leading to these wintertime ozone pollution events, the State of Utah, EPA Region 8, and oil and gas operators pulled together a multi-agency research team, including NOAA ESRL/CIRES scientists. The data gathering took place between January 15 and February 29, 2012.To document the chemical signature of various sources in the Basin, we outfitted a passenger van with in-situ analyzers (Picarro: CH_4, CO_2, CO, H_2O, $^{13}CH_4$; NOxCaRD: NO, NOx, 2B & NOxCaRD: O_3) meteorological sensors, GPS units, discrete flask sampling apparatus, as well as a data logging and "real-time" in-situ data visualization system. The instrumented van, also called Mobile Lab also hosted a KIT Proton Transfer Reaction Mass Spectrometer (suite of VOCs in situ measurements) for part of the campaign. For close to a month, the Mobile Lab traveled the roads of the oil and gas field, documenting ambient levels of several tracers. Close to 180 valid air samples were collected in February by the Mobile Lab for future analysis in the NOAA and CU/INSTAAR labs in Boulder. At the same time as the surface effort was going on, an instrumented light aircraft conducted transects over the Basin collecting air samples mostly in the boundary layer and measuring in situ the following species CH_4, CO_2 NO_2, O_3. We will present some of the data collected by the Mobile Lab and the aircraft and discuss some early analysis results.

Figure 1. Mobile Lab sampling downwind of an oil well pad near Horse Pool, Uintah Basin, February 2012.

NOAA Mobile Laboratory Measures Oil and Gas Emmissions

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A van capable of continuous real time measurement of CH_4, CO_2, CO, Water Vapor, Ozone, NO, NO_2, Volatile Organic Compounds (VOCs) (including aromatics) and other trace gases was driven in the oil and gas fields of the Uintah Basin in northeastern Utah. Compressor stations, processing plants, oil and gas well heads, separators, condensate tanks, evaporation pond disposal facilities, holding tanks, hydraulic fracturing sites, gas pipelines and more were studied using the van. The mobile measurements provide a powerful tool to get to the source of emissions and reveal the unique chemical signature of each of the stages and components of oil and gas production as well as overall basin and background gas concentrations. In addition to a suite of gas analyzers, the van includes a meteorological system, GPS tracking, flask sampling system, and a battery power system. Aspects of the vans hardware, sampling methods and operations are discussed along with a few highlights of the measurements.

Figure 1. The Van is shown on roads near Oil and Gas operations and a coal power plant in the Uintah Basin near Vernal, Utah.

Evaluating New High-frequency, High-precision Measurements of δ¹³C-CH₄ and δD-CH₄ for Top-down Emissions Estimation

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A new generation of observations of methane isotopologues are being developed based on quantum cascade laser spectroscopy. These new instruments, when combined with sample pre-concentration techniques, may allow *in situ* measurement of δ¹³C-CH₄ and δD-CH₄ at higher precision than previously possible and around an hourly frequency. If the anticipated precisions can be achieved, these new measurements should sample much of expected methane isotopologue variability on daily through annual timescales. Using model-generated time series' of δ¹³C-CH₄ and δD-CH₄, and estimates of source/sink-isotopologue sensitivity functions, we evaluate the benefit of these new observations in inverse estimates of methane sinks and emissions from four major sectors (microbial, fossil fuel, biomass burning and landfill). For global source estimation, we find additional uncertainty reductions of between 1 - 9 Tg/year for these source categories, compared to mole fraction-only inversions. On national scales, we obtain average uncertainty reductions of ~5-10% of the source strength for countries close to high-frequency monitoring sites, although the degree of uncertainty reduction on such small scales varies significantly (from close to 0% to almost 50%) for different sectors and countries.
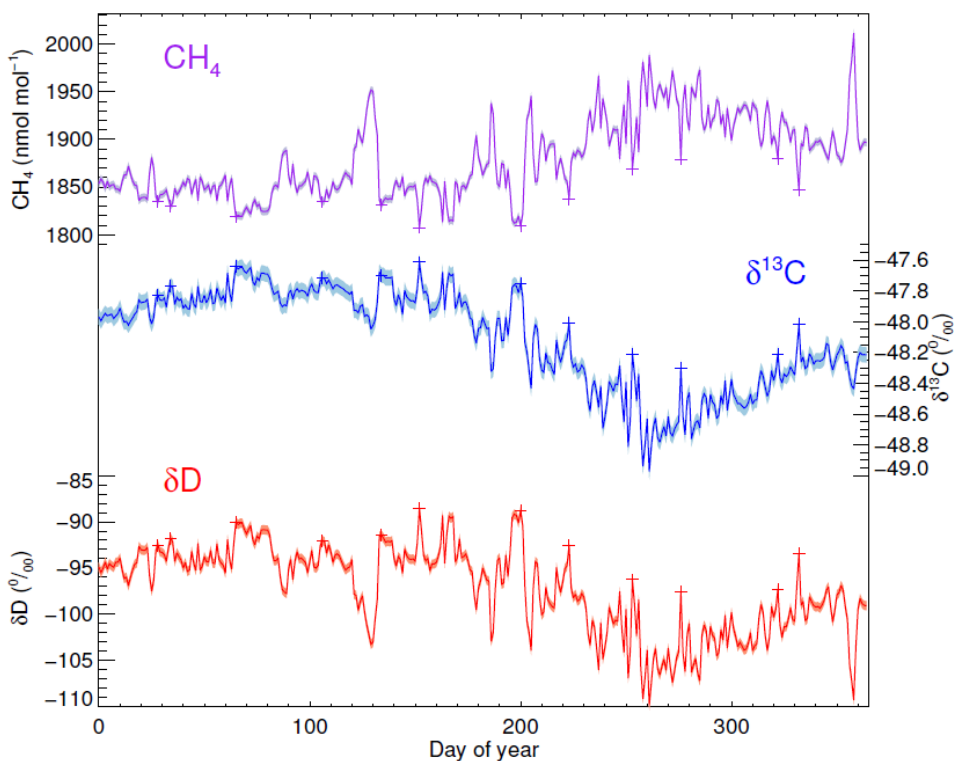
Figure 1. Model-generated daily average methane mole fractions (top panel, purple), and delta values for the two major isotopologues of methane (δ¹³C-CH₄, blue, and δD-CH₄, red) at Mace Head, Ireland. Anticipated measurement repeatabilities are indicated by the shading. The figure shows that much of the isotopologue variability should be resolved by the new observations.

The Identification and Quantification of Greenhouse Gas Point Source Emissions Using Cavity Ring-down Spectroscopy, Complementary to Other Techniques

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The provision of robust, accurate, stable, and mobile instrumentation for the determination of key greenhouse gases (GHGs) in ambient air is essential for assessing the emissions of these species from anthropogenic sources such as landfill sites, industrial processes, and agricultural facilities, for the purpose of process optimisation and carbon accounting activities. We report the details of a study where a commercial Cavity Ring-Down Spectroscopy (CRDS) based analyser (Tiger Optics Tiger-I 2000) has been developed to complement the measurement of point source emissions of GHGs using more established techniques such as open-path Fourier Transform Infrared Spectroscopy and Differential Absorption LIDAR. We give an introduction to the CRDS technique, its application to GHG measurements, and wider applications of the technique relevant to the environmental sector. We demonstrate that CRDS provides a reliable, fast response, calibration-free, relatively low-cost option for the identification of point sources and the subsequent quantification of emitted GHGs. We show how the technology provides the appropriate sensitivity in order to determine the output of gases at some distance from the emission source, and also the dynamic range to allow effective measurements of localised sources within the site of interest.
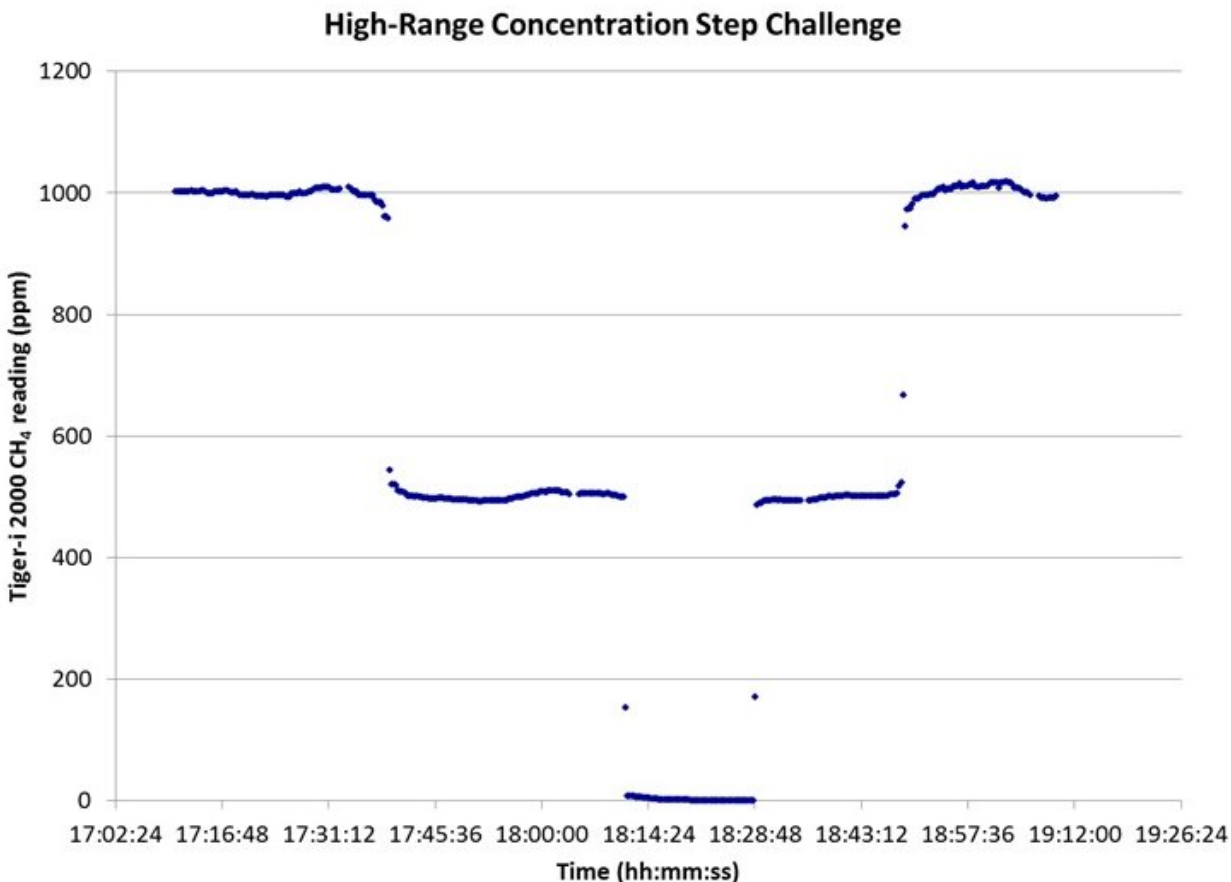

Figure 1. Tiger-I 2000 response to high concentration CH_4 intrusion.

Interannual Variability of Carbon Monoxide Emission Estimates Over South America from 2006 to 2010

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We present the first inverse modeling study to estimate CO emissions constrained by surface and satellite observations. Our 4D-Var system assimilates NOAA/ESRL Global Monitoring Division surface and Measurements Of Pollution In The Troposphere (MOPITT) satellite observations jointly by fitting a bias correction scheme. This approach leads to the identication of a slight positive bias of maximum 5 ppb in MOPITT column-averaged CO mixing ratios in the remote Southern Hemisphere. The 4D-Var system is used to estimate CO emissions over South America in the period 2006 - 2010 and to analyze the Inter Annual Variability (IAV) of these emissions. We infer robust, high spatial resolution CO emission estimates that show slightly smaller IAV compared to the GFED3.1 prior emissions. Inferred dry season (August and September) biomass burning emission estimates amount to 60, 92, 42, 16 and 88 Tg CO for 2006 to 2010, respectively (see Figure). Comparing the emission estimates with external factors we conclude that climatic conditions (such as the widespread drought in 2010) seem the most likely cause for the inferred IAV in biomass burning CO emissions. However, socio economic factors (such as the growing global demand for soy, beef and sugar cane ethanol) and associated deforestation fires, are also strong drivers of CO emissions but are difficult to link directly to CO emission.
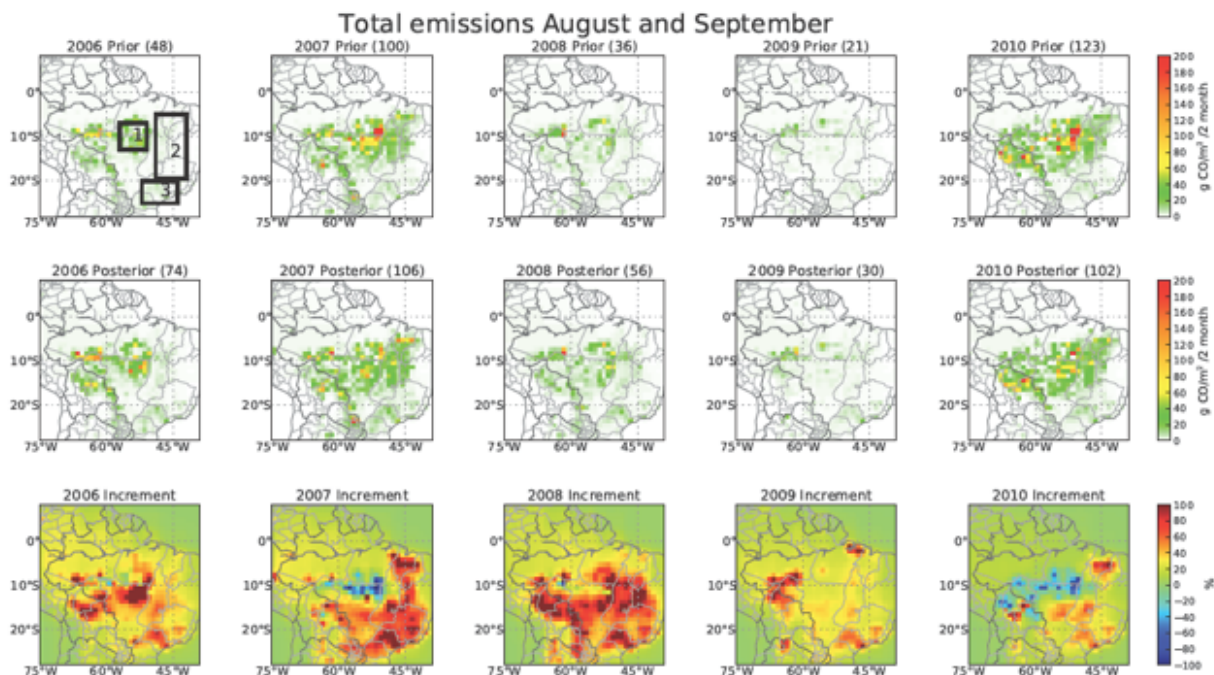
Figure 1. Prior emissions, posterior emissions and increments of the total CO emissions for August and September for the years 2006-2010 in g CO (2 month)/m^2: Numbers in the titles represent the two monthly total emission (Tg CO) for the 1x1 South American zoom region. Biomass burning emissions are derived by subtracting estimates for CO production from NMVOC, and fossil/biofuel CO emissions.

Temporal and Spatial Variability of the Stable Isotopic Composition of Atmospheric Molecular Hydrogen

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Molecular hydrogen (H_2) from different sources shows clearly distinct values in isotopic composition. This can be used to improve our understanding of the global atmospheric molecular hydrogen cycle, but few H_2 isotope data have been published so far. Within the EUROpean network for atmospheric HYDRogen Observations and Studies project (EUROHYDROS), weekly to monthly air samples from six locations in a global sampling network have been analysed for H_2 mixing ratio ($m(H_2)$) and the stable isotopic composition of H_2, (δD). The time series thus obtained now cover one to five years for all stations. This is the largest set of ground station observations of δD so far. Annual average δD values are higher at the Southern Hemisphere (SH) than at the Northern Hemisphere (NH) stations; maximum is observed at Neumayer (Antarctica), and the minimum at the non-arctic NH stations. The maximum seasonal differences in δD range from ≈18 ‰ at Neumayer to ≈45 ‰ at Schauinsland (Southern Germany). In general, seasonal variability is largest at the NH stations. The timing of minima and maxima differs per station as well. In Alert (Arctic Canada), the variations in δD and $m(H_2)$ can be approximated as simple harmonic functions with a ≈5-month relative phase shift. This out-of-phase seasonal behaviour of δD and $m(H_2)$ can also be detected, but delayed and with a ≈6-month relative phase shift, at Mace Head and Cape Verde. However, no seasonal δD cycle could be observed at Schauinsland, which likely reflects the larger influence of local sources and sinks at this continental station.

At the two SH stations, no seasonal cycle could be detected in the δD data. If it is assumed that the sink processes are the main drivers of the observed seasonality in $m(H_2)$ and δD on the NH, the relative seasonal variations can be used to estimate the relative sink strength of the two major sinks, deposition to soils and atmospheric oxidation by the hydroxyl (OH) radical. For the NH coastal and marine stations this analysis suggests that the relative contribution of soil uptake to the total annual H_2 removal increases with latitude.
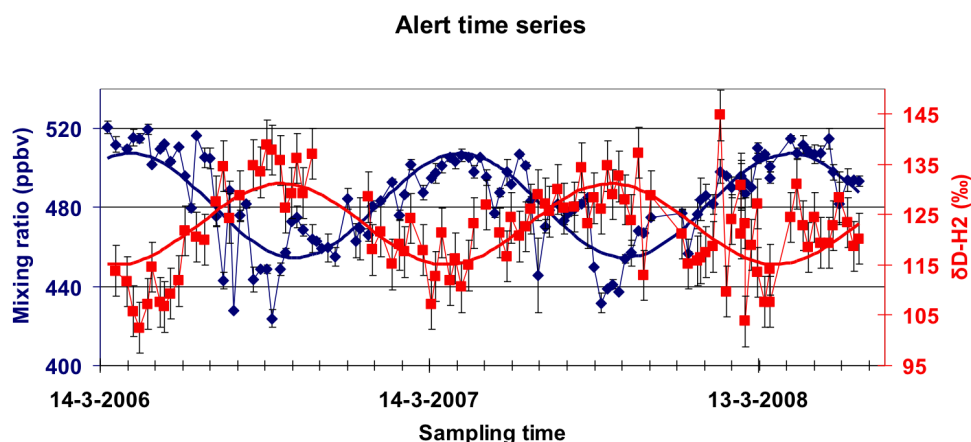

Figure 1. Time series of $m(H_2)$ (blue diamond, measured by UHEI-IUP, LSCE and MPI-BGC) and δD (red squares) measured by IMAU on air samples from Alert. Solid lines represent a harmonic best fit to the data. Error bars indicate one standard deviation

Decadal Trends in [18]O of Atmospheric CO_2

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The stable oxygen isotope [18]O is unique to isotope ecology in that it links the hydrosphere to the carbon cycle. Since land biosphere fluxes are the dominant influences on the [18]O of atmospheric CO_2 particularly on shorter times scales, analysis of atmospheric [18]O trends can provide useful insight into the terrestrial carbon cycle. The isotopic values imprinted by leaf water and soil water exchanges with CO_2 out-compete those from ocean exchange, fossil fuel and biomass burning, and stratospheric reactions. The opposing isotopic imprints of photosynthesis and ecosystem respiration therefore control the majority of atmospheric [18]O concentration. The resulting seasonal cycle in [18]O data of peaks during early summer, when photosynthesis dominates, and lows during early winter, when respiration dominates, has been clearly established. However, the reasons for the interannual variability of atmospheric [18]O remain unknown. Studies have shown that the size and isotopic value of the "retrodiffusion" flux- the CO_2 that enters and exits leaves without being fixed by photosynthesis- is a function of stomatal conductance, which is affected by the relative humidity in the surrounding atmosphere. We observe that data from numerous global sites shows a global decadal oscillation in ^{18}O, suggesting a climatological forcing. We compare decadal trends in [18]O with the climate oscillations, the 11-year solar cycle, as well as relative humidity records, examining correlations and proposing associated mechanisms. Understanding the decadal patterns in atmospheric [18]O of CO_2 will shed light on global terrestrial carbon fluxes and the carbon-water interaction on decadal time scales, potentially helping to scale human versus natural impacts on this coupled system.
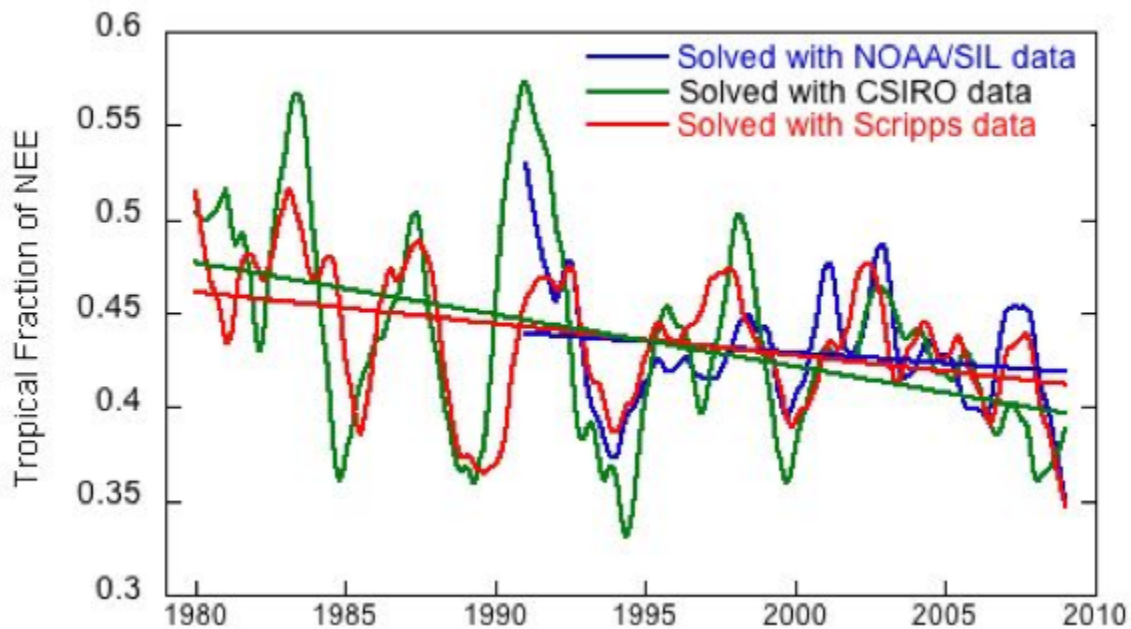
Figure 1. Modeled tropical fraction of Net Ecosystem Exchange (NEE) over 30 years, using isotope data from NOAA/INSTAAR Stable Isotope Lab, Commonwealth Scientific and Industrial Research Organization (CSIRO), and Scripps Institute of Oceanography.

The Monitoring Network of the MPI for Biogeochemistry, Jena for Atmospheric Greenhouse Gases, Oxygen and Their Isotopic Signatures

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Since 2004 the MPI for Biogeochemistry has been developing a small network of atmospheric monitoring sites for biogeochemically relevant species. The network currently comprises 8 sites and 2 has sites under construction (Figure 1). Locations of the sites were chosen based on: (1) filling critical gaps in the global i*n situ* observational network and, (2) close to biogeochemical "hotspots" in view of regional climate variability and future trends, such as Siberia, Amazonia and the subtropical upwelling regions off the west coast of Africa. Six sites include quasi-continuous measurements of atmospheric greenhouse gases (GHGs), 4 of which are augmented by continuous O_2/N_2 instruments. A comprehensive flask sampling program for quality control and isotopic analyses is performed at all sites. Here we report primarily on the flask observations. Pressurized 1-l glass flasks (1.6 bar) are routinely taken weekly or bi-weekly at all sites in triplicates for quality control and subsequently analyzed at the MPI for Biogeochemistry for CO_2, CO, CH_4, N_2O, H_2, SF_6, ^{13}C and ^{18}O in CO_2 and the O_2/N_2 and Ar/N_2 ratio. Oxygen fractionation effects caused by micro-leaks during extended storage times before analysis are corrected by normalization to a constant Ar/N2 ratio, which significantly reduces the scatter of the O_2/N_2 measurements of flask replicates. Comparison of the flask observations from the Alert Station shows a reasonable agreement with flask measurements from other monitoring agencies. Figure 2 shows as an example the complete record from the flask sampling site located at Sumburgh Head on the southern tip of the Shetland Islands (60.28N, 1.28W). The rather large scatter of the CH_4 measurements is most likely caused by gas leaks from oil platforms in the nearby ocean. Several of the records have already been used in modeling studies; the complete record is available upon request and is also currently being incorporated into the Word Data Center for GHGs.
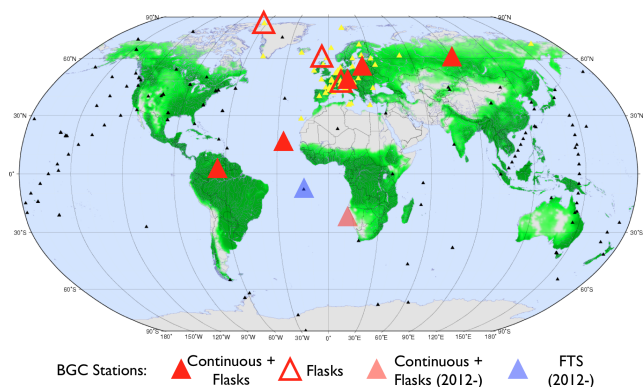

Figure 1. Map of the monitoring network of the MPI for Biogeochemistry. The Ascension Island Station in the South Atlantic will only be instrumented by a Fourier Transformation Spectrometer in 2012.
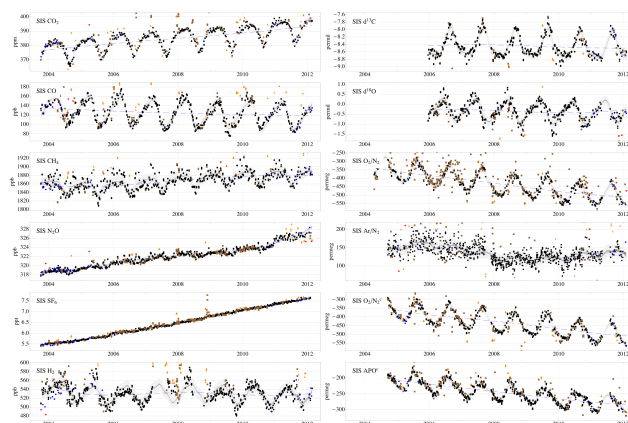

Figure 2. Complete flask measurements from the Shetland Islands station (60.28N, 1.28W) analyzed at the MPI for Biogeochemistry. The colors of the symbols represent quality/representativity indicators: a black circle indicates a good flask measurement from a good replicate. The fitted lines (seasonal cycles and trends) are for display purposes only.

Stable Isotopic Measurements of Carbon Monoxide in Air: Work In Progress

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Stable Isotopes of Carbon Monoxide shows promise as a tracer of fossil fuel emissions, and as a reliable and less expensive supplement to $^{14}CO_2$ measurements. The $C^{18}O$ signature of combustion is particularly of interest for source identification, as can be seen in the figure below. At INSTAAR, University of Colorado, we are developing an extraction system that will be capable of measuring the mixing ratio and isotopic signatures primarily from ice cores, but it will also have the capability to measure atmospheric air samples as well. Due to the small sample size extracted from ice, we are developing this system to reliably measure samples with CO concentrations on the order of 50 ppb using only 80 cc's of air. The small volume requirements of this system will make it an easy measurement to add to air sampling campaigns such as the Indianapolis INFLUX project without impacting other measurements. While this effort is still very much a work in progress, we have shown that we can extract CO from ice, as well as air standards, and measure both the CO mixing ratio and the isotopic composition with increasing reproducibility. If successful, this could become a new method that would help to constrain fossil fuel emissions fraction in atmospheric CO_2.
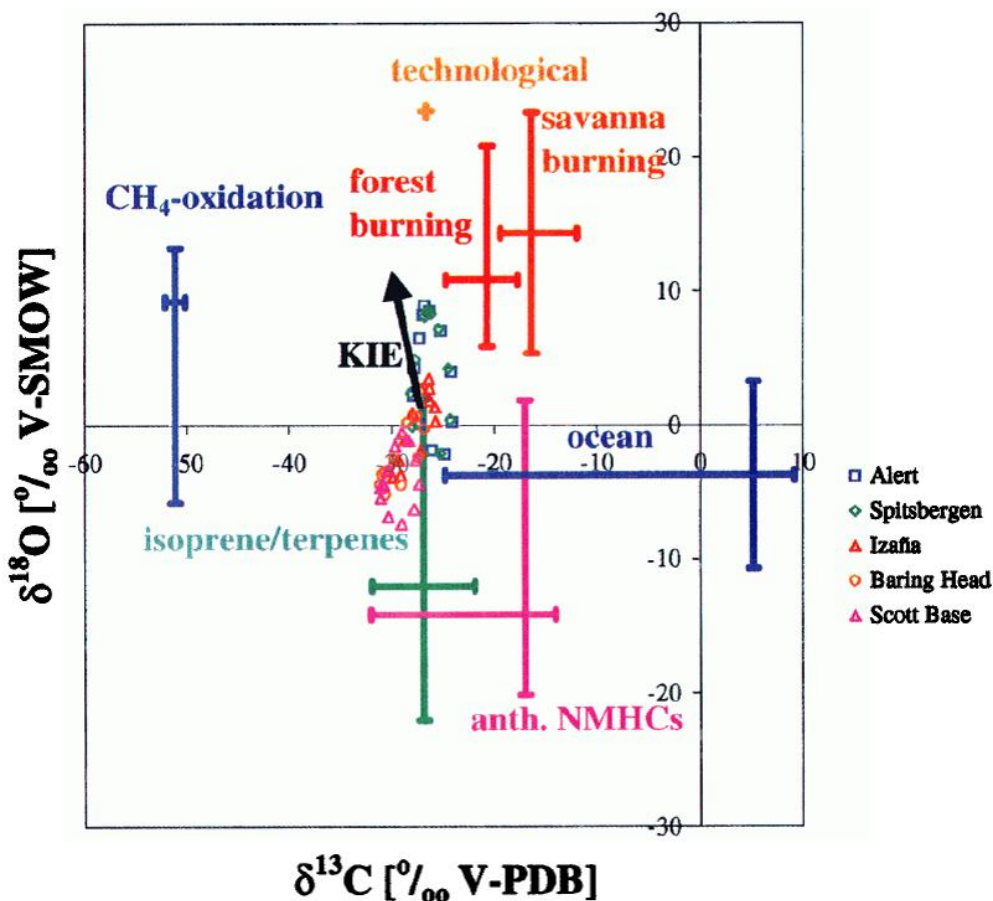

Figure 1. Isotopic Signatures of Carbon Monoxide Sources (Bergamaschi et al, 2000).

Twenty Years Measuring CO in the Troposphere: What Have We Learned and Where Do We Go?

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The GMD Carbon Cycle Group has measured carbon monoxide (CO) in the boundary layer from a globally distributed set of locations for twenty years. CO is an important component in tropospheric chemistry due its high affinity for OH. Prior to ~1994 it was widely held that CO was increasing. Chemistry Transport Models which included increasing CO predicted increases in Methane (CH_4) and other gases destroyed by OH. NOAA measurements in the 1990s were the first to show that CO was decreasing. The observed rates of decline are comparable to results from chemical transport models which include effects of pollution controls on emissions from Europe and the U.S. Vertical profiles, determined from aircraft during 1999-2007, show enhancements in the Northern Hemisphere (NH) free troposphere coincident with surface increases related to wildfires.

The NOAA measurements provide an extensive picture of CO in the lower troposphere and has provided unparalleled insight into its global cycle. Nonetheless, the data contain uncertainties which need review. These are largely related to: 1) The limitations associated with the analytical techniques available before the early 2000s. Methods developed during the past ten years have significantly improved how we measure CO and eliminated previous problems. 2) Uncertainties in the measurements are also due to difficulties producing and maintaining reference gases. Drift in primary and secondary standards at low rates have been difficult to quantify. In this paper we first provide a quick review of what we have learned about CO in the troposphere. We will then discuss the current data set, its limitations and the issues which have been resolved, and lastly, the work still in progress.
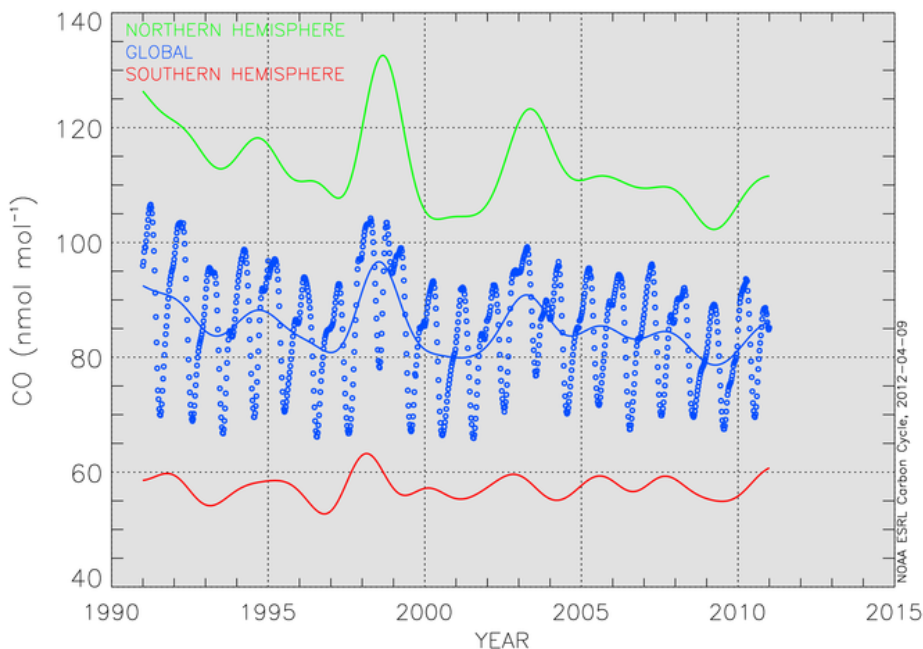

Figure 1. Global, NH and Southern Hemisphere (SH) spatially-averaged time series. Solid lines represent the zonal trends, the globally-averaged CO mole fractions are also shown. The world-wide enhancement seen in 1997-1998 was due to emissions from extensive fires in Indonesian and Boreal Forests. Fires in Russia during 2002-2004 are evident in the global and NH timeseries.

Linking Carbon Isotopes of Methane to International Standards – Can We Close the Loop on Calibration?

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The growth rate of the mole fraction of atmospheric methane (CH_4) has varied substantially over time: the last three decades have seen a globally averaged increase of more than 200 ppb, followed by a period of relative stability, and in the last five years, an increase. Understanding the sources and sinks of atmospheric CH_4 will advance our understanding of its variable growth rate and its effect on global climate change. Stable isotopes of CH_4 are a useful means to delineate sources and sinks of atmospheric CH_4. The Stable Isotope Laboratory at CU-INSTAAR has measured carbon isotopes of CH_4 in the NOAA Earth System Research Laboratory, Global Monitoring Division's Cooperative Air Sampling Network since 1998. These data—from a 15-site subset of the NOAA Network—show an overall decrease in $d^{13}C$ of atmospheric CH_4 in the last few years, with a maximum decrease of 0.3‰ amongst the sites. The significance of that observation, as well as the clear detection of trends, require well-calibrated CH_4 standards inter-compared among different laboratories. At INSTAAR, our $d^{13}C$ of CH_4 scale is tied to that of UC-Irvine through multiple compressed, whole-air cylinders filled at Niwot Ridge, Colorado. While data show that our scale has remained stable over the last decade, calibration to the primary carbonate standards (NBS-19 and LSVEC) remains a challenge. Although linking whole air standards to primary reference materials has proven difficult, this has been a goal of the atmospheric CH_4 isotope measurement community for some time, and was recently underscored by the International Atomic Energy Agency (IAEA)/World Meteorological Organization Scientific Advisory Group for Greenhouse Gases. Here we discuss the application of a new offline extraction system, developed to measure ^{14}C of CH_4 at INSTAAR, but which also allows for higher precision Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) measurements of $d^{13}C$ of CH_4-derived CO_2. INSTAAR's calibration for $d^{13}C$ of CO_2 is strongly tied to the VPDB scale; furthermore this will allow for direct comparison to IAEA carbonate standards. This is a significant step forward for methane isotope calibration at INSTAAR, and will contribute to efforts for worldwide inter-laboratory calibration.
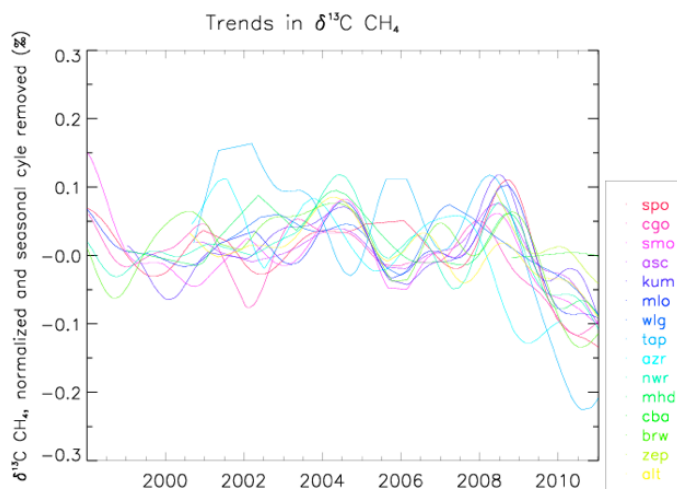

Figure 1. Atmospheric observations (1998—2011) of $\delta^{13}C$ of CH_4 from a 15-site subset of the NOAA/ESRL Global Monitoring Division Cooperative Air Sampling Network show oscillations in growth over the last decade and more negative trending over the last 4 years.

Methane Fluxes to the Atmosphere from Deepwater Hydrocarbon Sources

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Methane, one of the most potent greenhouse gases, has a warming potential 72 times that of carbon dioxide over a 20-year time horizon. It is also actively involved in atmospheric chemistry. Gas hydrates, ice-like mixtures of gas and water, are the largest methane reservoir. The total abundance of marine gas hydrates is equivalent to 400 times the total atmospheric methane. Whether the marine gas hydrates, especially the deepwater gas hydrates, contribute significantly to the atmospheric methane is under debate. To investigate this question, two studies (HYFLUX and PLUMES) were conducted over deepwater hydrocarbon plume areas in the Northern Gulf of Mexico. Continuous air-sea measurements were made with high spatial and temporal resolution during both studies using a "Weiss-type" equilibrator coupled with a Gas Chromatography-Flame Ionization Detector (during HYFLUX) or a Cavity Ring-Down Spectroscopy (during PLUMES). Results from both studies indicate that methane fluxes to the atmosphere from deepwater hydrocarbon sources are small (Figure 1) and deepwater hydrocarbon sources are not likely to play a significant role in contemporary climate change.
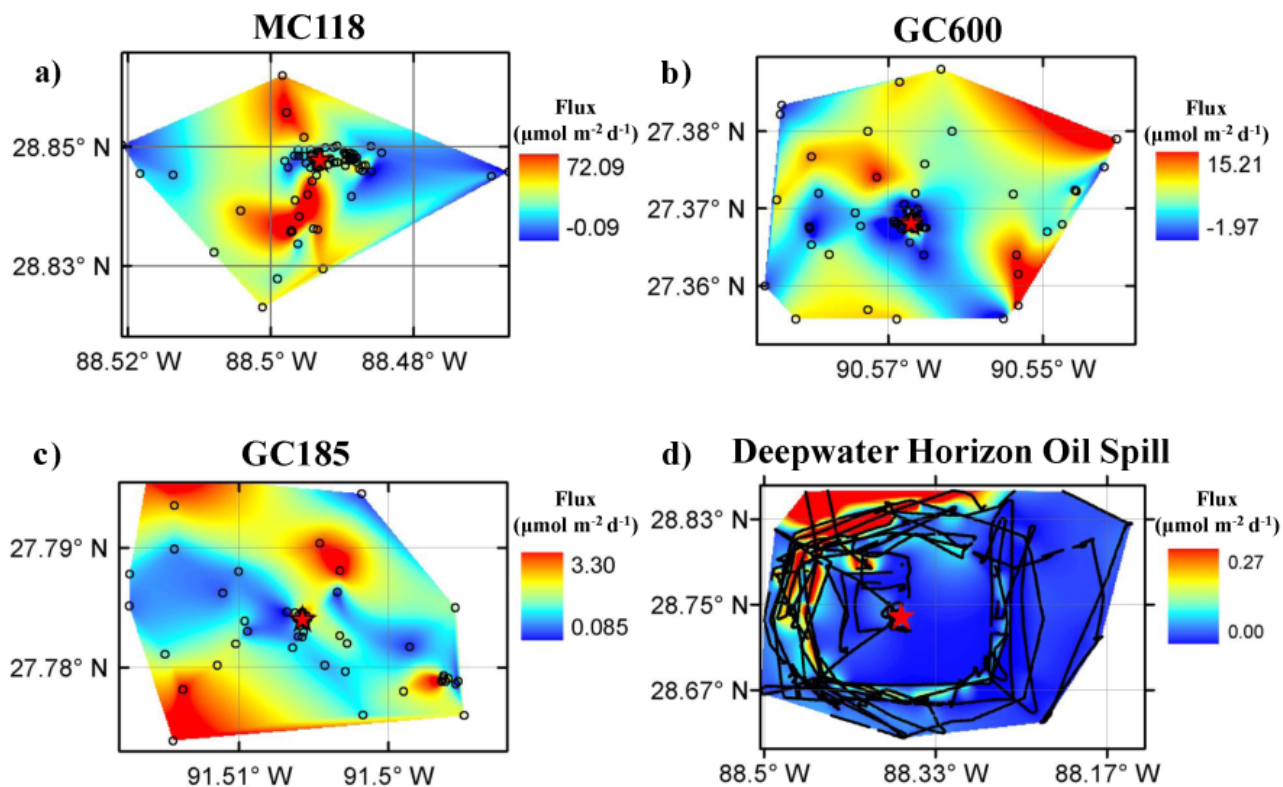

Figure 1. (a – c) Methane fluxes to the atmosphere from deepwater hydrocarbon seeps during HYFLUX (4 – 19 Jul, 2009). (d) Methane fluxes to the atmosphere from Deepwater Horizon oil spill during PLUMES (12 – 20 Jun, 2010). Black circles indicate sampling locations.

Toward a Combined Data-fusion Atmospheric Inversion System at Continental Scale: Structure of Flux Errors and Atmospheric Regional Variability Over North America

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Current efforts for the development of regional networks of CO_2 mixing ratios on continental surfaces aim at constraining regional carbon balances for mitigation and adaptation policies. The design of these networks remains unclear for both constraining the regional balance and capturing the spatial patterns in the surface fluxes. The Mid Continent Intensive (MCI) experiment offers a unique tower deployment over the U.S. Upper Midwest, with 8 surface towers located in a 700 x 700 km domain measuring *in situ* CO_2 atmospheric mixing ratios continuously. We used our mesoscale inversion system to perform sensitivity experiments, tower removal tests, and cross validations to investigate the robustness of the regional carbon balance and the flux spatial patterns to the network design. We also investigated the impact of our initial assumptions, in particular the spatial structures in the prior flux errors, affecting both our corrections of the regional biases and smaller scale flux signals. Finally, we compared our results to recent findings using eddy-flux observations and land vegetation modeling. The converging estimates around few hundreds of kilometers at the weekly time scale indicate clearly that spatial coherence is present in regional CO_2 flux errors, even though a more rigorous quantification is still limited by the lack of observations at finer scales.
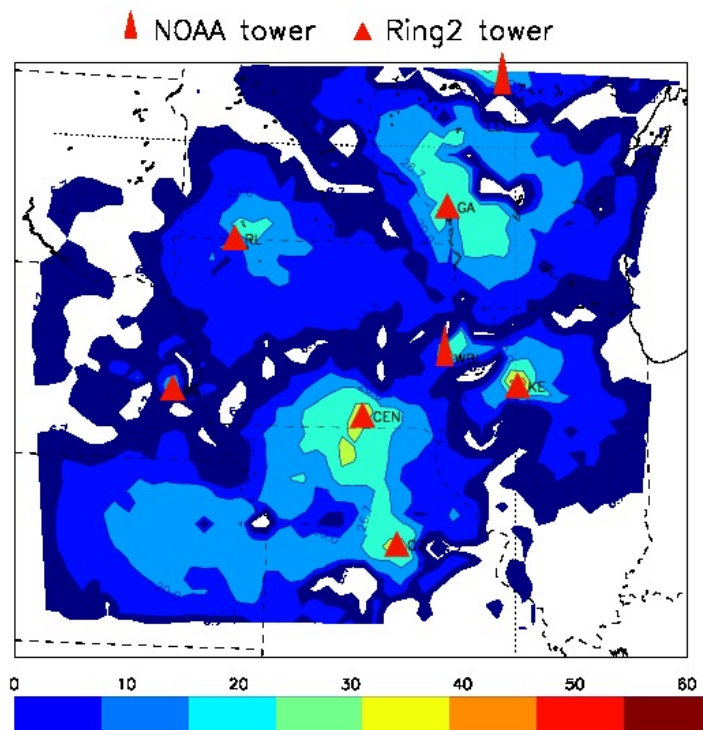
Figure 1. Error reduction in % for June to December 2007 using the MCI tower network at 20 km resolution, assuming prior flux error spatial correlations based on ecosystems and distances between pixels.

Seasonal Variation of the Global Carbon Fluxes Using CarbonTracker

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About half of CO_2 emission caused by fossil fuel combustion has been absorbed by the terrestrial ecosystem and ocean. Therefore, understanding the fundamental processes responsible for the net carbon sinks/sources and the primary control factors are remarkably important. Figure 1 shows the global distribution of annual accumulation and the seasonal cycle of zonal mean net fluxes of land ecosystem and ocean carbon over recent 10 years. The net sink area, for biosphere flux, is mainly in the northern hemisphere high latitude, especially over the east of Siberian and North America. For ocean flux, the Northern Atlantic Ocean and Pacific Ocean are the net sink area. Tropical regions are the most dominant source of both biosphere and ocean carbon fluxes. The large seasonal signal in land ecosystem flux is located in mid- and high-latitude regions where temperature influences the carbon cycle. However, although temperature has no significant variation in the tropical region, it still shows seasonal cycle of carbon fluxes. Our preliminary results suggest that this might be due to the relation between land ecosystem carbon flux and annual change of radiation and precipitation over the tropical region. Using CarbonTracker, we analyzed the seasonal cycle of land ecosystem and ocean carbon flux and will discuss how climate system, which is one of the carbon cycle control factors, effects on the terrestrial ecosystem, especially in tropical region, and ocean fluxes.
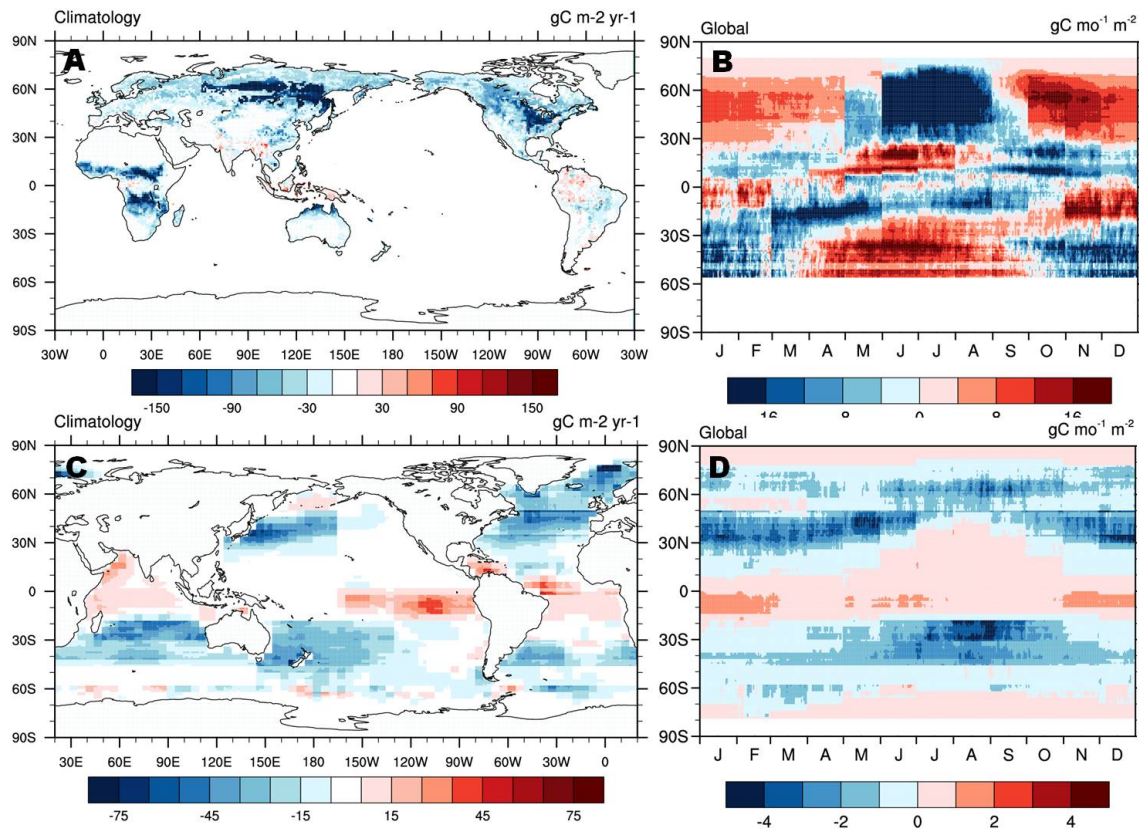

Figure 1. Ten-year (2000~2010) climatology for the global distribution of annual fluxes (A,C) and the zonal averaged seasonal cycle (B,D) for biosphere (A,B) and ocean (C,D) from CarbonTracker.

Studies of Carbon Isotopic Ratios in Atmospheric Methane and Some of It's Sources in India

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Methane (CH_4) is one of the important greenhouse gases with increasing concentration in the atmosphere. Methane currently has a globally averaged mixing ratio of ~1.8ppmV in the troposphere. Its concentration has been increasing in the atmosphere for the last 200 years and it has more than doubled to a present value compared to pre-industrial time. The carbon isotopic composition of methane is useful for constraining the global CH_4 budget and identifying CH_4 sources. This technique is widely used all over the world to identify the methane sources, especially in the Northern Hemisphere. Very limited work is done from India in the last decade to measure $\delta^{13}C$ of methane in the atmospheric air to identify its sources. We present here the data obtained using conventional method of CH_4 isotope analysis. Atmospheric air samples were collected during: 1) September-October 2002 for spatial variation, 2) during night time on 4-5 December 2002 & 10-11 June 2003 for diurnal variations from Ahmedabad (23°02′ N, 72°33′ E), India at a height of ~80ft above the ground to estimate the mean isotopic composition of the local methane source. The mean overnight source mix (for the period 23:45 until 06:45, 4-5 December), calculated using the Lever rule, was -51.7 ± 1.1‰ and suggests that the excess methane is mainly contributed by a single anthropogenic source, where as $\delta^{13}C$ of methane sources varies between -8.8 to -34.4‰ for the period 21:00 to 8:00 hours on 10-11 June 2003. The data (figure) suggests that two dominant sources (automobile exhaust and natural gas leakage) contribute during night time. Both the sources have equal contributions from 21:00 to 6:00 where as automobile exhaust dominates after 6:00 hours. We also determined the $\delta^{13}C$ signatures of different methane sources in India.

Sr.no	Source	Place	Location	No. of samples	$\delta^{13}C$ (‰)
1	Paddy fields	A.P state	16°97′ N ; 82°15′ E	10	-57.2 ± 0.5
2	- do -	Gujarat	22°20′ N ; 72°40′ E	5	-54.3 ± 0.5
3	Gas hydrates	Arabian Sea	10°51′ N ; 73°36′ E	2	-65 ± 1
4	Gas seeps	Manipur	24°48′ N ; 93°56′ E	2	-44.5 & -48.7
5	Coalbed	Jharkhand	23°47′ N ; 86°25′ E	4	-45 ± 1.0

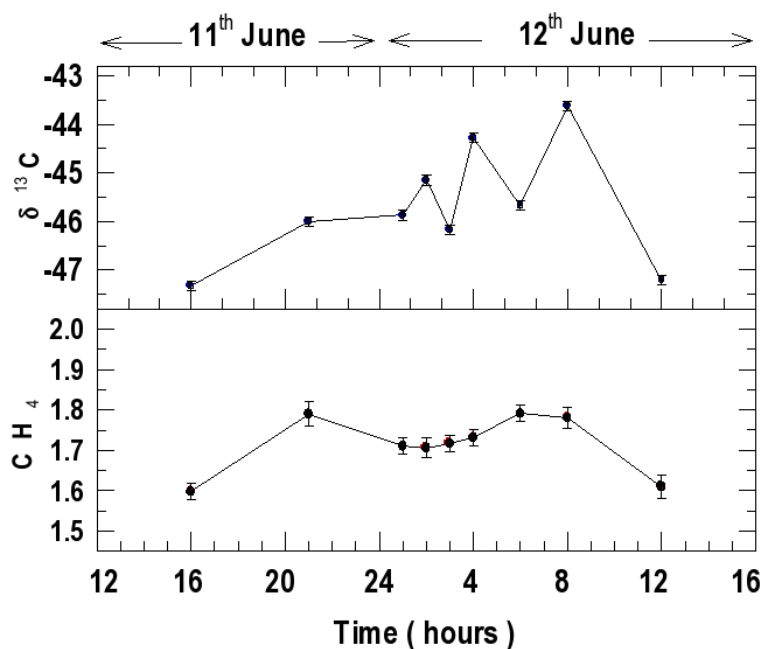Table: $\delta^{13}C$ of methane in some of the sources in India

Figure 1. Diurnal cycle of CH_4 (ppmv) mixing ratio and $\delta^{13}C$ (‰) in Ahmedabad city during 11-12 June 2003.

INFLUX: Model-data Comparison and the Detection Limit of the Observational Network

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The goal of the INdianapolis FLUX (INFLUX) project is to detect greenhouse gas emissions at an urban scale. The project involves combining data from atmospheric models, bottom up inventories, and observed greenhouse gas mixing ratios and associated tracers (CO_2, CH_4, CO and $^{14}CO_2$) from towers and aircraft. The test bed city is Indianapolis, Indiana. Indianapolis was chosen as the study location because it is a large city (12th largest by population in the U.S.) with a flat terrain which simplifies the detection of urban greenhouse gases from the city.

The focus of this presentation is model-data comparisons and the detection limit of the INFLUX observational network. The model-data comparison involves evaluating output from forward simulations that utilize the Weather Research and Forecasting Advanced Research Model and Vulcan/Hestia emissions inventories with INFLUX observations. The detection limit of the observational network is addressed by perturbing the surface fluxes and examining the changes in concentrations between the perturbed and control simulations.
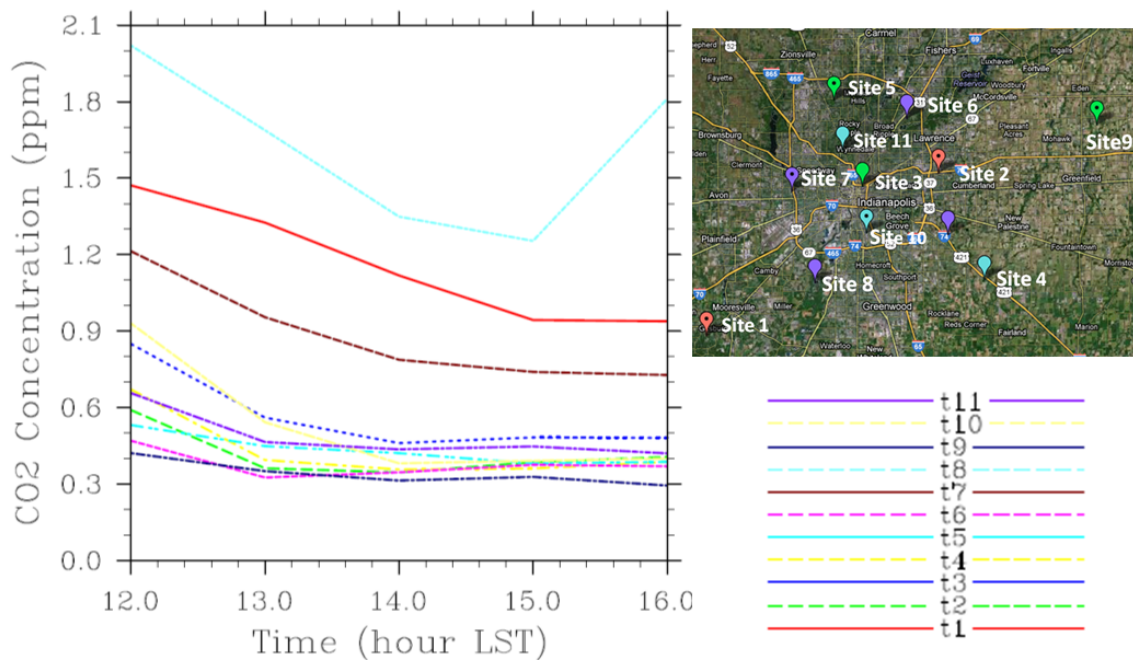
Figure 1. Observed midday boundary layer concentration changes of CO_2 at INFLUX tower locations due to a 20% increase in Vulcan surface fluxes on March 2, 2011. T1 corresponds with tower 1 at site 1 on the corresponding map, T2 corresponds to tower 2 at site 2, etc.

Isoflux Inversion Progress Report: Towards Building a Regional Bayesian Inversion for $\delta^{13}C$ of Terrestrial CO_2 Fluxes

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Year to year terrestrial CO_2 uptake and release is highly variable, and much uncertainty surrounds the links between CO_2 fluxes and local to regional weather and climate variability. Plant discrimination against the stable carbon isotope, ^{13}C, is related to stomatal conductance, and is therefore a useful tracer of plant water use efficiency. Furthermore, ^{13}C is a useful tracer of the differential responses of C_3 and C_4 plant functional types to climate and weather anomalies. Both aspects of the terrestrial carbon cycle are of great interest to those seeking to understand the potential effects of global climate change on croplands, forests and natural CO_2 sinks. For the first time, spatial and temporal density of $d^{13}C$ of CO_2 atmospheric observations is high enough to allow for regional inversions of $d^{13}C$ of CO_2 to optimize prior estimates of plant discrimination and disequilibrium flux (an isoflux resulting from the combination of a finite residence time of carbon in terrestrial biosphere pools and a changing atmospheric signature due to human burning of fossil fuels with a plant-derived $d^{13}C$ signature). We present a progress report on the first regional inversion of $d^{13}C$ of CO_2, performed using a traditional Bayesian synthesis framework and the fixed-lag Kalman smoother technique of Bruhwiler and others. Influence functions (footprints) are generated with FLEXPART, driven by National Centers for Environmental Prediction Global Forecast System meteorology. Prior isofluxes (CarbonTracker 2010 posterior net ecosystem exchange multiplied by biosphere $d^{13}C$ from SiB) are of 3-hour, 1x1 degree resolution. Unoptimized fire and fossil fuel emissions are also from the CarbonTracker system, and background CO_2 and $d^{13}C$ values are taken from NOAA/ESRL marine boundary layer and aircraft data. We are working towards discrimination and disequilibrium fluxes optimized at 5x5° resolution for multiple years over the North American region, from 145-25°W longitude and 10-80°N latitude.

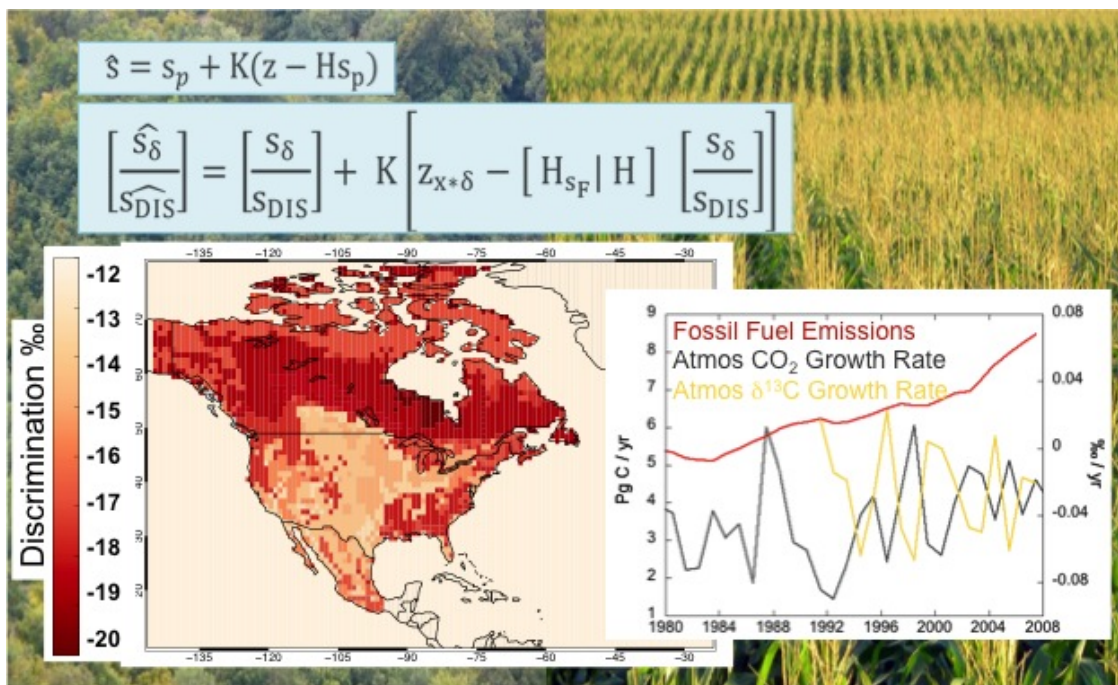**Figure 1.** Posterior plant discrimination results for May 2007 (LH panel) and global atmospheric CO_2 and delta ^{13}C growth rates and fossil fuel emissions (RH panel).

Single-Photon LiDAR for Measuring & Monitoring Forest Carbon Fluxes

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Remote-sensing for detecting areas of "deforestation and forest degradation" is a relatively mature field though not without challenges. In comparison, current methods for quantifying the carbon fluxes associated with those areas are much more expensive and much less accurate. Quantifying fluxes for a large number of discrete areas across a country is especially difficult, whether they are spread out across the U.S., as planned for California offsets, or across Indonesia as planned for Australian offsets.

At recent meetings of the National Aeronautics and Space Administration Carbon Monitoring program and the United States Government SilvaCarbon program, forest-monitoring experts confirmed that airplane-mounted LiDAR could play a unique role in improving estimates. It was also recognized that technical limitations of conventional LiDAR systems make the acquisition of large amounts of high-fidelity 3D images prohibitively expensive.

Sigma Space Corporation has built and demonstrated a Single-Photon LiDAR, which enables rapid and broad LiDAR coverage while maintaining the high 3D resolution and the density of range returns needed for accurate measurements of forest structure and above ground biomass. Consequently, Single-Photon LiDAR will allow, for the first time, cost-effective measurement and monitoring of large forested areas with sufficient accuracy to inform "results-based" payments for mitigation activities in the forest sector (e.g. REDD+).
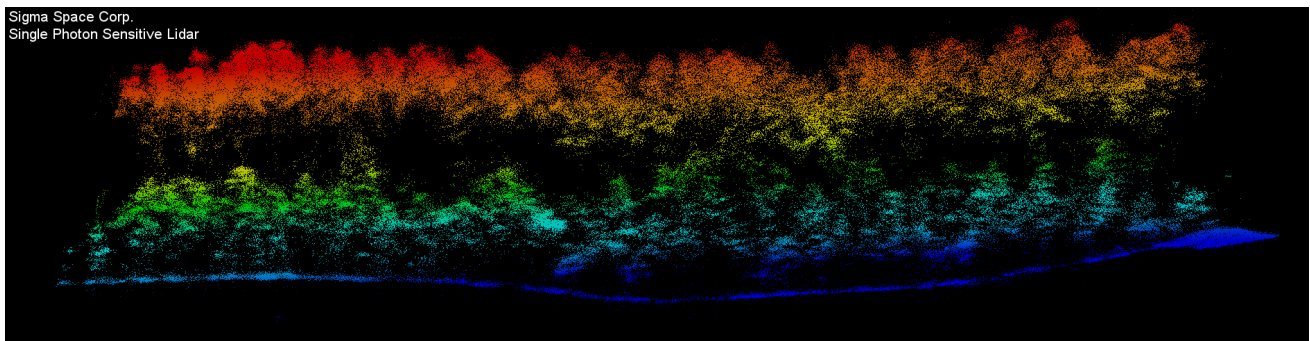

Figure 1. Sigma Space Corporation, Single Photon Sensitive LiDAR.

ICOS-ATC Lab Test for GHG Instrumentation: Presentation and First Results

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The Integrated Carbon Observation System (ICOS) European research infrastructure is dedicated to long-term quantification of the greenhouse gas (GHG) balance of Europe via a harmonized network of atmospheric, ecosystem and ocean observation sites. To ensure long-term high precision monitoring of GHG, a strategy of standardized instrumentation and methods has been defined. Also, the need to be up-to-date with new GHG instrumentation has been identified as a key point for the future ICOS atmospheric network. In this context, a test laboratory will be part of the ICOS Atmospheric Thematic Center (ATC) to: 1) interact with research institutes and private companies for evaluation of new sensors and prototypes, 2) perform and document tests of new sensors and 3) provide recommendations for the update and the evolution of the running ICOS Atmospheric Station. In the current preparatory phase, we defined the needs of the test lab in terms of instrumentation and methodology to fulfill the objectives. A first standardized test protocol has been established and a dozen instruments for atmospheric CO_2, CH_4, CO and N_2O analysis have been evaluated. We present in this poster the methodology used with some of the key results of the test lab.

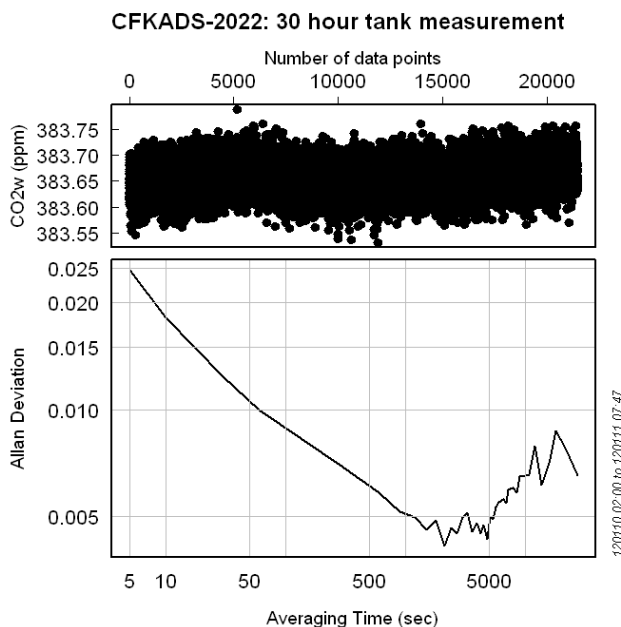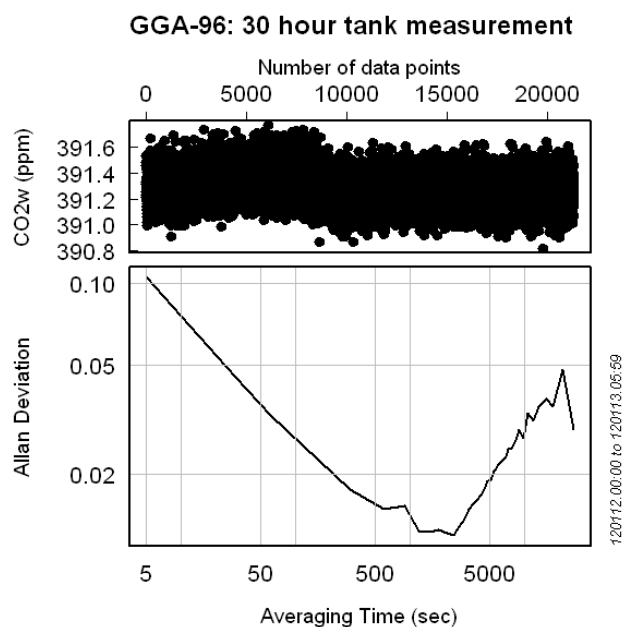**Figure 1.** Picarro G2401: CO_2 precision assesment.

Figure 2. LGR GGA: CO_2 precision assesment.

Improving and Extending a CO_2 Observation Network in the Pacific Northwest

A. Schmidt[1], M. Goeckede[2] and B.E. Law[1]

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Our CO_2 study in Oregon aims to improve understanding of the mechanisms driving carbon exchange processes and associated uncertainties within a region by maintaining and extending a ground-based network of CO_2 observation sites in Oregon and aircraft sampling of boundary layer profiles, and continuing development and application of a high-resolution data assimilation system with regional atmospheric inverse modeling. The Pacific Northwest and Oregon in particular is characterized by its strong precipitation and vegetation gradient from the mesic coast with its large carbon sink in evergreen forests to the inland cold desert. In addition, the region is characterized by relatively isolated larger urban areas and other anthropogenic CO_2 sources. Hence, the spatio-temporal distribution of sources and sinks can provide great insights into changes in atmospheric CO_2 from incoming air off the Pacific Ocean. The new towers within our model domain will greatly improve data quality and footprint coverage. Our modeling studies are considered a test for larger scale applications in a small scale and data-rich environment. The mixing ratio time series from these sites would also provide a valuable addition to the CarbonTracker database for constraining flux fields in the Pacific Northwest U.S., and monitoring incoming CO_2 boundary conditions at the transition from Pacific Ocean to the North American continent. This tower setup allows testing biosphere process models at different levels of complexity (BioFlux, CLM4) and evaluating the influence of resolution settings and data availability on final flux products and their uncertainties.
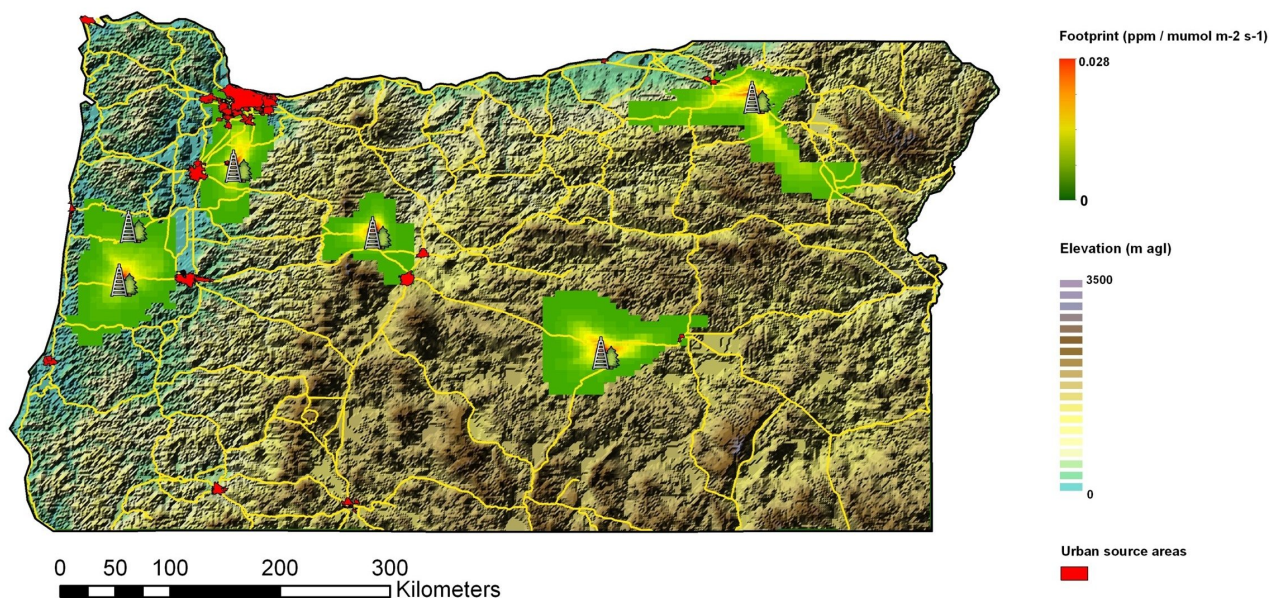

Figure 1. Map of Oregon showing the tall tower positions and the corresponding footprint strength of the surface area on the atmospheric CO_2 concentration at measurement height. The yellow lines mark major highways and roads.

University of Washington (UW)-NOAA Cooperation at the Mt. Bachelor Observatory (MBO)

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[3]NOAA Earth System Research Laboratory, Boulder, CO 80305

Since 2004 a team from the University of Washington has operated the Mt. Bachelor Observatory at 2.8 km on the summit of a dormant volcano in central Oregon. Measurements at the site have focused on understanding the climate and air quality impacts from gas and aerosol pollutants transported to North America. The site is unique in regularly sampling free tropospheric air on the west coast of North America and is operated with the cooperation of the Mt. Bachelor Ski Area. Data from the site have been used in more than 2 dozen publications on O_3, CO, aerosols, NO_x, mercury and other species.

Starting in October of 2011, the NOAA/GMD Carbon Cycle Greenhouse Gas (CCGG) Group installed a flask sampling package at MBO to collect daily whole air samples. These observations will provide new data for understanding the sources and sinks of key chemical compounds. Flask samples are collected at 12 (Global Mountain Time) every day, which is the time with the most frequent occurrence of free tropospheric air at the site. The flask data include all of the usual carbon, Greenhouse Gas and other species measured by the CCGG group. Since 2004 we have measured CO by non-dispersive Infrared technology. As part of our Quality Assurance procedures we have compared the CCGG flask measurements with our existing Nondispersive Infrared Sensor (NDIR) measurements for the first data period (Oct 2011-Jan 2012). The adjacent figure shows this comparison. Note that the NDIR measurements have a 1 sigma precision of 14 ppbv so this comparison does not suggest any bias in either method. In the near future we will install a Picarro cavity ring-down system for CO and CO_2, which will provide higher time resolution and better precision than the NDIR system.

This UW-NOAA partnership will provide one of the few records of long-term changes in the free troposphere. More information on the MBO including real-time and archived data can be found here: http://www.atmos.washington.edu/jaffegroup.

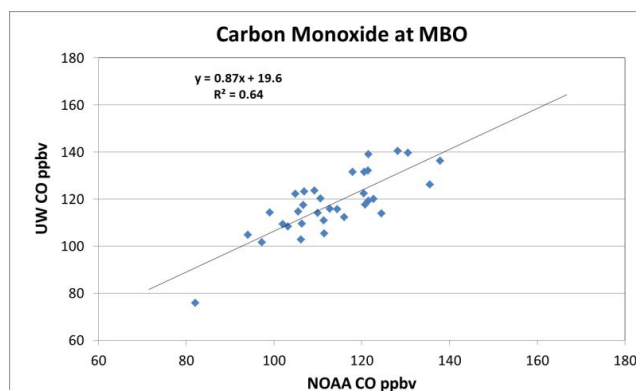**Figure 1.** Photo of Mt. Bachelor in central Oregon.

Figure 2. Comparison of CO measured by the UW and NOAA/GMD groups at Mt. Bachelor.

Synoptic Process and Higher Values of CO$_2$

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This study is based on CO$_2$ data from the Ulaan-Uul Station, Mongolia (UUM), comparing atmospheric CO$_2$ values between subsequent weekly flask samples that differed by greater than 3 ppm and the associated synoptic meteorology. The weekly differences were greater than 3 ppm when air masses were transported south-eastward from industrial regions of Russia and China located north and west of Mongolia.
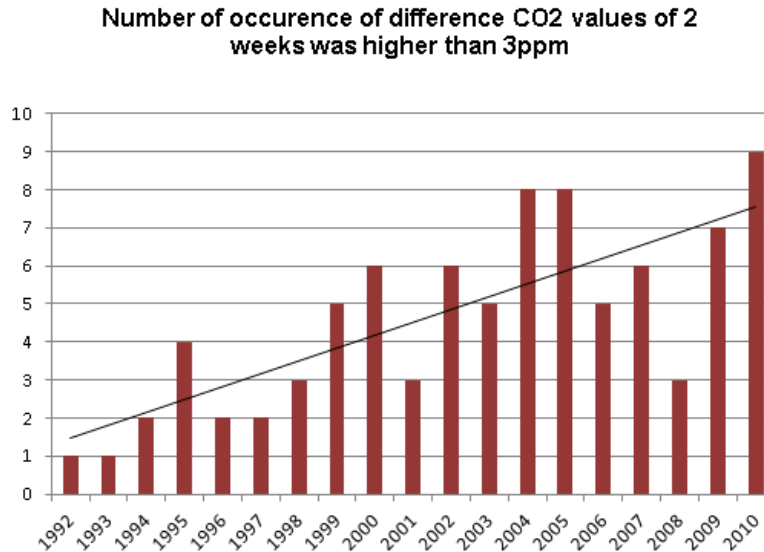

Figure 1. Occurrence of subsequent weeks when CO$_2$ values were greater than 3 ppm. The trend in the number of subsequent weeks with elevated CO$_2$ differences has been increasing over the past 18 years.
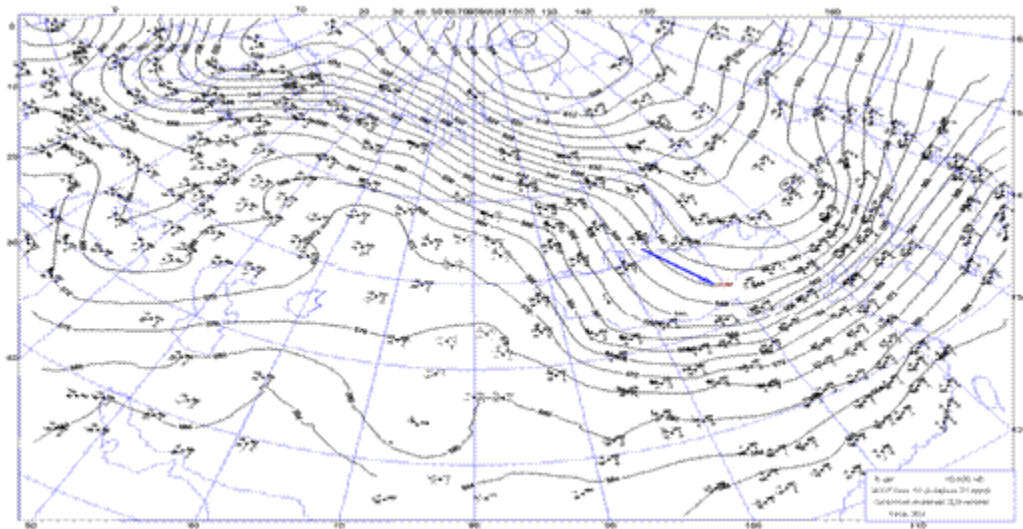

Figure 2. Typical 500 hPa synoptic map for periods with elevated CO$_2$ at the UMM, Mongolia flask sampling site.

Impact of Aerosols on Climate Changes in the 20th Century

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Climate impact by anthropogenic drivers gives high concerns in climate change simulation. Intergovernmental Panel on Climate Change AR4 emphasized the role of aerosol on climate, besides the greenhouse gases (GHGs), due to its negative significant radiative forcing. This study is interested in anthropogenic aerosol effects on long-term climate through direct and indirect radiative process and uses HadGEM2-AO developed by the United Kingdom Met office.

Unlike the long-lived GHGs, which are distributed uniformly over the globe, aerosol effects with the short lifetime appear more regional and less persistent than those of GHGs. In Figure 1, aerosol optical depth in Northern high latitudes has been dramatically increasing since the 1950s in East-Asia, North America and Europe. There are significant changes in Earth`s radiative balance indirectly through their effect on cloud properties such as cloud albedo, droplet size, number concentration, brightness, and amount. Especially, cloud amount response by aerosol, the increases in low level cloud, is shown in enhancing shortwave reflection. We found that radiative flux perturbation at the top of atmosphere is estimated to be –0.44 Wm^{-2}, globally in the middle of the 20th Century. This forcing is comparable in magnitude to GHGs forcing 0.43 Wm^{-2} but opposite in sign.

Reductions in the amount of solar irradiance lead to changes in the atmospheric temperature. In Figure 2, global temperature anomaly (HIST experiment, including all forcing) during the middle of the 20th Century remains cool and steady at approximately the same level in pre-industrial. Particularly, the largest temperature reduction is found in the Northern Hemisphere because of a larger aerosol burden there. As a result of this unbalanced cooling, the Intertropical Convergence Zone is displaced southward by a few hundred kilometers. After the late 1970s, GHGs forcing became the dominant factor, which significantly contribute to global warming.
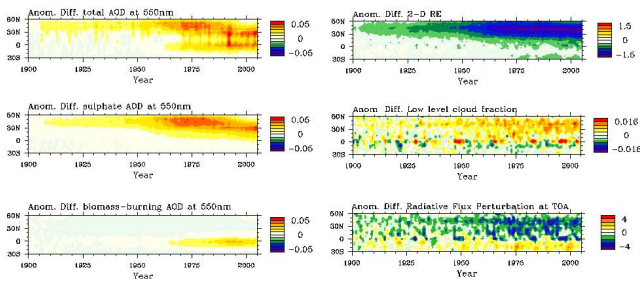

Figure 1. Latitude-time sections of zonal mean anomalies (total Aerosol Optical Depth, cloud effective radius, low level cloud fraction, net radiative flux perturbation) from 1900 to 2005.
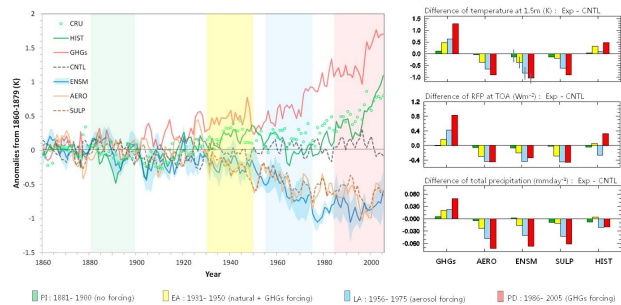

Figure 2. Global annual mean surface air temperature anomalies, for Climate Research Unit data (green open circle), all forcing historical experiment (green line), GHGs only (red line), no forcing control experiment (dotted black line), aerosol ensemble mean experiment (blue line), aerosol only experiment (brown line), and sulphate only experiment (dotted brown line) from the HadGEM2-AO climate model.

Developing Useable Black Carbon Information – Case Studies from the IASOA Network

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The International Arctic System for Observing the Atmosphere (IASOA) is an International Polar Year (IPY) legacy project whose founding vision was to coordinate pan-Arctic atmospheric observing research to address broad science questions about Arctic change. During the IPY, IASOA efforts developed observing inventories for nine partner stations (Figure 1), created a data portal to facilitate data sharing (iasoa.org), increased value-added observing assets at key locations, and contributed to the development of a clean air observatory in Tiksi, Russia to fill an important spatial gap. Moving beyond IPY, IASOA's long-term vision for enabling pan-Arctic synthesis and assessment science is poised for implementation. The network science leads have prioritized relevant and actionable assessment themes, which include: understanding the role of black carbon and other short lived climate forcers (SLCF's) on regional warming; understanding the role of Arctic clouds and aerosols in the regional climate system; and contributing to atmospheric-surface flux process understanding.
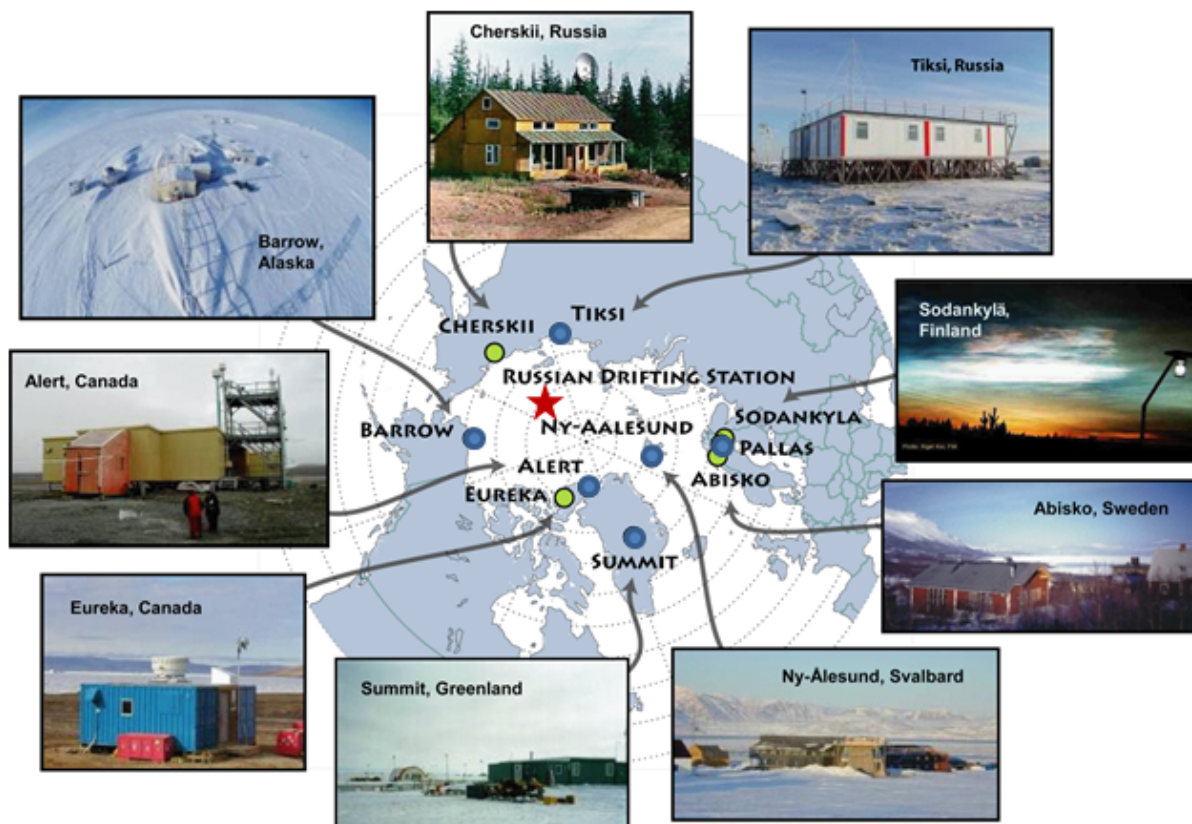

Figure 1. The IASOA member observatories. The red star represents the Russian North Pole drifting station which is the newest member of the consortium. Blue dots indicate current locations of relevant black carbon observations.

Soot Surveys in the Air and Snow During PAMARCMIP 2011 and DOSA Campaigns

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[2]Alfred Wegener Institute for Polar and Marine Research, Bremerhaven 0471 4831-0, Germany
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[5]On contract with Environment Canada

Particulate black carbon (BC) in the Arctic atmosphere and its deposition onto snow and ice surfaces contributes to atmospheric warming and a reduction in the surface albedo. However, the increase in absorption of solar radiation and its impact on the ice melt rate is unknown. Latitudinal and vertical gradients in soot were observed in the Arctic during the 2011 Polar Airborne Measurements and Arctic Regional Climate Model Simulation Project (PAMARCMIP) campaign. This collaborative effort with the Alfred Wegener Institute for Polar and Marine Research (Bremerhaven, Germany) conducted surveys between Barrow (Alaska), Alert (Canada) and Svalbard (Norway). Figure 1a illustrates the latitudinal and vertical gradients in the aerosol equivalent BC inferred from light absorption coefficient measurements made from 3-wavelength Continuous Light Absorption Photometer. A specific attenuation coefficient of 10 m^2g^{-1} was assumed to convert light absorption coefficient to Equivalent Black Carbon (EBC) mass. Figure 1b shows averaged vertical gradient of EBC for the entire campaign indicating higher EBC levels in the layer 2 to 3 km than at the surface.

At Alert, we extended the *in situ* measurements from aerosol light absorption derived BC/ aerosol scattering to include elemental carbon by Thermal Optical Transmittance as well as refractory black carbon by Single Particle Soot Photometer (SP2, DMT). Several vertical aircraft profiles were conducted over Alert with an effort to compare the surface based measurements of light absorption carbon to the levels aloft.

In the Deposition of Soot in the Arctic (DOSA) 2011 study, we employed micrometeorological methods (gradients, eddy covariance) to directly measure the dry deposition rate of BC onto an Arctic snow surface at Alert, Canada, over 20 days in April 2011. BC was quantified at high frequency with a SP2. Deposition rates were also obtained by daily snow / diamond dust collection on Teflon sheets for subsequent lab analyses. Preliminary results of this study will be disseminated.
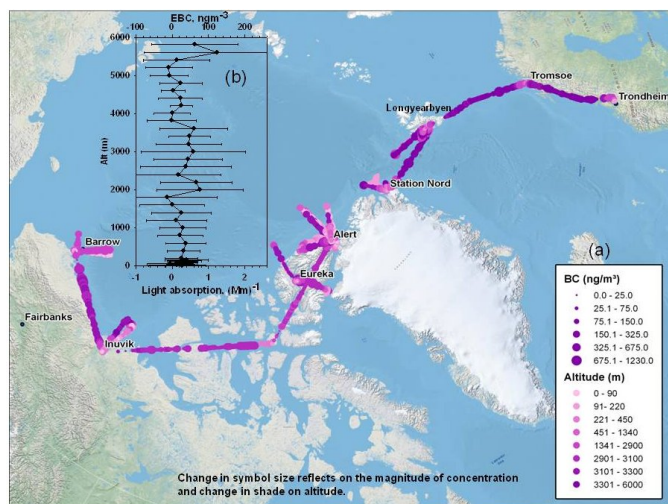

Figure 1. a: Latitudinal and vertical distribution of EBC. b: Vertical gradient (Average ± 1sd) in the light absorbing carbon during PAMARCMIP from April 2 to May 5, 2011. Elevated levels of EBC are observed between 2 to 4 km altitude. Light absorption conversion to EBC mass by using 10 m^2g^{-1}.

Seasonal & Annual Variations in Aerosol Elemental Carbon (EC) Observations Over Canada: Constraints on Changes of Fossil Fuel Emissions

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Although lots of attention has recently been paid to Black Carbon (BC), there are still large gaps in the knowledge of quantifying their emission sources and estimating their impacts on regional/global climate, particularly when compared to corresponding effects from CO_2 and other Greenhouse Gases (GHGs). An observation network of aerosol carbon has been strategically set up and co-located with CO_2 and other GHG measurements across Canada since 2006. These sites represent different geographic locations with various source influences, including Toronto (a typical urban site), Egbert (a rural site), Fraserdale (a boreal East site, in northern Ontario), ETL (a boreal West site in Saskatchewan), and Alert (an Arctic baseline site). Due to the short atmospheric life-time of EC, the changes in source emission may be inferred from the changes in atmospheric EC concentration. Weekly integrated quartz filter samples collected at these sites over the period of 2006 to 2010 were analyzed for EC concentration. The weekly values were averaged into two seasonal means of summer-fall (May-Oct) and winter-spring (Nov- Apr) for the entire data set. The results show that: 1) EC concentrations during warm seasons are higher than those in cold seasons at all sites except for Alert (where the opposite pattern is found), which are consistent with source influencing patterns; 2) All the EC concentrations during warm seasons at Toronto, Egbert, Fraserdale as well as those during cold seasons at Alert show a decrease trend from 2007 through 2009 and a slight increase in 2010, which are consistent with the changes of the fossil fuel emission inventories (CDIAC: http://cdiac.ornl.gov/trends/emis/meth_reg.html) in North America & Europe during the same period; 3) Large variations in EC concentration at the ETL site during the warm seasons in 2006, 2008 and 2010 indicates that the impact of biomass burning emissions can not be underestimated at the site. The relationship between EC concentration and excess CO_2 (i.e. the difference between the observation and the marine boundary layer value) at Fraserdale site will be also investigated to explore a potential approach for mutual constraints on fossil fuel emitted EC and CO_2.
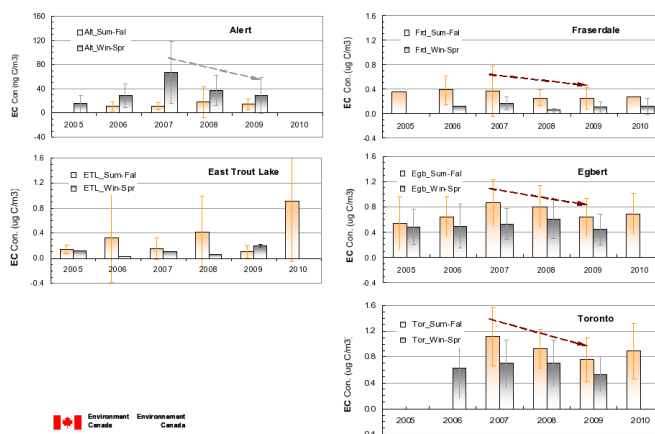

Figure 1. Seasonal variations of EC at five sites over Canada. Orange bars: warm seasonal means; gray bars: cold seasonal means. EC concentrations during warm seasons are mainly influenced by the polluted air masses from the south whereas during cold season major impacts on EC are from the clean air masses from the north at all sites except for Alert (where an opposite pattern is found). EC concentrations during warm seasons at Toronto, Egbert, Fraserdale and those during cold season at Alert show a decrease trend from 2007 through 2009 and a slight increase in 2010, which are consistent with the changes in fossil fuel emission inventory. (CDIAC: http://cdiac.ornl.gov/trends/emis/meth_reg.html).

Aerosol Optical and Radiative Properties Measured at Mt. Lulin During Biomass Burning Seasons

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[2]Taiwan Environmental Protection Administration, Taipei, Taiwan

This paper presents the parameters of aerosol optical properties including scattering, absorption, extinction, single scattering albedo, Angstrom exponent, aerosol optical depth, and derived radiative forcing efficiency at the Lulin Atmospheric Background Station (LABS) in central Taiwan, East Asia. The LABS held its grand opening for operation on 13 April 2006. It is located at the Mt. Lulin (2,862 m MSL; 230 28'07"N, 120052'25"E) in central Taiwan. The LABS is unique because its location and altitude can enhance the global network of Global Atmosphere Watch (GAW) in the Southeast (SE) Asian region where no high-elevation baseline station is available. Our site is located between the GAW Waliguan Station (3,810 m) in Tibetian plateau and Mauna Loa Observatory (3,397m) in Hawaii. In autumn of 2008, light scattering and absorption measurements were added to the suite of instruments at our site. Trajectory study indicates that this site provides us a great of chances to observe a variety of air mass originated from contaminated or clear source regions, giving a distinctive contrast of atmospheric changes. Till present time, the average values of light scattering and absorption (550 nm) are 40.57 Mm-1 and 4.76 Mm-1, respectively. To summarize the results, the maximum concentration of pollutants generally occurred during spring time, especially in March, the average values of light scattering and absorption (550 nm) are 103.89 Mm-1 and 14.45 Mm-1, corresponding to the biomass burning from SE Asia, which are significantly higher than those values in other seasons. Further relationship of those optical parameters with pollutants will be further studied.
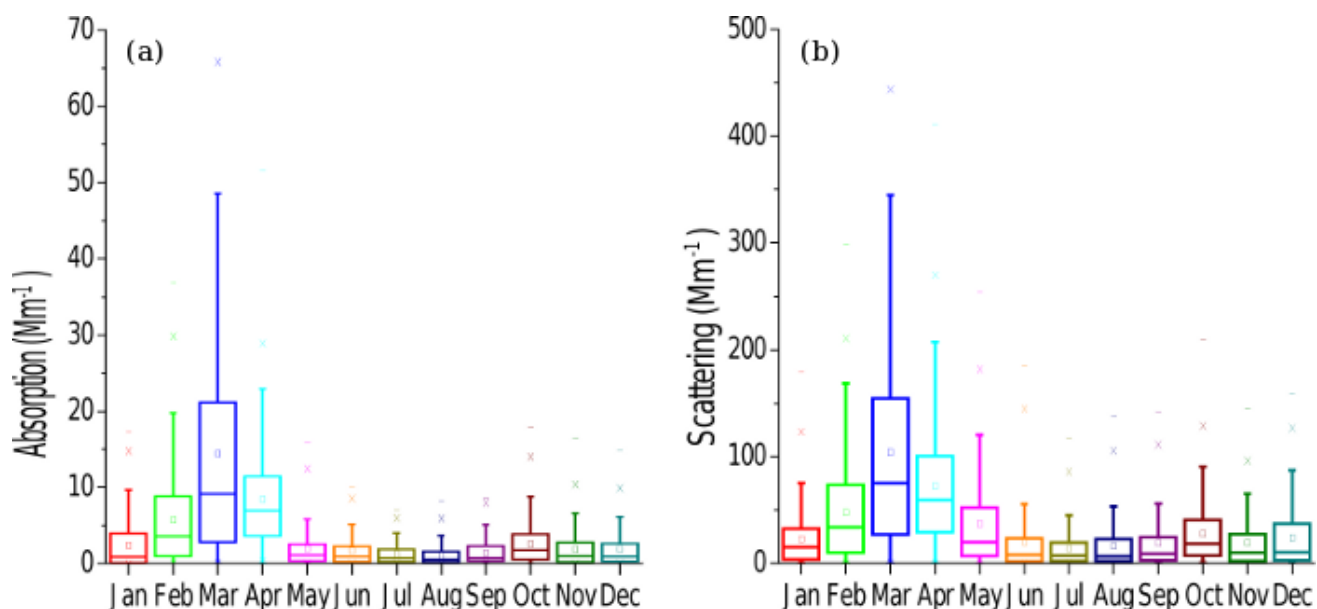
Figure 1. Seasonal variation of (a) aerosol light absorption coefficient, and (b) aerosol total light scattering coefficient.

Aerosol Optical Properties from the Himalayan Foothills Site During Ganges Valley Aerosol Experiment (GVAX)

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Aerosol at the Manora Peak GVAX site emanates from local vegetation, biofuel burning and pollution from the Ganges River Valley as well as long-range transport, especially during downslope periods. Source and seasonal variability of the aerosol optical and cloud-forming properties are presented for the summer monsoon season and fall transition to the dry season. Aerosol loading has a seasonal low during the summer with an average Jun-Aug aerosol scattering coefficient at 550 nm of 74 Mm^{-1} and a mid September to mid November average value of 205 Mm^{-1}. As evidenced by changes in the aerosol single scatter albedo and Ångstrom exponent the aerosol is slightly smaller and darker during the summer and may reflect wet scavenging of larger, more hygroscopic aerosol. A strong diurnal trend is apparent with higher loading around solar noon. The most remarkable feature of the GVAX aerosol during both seasons is its relatively large size. The average Ångstrom exponent for the 450/700 nm wavelengths is ~ 1.0. The large size persists through both seasons and during upslope and downslope conditions.
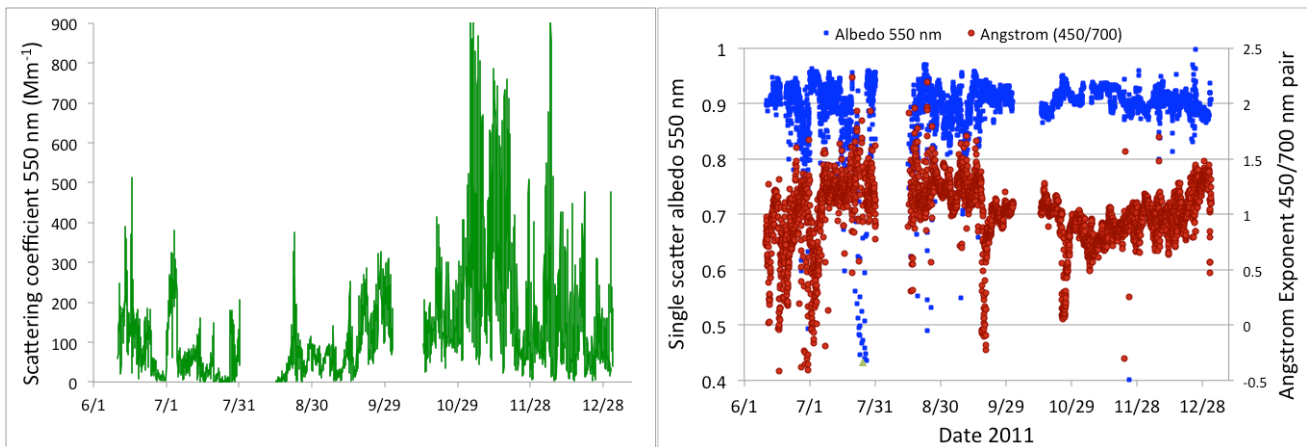

Figure 1. The aerosol scattering coefficient at 550 nm (left) and the aerosol single scatter albedo and Ångstrom Exponent at 550 nm (right) from June to December 2011 from Nainital, India.

**An Inexpensive Method for Estimating Particle Pollution**

M.M. Seltzer

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Air Pollution is crucial to understanding the health and environmental hazards that exist around us. Current real time measurement methods (such as PM2.5 which measures the mass concentration of particles that are under 2.5µg) are expensive, require extensive training, and are not portable. Through measuring the mass concentration of black carbon filtered through snow, this experiment seeks to create a viable, inexpensive, and transportable method of estimating particle pollution. Given that precipitation serves as the dominant method of air particulate cloud scavenging, there may be a relationship between PM2.5 and black carbon in snow.

Snow was collected from four sites around Denver, Colorado where PM2.5 air quality monitors were available. The snow was melted and filtered onto Pallflex membrane filters. The filters were then analyzed for their darkness (light ratio) and using Beer's Law and were compared to the PM2.5 data for each site.

PM2.5 in air and black carbon in snow showed a statically significant relationship. The data showed that this method is a viable way of estimating particle pollution.

The process of estimating particle pollution through measuring black carbon in snow yields many important implications. Most states in the U.S. have few air monitoring stations and these stations don't necessarily reflect the particle pollution at every area surrounding them. This method could provide a far increased amount of data. Finally, in developing nations, this method could empower individuals to cheaply measure their air pollution and understand the hazards around them.
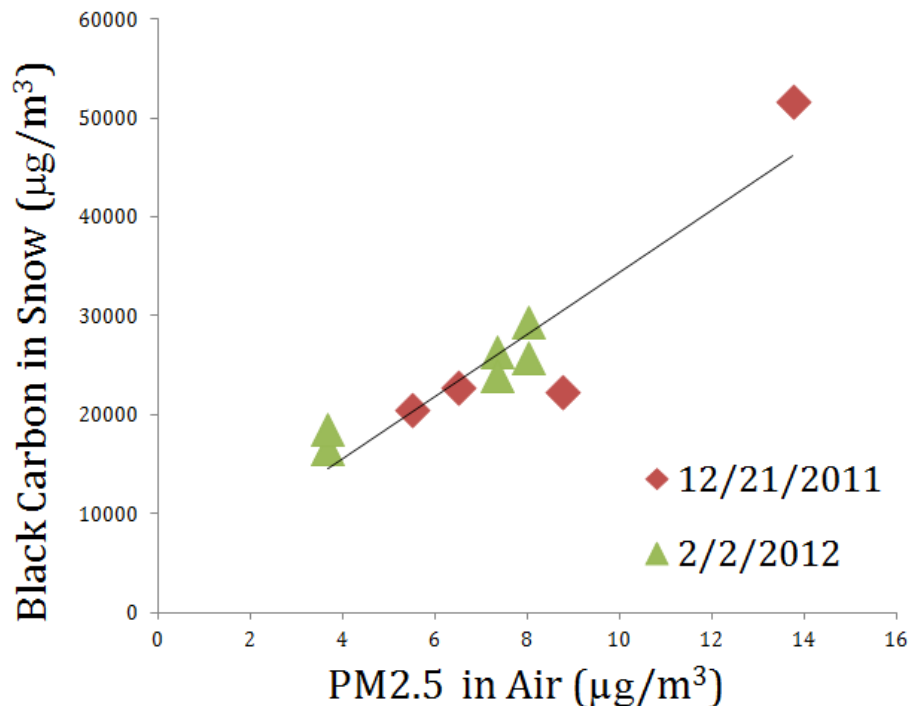
[1]PM2.5 readings from colorado.gov air pollution control division [6]

Figure 1. Black carbon in snow vs 3-hour average of PM2.5 mass concentration at local site.

A Field-deployable Polar Nephelometer

J.E. Barnes

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An instrument has been developed that addresses the measurement of the aerosol phase function, an important component in understanding radiative transfer in the earth's atmosphere. The aerosol phase function describes the scattering of light from aerosols as function of angle. There is a wide variation in phase functions which reflect aerosol size, shape and composition. The phase functions are fundamental to many satellite and lidar (laser radar) retrievals of aerosols and are often not well known. Calculations of the phase functions, instead of measurements, are often used and a simple change from spherical to non-spherical particles can have large impacts (50-100%) on the results.

An innovative imaging polar nephelometer has been developed at the NOAA/Mauna Loa Observatory. The instrument measures both the aerosol and molecular phase function *in situ* from approximately 5 to 175 degrees with resolution of better than one degree. The angles are all measured simultaneously with integration times of tens of seconds to a few minutes. The measurement of the molecular phase function, which is well known, provides an absolute calibration of the instrument both in total light scattered and in the angular dependence. The current absolute accuracy is a few percent for a one-minute integration. Multiple wavelengths, and both parallel and perpendicular polarizations of the light, can be measured for additional information about the aerosols.

Version 3 of the imaging polar nephelometer (PNeph) has been constructed and is being tested in the laboratory. The 1.5 meter PNeph is shown below. It can be operated horizontally or vertically. The camera and fisheye lens image the laser which enters the sample chamber on the left and exits on the right. One laser (532 nm) is shown and there is room for a second set of laser, optics, and alignment mirrors side-by-side for an additional wavelength or polarization. The same camera/lens pair will image both beams simultaneously and an 808 nm laser is planned. The 808 nm wavelength is readily available and still in the range of the camera sensitivity.
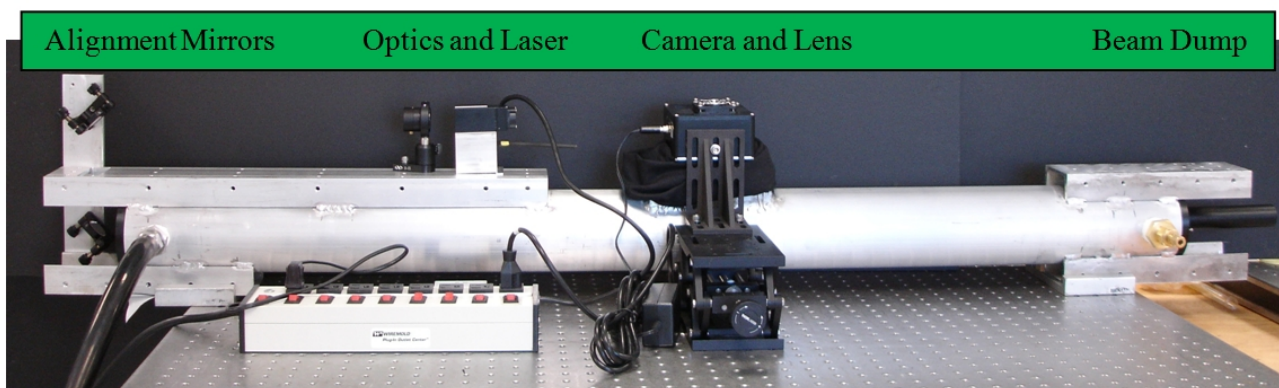

Figure 1. Imaging polar nephelometer in Hilo Laboratory for testing. The camera (center) is using a temporary external mount.

Assessing the Importance of Contact Ice Nucleation

Y. Huang[1], M.D. Brown[2], S. Dhaniyala[2], S. Garimella[1] and D.J. Cziczo[1]

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The indirect effect of aerosols on global radiative forcing via its impact on cloud formation is one of the key unknown in climate change science today. Though our understanding of warm cloud formation is fair, our inability to fully understand and describe cold cloud formation is what limits us in determining and predicting future climate change. It is believed that deposition freezing and immersion freezing are important ice nucleation mechanisms. Less known is the mode called "contact freezing", which involves particles coming into contact with a water droplet to form an ice nuclei (IN). Some experimental studies have shown that the IN formation due to contact freezing was initiated at higher temperatures compared with immersion freezing. However, few experiments were performed using atmospherically relevant conditions and parameters.

We are in the process of constructing a laboratory-based experiment to assess the importance of ice nucleation via contact freezing. The system diagram is shown in Figure 1. The system consists of an injector which is designed to bring a water droplet (diameter~ 15-25 microns) into contact with aerosol particles (diameter ~ 100 nm – 1000 nm) at cold temperatures. The collision between the water droplet and the aerosol particle(s) may induce IN formation, and the potential IN will grow as it travels down a glass flow tube supersaturated with respect to ice. A Bruker Fourier Transform Infrared (FTIR) spectrometer will be used to monitor ice presence and water vapor partitioning in the flow tube at multiple positions and help determine the onset temperature of contact freezing. At the end of the flow tube, a counterflow virtual impactor (CVI) is affixed to reject aerosol particles and let through only the large particles, i.e. the IN. The flow containing the IN will be directed to the Particle Analysis by Laser Mass Spectrometry (PALMS) instrument which performs *in situ* chemical analysis of a single particle. In PALMS, two 532 nm YAG laser beams set at a distance apart are used to detect particles and provide sizing information via scattering. A 193 nm excimer laser beam is then triggered to ablate and ionize the particle. The ions are accelerated into a reflectron mass spectrometer and detected. The water droplets and aerosol particles sent into the system will have different chemical signatures, as identified by PALMS, can confirm that contact freezing is the cause of the IN formation.

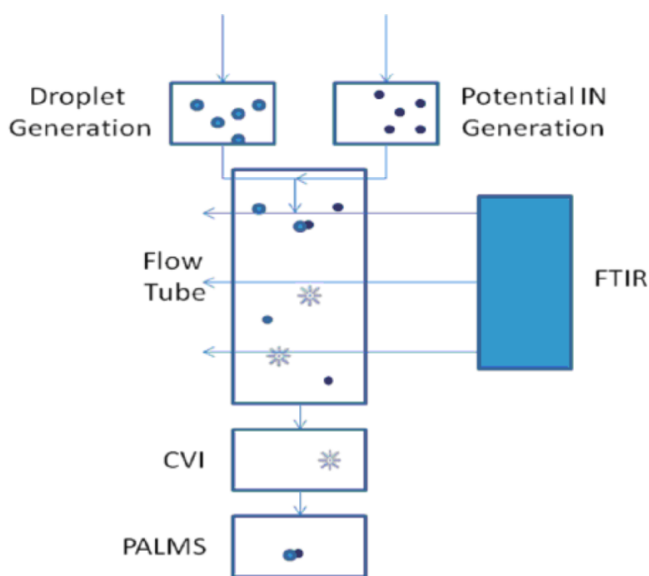**Figure 1.** System diagram. Droplets and potential IN will be generated and equilibrated with the flow tube temperature before interacting. A Bruker FTIR spectrometer will be used to determine ice nucleation in multiple locations. A CVI will be used to separate ice crystals from unactivated aerosol particles and evaporated drop residue. The PALMS instrument will be used for ice residue analysis.

How Does the Nature of Rain Affect the Climate? Black Carbon – Rain Interaction Over Eastern Himalaya, India

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One of the major sources of global warming is atmospheric Black Carbon (BC) which is generated by fossil fuel and biomass burning. Wet scavenging or wash-out by rain is the major process for the removal of BC from the atmosphere. This study is an attempt to investigate the effect of the intensity of rain on the removal of BC from the atmosphere and its consequent signature on the net radiative forcing over a high altitude hill station, Darjeeling (2200 m asl), Eastern Himalaya, India. The study has been made during several rain events in premonsoon (April – May) and monsoon (June – September) in the year 2009. BC had been continuously monitored using an Aethelometer, which measures the mass concentration of BC by measuring the attenuation of light transmitted through a quartz filter tape on to which the ambient particles are made to impinge. The intensity of rain was measured using a co-located optical rain gauge. The removal or wash-out of BC due to rain was determined from the BC concentrations just before and after the rain. Out of several rain events, the initial BC concentrations before rain were found to be almost equal in 11 events. Among those, 6 events were of lower intensity (less than 5 mm hr^{-1}), 3 events were of moderate intensity (5-10 mm hr^{-1}) and 2 events were of higher intensity (greater than 10 mm hr^{-1}). The wash-out of BC from the atmosphere was studied for each of intensity-classes for the equal duration (1 hr). Thus the initial BC concentrations and the duration of the rain were kept equal in order to better understand the extent of removal of BC depending on the nature of rains. It was observed that the wash-out of BC was highest for the lower-intensity rains (60-70 %) followed by moderate (40-55 %) and higher-intensity rains (20-30 %). It was also observed that to remove equal amounts of BC from the atmosphere, the time taken by higher-intensity rains was almost double than lower-intensity rains. In addition to those 11 events, four rain events were studied separately where BC, SO$_4^{2-}$ aerosol and Aerosol Optical Depth were measured before and after the rains. The radiative forcing and the radiative heating rate were determined using SBDART model both before and after the rains. It was observed that the lower intensity rains reduced the BC to SO$_4^{2-}$ ratio more compared to moderate and higher-intensity rains. Consequently atmospheric forcing and radiative heating rate were also found to be drastically reduced for the lower-intensity rain. Thus a light rain is much more able to cool the atmosphere by reducing the atmospheric forcing and radiative heating rate significantly and has a significant co-benefits to the climate than a heavy rain. Although this study represents the regional scenario of aerosol-rain interaction over Eastern Himalayan region, it is expected to be generally valid.
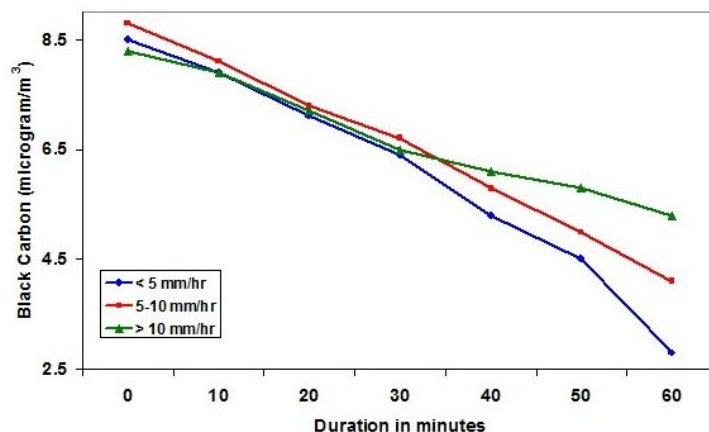
Figure 1. Wet scavenging of BC aerosol at different rain intensities.

Recent Science from the Cape Verde Atmopsheric Observatory (CVAO)

J. Lee[1], S. Punjabi[1], K. Read[1], L. Carpenter[1], A. Lewis[1], S. Moller[1], L. Neves[2], Z. Fleming[3], M. Evans[1] and S. Arnold[4]

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The CVAO (16,848°N, 24.871°W), a subtropical marine boundary layer atmospheric monitoring station situated at Calhau on the island of São Vicente, has been in operation since October 2006. Almost continuous measurements of the trace gases O_3, CO, NMVOC, NO, and NO_2 have been obtained. Other data from the CVAO, for example of greenhouse gases, aerosol (physical and chemical parameters), halocarbons, halogen oxides, are also available over various timescales (see http://ncasweb.leeds.ac.uk/capeverde/ for more details). The prevailing strong on-shore winds bring marine air masses with varying inputs of Sarahan dust and of long range transport from North American Europe, thus the CVAO is an appealing location for both short- and long-term research into a variety of atmospheric phenomena.

Aged air masses from North America, Europe, and Africa influence the measurements at the observatory, but fresh emissions from coastal Africa and the ocean may also play a major role. Through the use of the United Kingdom Met office's NAME model (http://www.metoffice.gov.uk/research/modelling-systems/dispersion-model) it has recently been possible to classify the air received by the site and this has since been employed in further interpretation of the datasets (Carpenter et al., 20102).

Measurements from the last six years will be presented at the conference together with comparisons with the output of the CAM-Chem and GEOS-Chem global chemistry transport models (Read et al., 2012). The GEOS model shows a significant underestimate in the NO_x concentration compared to the observations. The model calculates an annual mean NO_x concentration of 8.5 pptv +/- 2 pptv whereas the equivalent observation are 25 pptv +/- 24 pptv[3]. The impact of this on the composition of the marine troposphere is profound. Figure 1 shows the impact of forcing the tropical boundary layer NO_x in the GEOS model to be a minimum of 25 pptv (the observational mean), with significant (50 to 200%) increases in O_3 observed. It is clear that the tropical marine boundary layer is very sensitive to perturbations in the NO_x concentrations, that the model fails to simulate these concentrations at Cape Verde.

The CVAO is a Global Atmospheric Watch (GAW) station and so data is submitted regularly on daily, monthly and yearly timescales to the World Centre for the Greenhouse Gases http://gaw.kishou.go.jp/wdcgg/ in addition to the British Atmospheric Data Centre http://badc.nerc.ac.uk/home/index.html along with associated instrument metadata. GAW audits are planned for CO, O_3 and the greenhouse gas species later this year.
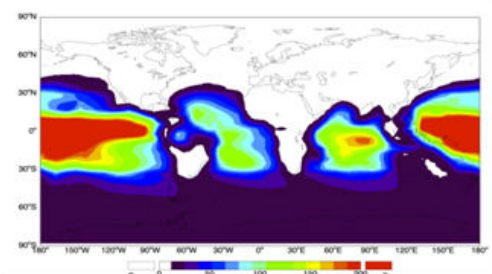

Figure 1. The impact on ground-level ozone of forcing the tropical boundary layer NO_x in the GEOS-Chem model to be a minimum of 25 pptv (the observational mean).

Ten Years of Observations of Ozone-depleting Substances at Monte Cimone (Italy) for Deriving Trends and Regional Emissions.

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Man-made halogenated gases that are potentially harmful for the stratospheric ozone layer are regulated under the United Nations Environment Prigramme Montreal Protocol on substances that destroy the ozone layer. The Protocol is a good example of how international agreements can be effective in tackling environmental issues of global significance. In fact, as a consequence of the implementation of the Protocol and subsequent amendments, tropospheric abundances and emissions of most ozone depleting substances (ODSs) started to decrease in the mid-nineties. However, the enhancement polar vortex strength and decrease in stratospheric temperatures in the Arctic, likely to be due to change in global climate, have been recognised as responsible of an unprecedented ozone loss observed over the Arctic in the Spring 2011. Therefore, notwithstanding the effectiveness of the Montreal Protocol, the attention on tropospheric levels of ODSs is still high. Through direct observations it is possible to correctly evaluate the global atmospheric budget of ODSs. Here will be presented the results of ten years of continuous measurements of ODSs carried out at the World Meteorological Organization-Global Atmosphere Watch Italian Climate Observatory "O. Vittori" on the top of Monte Cimone (Italy) , an Advanced Global Atmospheric Gases Experiment affiliated station. As an example the tome series for CFC-11 is reported in Figure 1.
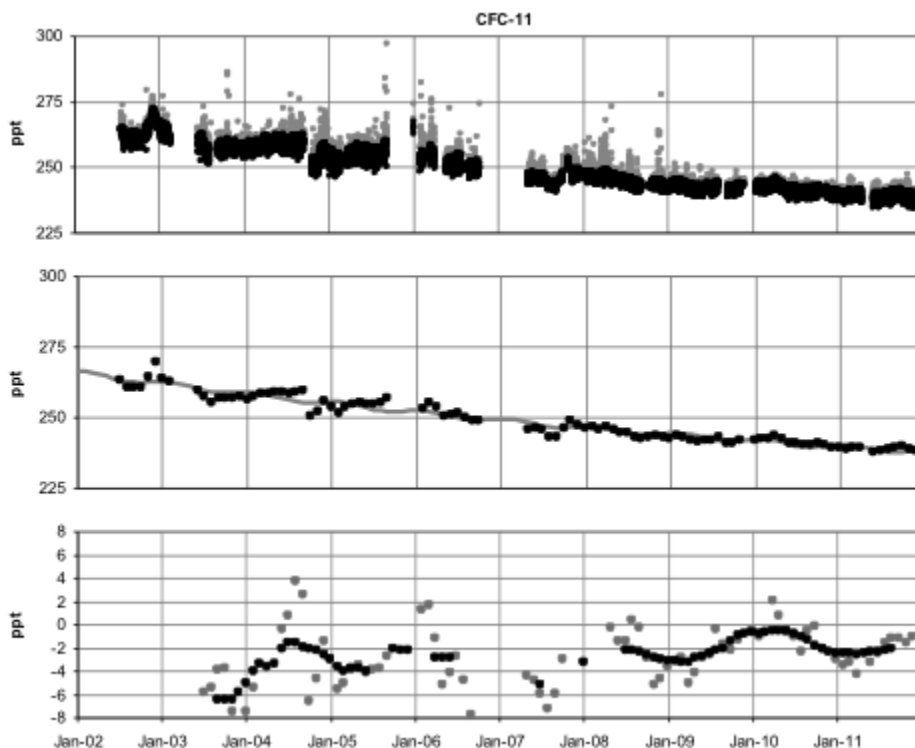

Figure 1. CFC-11 at ICO-OV. Top Panel: time series, black dot baseline values, grey dots pollution events. Middle Panel: best fit. Bottom Panel: annual growth rates.

Comparison of Surface Measurements of Equivalent Black Carbon at Four Arctic Stations

T. Uttal[1], A. Maskhtas[2], O. Blumenthal[3], C. Sandoval[3], K. Sanchez[4], S. Sharma[5], R. Schnell[1], J. Ogren[1], R. Albee[3], T. Mefford[6] and T. Hansen[7]

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[7]Magee Scientific Inc., Berkeley, CA

Black Carbon has received global attention as a potential significant short term climate forcer in the Arctic, however direct surface measurements in Arctic locations have been sparse. In order to better understand the effects of black carbon this study compares one annual cycle (2010) of Equivalent Black Carbon (EBC) for observatories in Tiksi (Russia), Barrow (Alaska), Alert (Canada) and Summit (Greenland). It is expected that this analysis will provide some direct observational evidence to test the hypothesis that black carbon distributed on Arctic snow and ice surfaces may have a significant impact on surface albedo.
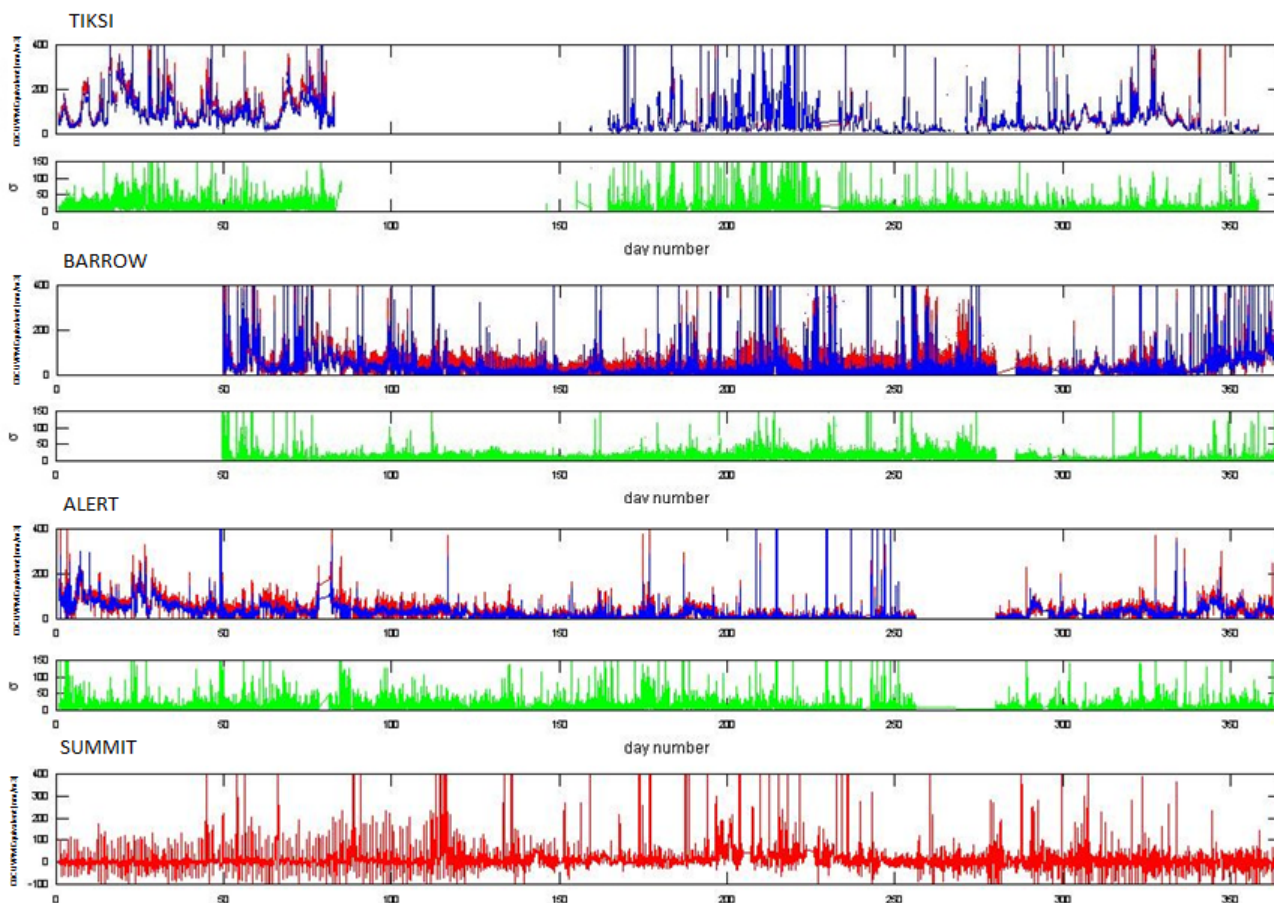

Figure 1. EBC estimates from 880 nm (red), 370 nm (blue); σ – standard deviation (green) of the 7 wavelengths from the Magee Scientific Aethelometer for Tiksi, Barrow, Alert and Summit Greenland.

The Tiksi, Russia Hydrometeorological International Facility for Atmospheric, Terrestrial and Ocean Observations: First Measurements and Future Plans

A. Makshtas[1], T. Uttal[2], O. Dmitrieva[3], T. Laurila[4], S.J. Oltmans[5], A. Reshetnikov[6], R.C. Schnell[2], E. Asmi[4], H.J. Diamond[2], M. Aurela[4], E.G. Dutton[2], V. Kustov[1], I. Repina[7], A. Artamonov[7], A. Konoplev[8], A. Rychkov[8], R. Albee[9], M. Okraszewski[9], D. Apartsev[1], B. Holben[10], M. Sorokin[10], A. Sinyakov[3], E. Volkov[3], M. Ivanova[3], V. Kondreyev[3], V. Ivakhov[6], E. Estes[11], B. Vasel[2] and A. Kuzmichov[1]

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[7]Russian Academy of Science, Moscow, Russia
[8]Research and Production Association "Typhoon" Institute, Obninsk, Russia
[9]Science and Technology Corporation, Boulder, CO 80305
[10]National Aeronautics Space Administration (NASA), Greenbelt, MD 20771
[11]Cherokee Services Group, Ft Collins, CO 80525, USA

During the International Polar Year within the framework of Activity 196 "International Arctic Systems for Observing the Atmospheres" key task was "Creation of the Atmospheric Observatory of Climatic Monitoring in Tiksi, Russia". This task has been realized by the combined efforts of Roshydromet, NOAA, National Science Foundation, NASA, the Russian Academy of Science, the Sakha Republic and the Finish Meteorological Institute. The current observatory features modernized communications, power, laboratory and office facilities which are suitable for supporting the collection of quantitative data on atmospheric structure and processes as well as associated ocean and land parameters in order to further studies of weather and climate. The Tiksi science program has had a preliminary focus on supporting International networks, such as Global Atmosphere Watch (atmospheric gases and aerosols), Baseline Surface Radiation Network (atmospheric radiation), Climate Reference Network (climate grade weather observations), the International Permafrost Association, and AeroNET (aerosol optical depth). The measurements are currently being made of a number of key measurements of surface and atmospheric radiation, the permafrost active layer, black carbon, surface ozone, atmospheric optical depth, aerosol concentrations, water vapor, methane and CO_2 fluxes, greenhouse gases and persistent organic pollutants.
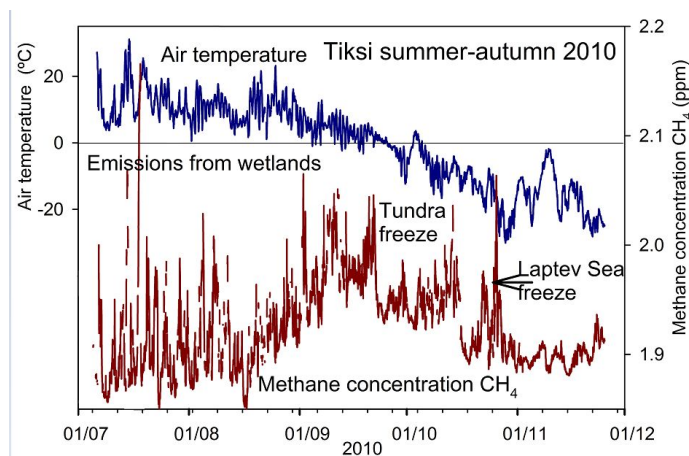

Figure 1. Methane flux signature during fall freeze of the tundra and sea-ice at the Tiksi Hydrometeorological Observatory in the Sakha Republic, Russia.

Atmospheric Data Management at ICOS Atmospheric Thematic Center: Collection, Processing, Archiving and Access

L. Hazan, J. Tarniewicz, P. Jegou, M. Schmidt, M. Ramonet, I. Pison, J. Paris, L. Rivier and P. Ciais

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ICOS (Integrated Carbon Observation System) is a new European research infrastructure for quantifying and understanding the Greenhouse Gas (GHG) balance of the European continent and adjacent regions. It consists of an harmonized and standardized network of long-term observation sites coordinated through a set of four central facilities including, for the atmospheric components, an Atmospheric Thematic Center (ATC) and a Central Analytic Laboratory (CAL). The aim of this infrastructure is to provide the long-term atmospheric and flux observations required to understand the present state and predict future behavior of the global carbon cycle and GHG emissions. ICOS is currently in its preparatory phase (ICOS PP, until March 2013).

The need of an ATC operating at the European level in ICOS is justified by the distributed nature of this infrastructure, with stations managed by different countries. A central facility is needed to ensure that: 1) all data collected at the atmospheric stations are processed with the same algorithms and properly archived for the long term, 2) the atmospheric stations can receive permanent and timely support for optimal operation during their lifetime, and 3) that technology watch on measurement techniques will allow efficient new sensors to be used in the network in the future. The ATC will also be responsible to link the ICOS atmospheric data collection program with international monitoring programmes.

The poster presents the different steps of the data management done at the ATC, from data collection to web broadcasting. A focus is done on data processing and access to measurements and elaborated data product.

References: ICOS infrastructure: http://www.icos-infrastructure.eu/ and ICOS ATC demonstration: https://icos-atc-demo.lsce.ipsl.fr/
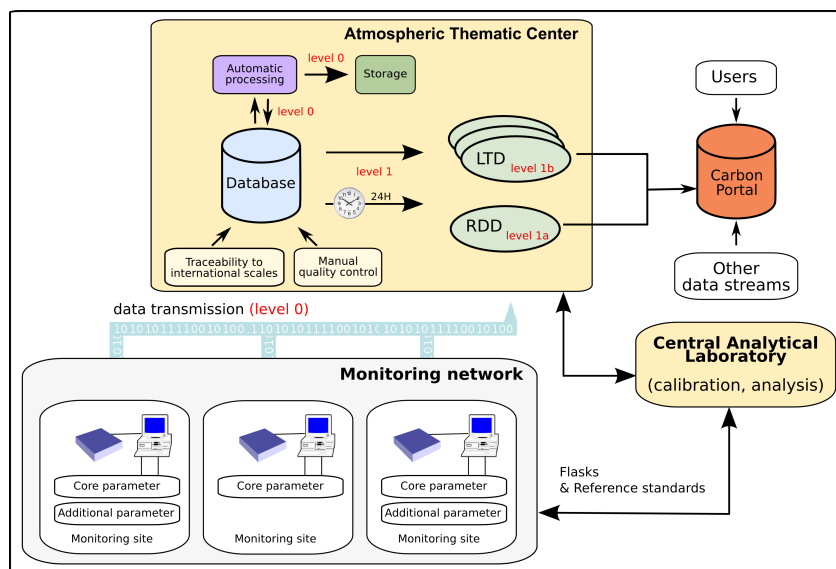

Figure 1. Data processing at ICOS ATC. Also presented is the relation between ATC and CAL central facilities.

The ICOS Atmospheric Network and Atmospheric Thematic Center (ATC)

M. Ramonet[1], P. Ciais[1], L. Rivier[1], T. Laurila[2], A. Vermeulen[3], M. Geever[4], A. Jordan[5], I. Levin[6], O. Laurent[1], J. Rangognio[1], M. Delmotte[1], B. Wastine[1], L. Hazan[1], M. Schmidt[1], J. Tarniewicz[1], P.Y. Jegou[1], J. Helle[1], T.G. Spain[7] and J.D. Paris[1]

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Integrated Carbon Observation System (ICOS) is a European Research Infrastructure (www.icos-infrastructure.eu) dedicated to understanding the greenhouse balance of the European continent and of adjacent regions. It integrates terrestrial, atmospheric and oceanic observations at various sites into a single, coherent, highly precise dataset. The need of an ATC operating at the European level in ICOS is justified by the distributed nature of this infrastructure. A central facility is needed to ensure that all the data are processed with the same algorithms and properly archived for the long term, that the atmospheric stations can receive permanent support for optimal operation during their lifetime, and that new sensors can be smoothly deployed in the network in the future. The ATC will also be responsible to link the ICOS atmospheric data collection program with other central facilities, in the framework of European and international monitoring networks.

A demonstration (Demo) experiment has been set up during the second semester of 2011 to demonstrate the feasibility of the ICOS infrastructure and its capability to manage properly a network of standardized instruments, with a centralized data processing performed in near real time. For that purpose, the Demo will rely on a small network made of four stations and central facilities (ATC, Ecosystem Thematic Center (ETC) and Central Analytical Laboratory (CAL)). The presentation will detail the tasks of the ICOS-ATC, and the preliminary results obtained during the Demo Experiment.
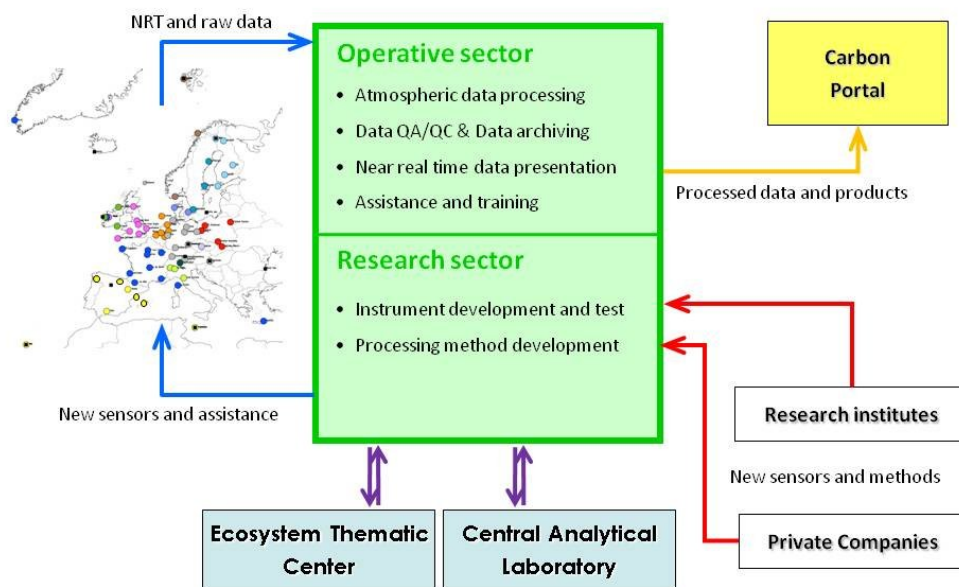

Figure 1. Schematic view of the main tasks of the ICOS-ATC.

Measurements of Trace Gases at Lulin Atmospheric Background Station (LABS) and Dongsha Island (DSI), Taiwan

C.-F. Ou Yang[1], N. Lin[2], C.-T. Lee[3], G.-R. Sheu[2], H.-C. Hsieh[1], S.-H. Wang[2], W.-T. Liu[1] and J.-L. Wang[1]

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Measurements of trace gases (CO, ozone, etc.) were performed at LABS (Lulin Atmospheric Background Station, 23.5°N, 120.9°E, 2,862 m a.s.l.) and DSI (Dongsha Island, 20.70°N, 116.73°E, 3 m a.s.l.). Based on the nearly six-year measurements, diurnal variations of these species at the LABS were found to be distinctively different from those at the surface. CO show maximum concentrations in late afternoon, and minima at night. Ozone however, shows a nearly opposite variation to CO with minima at noon, contradictory to the photochemistry production of maximum ozone at the surface. However, this pattern of ozone diurnal variation repeated for the last five years, but changed since July 2011. The results of flask samples analyzed by NOAA/ESRL/GMD were also discussed in this study.

For the measurements at Dongsha Island, a small island situated between Taiwan and the Philippines, both Greenhouse Gases and ozone were measured during the spring of 2010. Our measurements suggested that strong northeasterly winds arising from the winter Asian monsoon may have transported polluted air masses from the northern continent to locations as far south as Dongsha (latitude 20.70°N), as indicated by elevated ozone levels of approximately 60 ppbv. In contrast, during the calm periods when the monsoon subsided, low ozone levels of about 30 ppb were detected, which is typical for marine air masses.
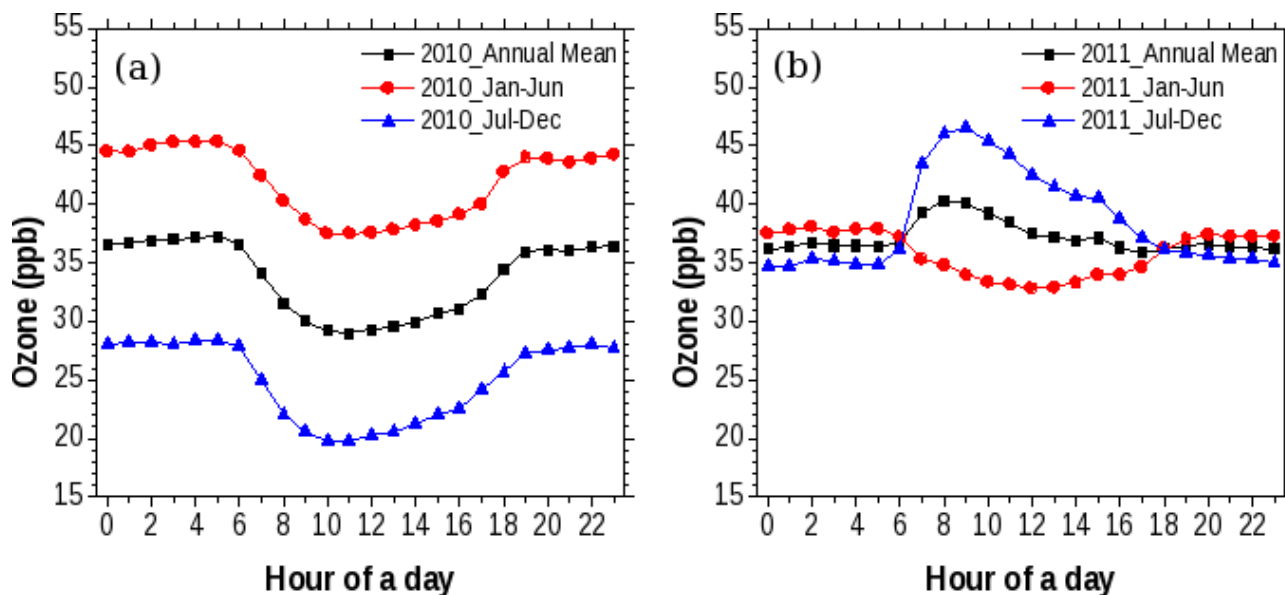

Figure 1. Diurnal variations of ozone observed at LABS in (a) 2010 and (b) 2011.

Atmospheric Radiation Measurement Program Data Quality Office Overview

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[2]Alliant Techsystems, Santa Barbara, CA

The U.S. Department of Energy's Atmospheric Radiation Measurement (ARM) Program collects a plethora of atmospheric data at several highly-instrumented permanent facilities, two mobile facilities, an aerial facility, and is adding two new permanent facilities. A primary objective of the ARM Program is to improve the understanding of clouds, aerosols, and radiative feedback processes in the atmosphere by collecting field measurements to aid in the advancement of global climate models.

To ensure the data collected are of the highest standard possible, the ARM Data Quality Office monitors and inspects data collected in near real-time. A system of automated and manual quality control techniques were developed to facilitate the systematic inspection of data and efficiently report instances of suspect data. This talk will review the tools and processes developed to create and monitor the quality control metrics, plots, interactive displays, notification methods, and documentation process for tracking instances of problems from detection to resolution.

Figure 1. Atmospheric Radiation Measurement Program logo.

Nocturnal Aerosol Optical Depth Measurements Using a Lunar Photometer

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Atmospheric aerosols drive many processes related to air quality, atmospheric chemistry, cloud formation, and directly impact the surface radiation budget. High quality records of aerosol properties are essential to better quantify the climate impacts of polar aerosols. To this end, the Scientific Committee on Antarctic Research has recommended the establishment of a network of Sun photometers to monitor columnar aerosol optical depth (AOD) at high latitudes. Such a network is now in place, with activities coordinated through the Polar-AOD community. However, nighttime observations are rarely made and require the use of costly Star photometers. Consequently, very little information about diurnal AOD variations is available, especially during the long polar night. During winter aerosols tend to accumulate within the Arctic vortex due to long-range transport and these may have significant impacts on the surface radiation balance.

We have been exploring the use of lunar irradiance to obtain nighttime AOD measurements using a small aperture photometer. The approach uses the United States Geological Survey lunar calibration system to provide high precision values of lunar exo-atmospheric spectral irradiance for any given location. Photometric measurements provide the column optical transmittance from which we can estimate AOD. To date, retrievals of multi-wavelength, nighttime AOD have been obtained in the vicinity of Baltimore, MD using a modified, commercial Sun photometer. More recently, NOAA/GMD has developed a prototype lunar photometer that is being evaluated at its Lab in Boulder, CO. In this presentation, test results (e.g., Figure) will be presented with an eye towards extending this approach for polar applications using a photometer system similar to that currently in operation at the NOAA baseline observatories. Barrow, Alaska is a target site for further testing and operations.
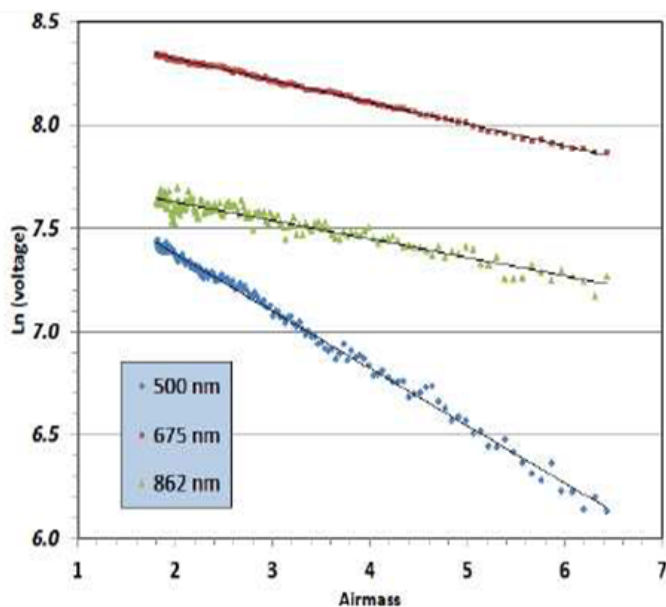

Figure 1. Examples of Langley calibration plots made from raw data collected the night of 9/10 March 2012 at NOAA/GMD-Boulder. Langley Plots are used to extrapolate the wavelength-dependent, top-of-the-atmosphere signals from which attenuation by atmospheric aerosols are measured to derive AOD. A fourth channel (420 nm) is to be added before deployment.

Surface Fluxes and Boundary-layer Measurements in Arctic at the Eureka (Canada) and Tiksi (Russia) Climate Observatories

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In this study we analyze and compare variability of turbulent surface fluxes including water vapor and carbon dioxide transfer based on measurements made at two different sites located near the coast of the Arctic Ocean at Eureka (Canadian territory of Nunavut) and Tiksi (East Siberia). Turbulent fluxes and mean meteorological data are measured continuously and reported hourly at various levels on 10-m (Eureka) and 20-m (Tiksi) flux towers. Sonic anemometers and Licor 7500 infrared gas analyzer are used to measure turbulent fluxes. Tower-based eddy covariance and solar radiation measurements provide a long-term near continuous temporal record of hourly average mass and energy fluxes respectively. The turbulent data are supported by additional atmospheric and surface/snow/permafrost measurements. The data show that sensible heat flux, water vapor and carbon dioxide fluxes were small and mostly irregular in the cold seasons when the ground is covered with snow. However, the turbulent fluxes increase rapidly when air temperatures rise above freezing during spring melt and eventually reach a summer maximum. According to our data, strong upward sensible and latent heat fluxes are observed throughout the summer months indicating unstable (convective) conditions on average. This study also shows that the sensible heat flux, water vapor, and carbon dioxide fluxes exhibit clear diurnal cycles during the Arctic summer. This behavior of the sensible heat flux is similar to the diurnal variations in mid-latitudes in summer. On average the turbulent flux of carbon dioxide was mostly negative (uptake by the surface) in summer indicating that the Eureka and Tiksi Arctic sites are net sinks for atmospheric CO_2 during the growing season. This result is not unexpected as both Eureka and Tiksi have a summer surface that is extensively covered with vegetation. It is also found that in a summer period observed temporal variability of the carbon dioxide flux was generally in anti-phase with water vapor flux (downward CO_2 flux and upward H_2O flux). During late summer and early autumn all turbulent fluxes rapidly decreases in magnitude when the air temperature decreases and falls below freezing. Although the Tiksi and Eureka sites have general similarities in annual surface fluxes, some more detailed differences in net characteristics are investigated resulting from such phenomena as the on-shore flow from the Laptev Sea in Tiksi which is absent at the more land-locked Eureka site.
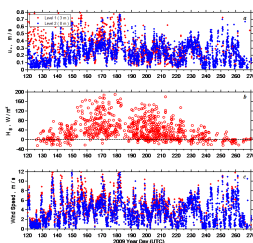

Figure 1. Time series of the hourly averaged (a) friction velocity, (b) sensible heat flux (Hs), and (c) wind speed for the Eureka site obtained during May-September 2009 (YD 120-270). Measurements were made by sonic anemometers located at 3 and 8 m above the surface. Positive values of Hs correspond to the unstable (convective) conditions and vice versa. Hourly averages of the sensible heat flux show large diurnal variations during summer.
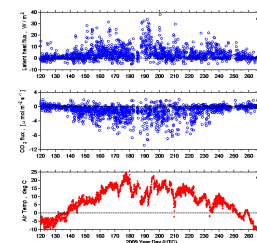

Figure 2. Time series of the hourly averaged fluxes of (a) H_2O, (b) CO_2, and (c) air temperature for the Eureka site obtained during May-September 2009 (YD 120-270). Measurements were made by sonic anemometers and Licor-7500. Negative signs mean downward fluxes and vice versa. Hourly averages of the fluxes and air temperature show large diurnal variations during summer.

Maps of Isolines of Ultraviolet (UV)-B Dose at the Republic of Panama

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The Laboratory of Atmospheric Physics of the University of Panama has been monitoring UV-B radiation as well as other meteorological variables since 1998. UV-B radiation is measured by means of broadband radiometers, 501 UV-Biometers, installed at the monitoring sites of the radiometric network managed by the University of Panama. Under clear sky conditions, extreme UV Indexes and high UV-B doses have been measured. It has been determined that these conditions are observed during 87% of dry season period. It has been established that, at the Republic of Panama, the incidence of skin cancers (basal, squamous and melanoma) has been increasing during the last decade. Due to this situation, in order to assess the UV-B dose distribution for all the country and for every month, maps of isolines of UV-B dose are extremely important.

As a first step for the construction of the maps of isolines mentioned before, a correlation between UV-B dose and solar global irradiation was established. It was accomplished by means of the data of both parameters measured, simultaneously, at the University of Panama under a day with clear sky conditions. The model used to fit the correlation was a sigmoidal function. Once that correlation was established, it was applied to solar global irradiation data captured by 23 stations managed by the National Hydrometeorological Center as well as 6 stations managed by the Panama Canal Authority. In this way, daily UV-B dose was obtained for all the sites where these stations are located. The data of UV-B dose captured by the radiometers managed by the University of Panama were also included. The maps mentioned before were constructed by means of the Kriging interpolation method.

According to those maps, highest levels of UV-B dose are observed at the Pacific seaboard during the dry season. Lesser levels of UV-B dose are observed at the Caribbean seaboard all over the year. These significant differences between the levels of UV-B dose at both seaboards are extremely linked to cloud cover. A discussion of the results of the UV-B dose isolines maps will be presented.
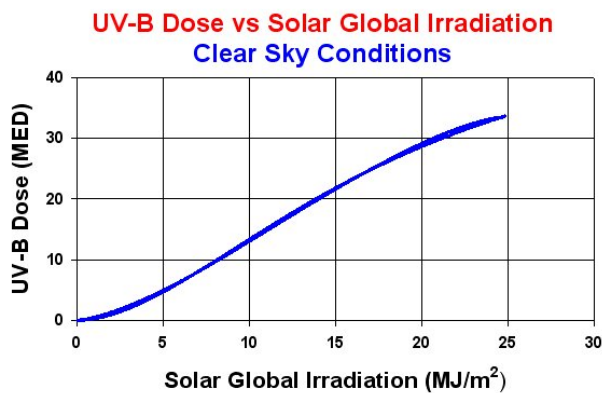

Figure 1. Correlation Between UVB Dose and Isolines of Monthly UV-B Dose - March Global Irradiation.
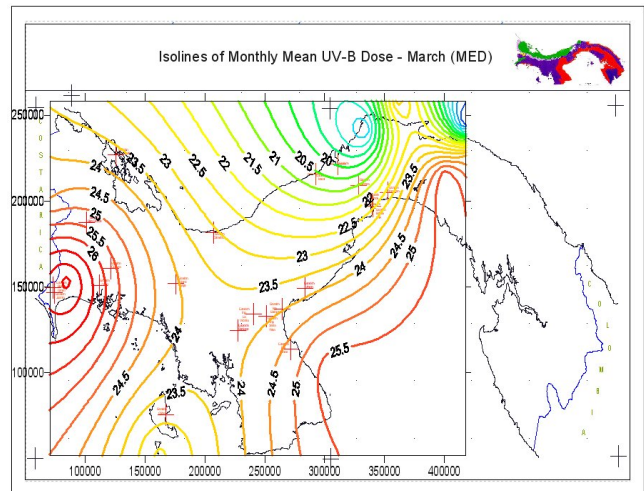

Figure 2. Isolines of Monthly UV-B Dose - March.

High Arctic Ultraviolet (UV) Radiation Levels in the Spring of 2011 Caused by Unprecedented Chemical Ozone Loss

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Ozone concentrations in the Arctic stratosphere during March 2011 were the lowest ever recorded. The record loss was mostly caused by chemical destruction of ozone, attributed to the existing stratospheric burden of ozone-depleting halogens and favored by an unusually prolonged cold period in the lower stratosphere in 2011. The low levels of total ozone led to elevated UV levels throughout the Arctic and sub-Arctic as shown in the figure below. UV radiation is characterized here in terms of the UV Index, which is a measure of the ability of UV radiation to cause sunburn in human skin. Changes in the UV Index anti-correlate with changes in total ozone (compare 2011 data in center and bottom panels). Noontime UV Indices of March 2011 exceeded historical measurements for this month at all Arctic sites where ground-based UV monitoring systems are located. The maximum enhancement of the UV Index relative to the climatological average was 122% (panel c). While these large relative changes are unprecedented, the absolute increases in UV levels were modest at all Arctic sites (e.g., increase by less than two UV Index units) because the low-ozone event occurred early in spring when the solar elevation was still small. However, larger absolute increases of UV Indices occurred at lower latitudes during excursions of the polar vortex in April. These larger increases were potentially harmful to life.

This presentation was motivated by an essay on Ozone and UV Radiation prepared for the "2011 NOAA Arctic Report Card", available at http://www.arctic.noaa.gov/reportcard/ozone_uv.html. It contains additional material not included in this presentation.
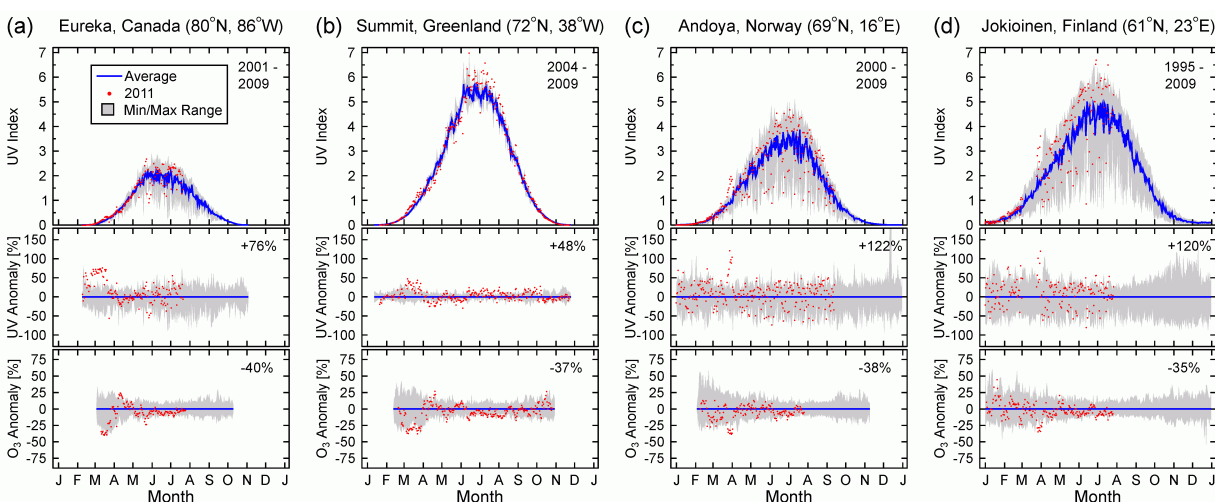

Figure 1. Seasonal variation of the noontime UV Index for four Arctic and sub-Arctic sites measured by ground-based radiometers. The upper panels compare the climatological average (blue line) with the measurements in 2011 (red dots), and historical minima and maxima (shaded range). Center panels show the anomaly in the UV Index, calculated as the percentage departure from the climatological average. Bottom panels show a similar anomaly analysis for total ozone derived from satellite measurements (TOMS and OMI).

The Antarctic, Boulder, and Mauna Loa Ultraviolet (UV) Monitoring Program Update

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The Radiation group of NOAA's Global Monitoring Division operates five UV monitoring stations. Three in Antarctica, one in Boulder, Colorado and one at the Mauna Loa Observatory, Hawaii. The Biospherical Instruments Inc-built spectroradiometers at the three stations in Antarctica have recorded more than 23 years of spectral UV and visible data. The NIWA-built spectroradiometers at the stations in Boulder and Mauna Loa have both acquired more than 12 years of data. Data from all five stations are used to advance radiative transfer studies and effects on plants and animals. Here we present some recent preliminary results on a study to validate recent work published on unexpected spectral variability found in the Solar Irradiance Monitor's data on the SOURCE satellite experiment in the waning years of solar cycle 23, 2004 to 2007. Data from both the Mauna Loa and south pole spectroradiometers was chosen due to low aerosols found at these sites. Data were chosen to duplicate the time periods chosen in the published studies. Additional data were chosen during maximum and minimal sunspot activity to determine their effects on the possible spectral changes in solar output.
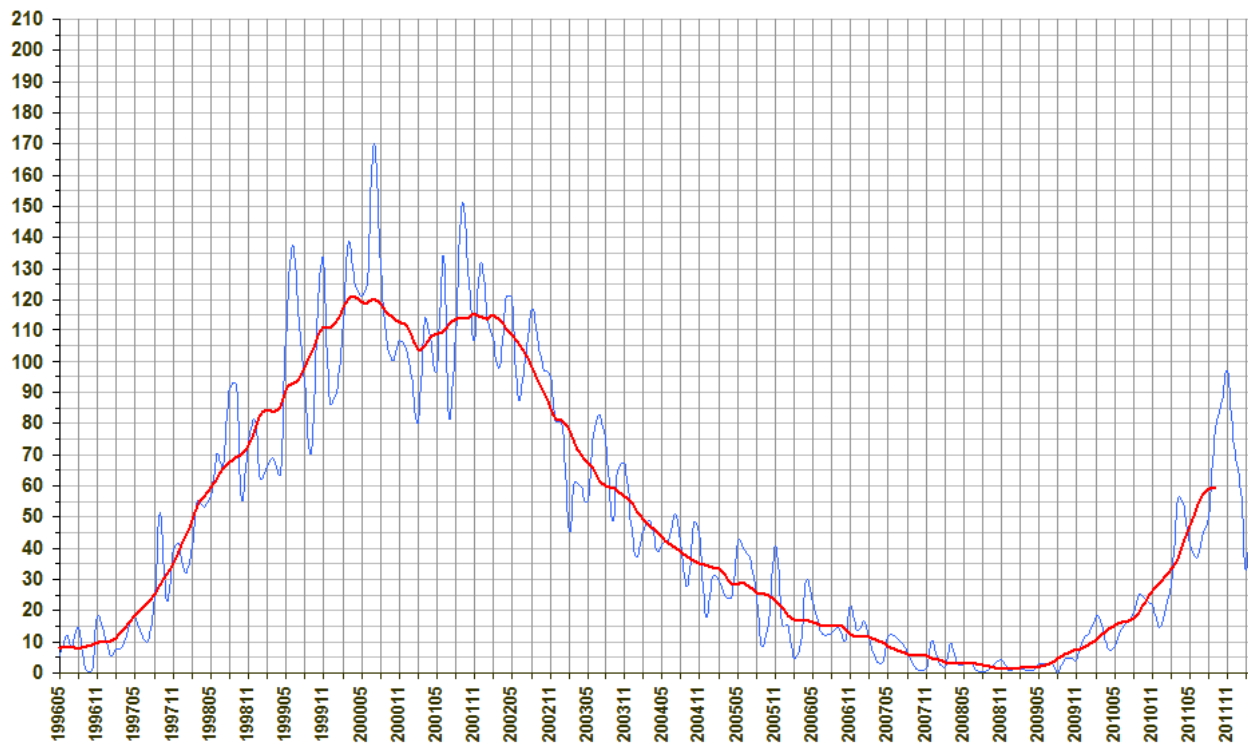

Figure 1. Sunspot activity during solar cycle number 23-24 (graph from http://www.solen.info/solar/solcycle.html).

NEUBrew - The NOAA/Environmental Protection Agency (EPA) Brewer Spectrophotometer Ultraviolet (UV)-Ozone Monitoring Network Update

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The NEUBrew network is a monitoring and research effort between NOAA's Global Monitoring Division and EPA's Office of Air Quality, Planning and Standards. The six station network is comprised of Brewer Mark IV spectrophotometers, chosen for their multi-function measurement capability. Presently the network is producing spectral UV irradiance, total column ozone, and ozone profile. The NEUBrew network was established in 2006 with stations located at Ft. Peck, MT, Table Mtn, Boulder, CO, the University of Colorado's Mountain Research Station at Niwot Ridge, CO, the University of Houston, Houston, TX, the Bondville Environmental and Atmospheric Research Site at Bondville, IL and the North Carolina State University's agriculture field site at Raleigh, NC. The sites were chosen because they represent a mixture of clean, mildly polluted and heavily polluted locations. In addition to the Brewer Mark IV spectrophotometers, each site is equipped with considerable ancillary instrumentation that allows for expanded research opportunities. The Brewer makes spectral scans of an internal reference lamp on a daily basis. This data along with opening and closing calibrations, a correction algorithm has been developed to update the instrument's response file on a daily basis. Results of its implementation are shown here. Additionally, a climatologically-based correction algorithm has been developed to adjust the total column ozone retrieval for seasonal ozone height and temperature dependence.
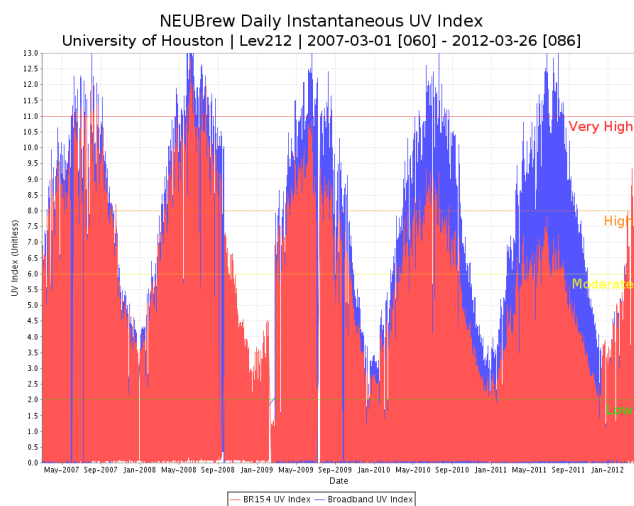

Figure 1. Brewer 154-Houston uncorrected UV index values from 2007 to 2011 compared to UV index from a collocated YES UVB-1.
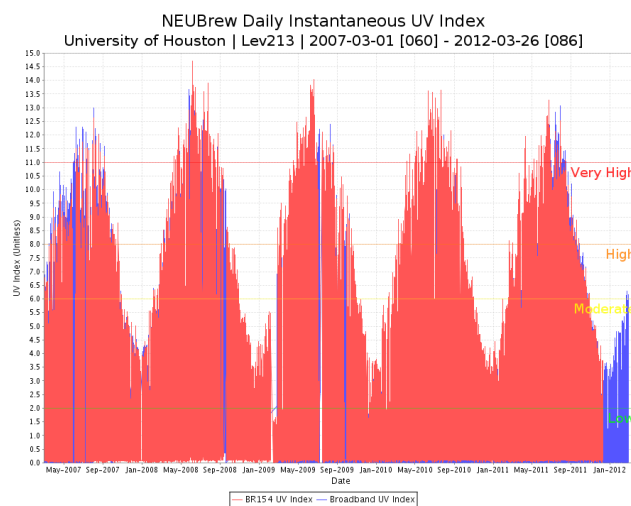
Figure 2. Corrected UV index values using an opening and closing calibration and incorporating a daily linear interpolation algorithm compared to UV index from a collocated YES UVB-1.

NOAA/GMD Participation in the Eleventh International Pyrheliometer Comparison (IPC-XI) September 26-October 15 2010 World Radiation Center (WRC) Davos, Switzerland
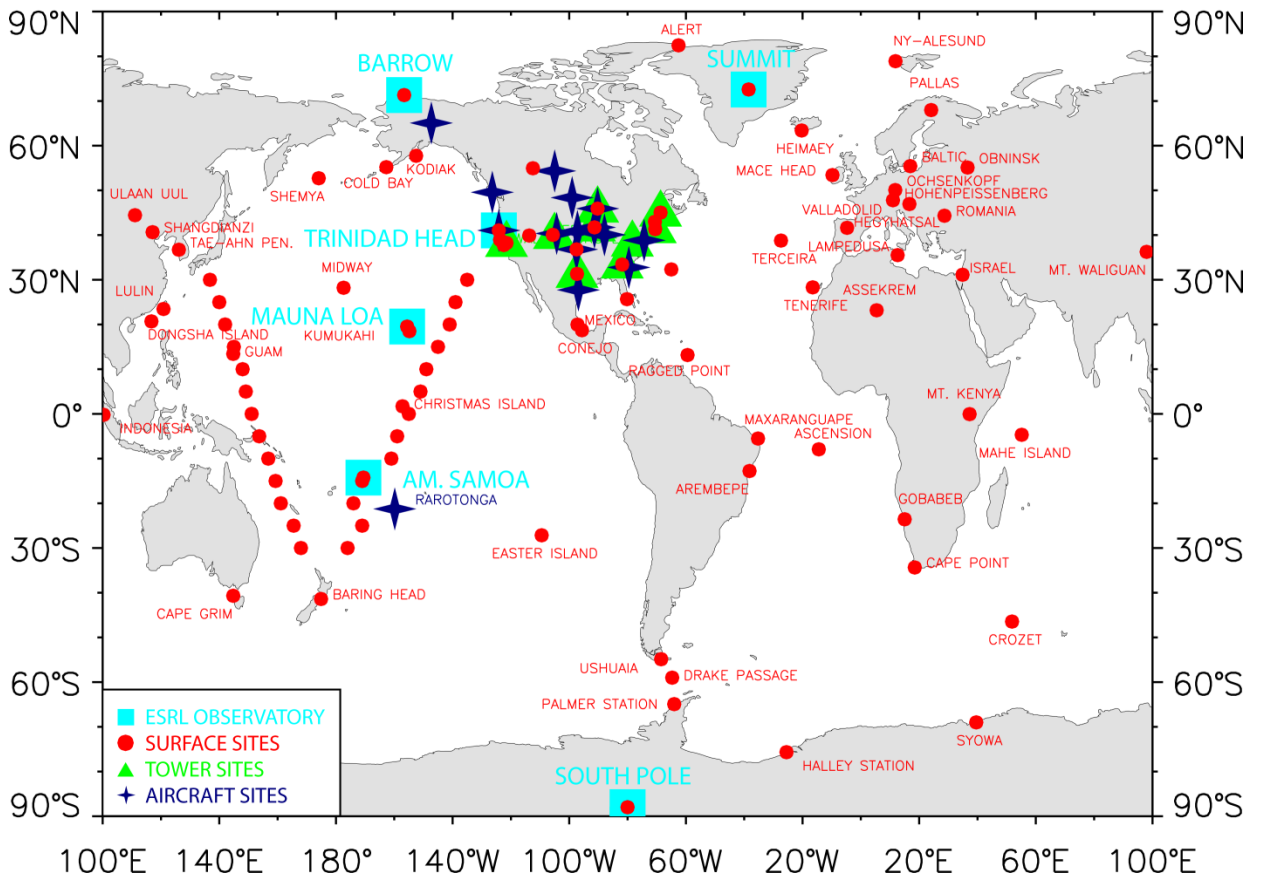
D. Nelson

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As one of the three Regional Radiation Centers (RRC) in WMO Region IV, the others being in Toronto and Mexico City respectively, NOAA broadband surface radiation measurements are referenced to the World Radiometric Reference (WRR). The WRR is defined by a group of dedicated radiometers maintained at the WRC in Davos. Every five years since the IPC-III held in 1975, NOAA/SRF standards have participated in a WMO-sponsored pyrheliometer comparison held at the WRC in Davos. Reference instruments from RCCs around the world are brought to Davos for comparison with the WSG defined WRR. Correction factors are established for relating the RRC reference instruments to the WRR. The goal is international standardization of solar irradiance measurements. Four NOAA/GMD radiometers plus additional NOAA/GMD instruments were also compared concurrently with other standards during the IPC. A Filter Radiometer Comparison (FRC) was conducted concurrently with the pyrheliometer comparison and optical depth data from participating instruments were compared with the reference sun photometers maintained at the WRC. There also was a comparison of pyrgeometers with the reference WRC black body calibration system. A NOAA/GMD sunphotometer, three rotating shadowband radiometers and a pyrgeometer were at Davos for participation in the FRC and pyrgeometer comparison. A final report summarizing the results of ICP-XI will be published by the IPC-XI host, the Physikalisch-Meteorologisches Observatorium Davos (PMOD). Over seventy individuals from forty three countries participated in IPC-XI.
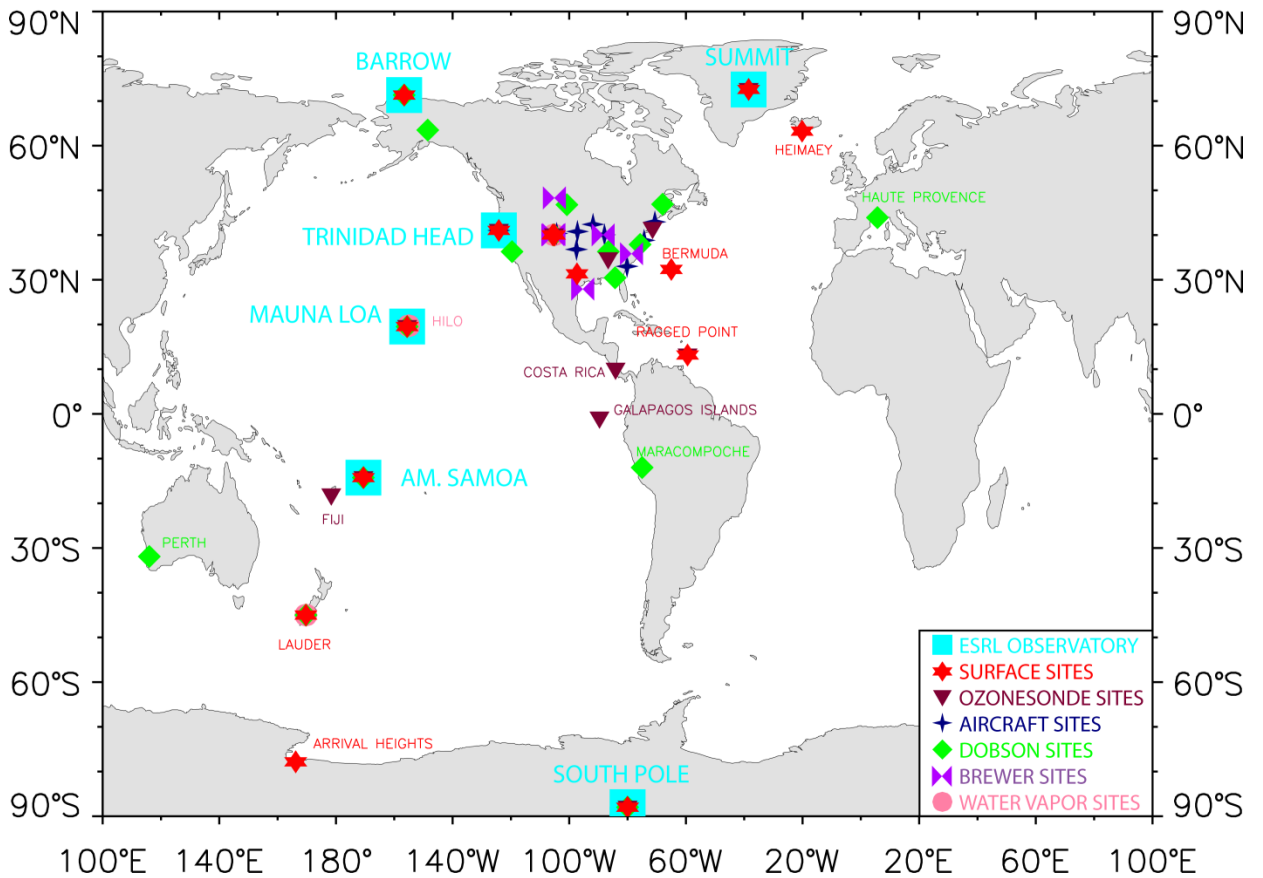

Figure 1. A photograph of the PMOD with observing tables in place for participants and their instruments.
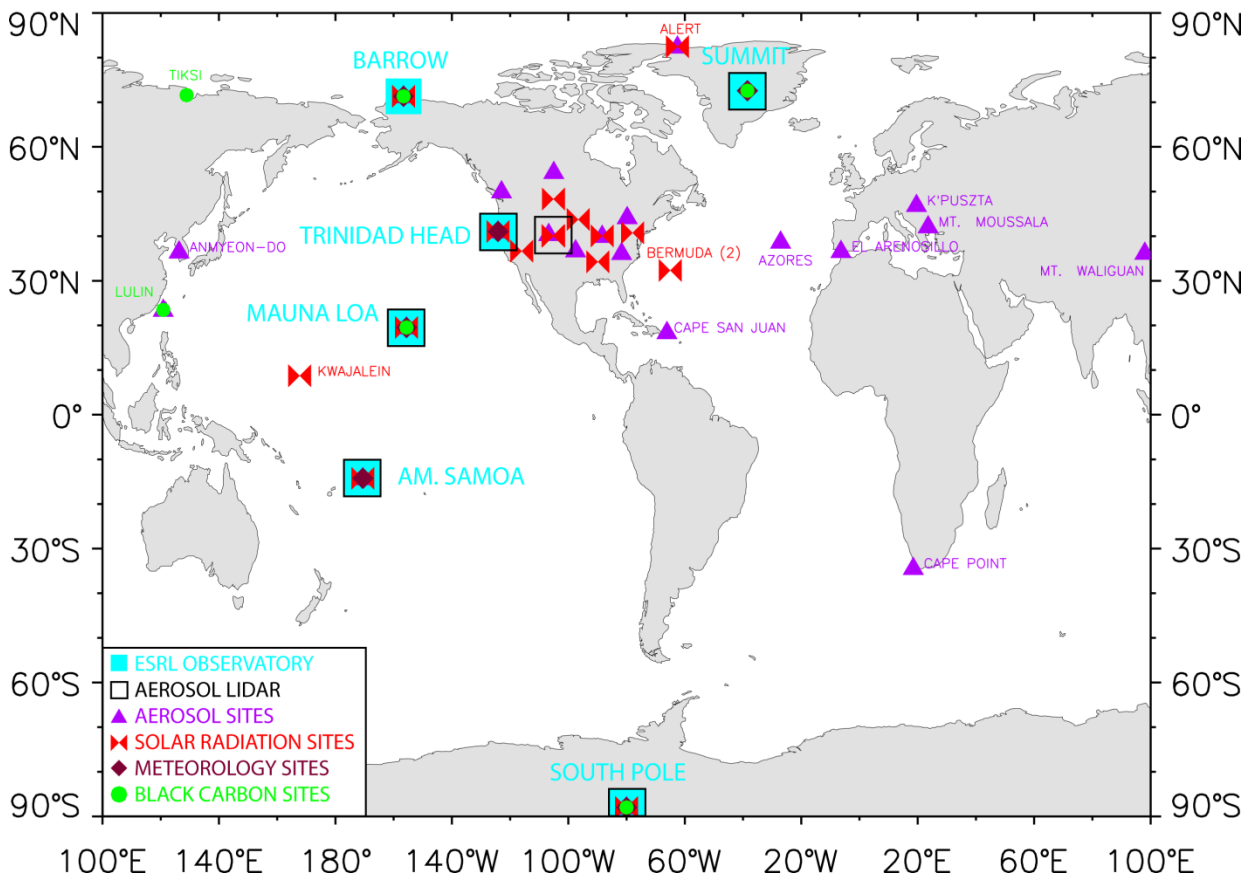
NOAA ESRL Carbon Cycle Greenhouse Gases

Legend:
- ESRL OBSERVATORY
- SURFACE SITES
- TOWER SITES
- AIRCRAFT SITES

Observatory labels: BARROW, SUMMIT, TRINIDAD HEAD, MAUNA LOA, AM. SAMOA, SOUTH POLE

Surface site labels: ALERT, NY–ALESUND, PALLAS, KODIAK, SHEMYA, COLD BAY, HEIMAEY, MACE HEAD, BALTIC, OBNINSK, OCHSENKOPF, HOHENPEISSENBERG, ROMANIA, ULAAN UUL, SHANGDIANZI, TAE–AHN PEN., VALLADOLID, HEGYHATSAL, LULIN, MIDWAY, TERCEIRA, LAMPEDUSA, ISRAEL, MT. WALIGUAN, ASSEKREM, KUMUKAHI, TENERIFE, DONGSHA ISLAND, GUAM, MEXICO, CONEJO, RAGGED POINT, MT. KENYA, INDONESIA, CHRISTMAS ISLAND, MAHE ISLAND, MAXARANGUAPE, ASCENSION, RAROTONGA, AREMBEPE, GOBABEB, EASTER ISLAND, CAPE POINT, CROZET, CAPE GRIM, BARING HEAD, USHUAIA, DRAKE PASSAGE, PALMER STATION, SYOWA, HALLEY STATION

NOAA ESRL Ozone and Water Vapor

Legend:
- ESRL OBSERVATORY
- SURFACE SITES
- OZONESONDE SITES
- AIRCRAFT SITES
- DOBSON SITES
- BREWER SITES
- WATER VAPOR SITES

Observatory labels: BARROW, SUMMIT, TRINIDAD HEAD, MAUNA LOA, AM. SAMOA, SOUTH POLE

Site labels: HEIMAEY, HAUTE PROVENCE, BERMUDA, HILO, RAGGED POINT, COSTA RICA, GALAPAGOS ISLANDS, MARACOMPOCHE, FIJI, PERTH, LAUDER, ARRIVAL HEIGHTS

NOAA ESRL Aerosols, Solar Radiation, Meteorology and Black Carbon

NOAA ESRL Halocarbons and Atmospheric Trace Species