# Global Monitoring Annual Conference 2011 Boulder, Colorado May 17<sup>th</sup> - 18<sup>th</sup>

"Ensuring Continuity and Reliability of Long Term Measurements"



# **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:

Timeline representing the long-term growth and measurement milestones of the Global Monitoring Division's six major themes.



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 2011 Global Monitoring Annual Conference

May 17-18, 2011 Boulder, Colorado

We at NOAA's Earth System Research Laboratory, Global Monitoring Division, would like to welcome you to our 2011 Global Monitoring Annual Conference. Each year, this conference brings in scientists from various agencies, universities, and international organizations to share the latest information on global monitoring trends and new approaches to obtaining long-term records of climate and the atmospheric constituents that force changes in climate. The theme for this year's conference is *Ensuring Continuity and Reliability of Long-Term Measurements*.

Well-defined, high-quality data sets are critical to understanding current and future changes occurring within the global climate system. In general, long-term scientific records are rare and their value to researchers and society inherently continues to grow each year. Multi-decadal records have been instrumental in discerning the differences between natural and anthropogenic contributions to the trends, distributions, and variability of climate-relevant phenomena. Maintaining long-term records requires the focus and dedication of scientists who believe in their mission. Each year, this meeting provides an opportunity for those scientists to gather and discuss significant findings and common issues relevant to both long-term and other supporting records, and we welcome you all to this, the 39<sup>th</sup> such event.

This year's conference will be attended by over 200 scientists, including almost 100 from universities and U.S. agencies other than NOAA and over 25 from 12 countries on five continents. The conference will address issues relating to climate change, ozone depletion, air quality, solar radiation, and renewable energy needs. Monitoring at all levels (ground based, *in situ* and satellite) will be addressed, as well as the use of reanalysis for integrating observations and producing relevant and timely products. The goal of the conference is to encourage thought about how long-term data sets can be used by other researchers, decision-makers, and society and how to best continue these records for many more decades into the future.

The conference agenda is posted at <u>http://www.esrl.noaa.gov/gmd/annualconference/</u>, along with abstracts from 107 presentations and posters being discussed at the 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

### **39th NOAA ESRL GLOBAL MONITORING ANNUAL CONFERENCE 2011** David Skaggs Research Center, Room GC-402 325 Broadway, Boulder, Colorado 80305 USA

### Tuesday Morning, May 17, 2011 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 - 08:15	Morning Snacks – Coffee, tea, fruit, bagels & donuts served	
	Page	No.
• Session 1	Introduction, Keynote Address, and Setting the Stage — Chaired by Russ Schnell	
08:15 - 08:30	Welcome	-
	Jim Butler (NOAA Earth System Research Laboratory, Boulder, CO)	
08:30 - 09:00	Keynote Address - Outlook for Long-Term Fossil-Fuel Emissions	1
	David Rutledge (California Institute of Technology, Pasadena, CA)	
09:00 - 09:15	CO <sub>2</sub> Emissions, Climate Change, and Human Development Pieter Tans (NOAA Earth System Research Laboratory, Boulder, CO)	2
09:15 - 09:30	A New Global Greenhouse Gas Observation Initiative	3
	Bob Marshall (Earth Networks, Inc., Germantown, MD)	
09:30 - 09:45	How Observations of Atmospheric O <sub>2</sub> Concentration Can Inform Our Understanding of Land and Ocean Processes in a Time of Global Change Ralph F. Keeling (Scripps Institution of Oceanography (SIO), University of California at San Diago La Jolla (CA)	4
• 09:45 - 10:15	Morning Break	
• Session 2	Halocarbons & Other Trace Species — Chaired by James Elkins	
10:15 - 10:30	Observational Constraints on U.S. Emissions of Climate-active and Ozone-depleting Trace Gases from NOAA Air Sampling Networks	5
	Steve Montzka (NOAA Earth System Research Laboratory, Boulder, CO)	
10:30 - 10:45	Review of Comprehensive Pole-to-Pole Airborne Survey of Greenhouse Gases	6
	James W. Elkins (NOAA Earth System Research Laboratory, Boulder, CO)	
10:45 - 11:00	National Institute for Environmental Studies (NIES) Monitoring of Atmospheric Halocarbons Yoko Yokouchi (National Institute for Environmental Studies, Tsukuba, Ibaraki, Japan)	7
11:00 - 11:15	Highlights from the UC-Irvine Global Monitoring Program (1978-2010)	8
	I.J. Simpson (University of California at Irvine, Irvine, CA)	
11:15 - 11:30	Urban Ambient Mixing Ratios of Hydrochlorofluorocarbons in China	9
	Xuekun Fang (State Key Joint Laboratory for Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China)	
11:30 - 11:45	Long-term Monitoring of Volatile Organic Compounds (VOCs) in the Free Troposphere Above the UK Shalini Punjabi (Department of Chemistry, University of York, York, United Kingdom)	10
• 11:45 - 13:00	Catered Lunch Service – Outreach Classroom GB-124 (pre-payment of \$10.00 required at registration table)	

### **39th NOAA ESRL GLOBAL MONITORING ANNUAL CONFERENCE 2011** David Skaggs Research Center, Room GC-402 325 Broadway, Boulder, Colorado 80305 USA

### Tuesday Afternoon, May 17, 2011 AGENDA

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

	P	age No.
• Session 3	Aerosols & Atmospheric Radiation — Chaired by John Ogren	
13:00 - 13:15	Lidar Remote Sensing of Stratospheric Aerosols and Comparison with Simulations from Whole Atmosphere Community Climate Model (WACCM)/Community Aerosol and Radiation Model for Atmospheres (CARMA)	11
	Ryan Neely (Cooperative Institute for Research in Environmental Sciences, University of Colord Boulder, CO)	ıdo,
13:15 - 13:30	Recent Observed Variations in Background Aerosol Optical Depth and Associated Direct Radiative Forcing Estimates	12
	E.G. Dutton (NOAA Earth System Research Laboratory, Boulder, CO)	
13:30 - 13:45	Radiative Forcing Efficiency of the Fourmile Canyon Fire Smoke Plume - A Near-Perfect Ad Hoc Experiment	13
	John A. Augustine (NOAA Earth System Research Laboratory, Boulder, CO)	
13:45 - 14:00	Organic Compositions of Baseline Marine Aerosol at Cape Grim, Australia	14
	Melita Keywood (Commonwealth Scientific & Industrial Research Organization, Marine and Atmospheric Research, Aspendale VIC, Australia)	
14:00 - 14:15	Empirical Estimates of Cloud Condensation Nuclei (CCN) from Field Observations	15
	Anne Jefferson (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)	
14:15 - 14:30	Decadal Trends in Observed Analytical Uncertainties for IMPROVE Elemental Data	16
	Warren H. White (Crocker Nuclear Laboratory, University of California at Davis, Davis, CA)	
• 14:30 - 15:00	Afternoon Break	
• Session 4	Ozone & Water Vapor — Chaired by Irina Petropavlovskikh	
15:00 - 15:15	Update on Stratospheric Water Changes	17
	Karen Rosenlof (NOAA Earth System Research Laboratory, Boulder, CO)	
15:15 - 15:30	Ozonesondes Show Record Low Stratospheric Ozone in the Arctic in 2011	18
	B. J. Johnson (NOAA Earth System Research Laboratory, Boulder, CO)	
15:30 - 15:45	Twenty-five Years of Ozone Soundings at South Pole: An Assessment of Changing Loss Rates	19
	Birgit Hassler (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)	
15:45 - 16:00	Measurement of Western U.S. Baseline Ozone from the Surface to the Tropopause and Assessment of Downwind Impact Regions	of 20
	<i>Owen Cooper (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)</i>	
16:00 - 16:15	Variability in the Distribution of Ozone Over Land and Marine Regions in the Indian Region S. Lal (Physical Research Laboratory, Ahmedabad, India)	21
16:15 - 16:30	Long-Term Observations from 1982 to 2009 of Ozone in the Southern Ocean Marine Boundary Laye from Cape Grim, Tasmania 41°S	er 22
	Melita Keywood (Commonwealth Scientific & Industrial Research Organization, Marine and Atmospheric Research, Aspendale VIC, Australia)	
16:30 - 16:45	Science Highlights at the Cape Verde Atmospheric Observatory (CVAO)	23
	K.A. Read (National Centre for Atmospheric Science, University of York, York, United Kingdom	<b>()</b>
• 17:00 - 20:00	Poster Session (DSRC Cafeteria) with appetizers & refreshments	

### **Outlook for Long-Term Fossil-Fuel Emissions**

### D. Rutledge

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**Figure 1.** Professor Rutledge is the Tomiyasu Professor of Electrical Engineering at Caltech, and a former Chair of the Division of Engineering and Applied Science there. He is the author of the textbook Electronics of Radio, published by Cambridge University Press. He is a Fellow of the IEEE, a winner of the IEEE Microwave Prize, and a winner of the Teaching Award of the Associated Students at Caltech. He served as the editor for the Transactions on Microwave Theory and Techniques, and is a founder of the Wavestream Corporation, the leading manufacturer of high-power millimeter-wave transmitters for satellite uplinks. In recent years, his research interest has been in developing methods for estimating fossil-fuel supplies in the long run.

### CO, Emissions, Climate Change, and Human Development

### P. Tans

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It is likely that the Intergovernmental Panel on Climate Change (IPCC)  $CO_2$  emissions scenarios are too high. In essence they are all still based on traditional economics that does not recognize fundamental physical limits to never ending growth. It is very unlikely that the finite Earth environment can sustain U.S. levels of resource consumption by 7 billion, and more, people. As resources increasingly have to be extracted from less attractive deposits, the rise of demand will be curbed by the increasing cost of extraction. A realistic projection of future atmospheric  $CO_2$  is lower than IPCC projections, but the very long persistence of  $CO_2$  in the atmosphere and oceans (see figure) makes it likely that slow climate feedbacks come into play. Slow feedbacks are hard to analyze and quantify until they actually occur, but they could be large enough to still make climate change hard to cope with. Climate change is expected to become an impediment to development, but rising costs of natural resources are likely to hamper development together with climate change, or even before climate change. We do not have a choice between mitigation of climate change and development. On the contrary, the latter can only occur in an economic system that functions well with little or no extraction of non-renewable resources, including fossil fuels, which then also mitigates climate change, decreasing the probability of disruptive changes in our ability to provide food, clean water, and other necessities.



**Figure 1.**  $CO_2$  in the atmosphere and oceans.

### A New Global Greenhouse Gas Observation Initiative

### B. Marshall

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Earth Networks operates the largest surface weather observing and total lightning detection networks in the world and has recently embarked on a new major initiative to deploy a global system of Greenhouse Gas (GHG) observation instruments. Earth Networks will use gas calibration standards from the NOAA that insure compatibility with the World Meteorological Organization scales for GHGs.

The initiative involves close collaboration with leading climate scientists and organizations including Scripps Institute of Oceanography, NOAA and National Institute of Standards and Technology. In addition, data from the network will be utilized for advanced inverse atmospheric modeling applications and the development of finer scale total carbon footprints and emissions estimates for various regions across the globe. This talk will discuss the emerging global monitoring capability of Earth Networks and outline its associated plans to help advance both scientific understanding and public awareness of atmospheric GHG concentrations.



**Figure 1.** Example of an Earth Networks 3D rendering from its GHG portal showing the concentration levels of carbon dioxide and its motion over the area during one day over San Diego. This animated visualization is based on operational forecast, and shows vertical distribution of  $CO_2$  in the air, which is affected by the weather and depends on topography of a particular region. The colors represent levels of  $CO_2$  – measured in parts per million units. The animation step is 30 minutes over a period of 24 hours.

## How Observations of Atmospheric O<sub>2</sub> Concentration Can Inform Our Understanding of Land and Ocean Processes in a Time of Global Change

### R.F. Keeling

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Time series of atmospheric oxygen  $(O_2)$  concentrations from the Scripps  $O_2$  program now span two decades. These series document a long-term decreasing  $O_2$  trend, cycles, and gradients, and will be discussed in terms of the constraints of long-term land and ocean carbon sinks, the stability of ocean biological production, rates of ocean deoxygenation, and testing depictions of ocean processes coupled ocean/atmospheric biogeochemical models.

The importance of the  $O_2$  data can be seen in relation to the limitations of current inverse calculations of carbon dioxide (CO<sub>2</sub>) fluxes. Because the high variability of land carbon exchanges tends to mask the oceanic exchanges, the CO<sub>2</sub> inverse calculations are better equipped to resolve fluxes on land than the oceans, and are better suited resolving flux variations than their mean value. The calculations are not as well suited to estimating long-term average fluxes or interannual variations of oceanic origin. Typically, the calculations are unable to improve much upon the ocean "priors" that are tied to sparse ocean observations.

In the future, global biogeochemical data assimilation will doubtless follow the lead of physical climate data assimilation, progressing from atmospheric-based assimilation to coupled ocean/atmosphere assimilation. Inversion calculations will also progress from the goal of estimating surface fluxes to the goal of optimizing process models that depict these fluxes. Progress toward making coupled biogeochemical inverse calculations is urgently needed, not just to address improvements in  $CO_2$  inverse calculations, but also to address a suite of important looming issues, such as ocean acidification, ocean deoxygenation, and climate impacts on ocean ecology. Coupled biogeochemical inverse calculations will require observing systems that can resolve ocean biogeochemical changes over broad space and long-time scales. The systems now deployed or planned (e.g. Argo floats, satellite systems, surface p $CO_2$  observations, repeat hydrography, time series, etc.) will provide essential components of this need. But a critical role will also be played by observations of atmospheric  $O_2$ .

The power of  $O_2$  data is harnessed via the tracer Atmospheric Potential Oxygen (APO  $\approx O_2 + 1.1CO_2$ ). The land biospheric effects on APO are near zero because of cancellation of the  $O_2$  and  $CO_2$  contributions. The observed trends in APO (see Figure), corrected for a small fossil-fuel effect, effectively constrain the combined exchanges of  $O_2$  and  $CO_2$  with the oceans. APO responds to ocean processes on the same space and time scales that influence atmospheric  $CO_2$  concentration, but are not resolvable in  $CO_2$  or its isotopes due to the high variability from the land. The 20-year records of APO reveal signals of ocean interannual variability not seen in other tracers or in hydrographic data. The continuity of these records will provide critically needed ocean-observing capability to aid in resolving threats to the ocean and the impacts on the carbon cycle.



Figure 1. Observed trends in APO.

# Observational Constraints on U.S. Emissions of Climate-Active and Ozone-Depleting Trace Gases from NOAA Air Sampling Networks

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 <sup>3</sup>Lawrence Berkeley National Laboratory, Berkeley, CA 94720
 <sup>4</sup>Science and Technology Corporation, Boulder, CO 80305

Precise measurements of trace gases in air sampled in the remote global atmosphere and in the continental U.S. air shed provide an opportunity to estimate U.S. emissions of ozone-depleting and greenhouse gases independent of inventory-based approaches. We have analyzed samples collected approximately weekly at two continental U.S. sites during the past 13 years. We also have shorter records (up to 6 years) from the analyses of flask samples collected daily at 5-10 tall tower sites and biweekly from aircraft (as vertical profiles) at 15-20 sites. Here we explore how emissions of ozone-depleting gases such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) have changed over time relative to emissions of hydrofluorocarbons (HFCs) used as substitutes. Results from surface sites sampled weekly since 1997 indicate a substantial increase in emissions of HFC-134a relative to HCFC-22 during this period as HFC use increased across the U.S. While some of these changes are captured by the U.S. EPA inventory emissions of these gases, others are not. When additional higher frequency data from tall towers and the more broadly distributed aircraft data are considered, emission ratios more representative of the entire U.S. are derived. Only with results from these additional sampling programs are we able to detect spatial and seasonal emission variations that are qualitatively consistent with expected geographical and seasonal use patterns of these refrigerants and, additionally, some new substitute HFCs (HFC-125 and HFC-143a).



Figure 1. Emission ratios of HFC-134a relative to HCFC-22 estimated from inventory techniques (U.S. EPA, black line) and atmospheric data (NOAA, colored lines). Emission ratios derived from atmospheric data are based on the correlation slope of measured mixing ratio enhancements above background of HFC-134a relative to those measured for HCFC-22. Results from weekly surface sampling at a site in Wisconsin (LEF, red symbols) and Massachusetts (HFM, blue symbols) are compared to the aggregated results from multiple sites sampled by aircraft and tall towers (green symbols).

#### **Review of Comprehensive Pole-to-Pole Airborne Survey of Greenhouse Gases**

<u>J.W. Elkins</u><sup>1</sup>, S.C. Wofsy<sup>2</sup>, F.L. Moore<sup>3</sup>, E.J. Hintsa<sup>3</sup>, B.R. Miller<sup>3</sup>, S.A. Montzka<sup>1</sup>, J.D. Nance<sup>3</sup>, D.F. Hurst<sup>3</sup>, C. Sweeney<sup>3</sup>, E. Atlas<sup>4</sup>, D.W. Fahey<sup>1</sup> and the HIPPO team<sup>5</sup>

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The collaborative research project: "HIAPER Pole-to-Pole Observations" (HIPPO) of carbon cycle, greenhouse gases study, and black carbon has measured cross sections of atmospheric concentrations approximately pole-to-pole, from the surface to the tropopause, three times during different seasons, with two more transects planned for 2011, to span a 2.7 year period. A typical survey comprises 10-12 flights over a 27-30 day period, traveling over 30,000 miles, and sampling the air from ~500 to 45,000 feet. A comprehensive suite of tracers of climate-forcing and ozone-depleting species are measured including  $CO_2$ ,  $O_2$ :N<sub>2</sub> ratio,  $CH_4$ , CO, N<sub>2</sub>O,  $\delta^{13}C$  and  $\delta^{18}O$  in  $CO_2$ , PAN, H<sub>2</sub>, SF<sub>6</sub>, COS, CFCs, HFCs, HCFCs, halogenated solvents, organic nitrates, and selected hydrocarbons from 24 instruments. HIPPO transects the mid-Pacific ocean with some excursions to its eastern and western coasts. HIPPO provides a unique and comprehensive global survey of atmospheric trace gases and black carbon covering the full troposphere in all seasons and multiple years. This campaign has achieved a "snapshot" of the atmosphere through measurements of temperature, pressure, humidity, and aerosol, black carbon, water vapor and ice crystals, and chemical composition, dramatically enhancing our understanding of our changing atmosphere and that of our model representations. This talk highlights the findings of the first three surveys, and plans for the final two surveys. These airborne profiles also bridge the information gap between ground-based networks and satellites.



**Figure 1.** Cross section of  $SF_6$  (ppt) from NOAA's UCATS instrument on the first southbound survey of HIPPO.



**Figure 2.** Cross section of  $CO_2$  (ppm) from NOAA's PFP flasks on the first southbound survey of HIPPO.

### National Institute for Environmental Studies (NIES) Monitoring of Atmospheric Halocarbons

Y. Yokouchi, T. Saito, Y. Nojiri, H. Nara, H. Tanimoto and H. Mukai

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Monitoring of atmospheric halocarbons was carried out at two remote sites in Japan; Hateruma Island (123.8°E, 24.1°N, 2004~) and Cape Ochiishi (145.5°E, 43.2°N, 2006~), as well as over the western Pacific Ocean (every ten-degree between 30°N and 30°S, 2005~) and over the Southeast Asian Sea (2007~) (Figure 1). The former is based on on-site hourly measurements and the latter is based on monthly sampling using NIES Voluntary observing ship (VOS) program (M/V Transfuture 5 for the western Pacific, M/V Fujitrans World for SE Asia). The target compounds included six CFCs, six HFCs, five HCFCs, three PFCs, SF<sub>6</sub>, and some natural halocarbons. Figure 2 shows the results for HFC-134a and HFC-152a as examples. Long-term changes of their baseline concentrations at low- and mid-latitudes in East Asia were derived from the data at Hateruma and Ochiishi, respectively. Occasional short-term enhancement, on the order of hours to days, could be used to analyze their emission rates from surrounding countries (China, Japan, Korea and Taiwan). The measurements over the western Pacific showed the gradients of halocarbon concentrations between northern and southern hemisphere. The gradients were lowest in summertime, when halocarbons observed at Hateruma were sometimes on a similar level as in the southern hemisphere. Over the Southeast Asian Sea, some halocarbons (e.g. HFC-152a) were found to be mostly close to the baseline concentration from the Western Pacific, while others (e.g. HFC-134a) were sometimes highly enhanced.



**Figure 1.** Monitoring and sampling points.

**Figure 2.** NIES measurements of HFC-134a (upper) and HFC-152a (lower) from Hateruma Island and over the Western Pacific (canister sampling), from Cape Ochiishi (on-site), and from over the Southeast Asian Sea (canister sampling). The thick color lines are the baseline mixing ratios. Gridded fields are shown for Southeast Asia.

#### Highlights from the UC-Irvine Global Monitoring Program (1978-2010)

I.J. Simpson<sup>1</sup>, S. Meinardi<sup>1</sup>, M.P.S. Andersen<sup>1</sup>, L. Bruhwiler<sup>2</sup>, F.S. Rowland<sup>1</sup> and D.R. Blake<sup>1</sup>

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The University of California, Irvine (UC-Irvine) has monitored global atmospheric trace gas mixing ratios continuously since 1978 using ground-based measurements in the Pacific Basin (71°N to 47°S). The measured gases include methane (CH<sub>4</sub>),  $C_2$ - $C_4$  alkanes, ethyne,  $C_1$ - $C_3$  alkyl nitrates, chlorofluorocarbons (CFCs), CH<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub> and H-1211. Long-term records of several of these gases are unique to the UC-Irvine global monitoring network, and here we present our program's research highlights. The global growth rate of  $CH_4$  has slowed considerably in the past three decades, from  $19 \pm 2$  ppbv yr<sup>1</sup> in 1985 to  $5.3 \pm 0.9$  ppbv yr<sup>1</sup> in 2010. Over the same time, the global mixing ratio of ethane ( $C_2H_6$ ) has declined by approximately 170 pptv (21%), from 791 ± 19 pptv in 1986 to  $625 \pm 12$  pptv in 2010. The global trends of CH<sub>4</sub> and ethane have shown remarkably good agreement in the past 25 years, both in terms of their long-term declines (most of which occurred prior to 2000) and short-term anomalies. Whereas the global CH, and ethane trends dissociated from each other for the first time in 2008, CH<sub>4</sub> and ethane increased together again in 2010, and the ethane growth rate in 2010 was  $31 \pm 11$ pptv yr<sup>1</sup>. The long-term global ethane decline has been accompanied by simultaneous decreases in global levels of propane and the butanes since 1996, as well as an 11% decline in global levels of the combustion tracer ethyne between 1996 and 2008. The anthropogenic tracer tetrachloroethene  $(C_2Cl_4)$  has shown a 60% decline in its global mixing ratio since 1989 and is currently approaching 2 pptv. Global mixing ratios of CFCs, CH<sub>2</sub>CCl<sub>2</sub> and CCl<sub>4</sub> have also continued to decrease, and our measurements show generally good agreement with other global monitoring networks. In contrast to many halocarbons, global levels of the industrial solvent chloroform (CHCl<sub>2</sub>) have increased by almost 20% since the late 1990s, from 9.0  $\pm$  0.3 pptv in 1997 to 10.7  $\pm$  0.4 pptv in 2008.



**Figure 1.** Global atmospheric mixing ratios and growth rates of selected gases measured by the UC-Irvine global monitoring network. (a) Global methane (CH<sub>4</sub>) growth rate and ethane mixing ratio; (b) global ethyne mixing ratio; (c) global tetrachloroethene (C<sub>2</sub>Cl<sub>4</sub>) and chloroform (CHCl<sub>3</sub>) mixing ratios. The data are plotted as running annual averages.

#### Urban Ambient Mixing Ratios of Hydrochlorofluorocarbons in China

### X. Fang, J. Wu, Y. Shi, J. Zhang and J. Hu

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In January and February 2001, a wide survey of 19 halocarbons in 45 cities was conducted in China. Up until now, ten years have passed and urban atmospheric levels of halocarbons in China may have changed greatly. In this study, 92 samples in 46 Chinese cities were collected in October and November 2010, and the levels of hydrochlorofluorocarbons (HCFCs) that were measured are similar to the research conducted in January and February 2001 by Barletta in 45 Chinese cities. One of biggest differences between the two studies is that HCFC consumption in China are very different geographically. Mixing ratios of HCFCs show a large enhancement with respect to Ammonia (NH<sub>3</sub>) background values, especially for HCFC-22 (585 pptv average in this study and 209 pptv for NH<sub>3</sub> background). Compared to the results of the previous study, it can be observed that levels of HCFCs have increased rapidly since 2001. HCFC-22, HCFC-141b and HCFC-142b have grown to 3, 2, 3 times higher (respectively) than that in 2001. Since the implementation of the Montreal Protocol, China has achieved remarkable successes in ozone protection (CFCs phase-out), while their replacements have become widely applied. In the next decades, this may bring about increasing emissions and atmospheric mixing ratios. Regions of urban clusters with high mixing ratios of HCFC-22 were identified, including the North China Plain, Yangtze River Delta and the Pearl River Delta, where further monitoring will be conducted in the future.



**Figure 1.** Map showing the geographical HCFC-22 mixing ratios of sampling sites. The pink solid circle represents the mixing ratio of HCFC-22 in different cities. The bigger circle represents the higher mixing ratio. The red hollow circle displays the relative "polluted" regions.

#### Long-Term Monitoring of Volatile Organic Compounds (VOCs) in the Free Troposphere Above the UK

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Preliminary results are presented from a long-term study of C2-C8 VOCs in the free troposphere above the UK. The study is conducted during UK flights aboard the FAAM BAe146 aircraft over the period Jan 2009 - Jan 2011. Samples are collected using the Whole Air Sampling system and subsequently analysed using a dual channel gas chromatograph with flame ionization detector. A seasonal cycle is exhibited by the majority of measured VOCs with concentration maxima in winter and minima in summer. Comparison with the Penkett et al. study (58°N) reveals a significant decrease (up to 45%) in acetylene, benzene, toluene, butane and pentane over the entire seasonal cycle. Ethane and propane, however, reveal relatively little change in winter maxima concentrations compared with the Penkett et al. study, but a large decrease in summer minima values (up to 50%). This is reflected by the increase in amplitude of the ethane seasonal cycle. The delay in the winter maxima in the Arctic cycle (using data from Laurila and Hakola (1996)) is observed due to the almost negligible photochemical activity during the extended winter of the polar region.



**Figure 1.** UK free troposphere data compared with North Atlantic (Penkett et al study (1993)), and Arctic site Pallas, Finland (Laurila and Hakola study (1994)) for ethane.



**Figure 2.** UK free troposphere data compared with North Atlantic (Penkett et al study (1993)), and Arctic site Pallas, Finland (Laurila and Hakola study (1994)) for acetylene.

### Lidar Remote Sensing of Stratospheric Aerosols and Comparison with Simulations from Whole Atmosphere Community Climate Model (WACCM)/Community Aerosol and Radiation Model for Atmospheres (CARMA)

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The quiescent volcanic period of the last ten years has provided a unique opportunity to observe the background state of stratospheric aerosols. Observations from this period of aerosol backscatter collected by Rayleigh/Mie lidars located in Lauder, New Zealand, Mauna Loa, Hawaii and Boulder, Colorado were explored with an emphasis on analyzing the seasonal cycles and decadal trends in the aerosol layer above 20 km altitude. The results from this analysis show an increasing trend in the backscatter cross-section over the last decade at all three sites that is modulated by a strong seasonal cycle with a winter maximum.

To further understand the differing roles of transport, chemical and microphysical processes of the aerosol layer, the results of the lidar data analysis are compared to output from a base run of the WACCM coupled to the CARMA that has been structured to include sulfate aerosols and meteoritic dust. This comparison shows overall agreement within the standard deviation of the annual mean aerosol profile at all three lidar locations. Correlation of the model aerosols and model N<sub>0</sub>O, lead to the conclusion that the observed seasonal cycle of stratospheric aerosols is controlled by the seasonally varying quasi-isentropic eddy transport associated with planetary wave breaking in the extratropical stratosphere. Comparisons between model profiles and observations also suggest that pollution from the Asian monsoon may be a leading cause of the observed trends in the aerosol record.



**Figure 1.** Comparison of the annual mean backscatter profile from each lidar and WACCM/CARMA (averaged at the model grid point closest to the corresponding lidar location).

### **Recent Observed Variations in Background Aerosol Optical Depth and Associated Direct Radiative Forcing Estimates**

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The direct solar radiative forcing of aerosols is primarily a function of aerosol optical depth (AOD), for which several observational techniques exist. The AOD variations over Mauna Loa Observatory (MLO) have been estimated for the past 55 years from "apparent solar transmission" observations. Because of MLO's unique geographic and topographic location, these AOD estimates have been considered generally representative of variations in the zonal-mean upper-tropospheric plus stratospheric background levels for the Northern Hemisphere lower latitudes. In more recent decades, refined observations of AOD utilizing supphotometers, lidars and satellites were subsequently implemented. These additional observations now permit more thorough and complete evaluation of changing AOD, although the MLO observations remain a rare long-term record to which the more advanced observations can be compared. Several of these records have been examined and indicate a sufficient increase in background AOD over the past decade (2000s) that, if global, could produce changes in radiative forcing over the decade that are significant but opposite in sign to that of CO<sub>2</sub>. However, confident long-term projections of aerosol loadings have not been made and in the last two years some reversal of the previous decade's change is now evident. The actual climatic forcing due to these changes in aerosols is dependent on the complete spatial and temporal extent of the variations, which is the subject of further investigation. The latest data and some speculation as to the origin and impact of the varying aerosols will be presented.



**Figure 1.** The main (left) plot is monthly average Mauna Loa apparent transmission (points) as computed from the Ellis & Pueschel pyrheliometer ratioing technique. The solid line is a 5-month running smoother. The timing and effect of major volcanic eruptions that injected high amounts of material into the stratosphere are indicated by the volcanoes' names. The annual oscillation in the 5-month smoother is due to seasonal zonal/hemispheric-scale transport from Asia. The expanded plot (right) shows daily apparent transmission for the past 14 years with an 85-point running smoother.

# **Radiative Forcing Efficiency of the Fourmile Canyon Fire Smoke Plume - A Near-Perfect Ad Hoc Experiment**

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On 6 Sep 2010 a wildfire in the foothills west of Boulder, CO grew explosively and sent a plume of smoke eastward. Fortunately, observations were made under and around the plume that were ideal for determining its radiative forcing efficiency (RFE), i.e., the change in net surface irradiance per unit aerosol optical depth at 500 nm (AOD<sub>500</sub>) [Stone et al. 2011]. Observations included two operational surface radiation budget (SRB) stations (Table Mountain and Boulder Atmospheric Observatory), four GPS water vapor sites, and three Weather Underground stations. Multiple channel Aerosol Optical Depth (AOD) was measured at the SRB sites and at the David Skaggs Research Center (DSRC) in Boulder, where air samples were also collected and analyzed for the aerosol's optical properties. The ideal nature of this situation was enhanced by clear skies that permitted unrestrained AOD and RFE calculations over a continuum of solar zenith angles (SZA). Our primary result was the documentation of RFE for shortwave (SW) and longwave (LW) irradiance over a wide range of SZA  $(35^{\circ}-73^{\circ})$  for a surface albedo of 0.15. RFE<sub>sw</sub> varied from  $-194\pm10$  Wm<sup>-2</sup>AOD<sub>500</sub><sup>-1</sup> at high sun to  $-81\pm9$  $Wm^{-2}AOD_{500}^{-1}$  at 73° SZA, while RFE<sub>1w</sub> was diurnally stable at +10±7 Wm^2AOD\_{500}^{-1}. Diurnally integrated RFE for SW, LW and all-wave net were -61.5, +10.0, and -51.5 Wm<sup>-2</sup>AOD<sub>500</sub>^{-1}, respectively. The net loss of incoming energy resulted in significant daytime cooling; observed air temperature anomalies under the plume were as much as -5°C. Published assessments of RFE are rare and often include a mix of limited ground-based data, error prone satellite retrievals, and model simulations that require assumptions on the optical properties of the aerosol. Our results were achieved entirely from highly accurate measurements and may be useful for refining model parameterizations and for improving assessments pertaining to smoke from northern wildfires.

Stone, R.S., J.A. Augustine, E.G. Dutton, N.T. O'Neil, and A. Saha (2011), Empirical determinations of the longwave and shortwave radiative forcing efficiencies of wildfire smoke, J. Geophys. Res., (in press).



**Figure 1.** NASA MODIS image of the Fourmile Canyon wildfire smoke plume at 12:15 LDT, 6 Sep 2010. Insert corresponds approximately to the green rectangle.

### Organic Compositions of Baseline Marine Aerosol at Cape Grim, Australia

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With 70% of the earths surface covered by oceans, aerosols in the marine boundary layer play an important role in the climate system, directly by scattering and absorbing radiation, and indirectly by acting as cloud condensation nuclei, thus influencing cloud droplet size distribution, cloud albedo and lifetime. While marine aerosol is dominated by sea-salt aerosol, organic compounds are also present. The species comprising organic aerosol provide information on the sources of the organic compounds, their production mechanisms and their likely interaction with the climate system.

Aerosol samples were collected at the Cape Grim Baseline Monitoring Station and their non-polar organic species composition determined. Several indices for *n*-alkanes were used to identify the contribution of biogenic and anthropogenic sources to the organic aerosol. In general, the baseline samples were dominated by biogenic sources and the contribution of the biological material was greater in summer than winter. Significant amounts of cycloalkanes were detected in all samples, indicating a biomass burning aerosol source in the marine boundary layer under baseline conditions. Back trajectory analysis and chemical transport modeling suggest that at five km the air masses had passed over land masses such as Southern Africa, Madagascar and Western Australia, before arriving at Cape Grim. While there is no indication that the air masses at five km directly interacted with the air masses at the surface at Cape Grim, we suggest that entrainment of aerosols from the free troposphere may provide a mechanism for supplying biomass burning aerosol to Cape Grim under baseline conditions.



**Figure 1.** Average summer and winter alkane concentrations measured in aerosol collected under baseline conditions at Cape Grim, Tasmania, Australia. The dominance of alkanes with carbon numbers greater than 22 indicate the importance of biogenic sources to the organic aerosol under clean marine conditions at Cape Grim.

### Empirical Estimates of Cloud Condensation Nuclei (CCN) from Field Observations

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The highest uncertainty associated with climate forcing comes from indirect forcing or clouds. How to parameterize the cloud spatial variance, lifetime, albedo precipitation and formation presents challenges to models and measurements. One such challenge is the characterization of aerosol activation into cloud droplets as a function of the percent water super saturation. Kohler theory of aerosol activation requires use of the size-dependent, aerosol composition to predict the CCN concentration. Several methods seek to simplify parameters within Kohler's equation to make the calculations feasible in large regional and global models.

This study presents an empirical method to predict the CCN concentration as a function of percent water super saturation. The aerosol optical properties of backscatter fraction and single scatter albedo function as proxies for the aerosol size and composition in a power law relationship to CCN. This method is tested at four sites with aged aerosol: SGP (Oklahoma, USA), FKB (Black Forest, Germany), HFE (Hefei, China) and GRW (Graciosa, Azores). Each site represents a different aerosol type and thus demonstrates the method robustness and limitations.



**Figure 1.** Correlations of calculated versus measured CCN from about 0.2 to 0.8 percent supersaturation for: a) Oklahoma, U.S. b) Black Forest, Germany c) Hefei, China, and d) Graciosa, Azore Islands. Least square fit and 1:1 lines are shown on each graph.

### Decadal Trends in Observed Analytical Uncertainties for IMPROVE Elemental Data

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The Interagency Monitoring of PROtected Visual Environments (IMPROVE) network has collected 24h PM2.5 samples for elemental and light-absorption analyses continuously since 1988, at a sustained frequency of twice a week or every third day. The network today includes about 170 sites, about 70 of these having operated continuously since 1995. The same size selective inlets and Teflon filters have been used throughout the measurements, and all analyses have been performed by Crocker Nuclear Laboratory at the University of California in Davis. All original sample filters collected since 1995 are archived on the Davis Campus.

The elements Na - Zr and Pb have been reported throughout the program, but the analytical methods have undergone some evolution. For example, the elements Na – Mn were determined by Particle Induced X-Ray Emission (PIXE) through November 2001, by X-Ray Fluorescence (XRF) analysis in a He-flushed atmosphere from December 2001 through December 2004, and by XRF analysis in vacuum since January 2005. In addition to these fundamental changes, incompletely-documented operational factors such as detector performance and calibration details have introduced other variations in the measurements.

Because the past analytical methods were all non-destructive, the archived filters can be reanalyzed with the current analytical protocol. For any one site, the historical series of consistently collected samples can be processed in a single analytical batch. The 15-year sample archive from Great Smoky Mountains National Park (Gatlinburg, TN) was recently selected to generate such an analytically homogeneous data set.

This presentation examines trends in the relationships between reanalyzed and originally-reported data for sample elemental composition at Great Smoky Mountains National Park. Figure 1 shows examples of the measurements' stability over time, a critical consideration when interpreting observed trends.



**Figure 1.** Long-term repeatability of analyses for sulfur and potassium. Each point represents one 24h PM2.5 filter sample from Great Smoky Mountains National Park, and shows the ratio of mass loadings (g/g) determined by the original analysis, performed shortly after sampling, and recent reanalysis with current system and protocol. Sample dates are indicated at the bottom, and major method distinctions are indicated at the top. Dashed horizontal lines indicate ratios of 9/10 and 10/9.

### **Update on Stratospheric Water Changes**

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A recent paper (Hurst et al. 2011) detailed temporal changes in stratospheric water vapor over Boulder for the period 1980-2010. This paper showed periods of varying change, some of which were due to changes in stratospheric methane oxidation. Using satellite observations, we are able to look specifically at the region of stratospheric entry in the tropics. This record, using UARS HALOE and Aura MLS data extends from the early 1990s to the present. There are some notable breakpoints in this record. The drop in water vapor at the end of 2000 has been described in detail (Randel et al. 2006; Rosenlof and Reid, 2007). More recently, in late 2010, another breakpoint occured; in this case the stratospheric entry value of water vapor increased significantly. This starts in late 2010, and a positive anomaly of greater than 0.5 ppmv is seen in the MLS 82 mb tropical data record (Figure 1). In this presentation, we will show the water vapor time series, both in the tropics and at higher latitudes, discuss possible reasons for the noted changes and potential radiative impacts.

Hurst, D.F., S.J. Oltmans, H. Vömel, K.H. Rosenlof, S.M. Davis, E. A.Ray, E.G. Hall, A. F. Jordon (2011), Stratospheric water vapor trendsover Boulder, Colorado: Analysis of the 30 year Boulder record, J. Geophys. Res., 116, D02306, doi:10.1029/2010JD015065.

Randel, W. J., F. Wu, H. Vomel, G. E. Nedoluha, and P. Forster (2006), Decreases in stratospheric water vapor after 2001: Links to changes in the tropical tropopause and the Brewer-Dobson circulation, J. Geophys.Res., 111, D12312, doi:10.1029/2005JD006744.

Rosenlof, K. H., G. C. Reid (2008) Trends in the temperature and water vapor content of the tropical lower stratosphere: Sea surface connection, J. Geophys. Res., 113, D06107, doi:10.1029/2007JD009109.



**Figure 1.** Top panel, MLS tropical water vapor at 82 mb. This corresponds to the entry value of stratospheric water vapor. Bottom panel, the same time series, shown in anomaly space, with anomalies calculated relative to monthly means.

### **Ozonesondes Show Record Low Stratospheric Ozone in the Arctic in 2011**

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The 2011 Arctic Polar vortex was uncharacteristically stable and cold allowing record stratospheric ozone depletion to occur late winter and early spring as reported by the Alfred Wegener Institute (AWI) for Polar and Marine Research. This was based on their analysis from an ongoing international network of about 30 ozone sounding stations in the Arctic and Subarctic. The winter time network program called "Match" coordinates ozonesonde balloon launches with air mass trajectories to sample specific air parcels for direct determination of ozone loss rates. One of the participating sites is at Summit Station, Greenland, where ozonesondes are launched weekly, and more often during the Match campaigns, by NOAA ESRL and supported by the National Science Foundation. Summit is located at 72.6°, N 38.5° W and often within the vortex and main ozone depletion area. Figure 1 shows the minimum ozone profile measured at Summit on March 28, 2011. The greatest depletion layer was from 18-21 km, 70% lower than the March average. This was consistent with loss rates observed over broad regions from Greenland to northern Scandinavia and Russia from AWI Match in 2011.



**Figure 1.** Ozonesonde launch at Summit, Greenland with temperature and minimum ozone profile measured on March 28, 2011. The shaded area represents the average  $\pm$  standard deviation for March since observations began in February, 2005.

### Twenty-Five Years of Ozone Soundings at South Pole: An Assessment of Changing Loss Rates

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In 2010, 25 years of continuous, year-round ozone soundings at South Pole station, Antarctica, were completed. These measurements provide unique documentation about the seasonality, trends, and variability of ozone depletion in the polar stratosphere at high vertical resolution. We have analyzed these ozone mixing ratios on pressure levels from about 200 to 15 hPa and have found that the onset of ozone loss at South Pole has moved forward by approximately 15 days during these 25 years. The onset of ozone destruction is earlier and not as severe at a lower latitude station (Georg-Forster/Neumayer station). We have found the highest loss rates at around 50hPa to 30hPa (see Figure 1). The loss rates have also changed over time: they grew from the late 1980s to the late 1990s and have remained roughly stable since then. During the early 1990s, loss rates were enhanced because of additional stratospheric aerosol due to the eruption of Mt. Pinatubo in 1991. We have normalized the estimated loss rates to the concentrations of equivalent effective stratospheric chlorine present at the same time. These are then used to estimate when loss rates are expected to be measurably lower than their peak values.



**Figure 1.** Profile of loss rates for five time periods (1986-1990, 1991-1995, 1996-2000, 2001-2005 without 2002, 2006-2010) at South Pole, as determined by a linear fit to all available data for each pressure level between day 235 and day 270. Loss rates are given in ppmv/day. Error bars represent 1  $\sigma$  uncertainties.

## Measurement of Western U.S. Baseline Ozone from the Surface to the Tropopause and Assessment of Downwind Impact Regions

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Monitoring of the full tropospheric baseline ozone flowing into the western USA from the Pacific Ocean has been limited to the weekly ozonesondes from Trinidad Head. To explore whether or not Trinidad Head is representative of baseline ozone at different latitudes, an ozonesonde network was implemented during May 10 – June 19, 2010, with four launch sites along 960 km of California's coastline. Three other sites were positioned inland to indicate the impact of ozone production downwind of the baseline sites. Modeling showed that the transport of North America pollution plumes over the California coast occurred primarily below 3 km. Removing ozone measurements impacted by these plumes resulted in no statistically significant change in the median baseline ozone. We found a high degree of vertical and latitudinal variation in free tropospheric baseline ozone with an enhancement at 6-10 km in the north sloping downwards to 2-4 km in the south. Polluted air masses and stratospheric intrusions that descend isentropically along the west coast likely explain this feature. Above 3 km, ozone precursor emissions (< 20 days old) most likely to impact ozone along the California coast originated in China or from international shipping. Below 2 km, international shipping is the greatest source of ozone precursors, but inefficient ozone production in the marine boundary layer results in much lower ozone values compared to the mid- and upper troposphere. Approximately 8-10% of the baseline ozone that enters California in the 0-6 km range goes on to impact the surface of the USA, but very little reaches the surface of the eastern USA. Focusing just on California, the major impact of baseline ozone that enters the state above 2 km is on the high elevation terrain of eastern California. Baseline ozone below 2 km has its strongest impact on the low elevation sites throughout the state. Compared to baseline sites, we found no increase in lower tropospheric ozone in the northern Central Valley, while ozone increases of 12-24% were found over the rest of the Central Valley. Enhancements above Joshua Tree were similar, 16-21%, while the greatest ozone enhancements occurred over the LA Basin, 29-60%.



**Figure 1.** a) Median ozone profiles during May-June 2010, with colors corresponding to the ozonesonde launch locations shown in b) Locations of the seven IONS-2010 ozonesonde sites. Also shown are the NOAA P3 sampling locations (blue dots) of the measurements used in the Central Valley and LA Basin ozone composite profiles.

### Variability in the Distribution of Ozone Over Land and Marine Regions in the Indian Region

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Measurements of surface ozone are being made at Ahmedabad (23.0°N, 72.5°E), an urban site, Mt. Abu (24.6°N, 72.7°E) and Nainital (29.4°N, 79.4°E). The latter two sites are high-altitude sites, the first one in Western India and the other in the Northern India. In addition to these surface level measurements, balloon borne measurements of ozone profiles up to an altitude of 32 km have been made using Electrochemical Concentration Cell sondes from Ahmedabad from 2003-2007 and over the Bay of Bengal (BoB) and the Arabian Sea (AS) during a cruise campaign in 2006. The surface-level measurements at all the three sites show strong seasonal variability with lowest levels during the summer monsoon period and higher levels during winter and spring seasons. Surface ozone levels at Nainital are highest (monthly average 60-70 ppbv) during April-May months (Fig.1) due to long-range transport and regional pollution. However, ozone at Mt. Abu is highest (~50 ppbv) in October-November months. Ozone profiles over Ahmedabad also show the increase due to regional pollution within the first 2 km while the effect of long-range transport is seen in the free troposphere above, an altitude of about 2 km.

Measurements of ozone profiles made over the BoB and the AS show the effects of transport from the Indo-Gangetic plain over the northern BoB in the 1-3 km height region. However, such an effect is not observed over the AS.

Further details of these results will be presented during the meeting.



Figure 1. Monthly average surface ozone levels with 1 sigma variability at Mt. Abu and Nainital in India.

# Long-Term Observations from 1982 to 2009 of Ozone in the Southern Ocean Marine Boundary Layer from Cape Grim, Tasmania $41^\circ S$

### I. Galbally and S. Molloy

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Ozone in the troposphere is an important greenhouse gas, ranked third in anthropogenic radiative forcing after  $CO_2$  and  $CH_4$ ; ozone in the troposphere makes up an important fraction of the atmospheric shield against ultraviolet radiation particularly when ozone depletion events occur, and tropospheric ozone drives tropospheric chemistry. Increases in background ozone, as have been observed to the present, have impacts also on the occurrence of urban and regional photochemical smog, related health effects and crop damage [Royal Society, 2008]. In the Southern Hemisphere there are few surface ozone monitoring stations and one can reasonably argue that around two thirds of the Southern Hemisphere lacks surface ozone measurements.

Ozone has been measured in the surface air at Cape Grim Tasmania, 41°S since 1976. These ozone measurements have been made with ultraviolet adsorption methods since December 1981. Dual instruments, an external daily zero and span check, and a separate calibrator have been maintained over most of the period. External calibration checks traceable to international primary standards were made in 1986, 2002 and 2010. The task of producing a homogeneous record via long-term instrument inter-comparisons and external calibrations will be described, along with the exploration of trends and their causes.

Selection of data by wind direction and speed and consistency of record, allows the determination of baseline ozone concentrations at Cape Grim, those concentrations that are representative of ozone in the Southern Ocean marine boundary layer. Surface ozone in Austral spring (SON) and summer (DJF) show positive trends in the 1980s and 1990s and non-significant trends in the 2000s and positive trends over the three decades combined. These trends and some associated variables will be described.



### Cape Grim Monthly Mean Anomalies: All Baseline Data

Figure 1. Surface ozone monthly anomalies from the long-term monthly mean mixing ratios, 1982-2009.

### Science Highlights at the Cape Verde Atmospheric Observatory (CVAO)

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Into its fifth year, the Global Atmosphere Watch international monitoring facility in Cape Verde is now well established. Measurements of the trace gases  $O_3$ , CO,  $NO_{xy}$  and VOCs continue to be made regularly and will be presented at the ESRL GMAC meeting. Ozone ( $O_3$ ) depletion is observed almost every day in this region, and this is due to low Nitrous Oxide (NO) concentrations and a low but significant presence of halogen oxides such as Bomine Oxide (BrO) and Iodide Oxide (IO) (< 2.5 and 1.5 pptv respectively) (Read et al., 2008i). Generally NO levels continue to be low (typical 11:00 – 15:00 average < 10pptv) but days with higher NO<sub>x</sub> are observed more often in 2008 and 2009 than in previously published data. Comparison of measurements with the output of the Goddard Earth Observing System (GEOS)-Chem global chemistry transport model show good agreement for  $O_3$  (see figure 1), but much more varied agreement with NO and  $NO_2$ . Possible reasons for this apparent discrepancy are discussed.

Comparisons of the seasonal cycles of various Non-Methane Hydrocarbons, and Oxygenated Volatile/Organic Compounds (OVOC) with CO indicate that although primary continental sources contribute to the concentrations in this region, the impact of secondary chemistry on the remote tropical marine environment is thought to be highly significant both in terms of year-round OVOC production and in the production of CO during summer (Read et al., 2009ii). This may not be fully understood in global models such as that of GEOS-Chem because of previously sparse measurements of VOC in the marine environment.

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 UK Met Office's NAME 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., 2011iii). Ongoing analysis of the trace gases using these classifications will also be presented here including the potential influence of dust on NO<sub>xy</sub> levels and the impact of different air masses on the primary and secondary sources of OVOC such as acetone and methanol.



**Figure 1.** Time series of daily averaged  $O_3$  mixing ratios measured at the CVAO and modeled using the GEOS-Chem global Chemical Transport Model.

NOTES:

# **39th NOAA ESRL GLOBAL MONITORING ANNUAL CONFERENCE 2011** David Skaggs Research Center, Room GC-402 325 Broadway, Boulder, Colorado 80305 USA

	Wednesday Morning, May 18, 2011 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 - 08:15	Morning Snacks – Coffee, tea, fruit, bagels & donuts served	
• Sagion 5	Page	No.
• Session 5	Curbon Cycle — Measurement Networks — Chairea by Jim Buller	~ (
08:15 - 08:30	China Meteorological Administration's (CMA) Capability and Effort to Serve the "Pilot Low-Carbon Action at 5 Provinces and 8 Cities in China" and the Global Network	24
	Lingxi Zhou (Chinese Academy of Meteorological Sciences, China Meteorological Administration, Beijing, China)	
08:30 - 08:45	Greenhouse Gas and Ozone Measurements from Aircraft in Alaska 2009 - 2011	25
	A. Karion (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)	
08:45 - 09:00	Long-term Methane Observations at the Global Atmosphere Watch Site Jungfraujoch with Gas Chromatography and Cavity Ringdown Spectroscopy	26
	M. Steinbacher (EMPA, Laboratory for Air Pollution/Environmental Technology, Duebendorf, Switzerland)	
09:00 - 09:15	Measurement of Uncertainty	27
	Stan Heckman (Earth Networks, Inc., Germantown, MD)	
09:15 - 09:30	Measuring CO, CH <sub>4</sub> , CO <sub>2</sub> & H <sub>2</sub> O in a Single Instrument; Using New CRDS Technology to Characterize Urban Plumes & the Well-Mixed Atmosphere <i>Gloria Jacobson (Picarro Inc, Santa Clara, CA)</i>	28
09:30 - 09:45	Towards On-line Monitoring of <sup>14</sup> C in Atmospheric CO <sub>2</sub> H.A.J. Meijer (Centre for Isotope Research, University of Groningen, Groningen, Netherlands)	29
• 09:45 - 10:15	Morning Break	
• Session 6	Carbon Cycle — Urban Emissions — Chaired by Arlyn Andrews	
10:15 - 10:30	Patterns and Variability in Δ <sup>14</sup> C of CO <sub>2</sub> in Northern Hemisphere Background Air H.D. Graven (Scripps Institution of Oceanography (SIO), University of California at San Diego, La Jolla, CA)	30
10:30 - 10:45	Evidence of Emissions from Oil and Gas Drilling Operations in Northeastern Colorado	31
	G. Petron (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)	
10:45 - 11:00	Observations of <sup>14</sup> CO <sub>2</sub> at the Boulder Atmospheric Observatory (BAO) Brian LaFranchi (Lawrence Livermore National Laboratory, Livermore, CA)	32
11:00 - 11:15	Quantification of Anthropogenic Emissions from an Urban Region: First Results of Time-integrated Flask Samples from the Indianapolis Flux (INFLUX) Project	33
	Jocelyn Turnbull (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)	
11:15 - 11:30	Quantification of Emissions from Methane Sources in Indianapolis Using an Aircraft-based Platform Maria Obiminda Cambaliza (Department of Chemistry, Purdue University, West Lafayette, IN)	34
11:30 - 11:45	Identification of Methane Emissions in an Urban Setting	35
	Eric Crosson (Picarro Inc, Santa Clara, CA)	
• 11:45 - 13:00	Catered Lunch Service – Outreach Classroom GB-124 (pre-payment of \$10.00 required at	

registration table)

# **39th NOAA ESRL GLOBAL MONITORING ANNUAL CONFERENCE 2011** David Skaggs Research Center, Room GC-402 325 Broadway, Boulder, Colorado 80305 USA

### Wednesday Afternoon, May 18, 2011 AGENDA

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

	Page	No.
• Session 7	Carbon Cycle — Observational Interpretation — Chaired by Pieter Tans	
13:00 - 13:15	Exploring the Recent Biennial Cycle in Observed CO <sub>2</sub> Growth Rate Using CarbonTracker Andrew R. Jacobson (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)	36
13:15 - 13:30	Can We Explain Recent Increases in Atmospheric CH <sub>4</sub> ? E.J. Dlugokencky (NOAA Earth System Research Laboratory, Boulder, CO)	37
13:30 - 13:45	Using CarbonTracker-CH <sub>4</sub> to Understand the Recent Methane Budget Lori Bruhwiler (NOAA Earth System Research Laboratory, Boulder, CO)	38
13:45 - 14:00	The Drivers of the CH <sub>4</sub> Seasonal Cycle in the Arctic and What Long-term Observations of CH <sub>4</sub> Imply About Trends in Arctic CH <sub>4</sub> Fluxes <i>Colm Sweeney (Cooperative Institute for Research in Environmental Sciences, University of</i> <i>Colorado, Boulder, CO)</i>	39
14:00 - 14:15	<ul> <li>The Isotopic Composition of Oxygen in Atmospheric CO<sub>2</sub> and El Niño: A New Constraint on Global Productivity</li> <li>L.R. Welp (Scripps Institution of Oceanography (SIO), University of California at San Diego, La Jolla, CA)</li> </ul>	40
14:15 - 14:30	Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC) Observations of CO, Uptake During the Indian Summer Monsoon Carl Brenninkmeijer (Max Planck Institute for Chemistry, Mainz, Germany)	41
• 14:30 - 15:00	Afternoon Break	
• Session 8	Carbon Cycle — Special Session — Chaired by Lori Bruhwiler	
15:00 - 15:15	Importance of Reliable Continuous Records of Earth System Parameters T.J. Blasing (Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak	42
	Ridge, TN)	
15:15 - 15:30	Assessment of the Long-Term Trend of Turkey's GreenHouse Gas (GHG) Emissions Using the Mann Kendall Test	43
15.20 15.45	Fatma Oztürk (NOAA Earth System Research Laboratory, Boulder, CO)	4.4
15:30 - 15:45	Brian Magi (NOAA Geophysical Fluid Dynamics Laboratory, Princeton, NJ)	44
• Session 9	Carbon Cycle — Remote Sensing — Chaired by Lori Bruhwiler	
15:45 - 16:00	Progress in Remote Sensing of Carbon Dioxide from Space - The ACOS Project	45
	Michael Gunson (Jet Propulsion Laboratory, Pasadena, CA)	
16:00 - 16:15	Atmospheric Infrared Sounder (AIRS) Retrieval of Atmospheric Carbon Dioxide (CO <sub>2</sub> ) in Three Layers Edward T. Olsen (Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA)	46
16:15 - 16:30	NDACC Fourier Transform Spectroscopy (FTS) Trace Gas Trends and the Revitalized Mauna Loa Observatory (MLO) FTS System	47
16.00 16.45	James Hannigan (National Center for Atmospheric Research, Boulder, CO)	40
16:30 - 16:45	Kemote Measurement of Greenhouse Gases Under Cloud With the Atmospheric Emitted Radiance Interferometer (AERI) Fourier Transform Spectomereter (FTS) Instrument <i>W.F.J. Evans (Northwest Research Associates, Redmond, WA)</i>	48

• Closing Remarks Dr. James H. Butler (NOAA/ESRL)

# China Meteorological Administration's (CMA) Capability and Effort to Serve the "Pilot Low-Carbon Action at 5 Provinces and 8 Cities in China" and the Global Network

### L. Zhou and colleagues

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Ambient GreenHouse Gases (GHGs) measurement (ground based site, tall tower, aircraft, etc.) and inverse modeling techniques have demonstrated that they are currently not sufficiently developed to provide a comprehensive routine and verification at the desired accuracy, especially on a smaller scale (e.g. regions and cities). Progress is to be gained from working together, to improve network coverage and verification techniques, as well as to gain better understanding of inventory estimates. The CMA leads the operational monitoring network for GHGs and climate change in China and plays a key role in the Intergovernmental Panel of Climate Change activities. The CMA represents the World Meteorological Organization (WMO) Commission for Atmospheric Sciences in China and is deeply involved in the Global Atmospheric Watch (GAW). The CMA and NOAA have a strong working relationship and renew bilateral agreements every two years (e.g. joint exchanges of scientists, calibration gases, flask air sharing, and the recent 10-day workshop in Boulder on high accuracy GHG measurements held September 2010). The "Pilot Low-Carbon Action at 5 Provinces and 8 Cities in China" by the Chinese Government is supervised by the National Development and Reform Commission (http://en.ndrc.gov.cn/). The CMA's capability and efforts look forward to expanding the number of ambient GHG and tracer monitoring sites as well as to develop a National Calibration Lab link to the WMO Central Calibration Labs so that China can evaluate its own atmosphere-climate change low-carbon system and contribute to the global network.



### CMA's Capability and Effort to Serve the "Pilot Low-Carbon Action at 5 Provinces and 8 Cities in China" and the Global Network

**Figure 1.** CMA's capability and effort to serve the "Pilot Low-Carbon Action at 5 Provinces and 8 Cities in China" and the global network.

#### Greenhouse Gas and Ozone Measurements from Aircraft in Alaska 2009 - 2011

<u>A. Karion<sup>1</sup></u>, C. Sweeney<sup>1</sup>, S. Wolter<sup>1</sup>, L. Patrick<sup>1</sup>, S. Montzka<sup>2</sup>, B. Miller<sup>1</sup>, T. Newberger<sup>1</sup>, H. Chen<sup>2</sup>, S. Oltmans<sup>2</sup> and P. Tans<sup>2</sup>

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The NOAA ESRL GMD Carbon Cycle and Greenhouse Gases Group's aircraft network consists of 18 sites, mostly in North America, that conduct bi-weekly flask sampling over given locations to altitudes of 8000 m above sea level (masl). Most sites sample 12 flasks during an altitude profile, and through collaboration with GMD's Ozone group, many conduct continuous ozone measurements as well. In March 2009, a new site in Alaska (site code ACG) was added to our network, through a collaborative effort with the U.S. Coast Guard (USCG). The USCG Air Station in Kodiak, AK, operates several C-130 aircraft and conducts routine bi-weekly flights for Arctic Domain Awareness (ADA flights) from March to November. These flights generally begin in Kodiak, continue on to Barrow, and then return back to Kodiak (see map) after passing at low altitudes over Kivalina and Galena. We have installed an inlet window-replacement plate on the USCG C-130 aircraft along with a pallet with NOAA instrumentation that is deployed on each ADA flight. Instrumentation on board consists of: two flask packages per flight, a compressor package for filling flasks, a continuous CO<sub>2</sub>/CH<sub>4</sub>/H<sub>2</sub>O analyzer (Picarro Cavity Ring-Down), a continuous ozone analyzer (2B systems), and an ambient temperature and humidity sensor. GPS time and location from the aircraft's navigation system are also collected. Flasks sampled in flight are analyzed at NOAA ESRL for the major greenhouse gases and a variety of halocarbons and hydrocarbons that influence climate, stratospheric ozone, and air quality. For the 2011 season, a new four-species Picarro analyzer was installed, adding continuous CO measurements to the site. We will present details on the deployed instrumentation as well as data collected from the 2009 and 2010 seasons along with some recent results from 2011.



**Figure 1.** April 4, 2011 flight path of the U.S. Coast Guard C-130 in Alaska. Continuous  $CO_2$  (shown),  $CH_4$ , CO, and  $O_3$  are measured during flight.

### Long-Term Methane Observations at the Global Atmosphere Watch Site Jungfraujoch with Gas Chromatography and Cavity Ringdown Spectroscopy

### M. Steinbacher, C. Zellweger and B. Buchmann

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*In situ* measurements of atmospheric methane (CH<sub>4</sub>) at Jungfraujoch started in February 2005 with gas chromatography and flame ionization detection (GC/FID). Ambient air measurements are performed every 24 minutes by analyzing discrete sample volumes. The sample air is dried prior to analysis by means of a Nafion dryer. In December 2009, a Cavity Ringdown Spectrometer (CRDS) for continuous CH<sub>4</sub> and Carbon Dioxide (CO<sub>2</sub>) observations was installed next to the GC/FID. During the first 8 months of operation, the sample air was also dried prior to analysis by means of a Nafion dryer. As the instrument is also capable of measuring H<sub>2</sub>O, no water vapor removal is used anymore (since August 2010). Thus, CH<sub>4</sub> dry air mixing ratios are currently determined by analyzing the fully unaltered humid gas stream and subsequently applying an empirical humidity correction accounting for dilution and pressure broadening effects. This presentation will provide a comprehensive analysis of the more than one year data set of the side-by-side CH<sub>4</sub> comparison. Besides a general evaluation of the GC/FID – CRDS agreement, particular attention will be paid to the long-term stability of the CRDS analyzer, the advantages of high time resolution monitoring at remote sites and the issue of sample drying. Figure 1 shows a 4-day time series of the CH<sub>4</sub> mixing ratios measured with both techniques giving a first impression that the overall agreement is very good, no significant bias exists and the observed CH<sub>4</sub> variability is well captured by both techniques.



**Figure 1.** 4-day time series of *in situ*  $CH_4$  mixing ratios at Jungfraujoch in June 2010 measured with CRDS and GC/FID. High-resolution data and 1min and 10min aggregates are shown for the CRDS, results of single injections are displayed for the GC/FID.

### **Measurement of Uncertainty**

### S. Heckman

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A measurement without an uncertainty is hard to use. Before one can use it, one has to do a lot of work to estimate the missing uncertainty. Manufacturers provide limited assistance by supplying detailed reports on their stability tests of a few 'typical' instruments. They understand their instruments better than users, but their work usually stops once the instrument leaves the manufacturing facility. This talk will discuss the Earth Networks design for continually measuring four sources of uncertainty at each site: instrument drift, tank drift, line contamination, and water vapor correction uncertainties. One measures uncertainty by measuring a known quantity and comparing the measurement to the known true result, or by measuring the same unknown quantity two ways and comparing the measurements to each other. For instrument drift we, like all others, compare to a calibration tank with known mixing ratios. For tank drift we continually compare two tanks at each site. For line contamination we continually compare two lines at each site. We were unable to measure water vapor two ways or compare to a standard. Since we cannot measure this uncertainty in the field, we instead try to make its contribution negligibly small by drying the gas before measuring the water vapor content. Details will be provided about how the Earth Networks calibration system allows us to measure each of these uncertainties.



**Figure 1.** Earth Networks, in collaboration with Scripps Institution of Oceanography, have developed a system for calibrating gas analyzes and monitoring their ongoing well-being. The system includes a calibration box and two air tanks filled with air containing known levels of gases.
# Measuring CO, CH<sub>4</sub>, CO<sub>2</sub> & H<sub>2</sub>O in a Single Instrument; Using New CRDS Technology to Characterize Urban Plumes & the Well-Mixed Atmosphere

## G. Jacobson, E. Crosson and C. Rella

Picarro Inc, 3105 Patrick Henry Drive, Santa Clara, CA 94054; 408-962-3925, E-mail: gjacobson@picarro.com

The ability to take inventory of critical greenhouse gases such as carbon dioxide  $(CO_2)$  and methane  $(CH_4)$  and quantify their sources and sinks is essential for understanding atmospheric change. Attribution of greenhouse gas sources has commonly been done using <sup>14</sup>C as a marker for fossil fuel combustion, however, current technology is not able to make continuous, real-time, <sup>14</sup>C measurements. As an alternative, researchers have adopted methods using carbon monoxide (CO) as a tracer for combustion emissions in the atmosphere. Therefore, measurement of carbon monoxide alongside relevant greenhouse gases provides a unique tool for characterizing anthropogenic emissions. Using Cavity Ring-Down Spectroscopy (CRDS) technology, Picarro has developed the capability to measure  $CO_2$  concentration to a precision (5 second, one sigma) of 150 parts-per-billion (ppbv),  $CH_4$  concentration to a precision of 1 ppbv, and CO to a precision of 30 ppbv, all within seconds, using the same instrument.

Research and development at Picarro have been focused on incorporating the fast optical switching and other technologies required to enable measurement of four species without compromising the high sensitivity, precision and low drift that make these instruments valuable to atmospheric scientists. In order to best serve the research community, two models have been developed, the G2401 for ground-based measurements and the G2401-*m* for flight-based measurements. The G2401 is designed for terrestrial atmospheric monitoring and is capable of meeting the World Meteorological Organization's data quality objectives for inter-laboratory comparability. The G2401-*m* includes unique pressure and vibration remediation technology to ensure optimal operation during the rapidly changing conditions present during aircraft flight. Current application work using the instruments includes: ground-based urban networks, remote atmospheric monitoring, mobile source identification, and flight-based vertical profiles, urban plume characterization and satellite data verification.



**Figure 1.** Picarro factory flight simulation test data for CO,  $CO_2$  and  $CH_4$  from a production G2401-*m* instrument. Testing is done in a custom-built hyperbaric chamber. The chamber pressure cycles between 760 to 250 Torr as the analyzer measures a constant-concentration gas stream delivered at the same pressure as the hyperbaric chamber.

## Towards On-Line Monitoring of <sup>14</sup>C in Atmospheric CO,

H.A.J. Meijer<sup>1</sup>, D. Paul<sup>1</sup>, E. Ilkmen<sup>2</sup> and D.E. Murnick<sup>2</sup>

<sup>1</sup>Centre for Isotope Research, University of Groningen, Groningen, Netherlands; 31503634609, E-mail: h.a.j.meijer@rug.nl <sup>2</sup>Department of Physics, Rutgers University, Newark, NJ 07102

For quantification of the net exchange of  $CO_2$  by the biosphere and the oceans, accurate knowledge about the spatial and temporal behavior of  $CO_2$  emitted by the combustion of fossil fuels ( $CO_2$ -ff) is essential. Determination of the amount of  $CO_2$ -ff is also of crucial importance by itself: Emission reductions in the framework of the Kyoto Protocol and successors should be independently verified, and a robust and accurate verification tool is important for policymakers and thus, for society. To identify and quantify atmospheric  $CO_2$ -ff concentrations, <sup>14</sup>C is the only direct tracer available. Since  $CO_2$ -ff contains no <sup>14</sup>C, the atmospheric <sup>14</sup>CO<sub>2</sub> concentration is diluted when  $CO_2$ -ff is added to the atmosphere. Indeed, the measurement of <sup>14</sup>C in air (and also in plant samples) has proven to be a very useful tracer for atmospheric  $CO_2$ -ff. However, the sampling and analysis procedures required are cumbersome, expensive, and essentially off-line. Atmospheric  $CO_2$  has to be collected (either in flasks or bags, or by bubbling air through a NaOH solution). Then, the samples have to be shipped to a <sup>14</sup>C laboratory, where the samples have to be prepared and analyzed (mostly in an Accelerator Mass Spectrometer).

Recently, Murnick and co-workers (Murnick et al., 2008) developed a totally different technique for <sup>14</sup>C detection, based on the opto-galvanic effect. The method combines the well-established technique for  $CO_2$ -lasers, the high spectral selectivity of such a laser filled with <sup>14</sup>CO<sub>2</sub>, and the subtle way in which impedance changes due to resonant radiation in a gas discharge can be detected. By placing the sample gas discharge cell intra-cavity, the necessary sensitivity for <sup>14</sup>CO<sub>2</sub> detection could be proven. The (desktop size) system operates in continuous flow mode, and can measure air directly. However, regarding the utmost accuracy needed for useful atmospheric <sup>14</sup>CO<sub>2</sub> monitoring, a CO<sub>2</sub> pre-concentration step will most likely be necessary. The talk will show the state-of-the-art, and illustrate the path towards accurate, time-resolved, *in situ* measurement of atmospheric <sup>14</sup>CO<sub>2</sub>.



Supported in part by National Science Foundation Grant 0922872, and in part by an RWE grant to the University of Groningen.

Figure 1. The Intra-Cavity Opto-Galvanic Spectroscopy setup.

#### Patterns and Variability in A14C of CO, in Northern Hemisphere Background Air

H.D. Graven<sup>1</sup>, T.P. Guilderson<sup>2</sup> and R.F. Keeling<sup>1</sup>

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The development of applications that determine fossil fuel-derived CO<sub>2</sub> and fossil fuel CO<sub>2</sub> emissions using observations of  $\Delta^{14}$ C in atmospheric CO<sub>2</sub> has advanced rapidly in recent years. The largest uncertainties associated with this method are contributed by measurement uncertainty and the specification of the "background" level of  $\Delta^{14}$ C, which provides the reference to which  $\Delta^{14}$ C dilution in polluted air is quantified. We will present measurements of  $\Delta^{14}$ C of CO<sub>2</sub> in Northern Hemisphere background air from the Scripps CO<sub>2</sub> Program's flask sampling network that were conducted at Lawrence Livermore National Laboratory. Meridional gradients in background air are evident in comparisons of  $\Delta^{14}$ C observed at Mauna Loa and Kumukahi, Hawaii (20°N), La Jolla, California (33°N) and Point Barrow, Alaska (72°N) between 2001 and 2007. La Jolla typically shows the lowest  $\Delta^{14}$ C. Seasonal cycles of  $\Delta^{14}$ C with maxima in fall are evident, with the largest amplitudes at Point Barrow, on average. The observations also show substantial year-to-year variability. For example, very little seasonality was observed in 2002-03 at La Jolla. We will discuss the influences that are likely to contribute to the observed patterns and variability in  $\Delta^{14}$ C of Northern Hemisphere background air and the implications for quantifying fossil fuel-derived CO<sub>2</sub> from Northern continents.



**Figure 1.** Measurements of  $\Delta^{14}$ C in CO<sub>2</sub> from Northern Hemisphere flask sampling sites in the Scripps CO<sub>2</sub> Program. Shown are smoothed curves for Point Barrow (PTB), La Jolla (LJO), Kumukahi (KUM) and Mauna Loa (MLO).

#### Evidence of Emissions from Oil and Gas Drilling Operations in Northeastern Colorado

<u>G. Petron</u><sup>1</sup>, G. Frost<sup>1</sup>, S. Montzka<sup>2</sup>, B. Miller<sup>1</sup>, A. Hirsch<sup>3</sup>, A. Karion<sup>1</sup>, C. Sweeney<sup>1</sup>, J. Kofler<sup>1</sup>, A. Andrews<sup>2</sup>, E.J. Dlugokencky<sup>2</sup>, M. Trainer<sup>2</sup>, D. Welsh<sup>2</sup>, D. Wolfe<sup>2</sup> and P. Tans<sup>2</sup>

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 <sup>3</sup>National Renewable Energy Laboratory, Golden, CO 80401

Since 2007, air samples collected regularly at NOAA tall towers and from aircraft across the U.S. have been analyzed for over sixty different species, including greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, SF<sub>6</sub>), CO, several hydrocarbons (propane, n-butane, pentanes, benzene, acetylene), and ozone-depleting substances. The Boulder Atmospheric Observatory (BAO) is a 300-m tall tower located 35 km north of the Denver metropolitan area in the northern Colorado Front Range. The BAO sits on the southwestern edge of the Denver-Julesburg fossil fuel Basin, home to over 15,000 oil and gas wells. Using *in situ* meteorological data, we analyze the air composition of the BAO samples for three different wind sectors: the North and East sector (with strong contributions from oil and gas production operations and cattle feedlots), the South sector (dominated by the Denver urban area), and the West sector (containing the foothills of the Rocky Mountains and a few oil and gas wells). Air samples from the BAO North and East sector exhibit enhanced levels of alkanes that are strongly correlated with each other. To put these BAO samples in a regional context, we drove a mobile laboratory around BAO during the summer of 2008. A continuous methane analyzer was used to detect regional enhancements in methane and local plumes from point sources (including a natural gas processing plant, feedlots, and waste water treatment plant). Targeted air samples within and outside of plumes were collected and later analyzed in the NOAA lab. We will present results from the analysis of the BAO and Mobile Lab data and use the atmospheric data together with a bottom-up estimate of propane emissions from oil and gas production operations in Weld County to derive source estimates for methane, n-butane, i-pentane, n-pentane and benzene.



**Figure 1.** Summertime and wintertime median mixing ratios of several species measured in air samples from the 300-meter level at the BAO tower for three wind sectors: North and East (N&E) where the density of gas drilling operations is highest, south (S) with Denver 35 km away, and west (W) with mostly clean air. The time span of the data is from August 2007 to April 2010. Summer includes data from June to August and winter includes data from November to April. Due to the small number of data points, we do not show summer values for the S and W wind sectors. Data outside of the 11am-3pm local time window were not used. Notice the different scales used for methane, propane and n-butane.

#### Observations of <sup>14</sup>CO, at the Boulder Atmospheric Observatory (BAO)

<u>B. LaFranchi</u><sup>1</sup>, G. Petron<sup>2</sup>, J. Miller<sup>2</sup>, S. Lehman<sup>3</sup>, A. Andrews<sup>4</sup>, E. Dlugonkencky<sup>4</sup>, B. Miller<sup>2</sup>, S. Montzka<sup>4</sup>, J. Turnbull<sup>2</sup>, P. Tans<sup>4</sup> and T. Guilderson<sup>1</sup>

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Atmospheric radiocarbon (<sup>14</sup>C) represents an important observational constraint on emissions of fossil-fuel derived carbon into the atmosphere due to the near absence of <sup>14</sup>C in fossil fuel reservoirs. The high sensitivity and precision that accelerator mass spectrometry (AMS) affords in atmospheric <sup>14</sup>C analysis has greatly increased the potential for using such measurements to facilitate carbon cycle studies and the validation of greenhouse gas emissions inventories. Here we report on the first-ever <sup>14</sup>CO<sub>2</sub> observations from the BAO, located in Erie, CO. The BAO tower is one of the tall towers in the NOAA ESRL greenhouse gas flask sampling network that has recently begun sampling for atmospheric <sup>14</sup>C, as well as other trace gases.

We will present observations of Delta<sup>14</sup>C in whole air samples collected between June 2009 and September 2010 at BAO. Values ranged from -20‰ ( $\pm$  1.8 ‰) to +46 ‰ ( $\pm$  1.8 ‰) corresponding to estimated fossil fuel CO<sub>2</sub> (CO<sub>2</sub>ff) concentrations as high as 25 ppm ( $\pm$  1 ppm) above the background. An analysis of the relationship between CO<sub>2</sub>ff and other combustion tracers provides information on the type of combustion contributing to the total fossil fuel signal and on co-located activities, such as oil and gas drilling operations to the northeast. We will focus, in particular, on the correlations of CO<sub>2</sub>ff with CO and CH<sub>4</sub>. The observed CO to CO<sub>2</sub>ff ratio is lower than has been seen in other regions, suggesting a relatively small contribution from mobile sources to total emissions in the region and a greater source from electrical utilities. Differences in the CH<sub>4</sub> to CO<sub>2</sub>ff ratio with wind direction indicates a larger source of CH<sub>4</sub> when winds arrive from the northeast, where significant oil and gas drilling operations are located, as opposed to the Denver metro area to the south and southeast.



**Figure 1.** Time series of  $\Delta^{14}CO_2$  (top,  $\infty$ ) and fossil fuel CO<sub>2</sub> (bottom, ppm) observed at the BAO, part of the NOAA Tall Tower Network. Solid circles represent individual measurements from discrete air samples collected at mid-day. Hollow circles are monthly (approx.) binned medians (with error bars representing the standard error of the mean). Fossil fuel CO<sub>2</sub> (CO<sub>2</sub>ff) is derived from an isotopic mass-balance equation using observed CO<sub>2</sub> mixing ratios, background [CO<sub>2</sub>] and  $\Delta^{14}CO_2$  estimated from observations at a nearby high elevation site (Niwot Ridge), an assumed  $\Delta^{14}C$  for fossil fuels of -1000 ‰, and estimated respired CO<sub>2</sub> correction ranging from 0.2 ppm (summer) to 0.5 ppm (winter).

# Quantification of Anthropogenic Emissions from an Urban Region: First Results of Time-Integrated Flask Samples from the Indianapolis Flux (INFLUX) Project

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INFLUX is a NIST-funded project to develop and assess methods of quantifying greenhouse gas emissions at the urban scale from top-down and bottom-up approaches, using Indianapolis as a test case. Indianapolis is an excellent test site, with relatively straight-forward meteorology; a contained, isolated, urban region; and relatively well-known emissions.

INFLUX incorporates atmospheric measurements from multiple platforms and methods, and bottom-up inventory estimates. This presentation focuses on flask measurements from the first two towers, installed in late 2010. These two towers are located upwind and downwind of Indianapolis in prevailing wind conditions (about 25% of the time). Flask samples are taken in mid-afternoon only on days when the appropriate wind conditions occur, determined each day using automatically generated HYbrid Single-Particle Lagrangian-Integrated Trajectory (HYSPLIT) back-trajectories. We will describe the newly-developed time-integrated flask sampling system used at the towers, which uses a 15 liter volume to integrate air from a one-hour period, before collecting a portion of the mixed air in glass flasks (figure 1).

Flasks are measured at NOAA ESRL and the Institute of Arctic and Alpine Research for ~40 species, including  $\Delta^{14}CO_2$  (as a proxy for  $CO_2ff$ ),  $CO_2$ , CO,  $CH_4$ , stable isotopes of  $CO_2$  and a suite of halocarbons and hydrocarbons. Species associated with urban emissions are consistently enhanced in the downwind samples relative to the upwind site (figure 2). Enhancements vary through time and are inversely correlated with wind speed and boundary layer height.



**Figure 1.** Time-integrated flask sampling system.

**Figure 2.** Enhancements in mole fraction of selected species at the downwind tower relative to the upwind tower.

#### Quantification of Emissions from Methane Sources in Indianapolis Using an Aircraft-Based Platform

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Methane is an important greenhouse gas that is 20 times more potent than an equivalent amount of carbon dioxide. Because of its relatively short lifetime and large global warming potential, reductions in its emission may lead to a considerable effect in the near-term. Urban city centers have been shown to be significant sources of anthropogenic methane with emissions much larger than currently reported in emission inventories. This discrepancy suggests that there remain a number of insufficiently characterized methane sources in urban environments. Using cavity ring-down spectroscopy, discrete flask sampling, and a mass balance approach, we determine methane emission fluxes directly downwind from the city of Indianapolis with an aircraft-based platform. By flying perpendicular to the prevailing wind direction in a horizontal flight transect across the city (Figure 1a), the methane distribution as a function of height above the ground and the horizontal distance is quantified (Figure 1b). Also shown in Figure 1b are methane hot spots that correspond to particular point sources within the city. In this work, we will describe in detail our approach to determine the city-wide emission flux as well as the source-specific methane emissions and show initial results from three flight experiments. Emission rates from specific sources of methane (e.g. landfill and wastewater treatment plants) will be investigated and quantified to determine the importance of each source to the total area-wide emission flux. As part of a collaborative effort called the Indianapolis Flux Experiment, this study will help us gain understanding into the nature of urban methane sources, specifically the magnitude of source-specific emissions, as well as the potential energy equivalent of these biogas emissions should they be captured and used to generate heat or electricity.



**Figure 1.** (a) Flight path on March 1, 2011, showing the horizontal flight segments perpendicular to the wind direction; also shown are the locations of potential methane sources in the city of Indianapolis. (b) Methane distribution as a function of the height above the ground and horizontal distance along the curtain flight segments; methane hot spots are observed at specific coordinates along the curtain flight segment.

## Identification of Methane Emissions in an Urban Setting

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The identification and quantification of greenhouse gas emissions from urban centers are becoming of more interest. Recent measurements indicate that urban emissions are a significant source of methane ( $CH_4$ ) and in fact may be substantially higher than current inventory estimates. As such, urban emissions could contribute 7-15% to the global anthropogenic budget of methane. Although it is known that the per capita carbon footprint of compact cities such as New York City, Boston, and San Francisco are smaller than sprawling cities such as Houston, the strengths of individual sources within these cities are not well known. Such information is of use to government policy makers because it can be used to incentivize changes in transportation and land use patterns.

In an attempt to identify major methane sources in Boston and Indianapolis, systematic measurements of  $CH_4$  concentrations were made at street level using a vehicle mounted cavity ringdown analyzer. A number of discrete sources were detected at concentration levels in excess of 15 times background levels. Background levels of methane were also measured to be 10% higher than the world-wide average of 1.860 ppm. Measurements of  $CH_4$  concentration levels along with detailed location information will be presented. In addition, chamber flux measurements of discrete sources will also be presented.



**Figure 1.** Methane concentration measurements in Boston displayed in Google Earth. Peaks correspond to methane concentrations up to levels five times background levels. These measurements were typical of measurements made throughout the city and surrounding suburbs.

## Exploring the Recent Biennial Cycle in Observed CO, Growth Rate Using CarbonTracker

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Since 2002, atmospheric  $CO_2$  growth rates estimated from NOAA Cooperative Air Sampling Network stations in northern extratropical latitudes have manifested an apparent oscillation with a period of about 2 years (Figure 1). Peak growth rates of around 3 ppm yr<sup>-1</sup> occur in January 2003, 2006, and 2008, and troughs below 1 ppm yr<sup>-1</sup> occur in spring 2004, January 2007, and January 2009. Time series of  $CO_2$  mole fractions extracted from CarbonTracker for the same stations were used to compute the growth rate surface, and we find that the model reproduces this oscillation. In CarbonTracker, this feature is almost exclusively due to variations in the terrestrial biosphere  $CO_2$  tracer--air-sea exchange and fossil fuel emissions do not contribute significantly. Intriguingly, the feature is also present in simulations using unoptimized "prior" land fluxes, but with a significantly smaller amplitude than in the optimized CarbonTracker product. Further analysis suggests that land flux anomalies cannot by themselves explain the observed growth rate variability, implying that interannual variability in atmospheric transport plays a large role in creating this feature. Using CarbonTracker as an analysis tool, we will explore the causes of this growth rate feature, and discuss implications for analysis of atmospheric time series.



Figure 1. CO<sub>2</sub> growth rates estimated from observed and modeled mole fractions.

### Can We Explain Recent Increases in Atmospheric CH<sub>4</sub>?

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Methane  $(CH_4)$  is the most important greenhouse gas influenced by human activities after  $CO_2$ . Its chemistry results in additional indirect climate effects from production of tropospheric  $O_3$ , which also affects air quality, and stratospheric  $H_2O$ . Natural emissions of  $CH_4$ , from Arctic wetlands and hydrates, are susceptible to changing climate, and they have the potential to cause strong positive climate feedbacks.

NOAA measurements of atmospheric CH, from the carbon cycle group's Global Cooperative Air Sampling Network began in 1983. From the beginning of the measurements through 2006, the rate of increase was decreasing from ~14 ppb yr<sup>1</sup> 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]. During 2007, atmospheric CH<sub>4</sub> began increasing again (see Figure). Dlugokencky et al. [Geophys. Res. Lett., 36, L18803, doi:10.1029/2009GL039780, 2009] attributed the increases in 2007 and 2008 to anomalously high temperatures in the Arctic (2007) and greater than average precipitation in the tropics (2007 and 2008). Near-zero CH<sub>4</sub> growth in the Arctic during 2008 suggests we have not yet activated strong climate feedbacks from permafrost and CH<sub>4</sub> hydrates. These inferences, directly from the data, are qualitatively consistent with recent model studies. Continuing increases in 2009 and 2010, each  $\sim$ 5 ppb yr<sup>-1</sup>, have not yet been analyzed. In 2010, we returned to a very strong La Niña, the same climate pattern responsible for large positive precipitation patterns in tropical wetland regions in 2007 and 2008. Indeed, strong precipitation patterns were observed in SE Asia in 2010. This is a likely cause of continued  $CH_4$  increase, and is consistent with the observation that the largest growth rates in 2010 were in the southern tropics. For 2009, when we were in a weak El Niño, no clear cause has emerged. The observations indicate the largest growth rates were observed in mid-latitudes of the northern hemisphere, a departure from 2007, 2008, and 2010 when signals were clearly dominated by the tropics.



**Figure 1.** a) Globally averaged  $CH_4$  dry air mole fractions (blue). Red line shows the deseasonalized trend. b) Rate of increase in atmospheric  $CH_4$  (red) and annual increases from Jan1 in year one to Jan 1 in the next year (blue symbols). Uncertainties are 68% confidence limits. 2010 increase is preliminary.

#### Using CarbonTracker-CH<sub>4</sub> to Understand the Recent Methane Budget

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Anthropogenic sources are thought to account for roughly 60% of the global atmospheric methane budget, with natural sources making up about 40%. Emissions from wetlands are the largest contribution from natural sources, while agriculture (rice and ruminants) and waste dominate anthropogenic emissions. Fugitive emissions from fossil fuel extraction are thought to make up about 20% of the global atmospheric methane budget. After declining over the past decades, the global growth rate of methane has started to increase again, and the cause of this trend is not currently understood. Climate-driven increases in wetland emissions likely played a role, especially in the tropics and the Arctic. Anthropogenic emissions as estimated from economic data have also been increasing, especially due to rapidly expanding Asian economies. In this paper we use a state-of-the-art ensemble data assimilation system (CarbonTracker-CH<sub>4</sub>) to attribute methane variability and trends to anthropogenic and natural source processes. We pay particular attention to the Arctic, where some recent years have been the warmest on record, and to the tropics and the potential role of ENSO in driving variability of wetland emissions. Finally, we explore whether a signal in anthropogenic emissions is present in the atmospheric network observation, and whether it is present in flux estimates from the methane assimilation. We find that high latitude and tropical wetland emission anomalies are readily identified by the assimilation, however, changes in Asian anthropogenic emissions are still difficult to estimate using the assimilation because of the sparseness of the global network. This highlights the importance of increased surface observations as well as the possible use of space-based observations.



**Figure 1.** Difference between modeled and measured methane for profiles measured at Carr, CO for the prior (bottom) and posterior (top) flux estimates. The white line shows the average difference for each altitude and the red lines show the 1-sigma confidence bounds.



**Figure 2.** The estimated total methane flux for North America. The dark blue line shows the posterior flux estimates with 1-sigma confidence bounds in light blue. The dark red line is the prior flux estimate and the light red area is the 1-sigma error bounds of the prior flux uncertainty.

#### The Drivers of the CH<sub>4</sub> Seasonal Cycle in the Arctic and What Long-Term Observations of CH<sub>4</sub> Imply About Trends in Arctic CH<sub>4</sub> Fluxes

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The large seasonal signal in Arctic  $CH_4$  is driven by two dominant processes: transport of  $CH_4$  from low latitude and local emissions. In collaboration with NASA Jet Propulsion Laboratory, the NOAA ESRL Carbon Cycle Group Aircraft Program is launching a new initiative entitled "Carbon in Arctic Reservoirs Vulnerability Experiment" (CARVE) to better understand the factors controlling the seasonal and spatial variability of  $CH_4$ and  $CO_2$  fluxes in the Alaskan Arctic. This initiative includes a new ground measurement site and three aircraft campaigns in early, mid and late summer of each of the next four years. Aircraft observations will include *in situ* measurements of  $CO_2$ ,  $CH_4$  and CO, as well as flask measurements of these same gases, plus  $N_2O$ ,  $SF_6$ ,  $H_2$ , haloand hydro-carbons and isotopes of  $CH_4$  and  $CO_2$ . Additionally, the payload includes the Passive/Active L-band System and a nadir-viewing Fourier transform spectrometer to deliver the first simultaneous measurements of surface parameters that control gas emissions (i.e., soil moisture, freeze/thaw state, surface temperature) and total atmospheric columns of carbon dioxide, methane, and carbon monoxide.

A 20-year record of ground observations made at Barrow, AK, and Alert, Nunavut show a pronounced increase in  $CH_4$  mixing ratios and decrease in C-13 isotopes of  $CH_4$  in the late summer, which are indicative of local  $CH_4$ emissions. Analysis of this late summer increase in  $CH_4$  shows inter-annual variability shared by many other  $CH_4$  analyses, but does not indicate that natural emissions in the Arctic are increasing due to observed warming. This presentation will review the major contributors to the seasonal cycle of methane over the Arctic and the likely source of the late summer increase in the methane mixing ratios observed throughout the Arctic.



**Figure 1.** Methane and  ${}^{13}C/{}^{12}C$  ratio in methane from Barrow and Alert Stations. Both methane time series show a very rapid increase in methane in late summer (red, top figures) which is coincident with a rapid decrease in  ${}^{13}C/{}^{12}C$  of CH<sub>4</sub> measurements (red, bottom figure).

# The Isotopic Composition of Oxygen in Atmospheric CO<sub>2</sub> and El Niño: A New Constraint on Global Productivity

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Three decades of oxygen isotope ratios in atmospheric CO<sub>2</sub> measured in the SIO global flask network have revealed a strong correlation with the El Niño-Southern Oscillation (ENSO). During the El Niño phase, the  $\delta^{18}$ O of CO<sub>2</sub> increased by approximately 0.5‰ at all stations. We have confirmed this general pattern by comparing SIO data with similar measurements made by NOAA and CSIRO. Station  $\delta^{18}$ O-CO<sub>2</sub> time series are positively correlated with predictions of the  $\delta^{18}$ O of precipitation in Southeast Asia and Northern South America from the IsoGSM model, and are negatively correlated with relative humidity in these same regions. We suggest that the redistribution of moisture and rainfall in the tropics during El Niño increases the <sup>18</sup>O/<sup>16</sup>O of precipitation and plant water, and this signal is then passed onto atmospheric CO<sub>2</sub> by vegetation-atmosphere gas exchange. Further exchange with the ocean and the biosphere, including the extra-tropics, provides damping of the  $\delta^{18}$ O-CO<sub>2</sub> to stable background levels.

We use a simple two-box model to estimate that the global turnover time of O-isotopes in atmospheric CO<sub>2</sub> from fitting the decay of the ENSO-related anomalies is 1.1 - 1.7 yrs. The turnover time of O in CO<sub>2</sub> is related to global gross primary production (GPP) and stomatal conductance. This study suggests that the response time of  $\delta^{18}$ O-CO<sub>2</sub> may be shorter than previously estimated and that the fast response can be accounted for by revising global GPP upwards from 120 Pg C yr<sup>-1</sup> to 150–175 Pg C yr<sup>-1</sup>. A detailed understanding of  $\delta^{18}$ O in the hydrologic cycle is not required to make use of this top-down damping constraint on gross exchange of O in CO<sub>2</sub>.



**Figure 1.** (a) El Niño Precipitation Index was used as a proxy for ENSO variability. Red arrows denote El Niño events. (b) Empirical ENSO model fit for the northern hemisphere (red line) compared against deseasonalized flask observations (black dots) and spline fits (grey line) at Mauna Loa, Hawaii Station. (c) Same as (b) but for the southern hemisphere model fit and the South Pole station.

# Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container (CARIBIC) Observations of CO, Uptake During the Indian Summer Monsoon

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During the Indian summer monsoon major changes in large scale atmospheric circulation take place. The Inter-Tropical Convergence Zone (ITCZ) travels 3\*10<sup>3</sup> km north, up to the Himalayas, and surface winds (especially the Somali jet) bring moisture-laden air deep into the sub-continent and neighboring regions. While low pressure systems are abundant, and deep convection is ubiquitous, an extensive upper tropospheric high pressure system develops that to some degree traps air that bears characteristics of surface trace gas emissions, and, in the case of CO,, uptake. The chemical regime across the anticyclone however does bear the characteristics of a strong north-south division as given by the presence of the ITCZ. Rainfall is abundant and intensive providing ideal conditions for strong CO<sub>2</sub> uptake by vegetation. The CARIBIC Observatory has been used to investigate the trace gas chemical composition of parts of the upper tropospheric anticyclone from 1998 to 2001 and in 2008. Systematic increases in SF<sub>6</sub> due to increased convection, and increase in CH<sub>4</sub> for the same reason, but also because of increased production, can be clearly discerned. Similarly, but somewhat later in the monsoon period, CO<sub>2</sub> decreases are recorded. Because quantitative information about the fluxes of CO<sub>2</sub> for India and more generally South Asia is scarce, we have tried to use our data to improve this situation. The flux of CO, can be derived when we assume the flux of  $SF_6$  to be known. Using this crude tool, the uptake of CO<sub>2</sub> was estimated. Later, using additional data from the CONTRAIL Project giving vertical profiles over Delhi and surface measurements (NOAA) and modeling a more refined estimate of CO<sub>2</sub> fluxes could be arrived at.



**Figure 1.** Trace gas mixing ratios measured at about 11 km pressure altitude over India and the Middle East in August and September 2008 by CARIBIC. The influence of surface air is clear from the increase in CO (light blue),  $CH_4$  (green),  $N_2O$  (yellow), and  $SF_6$  (red). The bottom panel shows the accompanying decrease in CO<sub>2</sub>.

## **Importance of Reliable Continuous Records of Earth System Parameters**

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Back in the 1970s we began to focus on questions involving carbon dioxide and climate change, in particular: (1) Is atmospheric carbon dioxide concentration increasing? (2) If so, is it anthropogenic? (3) Is the tropospheric near-surface air temperature increasing? and (4) Is the carbon dioxide influence on temperature strong in the context of other influences? Only reliable, consistent, long-term monitoring can provide answers to these questions as well as to others that have since arisen. Some of these other questions address radiatively active gases other than carbon dioxide, identifying sources and sinks of carbon at increasingly finer scales, social consequences of climate change, and mitigation strategies for greenhouse gas emissions. In this context, the Carbon Dioxide Information Analysis Center and other data monitoring and archiving groups continue to evolve. This presentation touches on monitoring and archiving of global temperature and anthropogenic carbon emissions to provide examples of the importance of (1) redundant measurements, (2) archiving, (3) record keeping, and (4) analysis.



**Figure 1.** Selected scientists and data addressing the monitoring of temperature, carbon dioxide and associated phenomena that provide clues as to: (1) causes of the  $CO_2$  increase, (2) anthropogenic emissions of  $CO_2$  and (3) the relative influences of  $CO_2$ , and other greenhouse gases on global tropospheric temperature.

## Assessment of the Long-Term Trend of Turkey's GreenHouse Gas (GHG) Emissions Using the Mann Kendall Test

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According to the United Nations Framework Convention on Climate Change data base, there has been about a 100% increase in the total green house gas (GHG) emissions of Turkey between 1990 and 2008. The long term trends of reported individual (GHG) emissions ( $CO_2$ ,  $CH_4$ ,  $N_2O$ ,  $SF_6$  and Perfluorocarbons (PFCs)) during this period were assessed by using non-parametric Mann- Kendall test. Carbon dioxide and  $CH_4$  showed increasing trend with p=0.001 significance level. Sulfur hexafluoride and  $N_2O$  increased during this period with p=0.05 and greater than p=0.1 significance level, respectively. However, a decreasing trend was recorded for PFCs with p=0.01 significance level. The rate of change of individual GHG emissions was calculated by Sen's slope estimated. The highest rate of increase was found for  $CO_2$  with a value of 8.4 Mt/year while the lowest one was calculated as 0.035 Mt/year for  $N_2O$ . Total rate of increase of GHGs within this time frame was calculated as about 9.75 Mt/yr. When one compared this value with the values recorded for other European Union countries, Turkey is the second highest GHG emitter in Europe after Spain, for which the rate of increase was calculated as 10 Mt/yr. The same methodology was also applied to the main sectors responsible to GHG emissions. While the emissions corresponding to agricultural activities fell down, those from energy, industry and waste rised with 99% confidence level within this period.



**Figure 1.** Global map showing the percent growth observed in total GHG emisisions (left top plot) (http://maps.unfccc.int/di/map/), in addition to variation of trends of individual GHGs emitted from Turkey between 1990 and 2008.

## Using Data to Improve a Global Fire Model for Use in Climate Models and Earth System Models

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We present a brief overview of Geophysical Fluid Dynamics Laboratory Earth System Modeling framework, and then discuss the development and implementation of an improved fire model for use in the coupled climate-biogeochemical cycles models. We discuss the observations we already use to improve the simulations, as well as what additional measurements would be useful. Thus, this presentation highlights the intersection of measurements and modeling with respect to biomass burning.

Biomass burning is a major disturbance in terrestrial ecosystems and a large source of carbon to the atmosphere. Natural and anthropogenic fires have been a part of the Earth system for millennia, but our understanding of global fire activity and the subsequent impacts on ecosystems and the atmosphere has only advanced significantly in the past three decades as a result of the availability of satellite-based data products. While climate is generally considered to be the dominant control on the distribution and timing of global fires, human activities directly shape global fire distribution through practices such as land-clearing, crop and pasture management, and fire suppression, and indirectly through anthropogenically driven climate change. This complex interplay results in fire characteristics that are dependent on the particular use of fire.

The fire model development is constrained by both global and regional scale datasets that are based on observations. The fire model simulates seasonal patterns in fire activity, burned area, and fire emissions, accurately reproducing timing and magnitude at regional scales when compared to observationally-based constraints such as fire counts from the NASA Moderate Resolution Imaging Spectroradiometer, burned area from the Global Fire Emissions Database (GFED) as shown in Figure 1, and emissions from fire emissions inventories. The goal of this research is to link the land process of fire to the atmosphere through emissions. Modeled aerosol optical depths can then be evaluated against satellite and ground-based data products.



**Figure 1.** Mean annual burned fraction of the gridcell simulated by (a) the fire model (BAREAt) and (b) reported by GFED Version 3 (BAREAGFEDv3). Total mean annual burned area is listed in the title in units of Mha (1 Mha = 10,000 km2).

### Progress in Remote Sensing of Carbon Dioxide from Space - The ACOS Project

### M. Gunson<sup>1</sup>, D. Crisp<sup>2</sup> and A. Eldering<sup>2</sup>

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The Atmospheric Carbon Dioxide (CO<sub>2</sub>) Observations from Space (ACOS) project has been processing Greenhouse-Gases Observing SATellite (GOSAT) data as a test of the algorithms and validation approach developed for NASA's Orbiting Carbon Observatory (OCO-2). Nearly two years of data have been processed and the retrieved  $X_{CO2}$  data products (see example below from April 2010) have been made available through the Goddard Earth Science Data and Information Services Center. These have already been used by a number of groups in assimilation studies to understand the improvements in surface CO<sub>2</sub> flux estimates. The comparison of these new satellite data with ground-based measurements from the Total Column Carbon Observing Network has revealed systematic biases of several parts per million in  $X_{CO2}$ . In efforts to reduce this overall error, the origins of this bias have been traced to sources in instrument calibration, uncertainties in spectroscopy, and the representation of aerosols and clouds. Progress in resolving these will be described with expectations for OCO-2, due for launch in 2013.



## 2010-04-01 -- 2010-04-30 Land

Figure 1. Retrieved X<sub>CO2</sub> over land scenes from GOSAT observations during April 2010.

## Atmospheric Infrared Sounder (AIRS) Retrieval of Atmospheric Carbon Dioxide (CO<sub>2</sub>) in Three Layers

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The AIRS mid-tropospheric global  $CO_2$  data product spanning September 2002 to the present may be freely downloaded from the Goddard Earth Sciences/Data and Information Services Center. Access links to the products are provided on the web page http://airs.jpl.nasa.gov/AIRS\_CO2\_Data.

We present a monthly global climatology of the mid-tropospheric  $CO_2$  for  $60^{\circ}S \le LAT \le 90^{\circ}N$ . The AIRS mid-tropospheric data product is now being used by several groups in modeling efforts to understand the sources and sinks and the lifting of  $CO_2$  from surface layers into the free troposphere.

We have retrieved Stratospheric  $CO_2$  at 30 km altitude, and global maps show significant interaction between the stratosphere and troposphere beyond the tropical pipe. The latitudinal variation of  $CO_2$  agrees well with the sparse *in situ* measurements but not with model results.

We are evaluating preliminary retrievals of lower-tropospheric  $CO_2$ , between the surface and 2.2 km (775 hPa) and will show global maps of early results.



**Figure 1.** Left panel shows January 2003 monthly average of AIRS retrieved stratospheric  $CO_2$  and right panel shows 3-D IMATCH stratospheric  $CO_2$ . The model  $CO_2$  profile has been convolved with the AIRS weighting function for this match. The tropical pipe is evident in both panels. The AIRS data show additional tropospheric intrusion at the high northern latitudes and a variation with latitude that is approximately a factor of four greater than in the model.

### NDACC Fourier Transform Spectroscopy (FTS) Trace Gas Trends and the Revitalized Mauna Loa Observatory (MLO) FTS System

J. Hannigan, M.T. Coffey and R.L. Batchelor

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The Network for the Detection of Atmospheric Composition Change (NDACC) is a global network comprised of several working groups focused on a particular measurement technique. The Infrared Working Group uses high-resolution, broadband solar viewing interferometers to measure more than 20 species and their isotopes. The remote sensing measurements are of the total column and course vertical profiles through the free troposphere and stratosphere. Among the 25 member and affiliated stations (see Figure 1) is the MLO FTS which began in 1991 and is currently undergoing a refurbishment and upgrade. From these sites we present multi-decade trends and model comparisons for several gases of total and partial columns. Figure 2 shows the time series of HCl above MLO and selected model simulations.



Figure 1. Map of NDACC stations. Locations designated with stars are current FTS sites.



Figure 2. Comparisons of daily average HCl above Mauna Loa between measurements (black diamonds) and several model calculations.

## Remote Measurement of Greenhouse Gases Under Cloud With the Atmospheric Emitted Radiance Interferometer (AERI) Fourier Transform Spectomereter (FTS) Instrument

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The remote measurement of tropospheric gas concentrations can be achieved by utilizing thermal emission under cloud. The cloud deck acts as a cold, optically thick, blackbody at the cloud base temperature. The emission features from the atmospheric gases below the cloud are superimposed on the cloud blackbody emission. In the thermal spectral region, there are bands and lines from ozone, carbon dioxide, water vapor, methane, nitrous oxide, chloroflurocarbons (CFC), nitric acid and many other gases.

Ozone is used as an example gas since it is both a major air pollutant and a strong greenhouse gas (GHG). The measurements made under cloudy conditions enable the radiative flux from tropospheric  $O_3$  to be determined since the downward emission from the stratospheric ozone are blocked by the cloud layer. The measurement of the surface forcing irradiance flux from gases requires a well-calibrated high-resolution measurement of spectral radiance in the thermal infrared region from 700 to 2500 wave numbers (cm<sup>-1</sup>): suitable measurements are conducted routinely with the AERI instruments at the Department of Energy Atmospheric Radiation Measurement (ARM) sites. Well-calibrated infrared spectral measurements of the downward infrared thermal radiation have been regularly taken by the robotic AERI instruments at the three main ARM sites for over 11 years with a 15-year record at the ARM South Great Plains site. The AERI instrument is an FTS which has internal blackbody calibration sources and is fully automated for long term operation.

Features from carbon dioxide, water vapor, ozone and several greenhouse gases are evident in zenith spectra of the radiance from clouds above the sites. Although the technique was designed for radiative forcing measurements of greenhouse gases, the conversion to mixing ratios is simple. Of particular interest is the measurement of ozone below cloud since the combination of the total column and the cloud base height yields a mean mixing ratio below the cloud base. Example measurements of the ozone mixing ratio in the lower troposphere are shown. A time series of the tropospheric ozone mixing ratio measurements will be displayed. Sample measurements of CFC11, CFC12 and HNO<sub>3</sub> mixing ratios will be demonstrated. Potential applications to the monitoring of GHG mixing ratios are discussed. Since AERI measurements are in the lower troposphere, these could augment the current ESRL GMD flask measurements and help assess the representativeness of the GMD gas mixing ratios. It would be highly desirable to have additional measurements of the average gas concentrations in the lower troposphere and at the surface since significant gradients have been observed in the gas profiles near large sources. Extra information could compensate for boundary layer effects on vertical profiles of gases. The combination of flask measurements and the AERI lower troposphere mixing ratio measurements of the temperature and humidity profiles from the surface up to cloud base.



Figure 1. The concept for measurement of gases by thermal emission spectra under a cloud.

NOTES:

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## • Carbon Cycle & Greenhouse Gases

P-1	Oxygen-18 of Atmospheric CO <sub>2</sub> : Decadal Trends and Climate Variability E.J. Zakem (Institute of Arctic and Alpine Research (INSTAAR), University of Colorado, Boulder, CO)
P-2	A Low-maintenance Drying System for Ambient Air Greenhouse Gas Monitoring
	L.R. Welp (Scripps Institution of Oceanography (SIO), University of California at San Diego, La Jolla, CA)
P-3	Comparison of Co-located Air Samples at Mauna Loa Observatory and CO, Observations at Mt. Fuji A. Sunaga (National Institute of Environmental Studies (NIES), Center for Global Environmental Research (CGER), Ibaraki, Japan)
P-4	Results from the North American Carbon Program Midcontinent Intensive Regional Experiment
	T. Lauvaux (Pennsylvania State University, University Park, PA)
P-5	Northern Hemisphere Trends in Carbon Monoxide: Effects of Changes in Anthropogenic Emissions and Biomass Burning
	Paul Novelli (NOAA Earth System Research Laboratory, Boulder, CO)
P-6	Active Sampling AirCore (ASAC) for Regional Trace Gas Sampling Surveys
	T. Newberger (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)
P-7	INFLUX: Tower-based Greenhouse Gas Measurements and Flux Estimates in an Urban Environment
	Laura McGowan (Pennsylvania State University, University Park, PA)
P-8	Quasi-Continuous Methane Measurements at Cherskii, Russia
	Molly J. Heller (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)
P-9	How Well Do We Know $\delta^{13}$ C of Atmospheric CO <sub>2</sub> ? Estimates of Uncertainty, Inter-laboratory Comparisons, and Calibrations to Carbonate Primary Standards Sylvia Michel (Institute of Arctic and Alpine Research (INSTAAR), University of Colorado, Boulder, CO)
P-10	Identification of Urban Zones Related to Carbon Emission Levels Using Moderate Resolution Nighttime Satellite Imagery From the International Space Station: Preliminary Results
	Chris Elvidge (NOAA National Geophysical Data Center, Boulder, CO)
P-11	Mid-stratospheric Measurements of CO <sub>2</sub> , CH <sub>4</sub> , and CO Using AirCore H. Chen (NOAA Earth System Research Laboratory, Boulder, CO)
P-12	Flask Versus In Situ Results at Tall Tower Sites
	B.M. Walsh (Science and Technology Corporation, Boulder, CO)
P-13	A Multi-Year Record of Airborne Continuous CO <sub>2</sub> in the U.S. Southern Great Plains Sebastien Biraud (Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA)
P-14	First Deployment of a New Mobile Laboratory for Greenhouse Gas Attribution Studies
	Ray Bambha (Sandia National Laboratories, Livermore, CA)
P-15	Development of High-Precision Gas Analyzers for Measurements of N <sub>2</sub> O, CO, CH <sub>4</sub> , CO <sub>2</sub> , and H <sub>2</sub> O Doug Baer (Los Gatos Research, Mountain View, CA)
P-16	An Approach for Estimating Multi-species Boundary Values for Air Entering the North American Domain A. Andrews (NOAA Earth System Research Laboratory, Boulder, CO)
P-17	Inverting <sup>13</sup> CO <sub>2</sub> for Terrestrial Carbon Fractionation in North America Caroline Alden (Institute of Arctic and Alpine Research (INSTAAR), University of Colorado, Boulder, CO)
P-18	The New Picarro G2311-f Methane, Carbon Dioxide, and Water Vapor Analyzer For Micrometeorological Applications
	Chris Rella (Picarro Inc, Santa Clara, CA)
P-19	2011 Tower Network Overview
	J.D. Kofler (Cooperative Institute for Research in Environmental Sciences. University of Colorado, Boulder, CO)
P-20	The Atmospheric Demonstration Experiment of the Integrated Carbon Observation System (ICOS)
	O. Laurent (Laboratoire des Sciences du Climat et de lEnvironnement (LSCE), Gif-sur-Yvette, France)

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## • Ozone & Water Vapor

P-21	Tropospheric Ozone Layer Attributes Quantified by Continuous Wavelet Transform (CWT) and Gradient Analysis
	Guanyu Huang (Department of Atmospheric Science, Huntsville, AL)
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- P-22 Modeling the Impact of Late 20th Century Stratospheric Ozone Changes: Sensitivity to Different Ozone Forcing Data Sets
  - Paul Young (NOAA Earth System Research Laboratory, Boulder, CO)
- P-23 Stratospheric Ozone Interannual Variability Measured by Lidar at Mauna Loa and Table Mountain Guillaume Kirgis (Jet Propulsion Laboratory, California Institute of Technology, Table Mountain Facility, Wrightwood, CA)
- P-24 Stratospheric Water Vapor Trends Over Boulder, Colorado: Analysis of the 30-year Boulder Record Dale F. Hurst (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)
- P-25 Long-term Tropospheric Ozone Variations at Background Measurement Sites Samuel J. Oltmans (NOAA Earth System Research Laboratory, Boulder, CO)
- P-26 Tropospheric Ozone During the Intensive Ozone Network Study (IONS) 2010/CalNex from Ozonesonde Observations: Stratospheric Influence and Long-Range Transport

Samuel J. Oltmans (NOAA Earth System Research Laboratory, Boulder, CO)

- P-27 Ozone Atmospheric Concentrations and Atmosphere/Ocean Fluxes During the TexAQS 2006, STRATUS 2006, GOMECC 2007, GasEX 2008, and AMMA 2008 Cruises *P Boylan (Institute of Arctic and Alpine Research (INSTAAR), University of Colorado, Boulder, CO)*
- P-28 Determination of Dobson Spectral Characteristics, A New Method Robert Evans (NOAA Earth System Research Laboratory, Boulder, CO)
- P-29 The RHUBC-II Campaign: Best-guess Water Vapor Profiles and Their Impact on Far-infrared (IR) Spectroscopic Studies

J. Delamere (Atmospheric and Environmental Research, Inc., Lexington, MA)

- P-30 Newly Identified Region of Rapid, High Concentration Wintertime Ozone Production Russell C. Schnell (NOAA Earth System Research Laboratory, Boulder, CO)
- P-31 Tropospheric Ozone Laminar Structures and Vertical Correlation Lengths Michael J. Newchurch (Department of Atmospheric Science, Huntsville, AL)
- P-32 Investigating Signatures of Large-scale Advection and Microphysical Processes on Vertical Profiles of Water Vapor and Aerosols Near Mauna Loa and Mauna Kea
  - Adriana Bailey (Department of Atmospheric and Oceanic Sciences, University of Colorado, Boulder, CO)

P-33 Can Ozone Cross-sections Be Verified from the Ground-based Measurements? P. Kiedron (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

- P-34 Continuity and Reliability of Measurements Made at the Cape Verde Atmospheric Observatory (CVAO) *K.A. Read (National Centre for Atmospheric Science, University of York, York, United Kingdom)*
- P-35 Long Term Changes in the Upper Stratospheric Ozone at Syowa, Antarctica Irina Petropavlovskikh (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

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## • Halocarbons & Other Trace Species

- P-36 Trends of Long-lived Halocarbons, Nitrous Oxide and Sulfur Hexafluoride Geoff Dutton (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)
- P-37 Global Trends in Atmospheric SF<sub>6</sub> Brad Hall (NOAA Earth System Research Laboratory, Boulder, CO)
- P-38 Airborne Measurements of Trace Gases During HIPPO: Comparisons with Satellite Retrievals from ACE-FTS and Aura Instruments

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

- P-39 First Results from UCATS During the GloPac 2010 Mission Eric J. Hintsa (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)
- P-40 Inexpensive Stratospheric Profiling as a Basis of Stratospheric Transport Monitoring Program *Fred L. Moore (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)*

## • Aerosols & Atmospheric Radiation

- P-41 NOAA GMD Participation in the Eleventh International Pyrheliometer Comparison (IPC-XI) September 26 October 15 2011 World Radiation Center (WRC) Davos, Switzerland
  - Donald Nelson (NOAA Earth System Research Laboratory, Boulder, CO)
- P-42 A Proposed Solar Radiation and Aerosol Optical Depth Network for the Continental United States Joseph Michalsky (NOAA Earth System Research Laboratory, Boulder, CO)
- P-43 Evaluation of Broadband Arctic Radiation Measurements: Introducing Tiksi Observatory Nobuki Matsui (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)
- P-44 NOAA's Antarctic Ultraviolet (UV) Monitoring Program: It's More Than Just UV Patrick Disterhoft (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)
- P-45 Typical Barrow Albedos Coupled with Solar Irradiance (Io) Variability: A Sensitivity Study Gail P. Anderson (NOAA Earth System Research Laboratory and Air Force Geophysics Laboratory, Boulder, CO)
- P-46 International Filter Radiometer Comparison Results Gary Hodges (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)
- P-47 The Effect of Measured Ozone Profiles on Ultraviolet (UV) Photolysis Rate Coefficients in the Troposphere K. Lantz (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)
- P-48 Development, Testing and Performance of a New Filter-Based Light Absorption Instrument P.J. Sheridan (NOAA Earth System Research Laboratory, Boulder, CO)
- P-49 Analysis of High-altitude Aerosol from Asia to Mauna Loa
   Elisabeth Andrews (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)
- P-50 Seasonal Aerosol Distributions at Summit, Greenland: EC, OC, <sup>14</sup>C and Individual Particle Analysis George Klouda (Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD)
- P-51 Data Quality Explorations Using Duplicate Measurements N.P. Hyslop (Crocker Nuclear Laboratory, University of California at Davis, Davis, CA)
- P-52 Aerosol Properties and Direct Radiative Effects Measured at a Representative Southeastern U.S. Site W.B. Beuttell (Department of Physics and Astronomy, Appalachian State University, Boone, NC)

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## • Observatories, Global Cooperative Measurements, & Instrumentation

- P-53 Extending the Use of the UK Based Research Aircraft to Provide a Long-Term Observation Platform James Lee (National Centre for Atmospheric Science, University of York, York, United Kingdom)
- P-54 Using Surface Weather Observations to Reduce Atmospheric Transport Errors in Regional Inversions Elena Novakovskaia (Earth Networks, Inc., Germantown, MD)
- P-55 Science at Summit Station, Greenland: Long-Range Plan Katrine Gorham (CH2MHill Polar Services, Englewood, CO)
- P-56 Correlation Between Cloud Cover Trends and Surface Temperature Trends: A Comparison Between Barrow, Alaska and Tiksi, Russia

Ludmila Matrosova (Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO)

- P-57 Global Atmosphere Watch Activities in Kenya and Characteristics of Some of the Gas Species C. C. Okuku (Kenya Meteorological Department, Nairobi, Kenya)
- P-58 Sonic Anemometer Angle of Attack Errors John Kochendorfer (NOAA Atmospheric Turbulence and Diffusion Division, Oak Ridge, TN, USA)
- P-59 The World Meteorological Organization: The International Dimension of Weather, Water, and Climate Renee Tatusko (NOAA National Weather Service, Silver Spring, MD)

## Oxygen-18 of Atmospheric CO<sub>2</sub>: Decadal Trends and Climate Variability

## E.J. Zakem and J.W.C. White

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The stable oxygen isotope <sup>18</sup>O is unique to isotope ecology in that it links the hydrosphere to the carbon cycle. The two gross land biosphere fluxes, photosynthesis and ecosystem respiration, are the dominant influences on the  $\delta^{18}$ O of atmospheric CO<sub>2</sub> on decadal timescales. Since these fluxes also dominate the interannual variability of atmospheric CO<sub>2</sub> itself, analysis of atmospheric  $\delta^{18}$ O trends could provide useful insight into the terrestrial carbon cycle. The reasons for the interannual variability of atmospheric  $\delta^{18}$ O remain unclear, particularly because the mechanisms of the interannual variability of the terrestrial biosphere carbon flux are not fully understood. Data from numerous global sites shows a global decadal oscillation in  $\delta^{18}$ O, suggesting a climatological forcing. We compare trends in  $\delta^{18}$ O with climate records, examining correlations and proposing associated mechanisms. Significant correlation is found with the Niño indices. Significant anti-correlation is found with tropical precipitation and tropical humidity. Possible mechanisms include strong effects on  $\delta^{18}$ O by relative humidity, the <sup>18</sup>O of precipitation, and the magnitudes of global photosynthesis and ecosystem respiration. Simple modeling of the  $\delta^{18}$ O in atmospheric CO<sub>2</sub> supports the plausibility of these mechanisms, but does not result in the pattern observed in the data. Results suggest errors in the methods used to calculate isotopic values of the terrestrial biosphere CO<sub>2</sub> fluxes, since data trends show the likelihood of global climate influence on  $\delta^{18}$ O communicated through the terrestrial carbon cycle.



Figure 1. Standardized  $\delta^{18}$ O of atmospheric CO<sub>2</sub> data from multiple sites and the resulting assimilation-weighted global composite.

#### A Low-Maintenance Drying System for Ambient Air Greenhouse Gas Monitoring

L.R. Welp<sup>1</sup>, W. Paplawsky<sup>1</sup>, R.F. Keeling<sup>1</sup>, R.F. Weiss<sup>1</sup> and S. Heckman<sup>2</sup>

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In preparation for the routine deployment of the Earth Networks greenhouse gas monitoring network, we have designed and tested a simple method for drying ambient air to below 0.1% mole fraction  $H_2O$  using a Nafion model MD-050-72S-1 dryer. We tested the prototype inlet drying system on a Picarro model G2301 Cavity Ring-Down Spectroscoy  $CO_2/CH_4/H_2O$  analyzer. The analyzer measures water vapor mixing ratio at the same frequency as  $CO_2$  and  $CH_4$  and then corrects for the dilution and peak broadening effects on the  $CO_2$  and  $CH_4$  mixing ratios. This analyzer is remarkably stable and performs well on water vapor correction tests, but we believe there is an added benefit of reducing the dependence on the  $H_2O$  correction for long-term field measurement programs. Unlike  $CO_2$  and  $CH_4$  measurements, which can be calibrated in the field with compressed gas standards, the  $H_2O$  correction is not easily calibrated in the field. Substantially lowering the amount of  $H_2O$  in the sample can reduce uncertainties in the applied  $H_2O$  corrections by an order of magnitude or more, and reduce the need to verify the  $H_2O$  correction algorithm stability.

Our Nafion drying inlet system takes advantage of the extra capacity of the external Picarro analyzer pump to redirect 30% of the dry gas exiting the Nafion to the outer shell side of the dryer. This method has no consumables and does not appear to alter the CO<sub>2</sub> and CH<sub>4</sub> concentrations of the sample gas within measurement precision. We restrict sample flow through the G2301 analyzer to 70 cc/min to conserve calibration gases during routine deployment. It is difficult to humidify air without changing its dry-gas CO<sub>2</sub> mixing ratio slightly because of the propensity of CO<sub>2</sub> to interact with water adsorbed on tubing walls. For this reason, we compared our Nafion dryer system with a proven cold trap at -95°C. Dry air from a standard tank was passed through a humidifier in the wet-gas test (or bypassed in the dry-gas test) and then alternately directed through the Nafion or cold trap at 15-min intervals. Differences between the Nafion dryer and cold trap in the dry-gas and wet-gas tests were less than the targeted precision of the measurements. Systematic differences between the drying methods were at the level of 0.01 ppm in CO<sub>2</sub> and 0.007 ppb in CH<sub>4</sub> for the wet-gas test (Fig 1) and 0.01 ppm in CO<sub>2</sub> and 0.04 ppb in CH<sub>4</sub> for the drygas test.



**Figure 1.** Time series of wet-gas experiment showing 1-min running means of the analyzer's 1-sec sampling. Tank air was humidified to 2.2%  $H_2O$  (mole fraction) and either passed through the cold trap (blue) or Nafion (red) in 15- min switching intervals. The first 2 min and last 1 min of each 15-min interval were excluded from the analysis because of transient artifacts. The moisture content of the Nafion-dried stream increased from 0.004% to 0.016% over the course of the experiment.  $CO_2$  and  $CH_4$  have been corrected for water vapor using factory default settings on the analyzer. Blue and red horizontal lines are means of cold trap intervals and Nafion intervals respectively over the entire experiment. The cause of the small drift in  $CH_4$  is unknown, but is subtracted in these tests.

#### Comparison of Co-Located Air Samples at Mauna Loa Observatory and CO, Observations at Mt. Fuji

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 <sup>4</sup>Institute of Arctic and Alpine Research (INSTAAR), University of Colorado, Boulder, CO 80309
 <sup>5</sup>A.S.L. & Associates, Helena, MT 59601

NIES CGER and NOAA ESRL started a comparison of co-located air samples from Mauna Loa Observatory (MLO: 19.54°N, 155.58°W, 3397 m.a.s.l) in May, 2010. To complement low-frequency measurement comparisons such as the cylinder-based World Meteorologial Organization (WMO) round-robin and flask-based projects [e.g. "sausage"], it was recommended at the WMO Expert Meeting in 2009 that more laboratories participate in more high-frequency real-air measurement comparisons. ESRL and CGER cooperatively developed and installed a sampling system on an existing intake line at MLO where both laboratories' flasks are filled from the same air stream at almost the same time. The CGER sampling part is the same as those used at other NIES sampling sites, and it was embedded in the ESRL sampling system. Samples are collected every week and analyzed data are updated every month. Although periodic re-calibration of working standard gases has not been done at CGER, due to the earthquakes in March 2011, so far most data agree relatively well for  $CO_2$ ,  $CH_4$  and  $\delta^{18}O-CO_2$ . Continued comparison is required to determine analytical tendencies at each laboratory (e.g. when standard gases are changed) and to quantify offsets because different standard scales are used for  $H_2$  and isotopic ratios. Frequent long-term comparisons of atmospheric measurements provide useful information to improve and maintain high quality observations and analysis.

CGER also has started CO<sub>2</sub> observation on Mt. Fuji ( $35.21^{\circ}$ N,  $138.43^{\circ}$ E, 3776 m.a.s.l,) with a battery-powered automatic system. CO<sub>2</sub> at Mt. Fuji compared to MLO flask data shows both similarities and differences. Mt. Fuji CO<sub>2</sub> observations can capture both global and regional CO<sub>2</sub> signals over Japan.







**Figure 2.** Mt. Fuji CO<sub>2</sub> (measured 1/day at 23 (JST)) compared to MLO CGER flask CO<sub>2</sub> data.

#### **Results from the North American Carbon Program Midcontinent Intensive Regional Experiment**

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The Midcontinent Intensive campaign presents a unique testbed for examining the ability of atmospheric inversions to constrain regional carbon balance and its spatial structure. We present here the high resolution inversion developed for the campaign, at 20km resolution from June to December 2007, and comparison of this inversion to the agricultural and forest inventories conducted in the region. Atmospheric transport was simulated with the non-hydrostatic atmospheric model WRF-Chem at 10km resolution, coupled to a backward Lagrangian Particle Dispersion model. Two different prior fluxes were used to evaluate the impact of the prior flux structure on the final flux estimate, one from the SibCrop model at 10km resolution, and the second from the CarbonTracker inverse system at one degree. The eight observation sites deployed in the area were used to constrain the  $CO_2$  fluxes at a weekly time step. We evaluated the impact of each site on the final estimates and tested different configurations (e.g. selecting sites in key areas or simply considering a sparser network). The study compares the observed impact on the final fluxes to the theoretical error reduction, and discusses the needs for future regional campaigns to assess the inverse carbon balance and its spatial structure at the mesoscale.



**Figure 1.** Posterior  $CO_2$  fluxes in TgC.deg-2 from June to December 2007, over the Mid-Continent Intensive region using prior fluxes from the SiBcrop vegetation model.

# Northern Hemisphere Trends in Carbon Monoxide: Effects of Changes in Anthropogenic Emissions and Biomass Burning

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The magnitude and direction of changes in tropospheric carbon monoxide (CO) during the past century are still debated, however it is most likely there have been extended periods of increase and decrease, overlaid with much shorter-lived changes. Carbon monoxide has been measured in air samples collected by the NOAA Cooperative Air Sampling Network since 1988. The results provide a spatial and temporal picture of CO in the marine boundary layer and suggest a long-term decrease in the Northern Hemisphere (NH). We previously reported a decline in CO through the 1990s with the greatest changes occurring between 30°-90°N. Here we examine how changes in Fossil Fuel (FF) and Biomass Burning (BB) emissions have impacted CO in the NH boundary layer during 2000-2008. We compare the changes in measured CO mixing ratios to variations in emissions developed for MOZART, a 3-D CTM. The major sources of CO in the NH are roughly evenly distributed between fossil fuel combustion (FF), oxidation of methane and non-CH4 hydrocarbons, and biomass burning (BB). Its primary sink is the Hydroxyl Radicals (OH). Only BB exhibits large inter-annual variation. A strong decrease in anthropogenic emissions from Annex 1 countries in the early 1990s contributed to a significant decline in CO. Continuing declines in their emissions during the late 1990s and 2000s added to the downward trend despite increasing emissions from developing nations. The NH decrease in background CO during 1990-2005 (i.e. change determined without the effects of the extreme NH fires of 1998 and 2003) compares well with FF emission inventories.



**Figure 1.** The LHS panel shows measured CO mixing ratios at Guam and the time series produced by MOZART. The results are presented as the smoothed fit to the data. The panel on the RHS shows the contribution of 5 major sources to CO at Guam.

## Active Sampling AirCore (ASAC) for Regional Trace Gas Sampling Surveys

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The NOAA ESRL GMD Carbon Cycle and Greenhouse Gases Group has developed and tested a prototype trace gas sampling system that utilizes a SulfiNertTM-treated (Restek Inc.) stainless steel tube (AirCore) to store continuously sampled air during horizontal surveys conducted by small Unmanned Aircraft Systems (UAS) such as the Scan Eagle. A trace gas analyzer such as a multispecies Cavity Ring Down Spectroscopic gas analyzer is used post flight to analyze the stored gas in the AirCore. The ASAC for UAS deployment (Figure 1) will have a total weight of approximately 6 kg. The 4.1kg AirCore tubing is the largest component in the ASAC system. The tubing outside diameter (1/8"), length (213 m), and wall thickness (0.01"), were chosen to maximize sampling resolution while remaining within the weight specifications for a Scan Eagle payload. Other hardware components in the system include a pump, a filter, a pressure-control system, a gas dryer, a mass-flow control device (a critical orifice), a data acquisition board, and a data logging system. We estimate the weight of these components to be close to 1.9 kg. We expect to maintain the gas pressure inside the AirCore tubing at two atmospheres to maximize total sample volume while sampling at 10 standard cubic centimeters per minute. Accounting for diffusive mixing of the sample during flight and post-flight analysis, approximately 240 discrete atmospheric samples over a 4-hour flight can be resolved. Assuming a 60-knot speed for the UAS, a distance of approximately 430 km will be traversed during a 4-hour deployment, providing an average sampling resolution of 1.7 km. Here we describe this sampling system and present results from both flight and driving tests.





#### INFLUX: Tower-Based Greenhouse Gas Measurements and Flux Estimates in an Urban Environment

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Independent verification of anthropogenic greenhouse gas emissions is an emerging need as legislation to regulate greenhouse gas emissions becomes increasingly likely. As part of the INFLUX Project,  $CO_2$ ,  $CH_4$  and CO mixing ratios are measured using wavelength-scanned cavity ringdown spectroscopy (Picarro, Inc.) at two towers surrounding Indianapolis, IN, with expansion underway to a network of twelve sensors, including <sup>14</sup>CO<sub>2</sub> flask sampling. Sampling was initiated in October of 2010, and is planned to continue through 2012. We plan to use these data to quantify spatial patterns in greenhouse gas fluxes within and around the urban center at high temporal resolution. We will present preliminary measurements from INFLUX towers as well as simulations of atmospheric greenhouse gas concentrations in the region. We will outline the analytic system being constructed to solve for urban emissions.



**Figure 1.**  $CO_2$  mixing ratios measured at the "Rural" site (top panel) and at the "Urban" site (bottom panel) on 8 November 2010. The wind direction was such that the urban plume was measured at the downwind "Urban" site.

**Figure 2.** Modeled  $CO_2$  mixing ratios corresponding to those shown in Figure 1. Although there is more stratification shown at the "Rural" site than was measured, the timing of the mixing and the overall shape of the diurnal cycle agree well with the measurements.

#### Quasi-Continuous Methane Measurements at Cherskii, Russia

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Atmospheric methane (CH<sub>4</sub>) mixing ratio has been measured quasi-continuously at Cherskii, Russia (68°30'N, 161°32'E) since September 2008. Samples are taken approximately every 5 minutes rotating between three different tower levels (2.6 m, 16.2 m, and 34.4 m). Measurements are made using an optical analyzer that uses off-axis, integrated cavity output spectroscopy, a robust measurement technique for remote sites. The uncertainty at 68% confidence limit is  $\pm$  2.4 ppb. The average seasonal cycle peak-to-peak amplitude at Cherskii is 33.4 ppb with a minimum in late spring and a maximum in late winter. A significant diurnal cycle is not observed throughout the year. Figure 1 shows CH<sub>4</sub> data from Cherskii plotted with a marine boundary layer reference for 72.8° N and ~ weekly discreet samples from five arctic sites. CH<sub>4</sub> data at Cherskii are highly variable with large enhancements especially after periods of low wind speed in the summer, when wetland emissions are greatest.



**Figure 1.**  $CH_4$  mole fraction (ppb = nmol mol<sup>-1</sup>) from Cherskii, Russia (CHS) plotted with the marine boundary layer reference (MBL reference) for 72.8° N and discreet samples from Summit, Greenland (SUM); Alert, Canada (ALT); Pallas-Sammaltunturi, Finland (PAL); Ny-Ålesund, Svalbard, Norway and Sweden (ZEP), and Barrow, Alaska, United States (BRW).

# How Well Do We Know $\delta^{13}$ C of Atmospheric CO<sub>2</sub>? Estimates of Uncertainty, Inter-Laboratory Comparisons, and Calibrations to Carbonate Primary Standards

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Measurements of stable isotopes of carbon dioxide are very useful for partitioning fluxes of  $CO_2$  between the terrestrial biosphere and oceans. However, in models that determine these fluxes, small changes in isotopic values have large effects. Therefore the utility of the models depends on robust quality assurance/quality control (QAQC) of isotopic data. Measurement uncertainty must be reduced as much as possible, a normal criterion for isotopic measurements. In addition, a consistent scale, traceable over decades, must be established and maintained. This is a task that is not commonly addressed by the isotopic community. The Stable Isotope Lab at University of Colorado/INSTAAR has been measuring isotope of  $CO_2$  from the NOAA Carbon Cycle Group's Cooperative Global Air Sampling Network since 1990. Here we present results of ongoing QAQC, including evidence to show the consistency of our scale over time. We also present a method for dynamic calculation of the uncertainty of our flask measurements, reflecting instrument performance and yielding varying uncertainties over time.

Comparison experiments with other stable isotope laboratories suggest that our  $\delta^{13}$ C scale is offset by approximately 0.03 per mil. Overall there is far less agreement in  $\delta^{18}$ O scales. Much of the discrepancy between laboratories is due to the inadequate calibration of CO<sub>2</sub>-in-air to carbonates, the international primary standards. We have designated a mass spectrometer for calibrations, and its customized extraction system enables direct comparison of CO<sub>2</sub>-in-air standards to CO<sub>2</sub> evolved *in situ* from carbonates and CO<sub>2</sub> equilibrations with water. Here we present results which prove the capability of the combined extraction systems to compare CO<sub>2</sub> from different sources. This new capability should enable us to resolve our offsets.



**Figure 1.** The top panel shows  $\delta^{13}$ C of CO<sub>2</sub> at Mauna Loa, plotted by sample date, with error bars reflecting the measurement uncertainty. Bottom panel, the  $\delta^{13}$ C of the "trap" tank run on the corresponding day, with error bars reflecting the standard deviation of three replicates. The trap tank allows us to follow instrument performance and confirm the consistency of our isotopic scale.

# Identification of Urban Zones Related to Carbon Emission Levels Using Moderate Resolution Nighttime Satellite Imagery From the International Space Station: Preliminary Results

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Fossil fuel CO<sub>2</sub> emission sources can be broadly divided into point sources (e.g. power plants) and distributed sources (vehicles, hot water heaters, furnaces, cooking, etc.). The spatial and temporal patterns of distributed carbon emissions cannot be measured from space due to atmospheric transport and the coarse spatial resolution at which atmospheric CO<sub>2</sub> can be measured from space. We are investigating the use of moderate resolution satellite observed nighttime lights as a proxy for the distributed component of fossil fuel CO<sub>2</sub> emissions. We analyzed 25 meter resolution nighttime color camera imagery that was acquired at Los Angeles, California from the International Space Station relative to county zoning maps. The preliminary results indicate that building in commercial and industrial zones have substantially brighter lighting than residential zones. The results indicate that it would be feasible to make high spatial resolution models of distributed CO<sub>2</sub> emissions within urban centers based on brightness levels of nocturnal lighting observed at moderate spatial resolution.



**Figure 1.** Twenty-five meter resolution color camera image of Los Angeles collected from the International Space Station on November 30, 2010.

**Figure 2.** Figure 1 image classified into four zones related to fossil fuel carbon emission levels: red = image margin, blue = no lights detection (very low carbon emissions), green = residential areas = low carbon emissions, magenta = commercial, industrial, and major streets/roads (high carbon emissions).
#### Mid-Stratospheric Measurements of CO<sub>2</sub>, CH<sub>4</sub>, and CO Using AirCore

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AirCore, a long tube descending from a high altitude with one end open and the other closed, has been demonstrated to be a reliable, cost-effective sampling system for CO<sub>2</sub> and CH<sub>4</sub> measurements. Previous studies show that vertical profiles from the ground level up to ~ 20 km (~ 40 mbar) can be achieved during a balloon flight. The ceiling of the profile is restricted mainly by the diffusion of air in the AirCore and the resolution of the analyzer used for the analysis. Here air with an extremely high CO mixing ratio (~ 10 ppm) has been employed as the initial filling air in the AirCore. This high CO filling gas is used to label the mixing process between the sampling and filling air at the top of the profile, thus, providing the ability to retrieve full profiles for CO<sub>2</sub> and CH<sub>4</sub> up to the balloon's ceiling height of ~ 30 km (~ 11 mbar). Stratospheric measurements of CO lack agreement among previous studies, (i.e. cryogenic sampling, in situ measurements, and remote sensing) due to difficulties that are inherent to the various techniques, and possibly due to latitudinal and seasonal variations that could not be represented by the available sparse observations. Efforts have been made to accomplish an accurate profiling of stratospheric CO using the AirCore, dealing mainly with the potential interactions of CO and high O<sub>2</sub> in the stratosphere. Stratospheric profiles of CO<sub>2</sub>, CH<sub>4</sub>, and CO can not only be used to validate total column measurements by remote sensing techniques, such as Fourier Transform Spectometer and satellite, and would be extremely valuable in characterizing stratospheric chemical processes, especially when such profiles can be made reliable and cheap enough for regular deployments in the field.



**Figure 1.** The AirCore balloon flight on March 12, 2011, for  $CO_2$  and  $CH_4$ . The red curves are the derived profiles based on the mixing processes labeled by a filling air with ~10 ppm CO, and the grey curves are the original parts of the profiles that are affected by the filling air.

#### Flask Versus In Situ Results at Tall Tower Sites

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Seven sites in the NOAA ESRL GMD Tall Tower network are equipped with both *in situ* systems for measuring CO and CO<sub>2</sub> and Programmable Flask Packages (PFP). Typically, daily flask pairs are sampled from the highest *in situ* level at the tower, and capture a snapshot of the planetary boundary layer during the most well-mixed time of the day. The daily samples are analyzed for fifty or more species of atmospheric trace gases and are used as an independent measure of comparison for CO and CO<sub>2</sub>. Paired samples provide a measure of repeatability for PFP measurements that includes sampling precision, analysis precision and atmospheric variability. PFP and *in situ* CO and CO<sub>2</sub> data from tower sites are included in the automated web-based Inter-Comparison Project, which is updated daily. Recent comparisons of flask versus *in situ* data have identified leaks in sample tubing and compressor packages, prompting investigation and timely repair. The flask measurements can also provide insight into pollution plumes and other local influences surrounding the tower. Variations between flask and *in situ* agreement differ from site to site, and seasonally. Analysis of the flask versus *in situ* statistics, as well as time series comparisons for each tower will be presented. Constraints in measurements, sampling time, and other problematic factors will also be explored. A brief overview of special projects and future instrument development will be presented.



**Figure 1.** Current 2011 flask (red) and *in situ* (blue) measurements from the Boulder Atmospheric Observatory (BAO) tower in Erie, CO. On the second graph, the running mean of the flask minus *in situ* CO<sub>2</sub> differences is indicated in red, while differences for individual samples are shown in green.

### A Multi-Year Record of Airborne Continuous CO, in the U.S. Southern Great Plains

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We report on three years of airborne measurements of continuous atmospheric  $CO_2$  concentrations over the Atmospheric Radiation Measurement Program (ARM) Climate Research Facility (ACRF) in the U.S. Southern Great Plains. These continuous measurements are collected weekly from a small aircraft (Cessna 206) on a series of horizontal legs ranging from 17,500 feet down to 1,500 feet above sea level. The continuous  $CO_2$  observations are measured using a  $CO_2$  analyzer built by Atmospheric Observing System Inc., based in Boulder, Colorado. The analyzer has non-imaging optics and negligible sensitivity to motion of platform. The NDIR Analyzer is the core element of the system. Accuracy, including bias, is approximately 0.1 ppm of  $CO_2$  Dry Mole Fraction at 1 Hz. Each flight lasts between 2.5 and 3 hours, yielding about 10,000  $CO_2$  measurements per flight. Since November 2007, more than 150 continuous  $CO_2$  vertical profiles have been collected, along with NOAA ESRL 12-flask (carbon cycle gases and isotopes) packages for validation. Comparison between the continuous and flask  $CO_2$  measurements indicates a difference of no larger than 0.2 ppm.



**Figure 1.** Weekly average continuous  $CO_2$  concentrations collected from 2008 through 2010 over the ACRF in the U.S. Southern Great Plains.

#### First Deployment of a New Mobile Laboratory for Greenhouse Gas Attribution Studies

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Anthropogenic sources of carbon dioxide  $(CO_3)$  represent a significant portion of the global carbon budget, but partitioning CO<sub>2</sub> measurements into their biogenic and anthropogenic sources has been difficult using only measurements of CO<sub>2</sub> abundances and those of a small number of additional tracers. An intensive field campaign was conducted in Fall 2010 at the Atmospheric Radiation Measurement-Southern Great Plains (ARM-SGP) Central facility near Lamont, OK to measure CO<sub>2</sub> and several tracers for its sources using a new mobile laboratory. Two trucks carrying over fifteen instruments for gases and particles were deployed along with a gas-calibration system. Air was drawn into both trucks from a 10-m tall mast. All measurements were made either from a common inlet or closely located inlets. Instruments were selected to provide measurements of tracers of both biogenic and anthropogenic sources. High-frequency measurements of abundances of CO, and its stable isotopologues (<sup>13</sup>CO<sub>2</sub> and C<sup>18</sup>OO) were made simultaneously with measurements of CO, SO<sub>2</sub>, NO<sub>3</sub>, O<sub>3</sub>, CH<sub>4</sub>, water vapor isotopologues (H<sub>2</sub>O, HDO, and H<sub>2</sub><sup>18</sup>O), volatile organic compounds, black and organic carbon aerosol, and particle count. Automated flask samplers collected whole air samples for off-line <sup>14</sup>C analysis using accelerator mass spectrometry. Redundancy between CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O measurements provided a valuable crosscheck for the calibrations and the measurements. Good agreement between CO, measurements from four different instruments was attained following careful post-processing and calibrations. Similarly good agreement was demonstrated between four instruments that measured water vapor and two instruments that measured CH<sub>4</sub>. The agricultural region that surrounds the ARM-SGP site had experienced little rainfall prior to the campaign, and land cover and crop growth were minimal during the period in which measurements were made (3 October -9 November 2010). Correlations between various tracers and CO<sub>2</sub> provide insight into the different sources, including the anthropogenic component, which includes biomass and fossil fuel combustion.



**Figure 1.** Time series of  $\delta^{13}$ C -CO<sub>2</sub>,  $\Delta^{14}$ C-CO<sub>2</sub>,  $\delta$ D-H<sub>2</sub>O, H<sub>2</sub>O, and CO measured during the campaign. High  $\delta^{13}$ C and  $\Delta^{14}$ C are associated with low CO,  $\delta$ D -H<sub>2</sub>O, and H<sub>2</sub>O and air from high altitudes. Low  $\delta^{13}$ C and  $\Delta^{14}$ C and high CO,  $\delta$ D-H<sub>2</sub>O, and H<sub>2</sub>O are associated with air from low altitudes within the past few days.

## Development of High-Precision Gas Analyzers for Measurements of N,O, CO, CH<sub>4</sub>, CO,, and H,O

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We report the continued development of two continuous-flow gas analyzers, based on cavity enhanced laser absorption spectroscopy, which measure important atmospheric constituents in real time, with high precision and accuracy, and over a wide range of mixing ratios. One instrument ( $N_2O+CO$  Analyzer) uses a tunable continuous-wave quantum cascade laser operating in the wavelength region near 4.56 microns to record measurements of carbon monoxide, nitrous oxide and water vapor in ambient air. The typical precision for continuous measurements at typical ambient levels of either CO or  $N_2O$  is about 0.1 ppbv (1-sigma, 10-second measurement time). The instrument also reports water vapor mixing ratio measurements simultaneously and employs those measurements to determine the effects due to dilution and line broadening to allow accurate determination of mixing ratios (CO,  $N_2O$ ) on a dry basis.

The other instrument uses two tunable continuous-wave near-infrared telecommunications-grade diode lasers operating in the wavelength regions near 1.6 and 1.65 microns to record measurements of carbon dioxide and methane in ambient air. This instrument employs an internal thermal control system to allow extremely low drift despite changes in ambient temperatures over the range from 0 to 40 degrees C. The instrument also reports water vapor mixing ratio measurements simultaneously and employs those measurements to accurately quantify the effects due to dilution and line broadening and provide accurate determination of the measured mixing ratios ( $CO_2$ ,  $CH_4$ ) on a dry basis. Both of these instruments require relatively low-power (150-250 watts) and no liquid nitrogen thus allowing for easy measurements in the field.



**Figure 1.** Thermally-stabilized gas analyzer provides simultaneous measurements of methane, carbon dioxide and water vapor.

# An Approach for Estimating Multi-Species Boundary Values for Air Entering the North American Domain

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Studies of North American greenhouse and pollutant gas budgets require knowledge of the upwind boundary condition. For  $CO_2$ , some studies have taken boundary values from CarbonTracker. However, no comparable product is available for other gases such as  $CH_4$ ,  $N_2O$  or CO. Furthermore, CarbonTracker residuals show strong seasonally-varying bias for certain Pacific marine boundary layer (e.g. Cold Bay and Shemya Island) and aircraft (e.g. Trinidad Head, Estevan Point, and Texas Gulf Coast) sites. Biased boundary values can lead to substantial systematic errors in inferred continental fluxes.

We have developed a method for creating empirical boundary value curtains for  $CO_2$ ,  $N_2O$ ,  $CH_4$  and CO that represent the time-, latitude- and height-variation of air entering the continent from the West. The product has 1km resolution in the vertical from the surface to 8km. The method assumes that the vertical gradient with respect to the Marine Boundary Layer (MBL) reference varies with season but is constant from year to year. This assumption is not valid for all species (e.g. certain refrigerants with rapidly changing abundance), but the method does seem to capture most of the observed variability for  $CO_2$ ,  $N_2O$ ,  $CH_4$  and CO. We also provide corresponding seasonal, latitudinal, and height-dependent error estimates for the product.

We will compare the empirical  $CO_2$  boundary values with corresponding estimates from CarbonTracker for selected sampling sites in North America. We will also present residuals for MBL and aircraft sites for all gases. Finally, we will use trajectories and data from Atlantic sites to examine to what extent it is valid to use only data from the Pacific to estimate the boundary condition for North America.



**Figure 1.** Afternoon mean carbon monoxide data collected at the Argyle, Maine Tall Tower (AMT) site (green; red=off scale) along with boundary values from our new empirical boundary product selected according to the latitude at the end of a 10-day back trajectory (black). The blue line is a smoothed representation of the AMT afternoon values.

#### Inverting <sup>13</sup>CO, for Terrestrial Carbon Fractionation in North America

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A variety of methods exist for constraining chemical fluxes at the earth's surface. Inverse modeling is often used to estimate regional-scale fluxes of the greenhouse gas carbon dioxide (CO<sub>2</sub>), by using atmospheric observations and particle transport models to optimize prior flux estimates. Fluxes of the rare stable carbon isotope in CO<sub>2</sub>, <sup>13</sup>C, have not traditionally been calculated with inverse models. Historically, <sup>13</sup>C has been used to partition CO<sub>2</sub> fluxes into land and ocean components, because major fluxes of this gas (fossil fuel, ocean, and land) impose distinctive and predictable fractionation patterns upon the stable isotope ratio. As measurement density improves, <sup>13</sup>C has the potential for an important new role in carbon cycle research: to illuminate mechanisms driving terrestrial biosphere exchange variability. Calculated time series of the global land flux, disequilibrium flux, and terrestrial discrimination from 1991 through 2008 that are consistent with bottom up net ocean fluxes suggest high interannual variability in terrestrial disequilibrium flux. The primary contributors to this variability likely include discrimination due to plant stomatal opening and the relative contributions of  $C_3$  and  $C_4$  vegetation to net ecosystem exchange. Discerning <sup>13</sup>CO<sub>2</sub> flux magnitude and variability on smaller space and time scales could therefore inform our understanding of the dynamics that exist between carbon cycling and environmental/climatic variability, as well as the impacts of biofuels on the <sup>13</sup>C budget. We determine "optimal" estimates of CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> surface fluxes across the region encompassing 10-80°N and 145-25°W. We use the Lagrangian particle dispersion model FLEXPART to generate partial derivative matrices or "influence functions", which relate fluxes in each 1x1 degree grid cell in the region of interest to concentrations at several North American NOAA ESRL Global Monitoring Division tower sites. By comparing modeled with observed <sup>13</sup>CO<sub>2</sub> concentrations at tower sites, we can then optimize our prior flux estimates. We will present comparisons between our simulated values and those observed at the monitoring sites, and we will present the preliminary results of our inversion.



Comparison of Modeled vs. Observed  $\delta^{13}$ C at a NOAA/ESRL tall tower in Park Falls, Wisconsin (LEF)

Figure 1. Comparison of Modeled vs Observed <sup>13</sup>C at a NOAA ESRL tall tower in Park Falls, WI.

## The New Picarro G2311-f Methane, Carbon Dioxide, and Water Vapor Analyzer For Micrometeorological Applications

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Picarro has developed a new analyzer, the G2311-f, a high speed Cavity Ring-Down Spectroscopy (CRDS) based analyzer for measuring carbon dioxide (CO<sub>2</sub>), methane (CH<sub>2</sub>) and water (H<sub>2</sub>O) at 10 Hz with both high precision and high accuracy. The new analyzer includes new capabilities and improves upon the performance demonstrated in the previous version, the G2301-f, launched in 2010. In an effort to prove out the viability of the G2301-*f* for micrometeorological applications, a number of land- and sea-based tests have been performed by research teams from NOAA, Oregon State University, and Columbia University using the G2301-f, including eddy covariance tests on land and at sea, and sea water head space equilibration tests in the Gulf of Mexico. As a result of this validation effort, Picarro has developed a new analyzer, the G2311-f, which is capable of measuring carbon dioxide to a precision (one standard deviation) of 200 parts-per-billion (ppbv), methane to a precision of 2 ppbv, and water vapor to a precision of 20 ppm. Concentration measurements are taken at a 30-Hz rate with the result that all three species are measured at a 10-Hz rate with extremely high accuracy. Water vapor is measured with sufficient precision for direct measurement of the latent heat flux as well as dilution and spectroscopic correction for carbon dioxide and methane. In addition, the data stream from a 3D sonic anemometer has been time-synched and integrated into the instrument graphical user interface and data logging software, and the environmental temperature range has been expanded to allow measurements over an even broader range of environmental conditions. This flexible device is capable of simultaneously measuring fluxes of carbon dioxide, methane, and latent heat using the eddy-covariance technique, but it can also be employed with other techniques that require the high accuracy and precision inherent to the time-based CRDS method, including the gradient flux method, relaxed eddy-covariance, headspace equilibration chambers, leaf / soil chambers, long-term tall-tower measurements, mobile plume mapping, and much more. We report the results of the validation test of the G2301-f and on the development of the new G2311-f instrument.

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**Figure 1.**  $CH_4$  and  $H_2O$  co-spectra of the Picarro Model 2301-*f* and  $CO_2$  and  $H_2O$  co-spectra of the Licor Li-7500. Data taken at the Mary's River site.

#### **2011 Tower Network Overview**

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Partnerships with external collaborators have enabled the NOAA ESRL GMD Tower network to expand from three sites in 2006 to eleven sites in 2010. Nine sites are equipped with *in situ* systems for continuous CO<sub>2</sub> and CO measurements. Collaborations have enabled continuous methane measurements at two sites. Programmable Flask Package samples are collected daily at ten sites. Expanding the network and upgrading the equipment has required a preventative maintenance schedule, routine testing procedures, hardware upgrades, error-checking software, and a web based utility for viewing processed data. These upgrades have improved data continuity and quality. A summary of the tower network and its measurement history, species data, statistics, maintenance, and notable towers instrumentation repairs are presented, including lessons learned.



Figure 1. The tall tower network May 2010 – Present (May 2011).

## The Atmospheric Demonstration Experiment of the Integrated Carbon Observation System (ICOS)

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ICOS is a new European research infrastructure for quantifying and understanding the greenhouse gas balance of the European continent and adjacent regions. It consists of a harmonized and standardized network of long-term observation sites coordinated through a set of central facilities including 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 greenhouse gas emissions.

ICOS is currently in its preparatory phase (ICOS PP). In conclusion of the ICOS PP, a 6-month demonstration experiment starts in April 2011 in order to demonstrate the feasibility of the ICOS infrastructure and its capability to properly manage a network of standardized instruments, with centralized data processing performed in near real time. For that purpose, the atmospheric demonstration experiment relies on a small demo network made of 4 Atmospheric Stations (AS) and central facilities (ATC and CAL). Moreover the demonstration experiment will allow us to validate the ICOS AS design pattern before the deployment of new ICOS AS within the infrastructure network during the construction phase. Indeed, a prototype of the ICOS AS pattern, designed by the LSCE and CEA with the assessment of the ICOS community, is installed in the atmospheric demo network at the OPE site (ANDRA, France).

The poster presents the Atmospheric Demo Experiment and focus on the design pattern of the ICOS Atmospheric Station.



Figure 1. ICOS Demo Atmospheric Network.

## Tropospheric Ozone Layer Attributes Quantified by Continuous Wavelet Transform (CWT) and Gradient Analysis

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Ozone laminar structures occur frequently in the troposphere. The formation of ozone laminar structures is believed to be due to the complex dynamical and chemical processes in the atmosphere. However, regional chemical models have difficulty reproducing the observed laminar structure. We developed two independent methods, the CWT method and the gradient method, to study the properties and climatology of ozone laminar structure based on data from ozonesonde and Ozone Differential Absorption Lidar (DIAL) observations. The DIAL profiles show high spatial and temporal variations of tropospheric ozone laminae due to complex dynamical and chemical processes, which suggest to us that the Lidar network would capture the characteristics of the ozone laminar structure.



**Figure 1.** Evolution of a Planetary Boundary Layer ozone enhancement event observed by lidar and sondes during an air stagnation event. High surface ozone (squares at zero altitude) was also observed by the EPA Station in Huntsville, AL. Large differences between ozone at the surface and ozone at higher altitudes often exist, especially during nighttime.

## Modeling the Impact of Late 20th Century Stratospheric Ozone Changes: Sensitivity to Different Ozone Forcing Data Sets

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Several climate model studies have addressed the role that 20th Century Antarctic ozone depletion has played in observed changes in both stratospheric and tropospheric climate: Polvani et al. (2011) have even suggested that the ozone depletion was the dominant driver of 20th Century climate changes in the Southern Hemisphere. However, the great majority of climate model studies have used either the ozone data set of Randel and Wu (2007) or the related one of Cionni et al. (2011), which do not capture the depth of the ozone hole. This issue has recently been addressed by developing a new ozone data set, drawing on the extensive database of observations collated by Hassler et al. (2009): the Binary DataBase of Profiles (BDBP). The BDBP data were used to develop a comprehensive statistical model to produce a spatially and temporally continuous data set suitable for global climate models.

We will show a series of climate model simulations to illustrate the sensitivity of the modeled ozone-hole signal to the ozone data set employed, comparing the Randel and Wu, Cionni et al., and BDBP-based data. Results will be presented in the context of existing studies to determine the importance of the climate model ozone data set for studying the impact of 20th Century ozone depletion.



**Figure 1.** Latitude-time plots of column (250-5 hPa) anomalies for the (a) Randel and Wu (2007), (b) Cionni et al. (2011) and (c) BDBP-based climate model ozone data sets, in Dobson Units (DU). Anomalies are computed relative to the 1979-2005 climatology for each data set.

#### Stratospheric Ozone Interannual Variability Measured by Lidar at Mauna Loa and Table Mountain

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Two Jet Propulsion Laboratory lidars, one at the Mauna Loa Observatory, Hawaii (MLO, 19.5°N, 155.6°W) and one at the Table Mountain Facility (TMF, California (34.5°N, 117.7°W), have been measuring vertical profiles of stratospheric ozone routinely since the early 1990's. Multi-linear regression analysis was performed on the deseasonalized monthly mean lidar ozone time series (from -2 ppmv to 4 ppmv) for each 1 km-altitude bin between 18 and 46 km from January 1995 to December 2010 (a period of low volcanic aerosol loading). We have selected interannual and annual components representing the 11-year solar cycle (SC), El Nino Southern Oscillation (ENSO), the Quasi-Biennial Oscillation (QBO), the Eliassen-Palm flux (EPf), horizontal and vertical transport, and a linear trend. Noise sensitivity on the regression model has been tested. Increasing the noise fraction on the original time series gives a limit beyond which the model becomes purely mathematical. For each station, proxies were chosen by a backward elimination method, and eventually selected if the percentage of variance exceed 5%. For both stations, the explained variances from the regression fit are between 40% and 80%. At MLO, a nearly-tropical site, the analysis revealed the dominance of the QBO (-1 ppmv to 1 ppmv), a strong positive springtime signature of the solar cycle and ENSO and a strong negative wintertime signature of the horizontal transport (~0.2 ppmv/indice). Linear trends obtained are between -0.2% and 0.5% per decade. The explained variance for the TMF time-series revealed a mixed influence of each proxy on each side of the ozone maximum altitude with a strong seasonal dependence, typical of mid-latitudes. The use of a mid-latitude Ozone Depleting Gas Index for TMF instead of the classical trend proxy increased the explained variance by 15% above 30 km and 9% below while reducing statistical error and increasing trends. Statistically significant maxima (~0.2 ppmv/indices) were found at 27 km in the annual response to SC, Ozone Depleting Gas Index (ODGI), ENSO and at 37 km for EPf. Higher maxima were found at 42 km in the annual response to Solar Cycle. QBO response is out-of-phase compared to MLOs. Trends are negative below 25 km (down to -0.5%) and positive above, reaching 1.5% with a linear proxy and 4% with the ODGI index at 42 km



**Figure 1.** LIDAR ozone response time series (ppmv) versus altitude. Left: response to QBO at MLO. Right: response to ODGI at TMF.

#### Stratospheric Water Vapor Trends Over Boulder, Colorado: Analysis of the 30-Year Boulder Record

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Trend analyses are presented for 30 years (1980-2010) of balloon-borne stratospheric water vapor measurements over Boulder, Colorado. The data record is broken into four multiple-year periods of water vapor trends, including two that span the well-examined but unattributed 1980-2000 period of stratospheric water vapor growth. Trends are determined for five 2-km stratospheric layers (16-26 km) utilizing weighted, piecewise regression analyses. Stratospheric water vapor abundance increased by an average of  $1.0 \pm 0.2$  ppmv ( $27 \pm 6\%$ ) during 1980-2010 with significant shorter-term variations along the way. Growth during Period 1 (1980-1989) was positive and weakened with altitude from  $0.44 \pm 0.13$  ppmv at 16-18 km to  $0.07 \pm 0.07$  ppmv at 24-26 km. Water vapor increased during Period 2 (1990-2000) by an average  $0.57 \pm 0.25$  ppmv, decreased during Period 3 (2001-2005) by an average  $0.35 \pm 0.04$  ppmv, then increased again during Period 4 (2006-2010) by an average  $0.49 \pm 0.17$  ppmv. The diminishing growth with altitude observed during Period 1 is consistent with a water vapor increase in the tropical lower stratosphere that propagated to the midlatitudes. In contrast, growth during Periods 2 and 4 is stronger at higher altitudes, revealing contributions from at least one mechanism that strengthens with altitude, such as methane oxidation. The amount of methane oxidized in the stratosphere increased considerably during 1980-2010, but this source can account for at most  $28 \pm 4\%$ ,  $14 \pm 4\%$ , and  $25 \pm 5\%$  of the net stratospheric water vapor increases during 1980-2010, 1980-2000, 1990-2000, and 1980-2010, respectively.



**Figure 1.** The smoothed 30-year Boulder record of stratospheric water vapor measurements by balloon-borne NOAA frost point hygrometers. Water vapor mixing ratios were binned in 2-km altitude intervals and assessed for trends in four different multiple-year periods using weighted, piecewise regression analyses. Net increases are evident for trend Periods 1, 2 and 4, as well for the entire record  $(1.0 \pm 0.2 \text{ ppmv})$ . The rapid downturn in Period 3 has been attributed to an anomalously cold tropical troppause and increased tropical upwelling. The root cause(s) behind the long-term stratospheric water vapor increase is (are) unknown.

#### Long-Term Tropospheric Ozone Variations at Background Measurement Sites

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The 35-year record of surface ozone measurements at four of the NOAA Baseline Observatories (Barrow, Alaska; Mauna Loa, Hawaii; American Samoa, and South Pole) represents some of the longest continuous records of tropospheric ozone at background locations. At these sites less than 5% of the data are influenced by nearby (<100 km) anthropogenic ozone precursor emissions. This data record is investigated for longer term changes with an emphasis on the 30-year period 1980-2009. The three ten-year periods are compared with particular emphasis on possible changes in the seasonal pattern over this time. At each of these sites strong seasonally dependent processes, such as the springtime boundary layer ozone depletion at Barrow, influence the year-to-year variability and can influence the longer-term changes. At several other regionally representative locations (Bermuda; Barbados; Iceland; Niwot Ridge, Colorado) there are 20+ years of observations, although in all cases there are multi-year gaps in the record. Earlier and more recent portions of the surface measurement locations there are also nearby longer-term ozonesonde observations (Mauna Loa – Hilo, Hawaii; Niwot Ridge – Boulder, Colorado; American Samoa; and South Pole). Changes represented by the surface (continuous observations) and profile (~4 times per month) time series are compared for the overlapping periods of observation.



**Figure 1.** a) Smoothed monthly surface ozone mixing ratios at Mauna Loa Observatory (solid black circles) and a linear fit to the monthly anomalies (solid red line). b) Ten-year average monthly values for three periods: 1980-1989, 1990-1999, and 2000-2009.

## Tropospheric Ozone During the Intensive Ozone Network Study (IONS) 2010/CalNex from Ozonesonde Observations: Stratospheric Influence and Long-Range Transport

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During a six-week period from mid May to mid June 2010, near daily ozone profile measurements were made at six sites in California as part of IONS 2010 during the CalNex Campaign. These sites were broadly distributed from north to south with four of the sites located along the California coast from Trinidad Head in the north to San Nicholas Island in the south. Two stations were located inland at Shasta State Historic Park in the north and Joshua Tree National Park in the south. While major local or regional pollution episodes were relatively few during this period, a number of stratospheric intrusion events were observed. Several of these reached the mid-troposphere down to as low as ~2 km. In two cases the intrusion event could be detected at nearly every location extending from the most northerly to southerly site. The extensive coverage in time and space of the ozone soundings allows them to be related to the broad scale meteorological pattern. The balloon launches were coordinated to take place at ~2200 GMT (1400 LST) near the synoptic analysis time of 0000 GMT. In addition to the "background ozone" associated with flow from the Pacific that reaches the coast of California, episodic events of enhanced ozone that appear to be related to more direct transport from Asia are also present in the multi-layered structure of the ozone profiles.



**Figure 1.** Ozonesonde profiles on May 11, 2010, from six sites in California during the IONS 2010/CalNex Campaign showing a strong stratospheric intrusion affecting all of the sites.

## Ozone Atmospheric Concentrations and Atmosphere/Ocean Fluxes During the TexAQS 2006, STRATUS 2006, GOMECC 2007, GasEX 2008, and AMMA 2008 Cruises

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Ozone ambient concentrations and atmosphere-ocean fluxes were measured on five cruises on board the NOAA Research Vessel Ronald Brown during 2006 to 2008. The cruises shown in Figure 1 resulted in ~3000 hours of open ocean ozone observations. The lowest ozone mixing ratios were measured in the Southern Atlantic during GasEx, with levels consistently in the 15–25 ppbv range. A similar narrow ozone mixing ratio distribution was observed in the South Pacific STRATUS cruise, but here ozone levels were approximately 10 ppbv higher, mostly in the 25–35 ppbv range. The STRATUS data collected during October 2008 on average appear ~5 ppbv higher than published oceanic data from Southern Hemisphere island locations. A wide range of ozone concentrations were measured during the GOMECC and TexAQS cruises. During southerly winds ozone was in the 20-30 ppbv range while concentrations reached 40-70 ppbv during winds coming from the coast. Similar observations were made during AMMA. In the outflow of urban areas reaching as far as ~100 km off the coast ozone levels were up to three times above background levels. These findings are in accord with previous ship-borne experiments in these and comparable regions, which have shown that ozone photochemical production continues to occur for several days in pollution outflow over the ocean. Ambient ozone concentrations measured on board the ships will be compared with land-based ozone measurements from the NOAA GMD surface ozone network.

The median of 10-min oceanic ozone deposition velocities (vd) results ranged from 0.009 cm s<sup>-1</sup> to 0.034 cm s<sup>-1</sup>. These directly-measured ozone deposition values are at the lower end of previously reported data in the literature for uptake to ocean water. Data illustrate a positive correlation (increase) of the oceanic ozone flux with wind speed, sea surface temperature, and biogeochemical conditions in the ocean surface microlayer, albeit the behavior of these relationships appears to differ during these cruises.



**Figure 1.** Tracks of the five ocean cruises with deployment of the ozone flux experiment.

### Determination of Dobson Spectral Characteristics, A New Method

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The Dobson instrument has been used for the determination of Total Ozone Column (TOC) since the mid-1920s. A complete description of the instrument operation, principles of measurement, and use is available elsewhere; briefly, the instrument measures the difference between the intensity of selected wavelength pairs in the 300-340 nm spectral range. ESRL GMD operates 16 of these instruments throughout the world, and serves as the Central Calibration Laboratory for the measurements with this instrument. The record of TOC starts in the early part of the 1900s, and the part of the record prior to 1979 is almost exclusively from measurements with the Dobson instrument. As the requirements for accuracy increase, a better understanding of the instrument characteristics is needed. In the past, only one Dobson instrument (D083, the World Primary Standard held at ESRL GMD) has had the slit functions measured, as this is a time-consuming process that required the instrument be taken to a special facility specializing in this characterization. The data processing algorithms were developed based on the characteristics of the reference instrument, and consistently applied to the world network. There are still differences in the TOC results of the individual Dobson instruments and stations, especially when compared to other measurement systems, ground-based and satellite-borne. The results of measurements using the possible combinations of wavelengths are also inconsistent. To understand these differences, a method is being developed for quick characterization of the individual Dobson instruments while at the instrument's normal operational site. NASA provided several Avantes AvaSpec-2048x14 Fiber Optic Spectrometers (specifications are compatible with the Dobson instrument spectral characteristics) to ESRL for investigation. We present the results of measurements inside the photomultiplier box of ten Dobson instruments, and a method for determining the slit functions. We show that the results of the new method predict the "real-world" response of one instrument, and produce a more consistent result with the wavelength combinations.

Info	Apair	Cpair	Dpair	AD	CD	Difference based on AD from official	Difference based on CD from official
						nom official	
Official	1.806	0.833	0.374	1.432	0.459		
D102	1.803	0.825	0.373	1.430	0.452	0.1%	1.5%
D080	1.796	0.832	0.381	1.415	0.451	1.2%	1.8%
D040	1.802	0.824	0.379	1.424	0.445	0.6%	3.0%
D102	1.804	0.826	0.374	1.430	0.453	0.2%	1.4%
D070	1.799	0.823	0.371	1.427	0.452	0.3%	1.5%
D065	1.805	0.831	0.376	1.429	0.455	0.2%	0.8%
D131	1.796	0.826	0.374	1.422	0.452	0.7%	1.5%
D067	1.806	0.828	0.375	1.431	0.453	0.1%	1.4%
D093	1.804	0.827	0.375	1.429	0.452	0.2%	1.5%
D087	1.802	0.825	0.374	1.428	0.451	0.3%	1.8%
Average	1.802	0.827	0.375	1.426	0.452	0.4%	1.6%

Figure 1. Absorption Coefficients for various test instruments determined by use of the Avaspec-2048x14.

## The RHUBC-II Campaign: Best-Guess Water Vapor Profiles and Their Impact on Far-Infrared (IR) Spectroscopic Studies

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The far-infrared (far-IR,  $15 < \lambda < 100 \,\mu$ m) is an extremely important spectral region. Nearly 40% of the outgoing longwave radiation and a significant portion of the infrared radiative cooling in the middle-to-upper troposphere are directly attributable to far-IR radiative processes. Surface radiation measurements in typical conditions contain no pertinent information about these radiative processes due to absorption by water vapor in the intervening lower atmosphere. The relatively high uncertainty in our knowledge of these processes is reflected in a corresponding uncertainty in climate models' predictions for the mid-to-upper troposphere. The Deptartment of Energy Atmospheric Radiation Measurement Program conducted a set of field experiments, the Radiative Heating in Underexplored Bands Campaigns (RHUBC), targeted at lowering these uncertainties. RHUBC-II was held from August–October 2009 at a site at 5400 m in the Atacama Desert of Chile, during which the precipitable water vapor (PWV) during clear periods was as low as 0.2 mm. RHUBC-II included a number of instruments that provided spectrally resolved measurements in strong H<sub>a</sub>O absorption bands in the far-IR and in the sub-millimeter. Improving spectroscopic parameters in these spectral regions using RHUBC-II measurements requires accurate specification of the water vapor profiles in the radiating column above the site. Vaisala RS-92 radiosondes were regularly launched during operational periods of RHUBC-II, but these radiosondes have well-known accuracy issues in conditions of low humidity and during daytime. This study utilizes an optimal estimation approach to refine the radiosonde profiles using observations from the 183.31-GHz GVRP instrument. Different retrieval approaches will be evaluated, as will the accuracy of the methodology specified by Miloshevich et al. (2009), for removing biases in radiosonde H<sub>2</sub>O profiles. The impact of the various water vapor profiles on far-IR and sub-millimeter radiance calculations will be shown.



**Figure 1.** Water vapor profiles above the RHUBC-II site are constructed from the original radiosonde measurements as well as 3 additional methods. The top panel is a model calculation of the far-IR radiance using the optimal-estimation retrieved profile (red). Differences in calculated far-IR radiances between the 3 additional methods and the original radiosonde profile are shown in the bottom panel. The total PWV for each method is given for reference.

#### Newly Identified Region of Rapid, High Concentration Wintertime Ozone Production

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Schnell et al. Nature Geosci. 2, 120-122 (2009) showed that high concentrations of wintertime photochemical ozone were produced rapidly at temperatures as cold as -18C in the rural Upper Green River Basin, Wyoming, USA. Here we note the identification of a ~15,000 km<sup>2</sup> region of high concentration and persistent wintertime ozone production in the Uinta Basin, Utah in the winter of 2009-2010 (40° N, 110° W; 300 km E-W x 200 N-S; basin floor ~1400 m above sea level). The Uinta Basin is ringed by mountain ridges of 1800-3300 m elevation and contains oil and gas extraction activities.



**Figure 1.** Hourly average max/min ozone and  $NO_x$ , average daily air temperature and snow depth for the Ouray, Utah monitoring station, 1 November, 2009 - 15 April, 2010. Through the summer and fall, ozone concentrations were at typical rural background levels of 20-50 ppb rapidly increasing to 60-120 ppb in mid-December, 2009 following sustained snow cover and abruptly decreasing from 115 ppb to 50 ppb the day snow melted and remaining in the 30-50 ppb range into summer. NO<sub>x</sub> concentrations were in the 2-10 ppb range prior to snow cover after which they rose to the 20-50 ppb range for the first half of the winter then decreased to the 10-30 ppb range until snowmelt, after which they returned abruptly to the 2-10 ppb range.

#### **Tropospheric Ozone Laminar Structures and Vertical Correlation Lengths**

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Tropospheric ozone profiles often show laminar structures in both the PBL and the free troposphere. We study the quantitative definition and evolution of ozone laminar structures, correlations of surface ozone with ozone aloft, and continuous ozone observations, based on twelve-year Huntsville ozonesonde data and the Huntsville Ozone Differential Absorption Lidar (DIAL). We conclude: (1) Ozone values at altitudes higher that 1-2 km above the surface carry little physical information about contemporaneous surface ozone, (2) Free-tropospheric and nocturnal residual-layer ozone values do affect surface ozone through processes that are not well understood, but do involve evolving physical/chemical processes, and (3) Ozonesondes are good for observing snapshots of atmospheric processes resulting in laminar structure, while DIAL is good for observing the evolution of atmospheric processes involving laminar structures.



**Figure 1.** Seasonal correlation of surface ozone with ozone aloft. Color spaghetti plots are one-year seasonal correlation of surface ozone with ozone aloft based on 1999-2010 Huntsville ozonesonde data. The solid black line represents the 11-year mean profile.

## Investigating Signatures of Large-Scale Advection and Microphysical Processes on Vertical Profiles of Water Vapor and Aerosols Near Mauna Loa and Mauna Kea

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While recent work suggests the isotopic composition of water vapor is controlled, to first order, by large-scale advection, other studies have proven isotopic measurements sensitive enough to investigate microphysical processes, such as rain recycling. On the one hand, this allows the stable isotope ratio  $2H:1H(\delta D)$  to serve as an effective tracer of atmospheric constituents important for climate and air quality. On the other hand, it creates the possibility that isotopic measurements could aid studies of aqueous processing of aerosol and trace gases. In this work, we examine both the large-scale/advective and microphysical signatures in vertical profiles of  $\delta D$  on the Big Island of Hawaii, home to NOAA's Mauna Loa Observatory. Simultaneous measurements of aerosol size distributions and CO<sub>2</sub> are used to verify inferences made from the water isotope information. Profiles were constructed by continuously measuring water isotopologues, CO<sub>2</sub>, aerosols (D<1000 nm), and temperature from a moving vehicle that was driven from sea-level to the summit of Mauna Kea several times daily. A total of nine profiles were obtained over three days, covering both the east- and west-facing slopes of the island.  $\delta D$ observations from this experiment clearly distinguish the moist marine boundary layer from the dry free troposphere, and also identify a transition layer in between, extending as much as 1000 meters above the trade wind inversion. Vapor mixing ratio and  $\delta D$  plots of the transition layer highlight the role of evaporation in mixing moisture upward from the top of the inversion cloud deck. Although air above the inversion is cloud-free, we are thus able to detect the traces of cloud-processing independent of aerosol number size distribution. Within the boundary layer, the isotopic profile is remarkably constant, except where falling precipitation is observed. In rainy conditions, strong isotopic depletion (lightening) is observed below the cloud layer, indicating the removal of heavier, condensed water. Conserved variable plots of total water and equivalent potential temperature are used to explore heating and cooling associated with rain removal and re-evaporation at lower altitudes.



**Figure 1.** δD (black), dewpoint (blue) and ambient temperature (red) profiles measured while driving from Mauna Kea summit down to Hilo, Hawaii. First observations of rain and cloud are marked.

#### Can Ozone Cross-Sections Be Verified from the Ground-Based Measurements?

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The recent World Meteorological Organization (WMO)/International Ozone Commission (IO<sub>2</sub>C) initiative recommends using Daumont, Brion and Malicet (1995: DBM) ozone cross-sections instead of the previously used Bass and Paur (1984: BP) cross-sections. The DBM cross-section measurements were performed at higher resolution and higher signal-to-noise ratio than BP measurements. Also they generate significantly lower residuals when quadratic parametrization with respect to temperature is performed. The change from BP to DBM cross-sections has surprisingly large impact on ozone column retrieval when Huggins region of 300nm-340nm is used. In particular, the measurements with Brewer spectroradiometers produce 2-3% lower ozone column with DBM. Also the ozone column obtained with UltraViolet-Rotating Shadowband Spectroradiometer (UV-RSS) at Table Mt., Boulder, Colorado shows 1% ozone column reduction. On the other hand, it was reported that Dobson instruments were unaffected. The ozone profile retrieval from GOME data are also affected by the choice of the cross-section. The WMO/IO<sub>3</sub>C recommendation disturbed the picture that emerged over last few decades of harmony among different measurements. We emphasize that no ground-based measurements verified which of the two sets of cross-sections is closer to the actual values in the atmosphere. We have attempted to perform verification of the cross-sections using two data sets: (1) 1998 Brewer MKIII at Mauna Loa, Hawaii and (2) 2003-2008 UV-RSS at Table Mt., Colorado. Both studies were aided by NOAA ozone sonde data at nearby locations as the comparisons are dependent on ozone and temperature profiles. So far root-mean-squared of residuals of measured spectra to synthetic spectra based on BP and DBM did not show statistically significant difference to render a judgment which of the cross-section is closer to the truth. Subsequently we performed extensive simulation studies to estimate measurement requirements in terms of noise, resolution and wavelength stability to find conditions when the detection of the difference is possible. Also we evaluate differential absorption technique that improves the detectability at the expense of lost low frequency components.



Figure 1. Ozone cross-section comparison at  $T = -45^{\circ}C$  with 0.6 nm resolution. Differences (Bottom) in optical depth for 300 DUs and Ratios (Top) shown for four data sets: Raw BP, temperature parametrized BP with Khomyr correction, DBM parametrized using 5-temperature data. These three compared to DBM parametrized using 4-temperature data. (Bands of Brewer (Top) and bands of Dobson (Bottom) are shown.)

### Continuity and Reliability of Measurements Made at the Cape Verde Atmospheric Observatory (CVAO)

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The CVAO is within a very small class of the World Meteorological Organization/Global Atmospheric Watch long-term observing stations, which measure a comprehensive range of atmospheric parameters. These include meteorological parameters, greenhouse gases, short-lived reactive gas species and aerosols. In this presentation we focus on the trace gas measurements and describe some of the ongoing efforts to ensure accurate, consistent and reliable measurements since the station began operation in October 2006. Standard operating procedures for all the measurements are in place and routine instrumental procedures are carried out by fully trained on-site personnel. Ozone (O<sub>2</sub>) measurements are almost always duplicated with the two instruments running in parallel and sharing an inlet. Carbon Monoxide (CO) measurements are almost always in triplicate and by three different methods (VUV Fluorescence, University of York; frequent flask sampling and online measurement by GC-MS, MPI, Jena). O<sub>2</sub> is linked to the primary standard reference photometer #2 (SRP#2) from the National Physical Laboratory (NPL) traceable through the National Institute of Standards and Technology (NIST), and CO to a standard provided by the GAW Central Calibration Laboratory (CCL) at NOAA/ESRL, through regular calibrations. GAW audits are planned for CO, O<sub>2</sub>, and the greenhouse gas species later this year. The CVAO is one of only a handful of observatories (see figure) making non-methane volatile organic compound (NMVOC) measurements and in December 2009 these were audited by the CCL at IMK-IFU, Garmisch-Partenkirchen, Germany, showing that the station measurements were within the accuracy and precision required by GAW. CVAO scientists are also involved in the new GAW expert group for the oxides of Nitrogen (NO<sub>w</sub>). Data analyses and Quality Assurance/Quality Control procedures for all measurements have been developed and streamlined since we began operating the site. The data is archived regularly to the British Atmospheric Data Centre (BADC) and to the World Data Centre for Greenhouse Gases (WDCGG).



Figure 1. The Cape Verde Atmospheric Observatory.



**Figure 2.** Global Atmospheric Watch GLOBAL sites which routinely make VOC measurements.

#### Long Term Changes in the Upper Stratospheric Ozone at Syowa, Antarctica

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Analyses of stratospheric ozone data recorded by Dobson Umkehr measurements since 1977 at the Syowa (69.0°S, 39.6°E), Antarctica station show a significant decrease in ozone above 4 hPa during the 1980s and 1990s. Ozone values over Syowa remain low since 2001. The time series of upper stratospheric ozone from the homogenized NOAA(/2) SBUV V8 overpass data ( $\pm$ 4 degrees, 24 hours) are in qualitative agreement with Syowa Station data. Ozone recovery during the austral spring over Syowa Station appears to be slower than predicted by use the Equivalent Effective Stratospheric Chlorine (EESC) curve. The long-term changes in station's equivalent latitude are derived from MERRA analysis at ~ 3 hPa and ~50hPa. These data are used to attribute some of the upper and middle stratospheric ozone changes to the changes in vortex position relative to station location. In addition, high correlation of the Southern Hemisphere Annular Mode (SAM) with polar upper stratospheric ozone recovery. Detection of stratospheric ozone recovery in the Antarctic region requires careful consideration of counteracting contributions from chemical and dynamical processes.



**Figure 1.** Long-term variations of ozone amount in layer 8+9+10 (above 4 hPa or 40 km altitude): Umkehr data (red circles) at Syowa and SBUV overpass data (blue squares). The red and blue lines show the EESC fit in Umkehr and SBUV data respectively. The dashed lines show linear ozone trends derived from 1979-200. The annual cycle, effects of solar activity, QBO, and SAM signals were removed from the data prior to the ozone record trend analysis. A symbol on the left edge of the plot represents averaged ozone from 3 stations, Faraday ( $65^{\circ}S$ ), King Baudoin ( $70^{\circ}S$ ), and Halley ( $73.5^{\circ}S$ ), measured between 1957 and 1972, and represents annual mean ozone.

### Trends of Long-Lived Halocarbons, Nitrous Oxide and Sulfur Hexafluoride

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In the mid-1970s, the NOAA's 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, 30+ year hemispheric and global mean records for CFC-11, CFC-12, and  $N_2O$ ; and 15+ year trends for Carbon Tetrachloride (CCl<sub>4</sub>) and sulfur hexafluoride (SF<sub>6</sub>). The combining technique takes advantage of co-located measurements and accounts for systematic differences between measurement programs. All data sets were placed on current NOAA scales for their respective gases. 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 greenhouse gases.



**Figure 1.** Nitrous oxide estimated global mean from 1977 to the present with 1- $\sigma$  uncertainties (gray bars). The changing uncertainties illustrate poorer instrumental precisions in the 1970s and 1980s. Improvements in measurement techniques and technology, as well as more sampling locations have reduced the global mean uncertainty since the mid 1990s. The red line is a linear fit to the global mean data demonstrating a fairly constant annual growth rate of 0.75 ppb yr<sup>1</sup>.

#### Global Trends in Atmospheric SF<sub>6</sub>

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Sulfur hexafluoride (SF<sub>6</sub>) is a potent greenhouse gas and useful atmospheric tracer. NOAA SF<sub>6</sub> measurements from two Earth System Research Laboratory/Global Monitoring Division programs (flask and *in situ*) were combined to produce global and hemispheric mean records. There were then were used to examine changes in the growth rate of SF<sub>6</sub> and corresponding SF<sub>6</sub> emissions. Global emissions and mixing ratios from 2000-2008 are consistent with recently published work. More recent observations show a 10% decline in SF<sub>6</sub> emissions in 2008-2009, corresponding with a decrease in world economic output. This decline was short-lived, as the global SF<sub>6</sub> growth rate has recently increased to near its 2007-2008 maximum value of 0.29 ppt yr<sup>-1</sup>. Interannual variability of the SF<sub>6</sub> growth is examined, along with implications for changing emissions.



Figure 1. Growth rate of SF<sub>6</sub> calculated from global and Northern Hemispheric mean SF<sub>6</sub> mixing ratios.

## Airborne Measurements of Trace Gases During HIPPO: Comparisons with Satellite Retrievals from ACE-FTS and Aura Instruments

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"HIAPER" is a Gulfstream-V research aircraft owned by the National Science Foundation and operated by the Earth Observing Laboratory of the National Center for Atmospheric Research. An ostensibly global, tropospheric survey of atmospheric carbon dioxide and other trace gases (dubbed the HIAPER Pole-to-Pole Observations of Greenhouse Gases and Aerosols field campaign, or "HIPPO") was initiated in January 2009. A total of five, wide-ranging sorties in about half as many years were to be flown by the HIAPER from its home base in Broomfield, Colorado. Each excursion was to occur during a unique segment of the seasonal cycle and would carry the aircraft between 85°N and 65°S latitude over the Pacific Ocean in the general vicinity of the international dateline while gradually ascending and descending almost continuously between the surface and the tropopause region. This first-of-its-kind airborne field campaign was designed to answer questions about the global distributions of many important atmospheric constituents – and the sources, sinks and transport process driving those distributions – with the hope of ultimately providing new and better constraints for global inverse and transport models. Integral to this effort is information about the upper troposphere/lower stratosphere to be drawn from satellite remote sensing, and the HIPPO data provide a unique opportunity for satellite retrieval validation. This poster will present comparisons of HIPPO data to retrievals from the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) aboard the Canadian SCISAT-1 satellite, as well as other instruments aboard the Aura satellite in NASA's A-Train constellation. The goal of this work is to validate satellite measurements with a set of precise and accurate aircraft data in order to create a combined dataset with global coverage from the surface to the upper atmosphere.



Figure 1. Flight tracks of the first three HIPPO missions.

### First Results from UCATS During the GloPac 2010 Mission

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Global Hawk Pacific (GloPac) 2010 was the first scientific mission of the Global Hawk Unmanned Aerial System (UAS), and included a payload designed for *in situ* measurement of trace gases and aerosols, remote sensing of gases and particles, and measurement of various meteorological parameters. The Global Hawk is capable of long-duration flights (30 hours; range = 20,000 km) at altitudes up to ~19 km, as demonstrated during GloPac by a flight from 34°N into the Arctic, with about 10 hours on location followed by a return to its base. The UAS Chromatograph for Atmospheric Trace Species (UCATS) instrument was used to measure N<sub>2</sub>O, SF<sub>6</sub>, H<sub>2</sub>, CH<sub>4</sub>, CO, and ozone during GloPac. Mission objectives addressed by these measurements include sampling of polar vortex fragments as they move into midlatitudes and break up, and observations of air from the tropics to high latitudes. Results are presented showing data from March/April 2010 and from previous aircraft missions, using tracer-tracer correlations to examine mixing and transport of high latitude air with lower latitude air in the stratosphere, and changes in the lower stratosphere since the mid-1990's.



**Figure 1.** Time series of  $N_2O$  and ozone on part of the 28-hour flight toward the North Pole. Note the strong anticorrelation of  $N_2O$  and ozone as the Global Hawk flew near the boundary between two distinct stratospheric air masses, one from midlatitudes and one from the vortex region.

### Inexpensive Stratospheric Profiling as a Basis of Stratospheric Transport Monitoring Program

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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. State-of-the-art coupled chemistry-climate models predict that the stratospheric overturning circulation has been strengthening in recent decades, and will continue to strengthen [e.g. *Butchart et al.*, 2010]. Knowledge of the strength of the stratospheric circulation and how it may change is of significant importance. Examples are the recovery of ozone [*Butchart, et al.*, 2010] and the concentration of stratospheric water vapor, which has been shown to influence climate [Solomon*et al.*, 2010]. 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<sub>6</sub> and CO<sub>2</sub> measurements over the past three decades to show that the mean age of stratospheric air had increased, in apparent opposition to the decreased mean age predicted by these models that have increase in stratospheric circulation.

This study highlighted the role long-lived trace gas measurements can play in helping to understand model predictions, but also clearly revealed 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 demonstrate that the data quality and cost is such that a sustainable long-term monitoring program for stratospheric circulation is feasible.



**Figure 1.** Decreasing mean ages caused by an increasing strength of the stratospheric circulation are consistent, robust results in nearly all  $CO_2$  Concentrating Mechanisms (CCM), (green lines) yet appear to be inconsistent with age of air data (black line) Ray et al. [2010].

# NOAA GMD Participation in the Eleventh International Pyrheliometer Comparison (IPC-XI) September 26 - October 15 2011 World Radiation Center (WRC) Davos, Switzerland

## D. Nelson

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The NOAA Global Monitoring Division (GMD) Solar Radiation Facility, as one of three Regional Radiation Centers (RCC) in the World Meteorological Oganization (WMO) Region IV (the others being in Toronto and Mexico City), 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 was held in 1975, NOAA Solar Radiation Facility 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 World Standard Group defined WRR. Correction factors are established for relating the RCC reference instruments to the WRR. The goal is international standardization of solar irradiance measurements. Four NOAA GMD radiometers and other instrument comparisons were also conducted concurrently with 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 also sent to Davos for participation in the FRC and pyrgeometer comparison. A final report summarizing the results of IPC-XI will be published by the IPC-XI host, the Physikalisch-Meteorologisches Observatorium Davos (PMOD). A photograph of the PMOD with observing tables in place for participants and their instruments is shown below in Figure 1. Over seventy individuals from forty three countries participated in IPC-XI.



Figure 1. The PMOD with facilities in place for conducting IPC-XI.

## A Proposed Solar Radiation and Aerosol Optical Depth Network for the Continental United States

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The U.S. ground-based measurement of solar radiation has been, to put it kindly, inconsistent. In the 1970s the Department of Energy (DOE) funded NOAA to install solar direct and diffuse measurement stations at 39 NOAA National Weather Service (NWS) sites. That funding lasted about five years and only a few stations continued to take data. Other efforts by the DOE and collaborators have had similar starts and stops. There are many existing networks of solar measurements that obtain global horizontal irradiance only, which is of limited usefulness and uncertain quality because of calibration and maintenance issues. This poster will present a possible network configuration that uses instrumentation capable of measuring global and diffuse horizontal and direct normal solar irradiances. Further, it is capable of accurate spectral measurements useful for photovoltaic (PV) prospecting. These spectral measurements can produce accurate aerosol optical depth (AOD) and water vapor retrievals, useful for prospecting for concentrating systems. A wavelength matched down-pointing radiometer is planned that would provide spectral albedo useful, not only to renewable energy, but to satellite retrieval and chemical transport model validation. Network, instrumentation, and value-added products will be described.



**Figure 1.** One possible siting strategy for the proposed solar and AOD network is to use the current Climate Reference Network sites shown here. This is attractive because the infrastructure exists and sites are remote to minimize pollution's interference with solar radiation. A modification of this would be to use suitable NWS sites near cities that have a low probability of widespread use of concentrating systems for solar energy, but have a preference of rooftop thermal and PV systems.

#### Evaluation of Broadband Arctic Radiation Measurements: Introducing Tiksi Observatory

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The Arctic is a challenging environment for making *in situ* measurements and broadband surface radiation measurements are no exception. A standard suite of radiation sensors is typically designed to measure the total, direct and diffuse components of incoming and outgoing long-wave (LW) and short-wave (SW) radiation and enhancements can include various sensors for measuring radiation in various narrower bandwidths. Many radiation sensors utilize protective glass domes and some are mounted on complex mechanical platforms (solar trackers) that rotate sensors and shading devices that track the sun. High-quality measurements require striking a balance between locating sensors in a pristine undisturbed location free of artificial blockage (such as buildings and towers) and providing accessibility to allow operators to clean and maintain instruments. Three significant sources of erroneous data include solar tracker malfunctions, riming of the instruments and operational problems due to limited operator access in extreme weather conditions. In this study, a comparison is made between the Global Shortwave (GSW) measurements and the component sum (cosine corrected direct + diffuse) SW measurements. The differences between these two quantities (that theoretically should be equivalent) are used to illustrate the magnitude and seasonality of radiation measurement problems. The problem of riming is investigated in more detail for one case study utilizing both SW and LW measurements. Solutions to these operational problems are proposed that would utilize measurement redundancy, more sophisticated heating and ventilation strategies and a more systemized program of operational support and subsequent data quality protocols.



**Figure 1.** Global SW and DIF+DIR: Comparison of a) Alert, b) Barrow, and c) Eureka in 2008. The top panels show GSW and the component sum. The bottom panels show the difference between the component sum and GSW.



**Figure 2.** Clear sky example with flux tower (LW and GSW) and DIF and DIR from SAFIRE in Eureka, Canada: March 26, 2010.

## NOAA's Antarctic Ultraviolet (UV) Monitoring Program: It's More Than Just UV

### P. Disterhoft and S. Stierle

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Since the discovery of the Antarctic ozone hole the National Science Foundation has supported a polar (Arctic and Antarctic) UV monitoring program. This monitoring effort has produced a continuous dataset for more than 23 years at several polar sites, which include the three Antarctic stations, the South Pole, McMurdo and Palmer. The Global Radiation group (G-RAD) of NOAA ESRL's Global Monitoring Division took over the operations of the three Antarctic stations in May 2010. In the short period that G-RAD has operated the network we are finding more utility in the long-term dataset than what was originally intended. The measurement of the biologically effective UV-B is important for studying how changes in UV-B irradiance affect humans and the biosphere. However, the spectral range of the SUV-100 beginning at approximately 300 nm and extending out to 600 nm makes this a very unique dataset in that it consists of both spectral UV and visible irradiances. Research that requires irradiances in both the UV and visible spectral regions can be pursued with this high quality dataset. One such research avenue we are pursuing is the validation of work by Haigh et. al. who recently, in a letter published in Nature noted unusual solar activity in the declining phase of solar cycle number 23 from 2004 to 2007. When analyzing the Spectral Irradiance Monitor (SIM) data on the SORCE satellite, they found a 4-6 times larger decline in the UV than what was expected from model data produced by Lean. This is offset by a small increase in visible solar output yielding comparable total solar output as measured by the SIM and the Lean model, but with considerably different spectral signature. According to Haigh this has ramifications in computing radiative forcing. We believe that this level of change in the spectral solar output can be seen in the long-term Antarctic dataset. We specifically chose the South Pole for an initial study on the data due to the extremely clean air at this site, thereby greatly reducing any complications due to aerosols in the comparison. The precision of the Antarctic spectroradiometers is very good, so the ratio of the change stated by Haigh in UV to the change in the visible over this time period should reveal itself in these ground-based measurements. Here we present our initial results of this comparison. Additionally, we show examples of the important network data such as spectral UV irradiance and some of the derivative products such as total column ozone, UV index, DNA response, to name a few. The NOAA Antarctic monitoring program website was recently launched and its URL is ersrl.noaa.gov/gmd/grad/antuy. All metadata, data, relevant publications and pertinent documents can be obtained through this web portal.

Year	340 nm irradiance μW/cm <sup>2</sup> *nm	500 nm irradiance µW/cm²*nm	Ratio 340/500
2004	32.07869	64.73205	0.496
2007	32.61054	65.68092	0.496
Ratio 2004/2007	0.984	0.986	0.998

**Table 1.** The South Pole SUV-100 data are presented in table 1 and show an approximate 1.6% increase in the UV at 340 nm from 2004 to 2007 and a similar 1.4% increase in the visible at 500 nm. The fact that they are both increasing does not agree with the spectral signature discussed by Haigh et.al. when comparing the SIM data from 2004 to 2007. These are preliminary results and more work needs to be done to better understand how the SIM data compare to the SUV-100 ground-based measurements before any conclusions can be drawn. This does, however, show the utility of the long-term Antarctic data set.

### Typical Barrow Albedos Coupled with Solar Irradiance (Io) Variability: A Sensitivity Study

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A new set of incident solar irradiance spectra has been computed at extremely high spectral resolution, based on published solar atmosphere physical models representing various magnetic activity features (Fontenla, et al.). This set of spectra can be linearly combined to produce the Solar Spectral Irradiance for any solar activity level, as a weighted sum of the activity drivers. A subset of irradiances have been convolved at spectral sampling compatible with MODerate Resolution Atmospheric TRANSmission (MODTRAN®5.2.0.0), that is at 0.1, 1.0, 5.0 and 15.0 cm<sup>-1</sup>. Since the MODTRAN radiative transfer calculations are linear with respect to the incident radiation, results of the computed cooling rates can also be linearly combined to yield the atmospheric cooling rate for any solar activity level. For this study, 3 simple levels of solar activity have been adopted, Low (quiet), Medium, and High. These have been coupled with 3 typical albedos near Barrow: sea ice, open ocean, and tundra. In order to delineate the altitudes of impact of the Io variability, 3 continguous spectral ranges were selected: Ultraviolet (UV), with Io heating and variability peaking near the stratopause, Chappuis (visible), peaking at 35km, and Short-wave Infrared, peaking in the troposphere (not shown). Sea ice preferentially enhances the small atmospheric heating near the surface, due to the reflection, while the darker albedos show much less surface impact.



**Figure 1.** MODTRAN5.2 calculations ('yellow to red' heats, 'blue to white' cools) for an ocean albedo. The top pair show UV negative cooling (heating) peaked at the troposphere with the capability of isolating detailed studies in the Huggins band near  $0.3\mu m$ . The lower pair show the visible spectral range (centered on  $0.6\mu m$ ) where the O<sub>3</sub> Chappuis band dominate. The difference spectra in the right pair of images show the variability in the 'low' vs 'high' solar irradiances over these spectral range, while the Io irradiance arriving at the surface is depicted in the left pair.

## **International Filter Radiometer Comparison Results**

## G. Hodges<sup>1</sup> and J. Michalsky<sup>2</sup>

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In conjunction with the Eleventh International Pyrheliometer Comparison held in Davos, Switzerland, from September 27 to October 15, 2010, the Physikalisch-Meteorologisches Observatorium Davos/World Radiation Center (WRC) also conducted the 3rd Filter Radiometer Comparison (FRC III). Two refurbished Atmospheric Radiation Measurement (ARM) multifilter rotating shadowband radiometers (MFRSRs) were included in the comparison, along with a new version of the MFRSR that uses a thermopile sensor for broadband solar measurements replacing the silicon photodiode that is used in the earlier (and all of ARM's) MFRSRs. The unprecedented temperature stability, required to successfully operate the thermopile, also improves the narrowband filter measurements significantly. All the participating instruments were compared to a group of precision filter radiometers that are owned and operated by the WRC. Initial results show that the MFRSRs compare favorably to the reference group, and are, in fact, within the limits for direct sun-pointing instruments set by the FRC II working group in the previous comparison, i.e.,  $\pm 0.005 + 0.01/air mass$ .



**Figure 1.** Time series of Aerosol Optical Depth at (nominally) 500 nm as measured during the FRC in Davos, Switzerland on 12 Oct, 2010. The reference triad is shown as filled black dots. NOAA GMD operated the Thermopile Spectral Radiometer (magenta open circles) and the MFRSR (blue plus signs).
# The Effect of Measured Ozone Profiles on Ultraviolet (UV) Photolysis Rate Coefficients in the Troposphere

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The Tropospheric UV and Visible Radiative Transfer Model (TUV-RTM) is used to evaluate the impact of measured ozone profiles on UV photolysis rate coefficients in the troposphere compared to the default U.S. Standard atmosphere ozone profile often used in photochemical models. The ozone profiles used in the calculations are from three sources: 1) Ozonesondes from the Earth System Research Laboratory of NOAA during the summer and fall of 2000; 2) Brewer Umkehr retrievals from the NOAA-EPA Brewer spectrophotometer Network (NEUBrew) during the winter, spring, summer, fall of 2007; and 3) ozonesondes from Valparaiso University during IONS and INTEX-B campaigns in the summer of 2004 and spring/summer 2006. The radiative transfer calculations are performed from the surface to 12 km. Sensitivity studies are performed for the effect of redistribution of ozone to the boundary layer and for a shift in the altitude position of the ozone peak on UV solar radiation. Larger effects are seen in shorter wavelengths of the photoyolysis rate coefficient of ozone  $(jO_3)$  and at larger solar zenith angles. Usage of the U.S. standard atmosphere ozone profile in computations of  $iO_2$  will slightly underestimate by 1-2% the photolysis rate constants for small surface ozone amounts and will overestimate the surface photolysis rate constant by 2-8% for larger amounts of surface ozone. In the vertical, the standard ozone profile has the ozonepause 5 km lower than observations for the Houston area. As a result, usage of the standard profile will increasingly underestimate the ozone photolysis rate constant by approximately 0-10%. Changes in  $jO_{2}$  will affect the concentration of the hydroxyl radical in the atmosphere and therefore the oxidative capacity of the atmosphere.



**Figure 1.** Ozondesondes from NOAA Global Monitoring Division in summer and Fall, 2000 (left). Umkehr Ozone profiles from NEUBrew Network for clear-days across the year, 2007 (right).

## Development, Testing and Performance of a New Filter-Based Light Absorption Instrument

## P.J. Sheridan, J. Wendell and J. Ogren

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Light absorption by atmospheric aerosols is an important factor in determining the radiative forcing of climate. The long-term measurement of the aerosol light absorption coefficient at surface monitoring stations is complicated by shortcomings in existing methods. Photoacoustic and absorption by difference (extinction minus scattering) methods are expensive and require highly trained operators and frequent attention, and thus are not ideal for long-term deployment at remote stations. Filter-based methods collect the aerosol particles on a filter and measure the increase in attenuation of light through the filter caused by the particles, and through calibration procedures the amount of light absorption from the particles can be determined. Since the late 1990s the ESRL Global Monitoring Division (GMD) and organizational precursors have been using a filter-based instrument, the Particle Soot Absorption Photometer (PSAP, Radiance Research, Seattle, WA) to measure the aerosol light absorption coefficient at the stations in the NOAA Global Collaborative Aerosol Monitoring Network. One of the major difficulties in the operation of the PSAP is the fact that the filters need to be changed frequently, on the order of a few hours to one day at most locations. This requires operators to visit the station frequently to avoid PSAP data loss, something that became a significant problem at some stations (e.g., very long driving distance from town, over weekends, etc.). For this reason GMD scientists and engineers have developed an inexpensive filter-based instrument that can measure aerosol light absorption from particles on eight filters in succession before requiring a filter change. This new instrument has been named the Continuous Light Absorption Photometer (CLAP), and is already deployed and making measurements at several of the Network stations. This presentation will provide an overview of instrument development, testing, performance characterization, and attempts at technology transfer to the private sector.



19.79 19 74 19.62 20110404a #10.009 Tr=0.7 20.02 19.46 19.70 9.77 19.74

**Figure 1.** Photos of the new CLAP instrument and an exposed filter showing the eight sample spots and spot areas determined by our automated image analysis program.

#### Analysis of High-Altitude Aerosol from Asia to Mauna Loa

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High-altitude mountaintop observatories provide the opportunity to make long-term, continuous measurements of aerosol properties in the free troposphere without the added expense and difficulty of operating aircraft. Here we present an analysis of aerosol optical property measurements from three mountaintop sites in Asia (Pyramid, Nepal; Waliguan, China; and Lulin Mountain, Taiwan) and compare the results with aerosol measurements at Mauna Loa, Hawaii. The seasonal variation and systematic relationships among aerosol properties change from site to site but the timing and links among parameters can be related to aerosol sources known to impact the individual sites. We focus on differentiating air masses based on their combined aerosol properties (Figure 1). Specifically we use data clustering techniques to identify different air mass types at these four sites and to determine if the resulting clusters can be related to specific aerosol events (e.g., dust, smoke). This allows us to determine the contribution of aerosol type. Furthermore, these rules could help constrain both model parameterizations and remote sensing algorithms which are often based on an assumed aerosol type.



**Figure 1.** Aerosol extinction (a), single scattering albedo (b) and Ångström exponent (c) as a function of trajectory (d) for Lulin Mountain. Colors indicate which back trajectory the aerosol properties are associated with.

#### Seasonal Aerosol Distributions at Summit, Greenland: EC, OC, <sup>14</sup>C and Individual Particle Analysis

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Aerosol is known to affect the Earth's atmosphere and surface albedo thus having an influence on climate. In the case of carbonaceous aerosol, Organic Carbon (OC) tends to scatter sunlight while Elemental (soot) Carbon (EC) aerosol absorbs light. Considering the importance of these aerosols on snow and ice albedo (Hansen and Nazarenko, 2004),  $PM_{2.5}$ ,  $PM_{2.5-10}$  and snow-melt filters were collected at Summit, Greenland from August 2000 to August 2002 to measure particulate EC, OC, and <sup>14</sup>C of total carbon; the latter to assess natural and anthropogenic source contributions. Additional source information was gleaned from scanning electron microscopy images (SEM) of single particles from selected filters. All samples were collected within a clean air sector upwind from the campsite only when winds were within–sector (180 °S ± 150 °) and –wind speed (> 1.3 m s<sup>-1</sup>). Preliminary analyses of  $PM_{2.5}$  results suggest spring-summer maxima of EC and OC (Figure 1). Summer concentrations are consistent with summer 2006 measurements reported by Hagler et al. (2007). The average percent modern carbon from a subset of filters over the two-year period was 44% (SD=18%; n=19). Figure 2 shows focused ion beam SEM images of soot (left) and likely mineral dust (center, right).



Figure 1. Greenland PM<sub>2.5</sub> EC, and OC concentrations.



**Figure 2.** FIB-SEM images of  $PM_{25}$  collected during 3 – 10 July 2001.

## **Data Quality Explorations Using Duplicate Measurements**

### N.P. Hyslop and W.H. White

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Environmental measurements are subject to uncontrolled natural variations that are difficult to reproduce in the laboratory. Collocated measurements are the most direct and comprehensive approach to characterizing measurement quality because the observed differences reflect the actual measurement performance under the natural environmental variability. Collocated data have been used extensively to estimate measurement precision, but these rich data sets can be used to explore several additional data characteristics. This presentation uses collocated measurements from the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network to explore relationships between measurement precision and concentration, the existing model of precision, measurement distributions, detection limits, and relationships among measurement errors in different species. Figures 1 and 2 illustrate a few of these features.



Figure 1. Differences between collocated measurements of selenium at several sites in the IMPROVE network.



**Figure 2.** Scatterplot matrix of observed differences,  $\Delta x$ , between the collocated measurements, where x = Br, S, mass, Fe, Ca, and Si. Along the diagonal are histograms of the observed differences for each species. Off the diagonal are scatterplots of the observed differences in one species versus the observed differences for another species. For example a point in the lower left graph represents the observed difference in duplicate Si measurements versus the observed difference in the duplicate Br measurements from a single day.

#### Aerosol Properties and Direct Radiative Effects Measured at a Representative Southeastern U.S. Site

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The southeastern U.S. is one of only a handful of regions worldwide which has not exhibited warming over the past century. Long-term measurements of key aerosol properties from a regionally representative site are necessary to corroborate recent studies indicating the potential role of aerosols in this lack of regional warming, especially during warm-season months. The semi-rural mountain location (1080m ASL) of the Appalachian Atmospheric Interdisciplinary Research facility at Appalachian State University (36.214°N, 81.693°W) is home to NOAA ESRL and NASA AERONET collaborative aerosol measurements, along with a suite of trace gas, meteorological, solar irradiance, and cloud-monitoring instrumentation. Two years of *in situ*-measured aerosol optical properties are presented here, placed in the context of those measured at other NOAA ESRL sites in the U.S. The *in situ* aerosol measurements and ten years of satellite-based aerosol optical depth (AOD) measurements highlight the large seasonal variability in regional aerosol optical properties and loading. Aerosol source types will also be presented, along with box model estimates of top-of-the-atmosphere direct aerosol radiative effect (based on the *in situ* and remote measurements) and recently-added aerosol hygroscopic growth measurements. Comparisons of aerosol direct radiative effects and optical properties between two very meteorologically-different summers could provide some insight into the possible aerosol response to future regional climate change.



**Figure 1.** Comparison of monthly-binned sub-micrometer aerosol radiative forcing efficiency at 550nm, measured at five NOAA ESRL North American sites during the period 6/09-3/11 (Left), including the Appalachian State University (APP site). Ten years of MODIS-measured aerosol optical depth measurements made above Boone, NC (right).

### Extending the Use of the UK Based Research Aircraft to Provide a Long-Term Observation Platform

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The region of the atmosphere from the surface through to the upper troposphere is currently difficult to probe from space. Although satellites give good global coverage, they are less quantative than *in situ* measurements and there can be interference from cloud coverage and aerosols. The availability of high quality and high resolution aircraft observations are of great value to improve our knowledge of atmospheric dynamics and composition.

The Facility for Airborne Atmospheric Measurements UK BAe 146 aircraft has been collecting data since July 2004 for individual projects and there has never been any attempt to link the datasets together. There is currently a database of over 500 flights. Ozone, CO,  $NO_x$  and temperature data collected over the UK has been averaged from 2005 to 2010, producing total and regional monthly averages for the UK at height intervals of 1000m – 10000m as well as distribution plots over the UK for the boundary layer, free troposphere and the lower troposphere/upper stratosphere.



0 50 80 110 140 170 200

**Figure 1.** Ozone distribution over the UK using data collected from the UK research aircraft between 2005 - 2010.



**Figure 2.** CO distribution over the UK using data collected from the UK research aircraft between 2005 - 2010.

## Using Surface Weather Observations to Reduce Atmospheric Transport Errors in Regional Inversions

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Over the next five years, Earth Networks will be deploying 100 GreenHouse Gas (GHG) measuring instruments, consisting of 50 in the United States, 25 throughout Europe and another 25 in other worldwide locations. Measurements provided by this network will represent regional to local scale atmospheric signals of carbon dioxide  $(CO_2)$  and methane  $(CH_4)$  gases and will be used for inverse modeling to estimate natural and anthropogenic sources and sinks of GHGs. Inversion approach utilizes backward trajectories and carbon footprint calculations based on meteorological fields provided by the Weather Research and Forecasting model. Errors in atmospheric transport are commonly considered as the largest source of error in inversions and of uncertainties in estimated surface fluxes of carbon. Assimilation of weather observations from the largest surface network with more than 8,000 sites within the U.S., operated by Earth Networks, improves accuracy of the transport model. GHG sensors, used in this study, are located in California and in Maryland, where Earth Networks has more than 610 and 570 surface weather sites, respectively. Root mean square error of resulting near-surface wind fields is reduced comparing to the errors before assimilation. Differences between the original footprints and footprints based on resulting analysis fields show the impact due to assimilation of surface observations. More accurate wind patterns resulted in more accurately calculated footprints and, therefore, reduced the inversion uncertainties in  $CO_2$  and  $CH_4$  emission estimates.



**Figure 1.** Example from the Earth Networks GHG portal showing live GHG observations and weather at a sensor site in California.

### Science at Summit Station, Greenland: Long-Range Plan

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Summit Station (72°36' N, 38°25' W) is a National Science Foundation (NSF)-supported remote field camp located near the highest point of the Greenland ice sheet at an altitude of 10,500 feet. Initially established in 1989 to support the Greenland Ice Sheet Project 2 (GISP 2), Summit Station has established itself over the last 20 years as a world-class research facility. The modern Summit supports research in many disciplines - including meteorology, glaciology, atmospheric chemistry, and astrophysics - and is home to one of the six NOAA Earth System Research Laboratory baseline observatories. Historically, Summit has supported a wide range of campaign and short-term projects, as well as year-round studies. To focus Summit as a NOAA baseline observatory and location for many NSF Arctic Observing Network (AON) projects requiring clean air and snow, the future direction of Summit Station is changing; NSF is transitioning the station to a model focused on long-term measurements. A first step in moving Summit towards this new model is the detailed design for an Atmospheric Watch Observatory – a structure designed to house instrumentation in support of long-term measurements by NOAA and AON projects. Redevelopment of the supporting station infrastructure is in the planning stages, with the goal of establishing a station supported year-round by a small staff with minimal air support.



Figure 1. Rendering of Summit Station 'Model 5'. Image provided by Kumin Assoc.

# Correlation Between Cloud Cover Trends and Surface Temperature Trends: A Comparison Between Barrow, Alaska and Tiksi, Russia

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Barrow, Alaska USA (71.323 °N, 156.609 °W) and Tiksi, Sakha Republic Russian Federation (71.580 °N, 128.92 °E) are two coastal Arctic observatories at almost identical latitudes. These two stations have unusually long meteorological records, and the analysis of monthly temperature trends show significant differences in how temperatures in the two locations are changing. In Barrow, temperature trends between 1945 and 2008 range from +0.015 °C/year to +0.075 °C/year (warming in all months) and in Tiksi, trends between 1935 and 2007 range from -0.02 °C/year to +0.02 °C/year (warming in January, February, May, June, July and cooling in March, April, August, September, October, November).

Clouds have strong radiative interactions with the surface and resulting impacts on surface temperatures. In Barrow, cloud cover trends between 1965 and 1998 range from +0.045 tenths/year to -0.04 tenths/year (decreasing in May, July, November and December and increasing in January, February, March, April June, August, September and October) and in Tiksi cloud cover trends between 1936 and 2007 range from -0.02 tenths/year to +0.038 tenths/year (increasing in all months except June, July, and August). Not all trends were significant, but Barrow seems to have coherent increased cloudiness in late winter and Tiksi seems to have coherent increased cloudiness in summer.

To investigate the possibility of regional connection between cloud cover and surface temperatures, monthly cloud cover trends (in tenths) were then correlated with monthly mean temperatures (°C) for Barrow and Tiksi (Fig 1). The period of comparison was limited to the period between 1965 and 1998 which is the extent of the surface observer cloud cover record for Barrow. Both sites showed a pattern of increasing clouds resulting in warmer surface temperatures in winter, although in Barrow the connection appears to be more statistically robust. In the Barrow summer, there was no statistically significant relationship between cloud cover trends and temperature trends. Tiksi shows a tendency for summer time cloudiness to be negatively correlated with surface temperatures. It is likely that future studies that take into account cloud phase, height and microphysics will contribute to a more robust linkage between cloud and surface properties.

The differences between Barrow and Tiksi are not unexpected given that Barrow is influenced by flows through the Bering Strait and Tiksi is on the edge of the massive Eurasian continent.



**Figure 1.** Correlation between Sky Cover Fraction and Surface Temperature Monthly Means observed in Barrow and Tiksi at the period of 1965-1998.

#### Global Atmosphere Watch Activities in Kenya and Characteristics of Some of the Gas Species

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Kenya serves as host to Mt. Kenya Global Atmosphere Watch Station (MKN), which is complemented by the Nairobi Ozonesonde Station. In this study, the characteristics of ozone data from both stations and carbon monoxide and volatile organic compounds data from MKN were investigated. At MKN, Ozone ( $O_3$ ) and Carbon Monoxide (CO) show strong diurnal variability due to dynamic processes. There are strong seasonal variations of  $O_3$  and CO due to seasonal variation in advection of depleted marine air.  $O_3$  concentrations tend to be more from May to September and lowest in November. Low CO occurs in April-May and November but have high peaks in February and July. These  $O_3$  and CO variations are due to monsoon transport and mountain venting. Volatile organic compounds show almost a similar annual cycle, having minimum values during the months of April and May and maximum values are varying (e.g. for ethane being December and January, butane July and August, and Pentane June). In Nairobi, ozonesondes show that minimum values in September and minimum values in March.



Figure 1. Nairobi vertical ozone profile.



Figure 2. Nairobi total column ozone trend.

### Sonic Anemometer Angle of Attack Errors

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Angle of attack or (co)sine errors are caused by the wakes formed downwind of sonic anemometer transducers. These errors occur when the vertical component of the wind velocity is non-zero, and they cause underestimation of the measured vertical wind speed. The importance of (co)sine errors in eddy covariance based mass and energy budgets have been established by past wind tunnel studies. In more recent field studies, these errors have been quantified in turbulent surface-layer flows. In the present study, (co)sine errors were estimated for over 100 combinations of angle of attack and wind direction using an RM-Young (8100VRE) sonic anemometer and a novel technique to measure the true angle of attack and the wind velocity within the turbulent surface layer. Corrections to the vertical wind speed varied from -5% to 37% for all angles of attack and wind directions examined. When applied to eddy covariance data from two Ameriflux sites, the (co)sine error corrections increased the magnitude of CO<sub>2</sub> fluxes, sensible heat fluxes, and latent heat fluxes by ca. 10%. A sonic anemometer designed with one pair of transducers aligned with the vertical axis (Applied Technologies, Inc., "VX" style) was also tested at four angles of attack (Fig. 2). Corrections to the vertical wind speed measured using this anemometer were within  $\pm 1\%$  of zero. Sensible heat fluxes measured using the Applied Technologies anemometer were ca. 9% greater than fluxes of sensible heat fluxes measured using the RM-Young. These results indicate that sensors with an off-axis transducer orientation, such as the RM-Young (Fig. 1), Gill, and CSAT anemometers, should be redesigned to allow for measurement of the vertical velocity using one pair of vertically aligned transducers, like the "Vx" style Applied Technologies anemometer (Fig. 2).



**Figure 1.** Photograph of a transducer wake in laminar wind tunnel flow.



**Figure 2.** Photograph of the Applied Technologies sensor (center) tilted 30° during the experiment.

# The World Meteorological Organization: The International Dimension of Weather, Water, and Climate

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The World Meteorological Organization (WMO) is a specialized agency of the United Nations (UN). It is the UN system's authoritative voice on the state and behavior of the Earth's atmosphere, its interaction with the oceans, the climate it produces, and the resulting distribution of water resources. Under WMO leadership and within the framework of its programmes, the national hydrometeorological services of the 189 Member nations contribute substantially to the protection of life and property against natural disasters, safeguarding the environment, and enhancing the economic and social well-being of all sectors of society in areas such as food security, water resources and transport. This poster will provide an overview of the WMO programmes and show, through its Technical Commissions and Regional Associations and in support of the U.S. Permanent Representative to the WMO, how YOU can play a role in contributing to the safety and welfare of humanity.



World Meteorological Organization

Working together in weather, climate and water

Figure 1. The WMO logo.

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