

## Annual Scientific Report 2002

NCAR | UCAR | NSF | ASR 2001

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### **Director's Message**



**Tim Killeen - NCAR Director** 

I am very pleased to report on our activities over the past year at the National Center for Atmospheric Research (NCAR). By any token, this has been an exciting year with successful field campaigns, the release of and progress on community models, dramatic advances in our supercomputing capabilities and the contractor's completion of the airframe for the new National Science Foundation research aircraft. We have also made significant steps in the implementation of our strategic plan and in our continuing efforts to broaden and balance the demographics of NCAR's scientific staff -- we look forward to the arrival of 12 new Scientists I in 2003. We were also very busy hosting visitors and guests for two meetings of the NCAR Advisory Council, as well as more than 70 scientific workshops and symposia covering topics such as instrumentation for the new research aircraft, carbon sources and sinks, weather modeling verification, cyber-infrastructure for environmental research and education, megacity impacts on regional and global environments, geographic information systems, and the ASP summer colloquium on aerosols, to name just a few.

As I reported to you last year, NSF conducted a thorough review of all NCAR divisions and UCAR and NCAR management. After the successful review, NSF decided not to compete the next cooperative agreement for the management and operation of NCAR and invited UCAR to submit a proposal for the management of NCAR for another five years. After we submitted our proposal in early October 2002, NSF distributed the proposal for an anonymous peer review and conducted a site review in December 2002.

As you page through the Annual Scientific Report for 2002, you will see we are working hard to implement our strategic plan through cross-divisional initiatives and with the National Science Foundation and our university partners. Below are just a few highlights; you can learn more about these and other activities throughout the report.

### Implementation of Our Strategic Plan

When I last reported to you, we had just completed the NCAR Strategic Plan, NCAR as an Integrator. That document sets forth our mission, vision, values and goals for the next decade. We have moved into the implementation phase for the Strategic Plan and have started work on several high priority scientific initiatives, with the strong support and involvement of the university community. These new initiatives include new efforts in weather and climate modeling, biogeosciences, the water cycle across scales, data assimilation, coronal magnetic fields and space weather modeling, geographic information systems, geophysical turbulence, climate and weather assessment science, and wildfire research. These efforts, now entering their third year of funding,

have made real progress in developing and maintaining collaborative research activity across divisions and with increasing university partner participation. We have also instituted a mentoring element to the initiative process that fosters further collaboration among the strategic initiative leads and the NCAR Directors.

#### **Progress on Community Models**

In 2002, NCAR released a new version of the Community Climate System Model (CCSM-2) after more than two years of preparation involving many NCAR and community scientists. Some of the improvements of CCSM2 are an improved longwave radiation and cloud scheme and an improved prognostic cloud water formulation in the atmosphere component (CAM), an improved anisotropic horizontal viscosity formulation and an increase in horizontal resolution in the ocean component, a new elastic-viscous-plastic ice rheology in the sea ice component, and a new biogeophysics formulation and a river runoff scheme in the land component. The CCSM-2 will be used to contribute to the IPCC Fourth Assessment Report, due in 2007.

Similarly, with partners from many agencies and institutions, we have developed and released the beta version of the new Weather Research and Forecasting (WRF) model, which has been downloaded by more than 1000 scientists worldwide. The WRF model and assimilation system will incorporate advanced numerics and data assimilation techniques, a multiple relocatable nesting capability, and improved physics, particularly for treatment of convection and mesoscale precipitation. It will also incorporate a new software framework that provides a modular, flexible, single-source code for use across diverse computing architectures. WRF is expected to set a new standard for the integration of research and operational forecast models, and to promote closer ties between the research and operational forecasting communities. The WRF is scheduled to become an operational model for both NOAA and DOD agencies in 2004.

Finally, with funding from NASA, we and our partners have started work on the development of a new Earth System Modeling Framework (ESMF), which has the potential to revolutionize numerical simulation of climate, weather, and space weather, by providing a common modeling infrastructure designed for code reuse and enabling extensive interoperability of software components.

### **HIAPER and Supercomputing**

We have continued to support the university community through the provision of research infrastructure and facilities. Atmospheric scientists using NCAR's supercomputing facility have already benefited greatly from the Advanced Research Computing System (ARCS) augmentation, which has brought the total computing capability to the level of approximately 9 Teraflops, peak (read more). The latest NCAR computer system, termed "Bluesky", has now passed its acceptance review and is on line for our users.

HIAPER (High-performance, Instrumented Platform for Environmental Research) In early June 2002, the completed HIAPER "green" (basic) airframe rolled off the Gulfstream assembly line in Savannah, Georgia. In July, Gulfstream transferred the green aircraft to Lockheed Martin's modification facility in Greenville, South Carolina where the aircraft will now reside until its completion and delivery to UCAR in October 2004. The NSF-led HIAPER Community Instrumentation Workshop took place at NCAR from November 4-6, 2002 where participants worked to identify the science thrusts and types of measurements for the HIAPER platform, ensure that the broad research community has a clear understanding of the HIAPER airframe and its basic infrastructure, and discuss the upcoming NSF Announcement of Opportunity (AO) for HIAPER research instrumentation development.

### **IHOP Field Campaign**

In May and June of 2002, the International H20 Project (IHOP) took place in the Southern Great Plains of Oklahoma, Kansas, and the Texas Panhandle. While data analysis will continue for many years, NCAR researchers have already identified two potential dramatic impacts of the IHOP 2002 efforts in improvements in nowcasting convective activity and nocturnal convection. The primary objective of this campaign was to characterize the four-dimensional distribution of water vapor in the lower atmosphere, and apply this improved understanding to the study and prediction of convection initiation. The primary scientific objectives of IHOP consisted of the study of convective initiation, boundary layer heterogeneity and evolution, morning and evening low-level jet, and prefrontal Bore events. The project was also motivated in part by the impact of flash floods on society, which in the US cause billions of dollars in property damage and the largest number of weather-related fatalities. You can read more about this project in this report.

### **Prominence Magnetic Fields**

At NCAR, scientists have made exciting new Solar prominence magnetic field observations using the Advanced Stokes Polarimeter at the Dunn Solar Telescope. This is the first time that prominence magnetic fields have been observed simultaneously in all four Stokes parameters, with a spectral range of 20 Angstrom encompassing three magnetically sensitive

lines with coverage all the way down to the solar limb. Preliminary results confirmed previous evidence that the prominence is permeated with mostly horizontal fields. These preliminary results are dramatic because initial broadband analysis of the polarization signatures suggests that the fields in the prominence feet are horizontal and brings into question some solar models requiring vertical fields. Images and detailed information about these results is available in this report.

This has been an exciting and rewarding year, and I believe that the Scientific Report for 2002 reflects this. I encourage you to explore the many project descriptions and their links, to learn more about NCAR's people, programs and accomplishments.

Tim Killeen

Director



# Annual Scientific Report 2002

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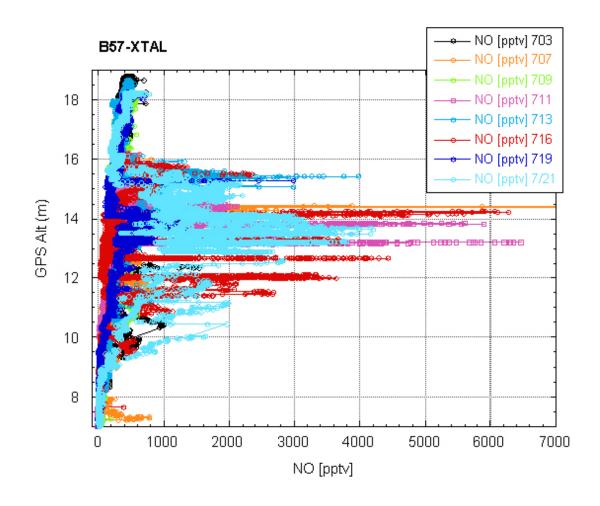
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## **Highlights**

Please click on the division names above to scroll directly to each division's highlights.

### ATMOSPHERIC CHEMISTRY DIVISION

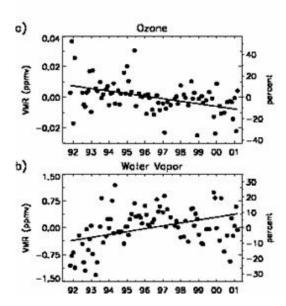
### **Lightning Production of NO in Florida Thunderstorms**



A significant uncertainty in current global chemistry/transport models and their estimates of the tropospheric ozone burden is the input of NOx to the atmosphere by lightning activity. Current global estimates have a wide range of 2-20 Tg(N)/yr. The models are also quite sensitive to how the NOx is distributed vertically by the deep convection since the lifetime of NOx increases strongly with altitude. NOx is also the rate-limiting constituent for production of tropospheric ozone in much of the middle and upper troposphere, the region where the ozone abundance has its largest influence as a "greenhouse" gas. During the recent NASA-sponsored CRYSTAL-FACE program, AON measured NO and total odd nitrogen (NOy) on board the WB-57 aircraft as it penetrated the anvil outflow regions of thunderstorms over southern Florida during the month of July. The results from a number of flights are shown below. In the case of no deep convection or electrical activity, mixing ratios of NO in this altitude range would be of the order of 100 parts per trillion or less. Clearly, the electrical activity has increased the mixing ratios by factors of 25-50 and this increase will have a large effect on ozone production as the outflow mixes over several lifetimes of NOx. By comparison with studies we have made in New Mexico and over Colorado, it appears from preliminary analyses that the Florida storms on average produce significantly higher mixing ratios. The three studies have also shown that a large fraction of the lightning produced NOx accumulates in the anvil outflow region rather than being distributed throughout the vertical extent of the storm.

### **Increasing Trend of Mesospheric Water**

Using a 10-year data set from the UARS/HALOE instrument, Marsh et al. has found that mesospheric water has an increasing trend of about 1% per year, similar to the trend previously reported in the stratosphere. (J. Geophys. Res., in press) In addition, it has been found that ozone measured at sunset has a strong negative trend that peaks at -4% per year around 75 km. The ROSE model calculations indicate that current photochemical understanding can account for a) the trend in sunset ozone, while there is no ozone trend at sunrise; b) the vertical structure of the observed ozone trend, which varies sharply with altitude, and c) the magnitude of the ozone trend, given the observed water changes.



Monthly anomalies (filled circles) at 0.023 hPa (approx. 75 km) for a) ozone and b) water vapor. Data shown are for sunset observations between 17N and 52.5N. Solid line represents the linear trend in the data.

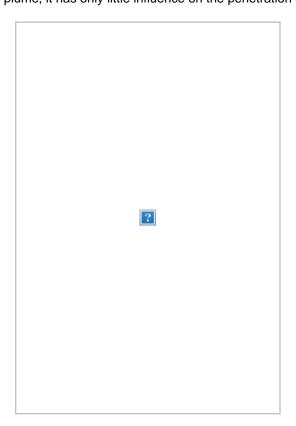
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### **ADVANCED STUDY PROGRAM**

### The nature of transport processes at the base of the solar convection zone:

An example of the research contributions of ASP postdoctoral fellows is the research of first-year postdoc Matthias Rempel, who used two modeling approaches to investigate the nature of transport in the "overshoot region" at the base of the convection zone in the Sun. In the first, he modified the MHD code of Mark Rast (HAO) to allow for separation of the thermal conductivity into a turbulent and radiative component. This separation enables adjustment of the convective properties apart from the radiative ones in the lower half of the convection zone. He then employed a thermal relaxation scheme to accelerate the approach to equilibrium

in the deep radiative layers. These modifications allowed him to apply the model to studies of the overshoot region at the base of the solar convection zone, where crucial storage of strong toroidal magnetic field is thought to play an important role in the solar dynamo. A 2D model with these modifications was able to reproduce many characteristics of previous overshoot models through different assumptions regarding the energy flux and Prandtl number. The model also shows how sensitively the overshoot depends on the structure of convection, which has to be considered when applying numerical results to solar overshoot. The accompanying figure shows a simulation of single downflows driven by cooling from the top boundary and entering a subadiabatic layer (below z = 2). Shown are the temperature perturbations with respect to the initial stratification. The length scale is made dimensionless with the pressure scale height at z = 2. In the upper part (z < 2) the Prandtl number is 1 in both cases, whereas in the lower part (z > 2) the Prandtl number is 0.25 for the left and 4 for the right case. Even though the Prandtl influences significantly the internal structure of the plume, it has only little influence on the penetration depth.



In a parallel study Rempel (collaborating with Mark Rast, HAO) investigated properties of single downflows driven by cooling at the top boundary (see Fig.1). In contrast to the full convection simulations these studies allow a much higher resolution of a single downflow. It was shown that the Prandtl number has nearly no influence on the penetration depth of a single downflow, whereas the full convection simulations show a significant increase of the overshoot depth with decreasing Prandtl number. Thus the dependence of the overshoot depths on the Prandtl number is caused by the different thermal adjustment of the mean stratification and not by a change of the deceleration of a single downflow. With the help of a semi-analytical convection model based on the assumption that the convection is driven by dominant downflows, fundamental results of the numerical simulations could be verified: the structure of the overshoot region is mainly determined by a) the Mach number of the downflows at the base of the convection zone and b) the efficiency of the mixing between downflow material and the surrounding plasma in the overshoot region.

### Mercury released to the atmosphere by biomass burning:

Senior Research Associate Hans Friedli (ASP and ACD), with colleagues from NCAR, U. Washington, Meteorological Services of Canada, Canadian Forest Service, has advanced the understanding of the cycling of mercury during biomass burning, progressing from laboratory to airborne measurements on wildland fuels and expansion to agricultural waste fuels The data indicate that all mercury contained in fuel is released as mostly elemental gaseous mercury with some fuel-dependent portion present in particulate form. The mercury release from fires in temperate US forests is relatively small (2-4 Mg/y), about 22 Mg/y for horsel

forests and about 500 Mg/y for all biomass burning. These estimates reflect the carbon release from biomass burning and landscape-specific emission factors. For reference, the total mercury released to the atmosphere is about 6000 Mg/g.

Friedli and Larry Radke also measured elemental gaseous mercury from sea level to the tropopause as part of the ACE-Asia and ICTC2K2 experiments and detected its transport from the western to the eastern pacific. The ACE-Asia data are extremely

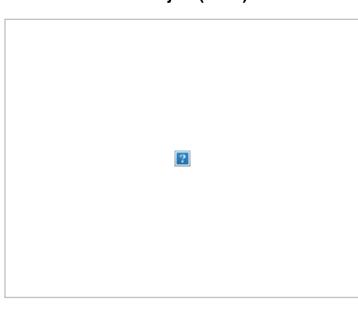
complex representing dust storms, anthropogenic, volcanic and possibly biomass burning signatures contained in multiple layers. The mercury profiles measured over the eastern pacific challenge the currently accepted lifetime for elemental mercury of one year; they indicate that the lifetime may be closer to 100 days. They also identified a large new sink for mercury in the stratosphere as revealed by a stratospheric intrusion depleted of elemental gaseous mercury. An anthropogenic plume encountered off the California coast had back trajectories out of China and Mongolia passing over Korea and Japan.

With coworkers from ACD, CU and as part of the Wildland Fire R&D collaboratory, Friedli also initiated laboratory experiments to determine the type and quantity of compounds emitted from live vegetation, simulating the conditions of an approaching wildfire. An understanding of the evolution of flammable volatiles is important because they are expected to modify flammability, fire dynamics, influence combustion chemistry and physics and, if not combusted, contribute directly and indirectly to the air pollution associated with wildfires. Roasting green or dry vegetation at increasing temperature to 300°C released methanol, acetaldehyde and acetone, readily measured by proton transfer reaction mass spectroscopy. The source of these compounds is not known at this time. They may be stored in the plant, be decomposition products of wood components or be partial oxidation products.

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### ATMOSPHERIC TECHNOLOGY DIVISION

### **International H2O Project (IHOP)**



IHOP focused on improving the ability to forecast convective rainfall amounts by deploying and evaluating an unprecedented suite of water vapor sensors. The IHOP PI's concentrated on designing aircraft tracks for multiple aircraft missions; coordinating various investigator's activities; organizing and running planning meetings; serving on the P-3 transition team to ensure the firstever P-3 deployment of ELDORA and the French Leandre II water vapor DIAL; and overseeing logistical planning for field operations. The yearlong planning effort culminated in a 2-month-long intensive field campaign. Over 200 researchers coordinated activities and obtained measurements on convection initiation events, low-level jets, bores, clear-air boundary layers and heavy rainfall events. Initial analysis of data and reports from investigators indicate that this project was a complete success. For complete information on IHOP, please visit the following link: http://www.atd.ucar.edu/dir\_off/asr02/ASR02accomp1.html

Shown above is one of the most complicated flight tracks that was flown during IHOP, involving all six research aircraft.

### Instrument Development and Education in Airborne Science (IDEAS)

IDEAS was a RAF-led effort that combines improving instrumentation for future NSF airborne research while exposing students from various universities to airborne research on the NSF/NCAR C-130. The program consisted of two phases, one in April and one in October 2002 with a total of 40 flight hours divided between the two periods. Students were required to select a mentor from among the participating scientists and then joined the flight crew operating instrumentation and data systems after suitable instruction by NCAR

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### **CLIMATE AND GLOBAL DYNAMICS DIVISION**

### **Climate Change Research Section**

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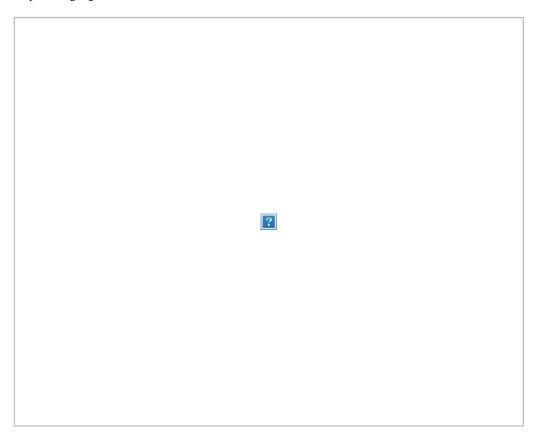
Recent simulations of PCM were done using the new volcanic forcing data put together by of Caspar Ammann (postdoc, Advanced Study Program). These simulations show the additional factor of volcanic forcing, using the same method described in the above paleoclimate simulations, improves agreement of simulated globally averaged temperature with observations.

This **figure** shows the globally averaged surface air temperature anomaly from 1880 to present. Also, the range of observed temperature estimates from several sources is shown in the gray color. Note that the simulated variations of temperature change closely match the increase of the temperature from the 1880s to the present, and the cooling effects of particular volcanoes are striking. The addition of volcanic forcing helps explain the short-term cooling events that are well observed.

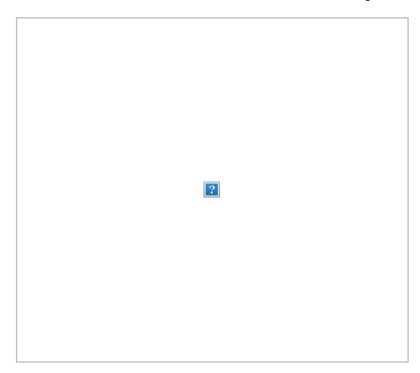
### **Climate Analysis Section**

Aiguo Dai (Climate Change Research Section) and Kevin Trenberth (Climate Analysis Section, CAS) have estimated annual and monthly mean values of continental freshwater discharge into the oceans at 1 degree resolution using several methods. The most accurate estimate is based on stream-flow data from the world's largest 921 rivers, supplemented with estimates of discharge from unmonitored areas based on the ratios of runoff and drainage area between the unmonitored and monitored regions. Simulations using a river transport model (RTM) forced by a runoff field were used to derive the river mouth outflow from the farthest

downstream gauge records. Separate estimates are also made using RTM simulations forced by three different runoff fields, including those from estimates of precipitation P minus evaporation E computed as residuals from reanalyses. Compared with previous estimates, improvements are made in extending observed discharge downstream to the river mouth, in accounting for the unmonitored stream-flow, in discharging runoff at correct locations, and in providing an annual cycle of continental discharge. Snow accumulation and melt are shown to have large effects. The use of river mouth outflow increases the global continental discharge by 19% compared with unadjusted stream-flow from the farthest downstream stations. The river-based estimate of global continental discharge is  $37288 \pm 662 \text{ km}3/\text{yr}$ . The river flow and discharge data are available from the CAS data catalog (http://www.cgd.ucar.edu/cas/catalog/).



This figure shows annual discharge rate ( $10^3 \text{ m}^3 \text{ s}^{-1}$ ) from each 4° lat by 5° long. coastal box. The numbers are the total discharge (in  $10^3 \text{ m}^3 \text{ s}^{-1}$ ) from the coasts behind the solid lines. Blank coastal boxes have zero discharge.



This figure shows annual discharge into the global ocean smoothed using 5° lat running-mean from the new four different cases, compared with that of Baumgartner and Reichel (1975). The one based on the 921 rivers is believed to be best.

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### **ENVIRONMENTAL AND SOCIETAL IMPACTS GROUP**

### Climate Projections, Uncertainty, and Scenarios for Impacts Assessment



This multidisciplinary workshop, organized by Linda Mearns and Warren Washington (CGD), brought together members of the impacts assessment community, decision makers, climate modelers, researchers of uncertainty and emissions scenarios, as well as representatives from various user agencies and programs. Held at NCAR on 17-19 July 2002, discussion centered around user-oriented climate projections and scenarios at the major climate modeling centers in the United States (NCAR, GFDL, and GISS). More than 75 participants assessed needs and opportunities in the generation of climate projections and scenarios, uncertainty in future climate projections, and also formulated a five-year Action Plan to accomplish the creation of a unified program for developing and distributing climate projections and scenarios in the United

States. The workshop is on line at www.esig.ucar.edu/projections/.

### La Niña and Its Impacts: Facts and Speculation



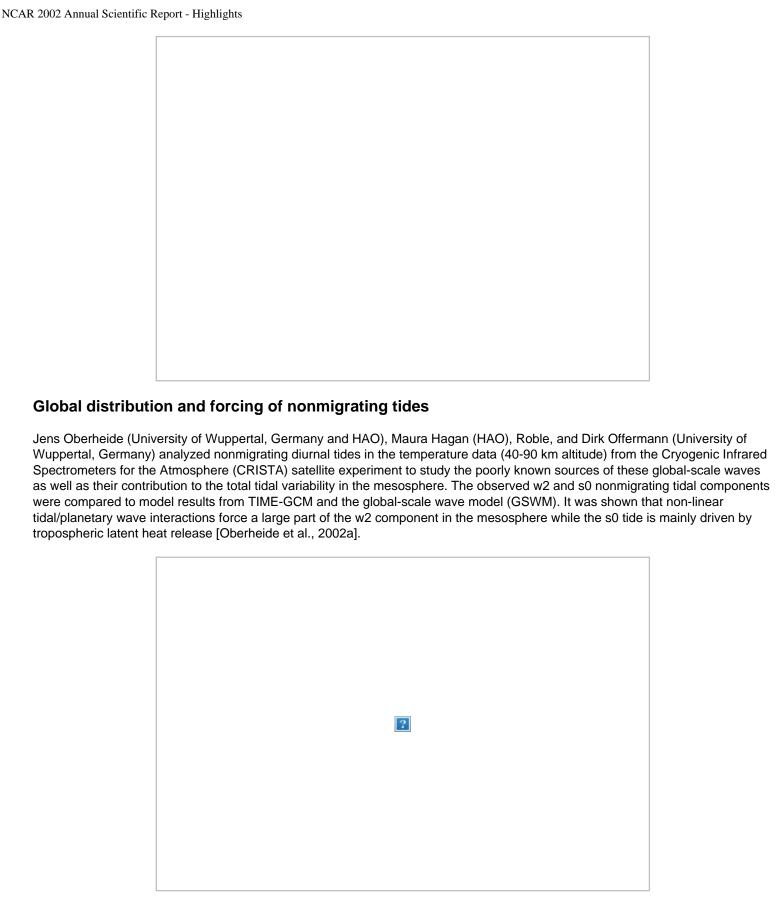
In 1998, Michael Glantz held the first-ever La Niña Summit at NCAR, bringing together researchers, forecasters, and users of LaNiña forecasts to draw attention to the importance of improving our understanding of the La Niña phenomenon, the cold phase of the El Niño-Southern Oscillation cycle. Although people have become familiar with El Niño and its impacts, La Niña is not so well known. A book based on that Summit, which presents updated information about La Niña, was published in FY02 by the United Nations University Press, La Niña and Its Impacts: Facts and Speculation. The book introduces the reader to the La Niña phenomenon, provides a view of the current state of scientific knowledge, presents case studies of La Niña impacts from around the globe, and examines the role of the media in reporting on ENSO, among other topics. More information on the book can be found at www.esig.ucar.edu/lanina.html.

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#### HIGH ALTITUDE OBSERVATORY

### Radiometric Variability and Convection

Mark Rast, Ilaria Ermolli (Astronomical Observator of Rome, OAR), Francesco Berrilli (Universita' Degli Studi Di Roma), and J. Summer Sands (SOARS) have made a three sigma detection of the convective contribution to the supergranular continuum intensity contrast. After careful alignment of CallK and red and blue continuum images, network cells were identified and azimuthally averaged continuum intensities were measured as a function of distance from cell centers. These were then averaged over many Supergranular cells to reduced granular noise. This was done both on unmasked images and after masking out magnetic contributions based on their CallK intensity. Without masking a 0.3-0.4% continuum enhancement due to magnetic network is observed. This is consistent with previous studies. After masking out the magnetic contribution a residual 0.1-0.2% continuum enhancement of supergranular cell centers is observed. This is the first measurement of the thermal signature of the supergranular flow.



Oberheide and Oleg Gusev (University of Wuppertal, Germany) extended the tidal analysis of CRISTA temperatures into the lower thermosphere. They analyzed the migrating diurnal tide and 8 nonmigrating diurnal components up to an altitude of 120 km.

were the first global measurements of nonmigrating temperature tides in this altitude region. The analyzed temperatures account for the deviation from the local thermodynamical equilibrium (non-LTE, NLTE). The nonmigrating tides became the dominant tidal components above 90 km and exceeded the migrating tidal amplitude by an order of magnitude at 110 km (80 K compared to 8 K)

[Oberheide and Gusev, 2002].

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### MESOSCALE AND MICROSCALE METEOROLOGY DIVISION

# Ensemble Forecasting on the Mesoscale: Storm-scale prediction with the ensemble Kalman filter (EnKF)

One major difficulty of mesoscale data assimilation is that observations that are plentiful involve only a subset of atmospheric variables while observing platforms that measure all variables are sparse. Balances that are relevant at large scales are questionable at the mesoscale. A method to address this problem is to explore the potential of Ensemble Kalman filter (EnKF) for mesoscale assimilation. Chris Snyder and Fuqing Zhang (Texas A&M University) applied the EnKF to the analysis and prediction of convective scale motions using a simple cloud model. They have shown that a 50-member EnKF is able to



estimate tangential and vertical velocity and temperature, given 4--6 scans (or about 20--30 minutes) of simulated observations of radial velocity extracted from a reference simulation of a supercell thunderstorm. These results are the first for the EnKF, outside of global atmospheric models, and they hold substantial promise for the application of the EnKF to meso- and convective scales.

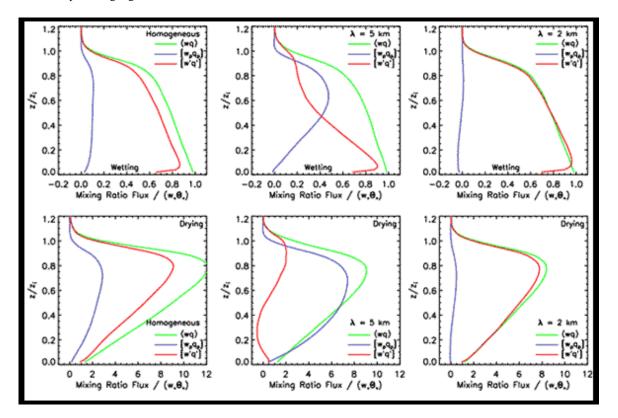
# Surface-Atmosphere Interactions: Influence of soil moisture heterogeneity on the planetary boundary layer (PBL)



Select one of the following links to view the above movie: Animated GIF | AVI format | MPEG format



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An important goal in mesoscale research is to understand the influences of surface heterogeneity surface-atmosphere interactions. Edward Patton (long-term visitor, Penn State), Peter Sullivan, and Chin-Hoh Moeng used their clear-PBL large-eddy simulation (LES) code, which was recently coupled to the NOAH (National Center for Environmental Prediction/Oregon State University/Air Force/Office of Hydrology) land-surface model, to study the PBL response to large-scale soil moisture heterogeneity (ranging from 2-30 km). In the presence of heterogeneity, the atmosphere transports moisture differently depending on the initial moisture state in the overlying atmosphere, wet versus dry. In both situations, land-surface heterogeneity induces organized motions that scale with the heterogeneity (see movies, above). However, depending on the moisture state of the overlying atmosphere, the phase-correlated component can either be the sole contributor to the vertical water vapor mixing ratio flux, or make zero contribution (see figure, above). One of the important findings of this study is that if researchers plan to use the eddy-correlation technique to measure vertical water vapor mixing ratio fluxes at a point within a region of large-scale moist or dry soil conditions, they could dramatically misestimate the vertical fluxes if they ignore the contributions to the flux from organized motions induced via heterogeneous surface forcing.

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### RESEARCH APPLICATIONS PROGRAM

### **Aviation Weather Program**

For the past 20 years the Research Applications Program has conducted aviation weather research, development, and technology transfer programs for the Federal Aviation Administration. In 2002 this work was recognized with two prestigious awards. The first, the FAA's Excellence in Aviation Award, was presented to NCAR and other national laboratories and universities that participate in the Aviation Weather Research Program (AWRP). The award recognized the team's superior research efforts that have provided significant benefit to the public through "more accurate and accessible weather observations, warnings, and forecasts." The second, The Aviation Meteorology Award from the National Weather Association (NWA), recognized the AWRP for funding research, development and phased implementation of products, displays, and a user-friendly dissemination system "for the safe and efficient flow of air traffic well into the future."

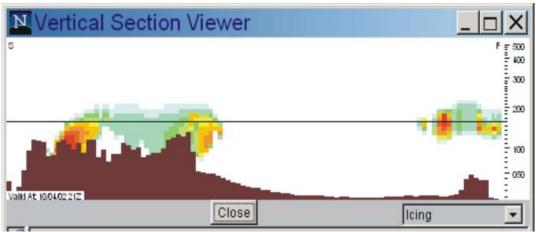
One of the new products mentioned in the NWA award was the Current Icing Product (CIP), developed at RAP over the course of a 12-year in-flight icing research effort and approved for operational use in 2002 by the FAA and the National Weather Service. The "operational" designation was the final step in a rigorous review process by the FAA and NWS' Aviation Weather Technology Transfer (AWTT) Board designed to ensure that new products meet the highest standards for quality. CIP is an excellent example

of an end-to-end research, development, and technology transfer effort with clear benefit to the public.

The algorithm combines information from a numerical weather prediction model and observations to provide a 3D gridded depiction of the likelihood of icing over the CONUS. The observations, from the GOES 8 and 10 satellites, NEXRAD radar mosaic, NWS surface observations, and voice reports from pilots, are mapped to the NCEP Rapid Update Cycle (RUC) model grid, which has 40-km horizontal resolution. Vertical resolution is re-mapped to 1000-ft levels. A 20-km version, matching the current, higher, resolution of the model, is being tested. From these maps, "interest maps" are constructed which reflect how that information is related to the presence or absence of supercooled liquid water within any gridded box. The interest maps are combined using fuzzy logic methods to come up with a final product of the likelihood of encountering icing conditions.

CIP has been transferred to the NWS' Aviation Weather Center in Kansas City and tailored for the different data sources and formats used there. Code was streamlined to run more quickly and hardened to avoid failures. Additional effort was required to produce graphical and gridded products on the Aviation Digital Data Service (ADDS, see <a href="https://www.aviationweather.gov">www.aviationweather.gov</a>) from the transferred code. Output is now available on ADDS in graphical format including constant-altitude views and vertical cross-sections along user-selected flight paths. Gridded output is also available in GRIB format. The user may also link to a page that provides information on the quality of the algorithm's performance, thus gaining a measure of confidence in the product.





### **Maintenance Decision Support System**

Each year, 6,600 people die, 470,000 people are injured, and 544 million hours of time are lost on America's highways during bad weather. In an effort to address these problems, the Federal Highway Administration (FHWA) has sponsored the development of a next-generation road weather information system. A team of national laboratories led by NCAR was tasked with designing and developing a new information tool, the

winter road Maintenance Decision Support System (MDSS). In 2002 the team delivered the prototype system to the FHWA. Designed with the needs of state Departments of Transportation in mind, the MDSS will allow winter maintenance managers to view predicted weather and road conditions and generate road treatment plans on a route by route basis before deteriorating road conditions occur. An improved capability for predicting the impact of weather on road conditions will allow managers to plan treatment scenarios based on available resources, as well as receive treatment recommendations based on proven rules of practice.



"Having access to proper weather and road condition information before and during adverse winter weather conditions will help transportation system managers take appropriate measures to keep roads open," FHWA Administrator Mary E. Peters said. "MDSS will help make roads safer."



The system combines standards of practice with the latest weather forecasting techniques and road condition models. It uses advanced winter prediction capabilities to recommend maintenance courses of action. The system displays various maintenance alternatives and their resulting benefits, which will allow highway departments to deploy snowplows, choose chemicals, and improve road conditions more effectively while also reducing response costs. The system also will lead to more efficient use of chemicals, which will reduce the impact on the environment. Private industry has been engaged in the development process from the beginning and is expected to build new products and services around the core capabilities of the prototype MDSS.

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### **SCIENTIFIC COMPUTING DIVISION**

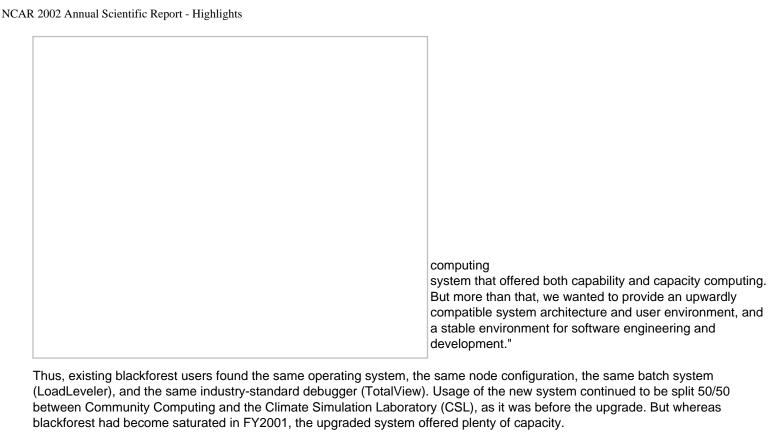
### Distributed Shared Memory (DSM) systems grow in prominence and performance at NCAR

The production supercomputer environment managed by SCD for NCAR has evolved over the decades. During the last 18 years, SCD has brought NCAR's science into the world of multiprocessing supercomputers. Prior to the introduction of the four-CPU Cray X-MP in October 1986, all modeling was performed with serial codes. Since then, the focus has been on redeveloping codes to harness the power of multiple CPUs in a single system, and most recently, in multiple systems.

SCD's computer room is now dominated by Distributed Shared Memory (DSM) systems, most notably the IBM SP system blackforest, with preparations well underway to install the larger and more powerful IBM Cluster 1600 system bluesky.

Early in FY2002, phase I of the Advanced Research Computing System (ARCS) was delivered. This more than doubled the size of blackforest, to 1,308 processors. Shortly after this upgrade, a new IBM p690 system with 16 POWER4 processors was delivered. This machine was used for testing and system development in preparation for a large IBM Cluster 1600 system scheduled for delivery in October 2002. Also during FY2002, four systems were decommissioned and two new systems installed. In addition, there were major system software upgrades performed on all major supercomputers.

SCD Director Al Kellie said, "When we designed the ARCS RFP, we wanted a production-level, high-performance

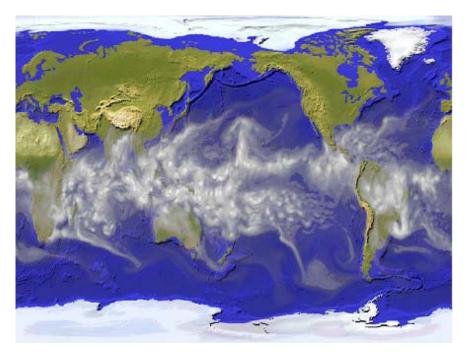


To prepare NCAR's computer room for the new ARCS equipment arriving in FY2002, SCD staff started work in early FY2001 to specify, procure, and install a new electrical power distribution system to support the next three years of the ARCS contract. This forms the cornerstone of a solid infrastructure for SCD to continue providing reliable, production-oriented services and equipment as tools for science.

The upgraded blackforest system went into production in December 2001, and it is accelerating research in global and regional climate change, droughts, short-and long-range weather prediction and warnings, wildland fires, turbulence, atmospheric chemistry, space weather, and other critical areas. The NSF purchased the machine for use at NCAR to advance a wide range of research topics in the agency's ten-year plan for the geosciences.

### Progress in the multi-institutional collaboration on the Earth System Modeling Framework

The Earth System Modeling Framework (ESMF) is building software infrastructure for climate, weather, and data-assimilation applications. This effort is being conducted with an exceptionally broad group of collaborators: SCD, CGD, and MMM at NCAR; NOAA GFDL and NCEP; MIT; the University of Michigan; DOE ANL and LANL, and NASA-GSFC DAO and NSIPP. The project is organized around a series of 11 milestones, the first four of which were submitted during FY2002. Detailed information is provided in this report and at <a href="http://www.esmf.ucar.edu/">http://www.esmf.ucar.edu/</a>.



The Community Climate System Model-2 is one of 15 testbed applications planning to adopt the Earth System Modeling Framework. The plot above shows precipitable water at T170 resolution.

During FY2002, the Earth System Modeling Framework team accomplished the following:

- Negotiated a three-year, \$9,800,000 contract with the NASA Earth Science Technology Office,
   \$2,600,000 of which will go to NCAR SCD for implementing the core framework
- Established a collaborative development environment and communal repositories
- Collaboratively created an ESMF Software Developer's Guide and an exhaustive ESMF Requirements
   Document
- Organized a community meeting with 80+ attendees in Washington, DC, in May 2002 to review the Requirements Document and solicit additional input
- Assembled the ESMF Validation (EVA) Suite and performed performance baselines on application codes that will be adopting the framework
- Collaboratively developed an ESMF Architecture Document, an ESMF Implementation Report, and a Build and Test Plan
- Selected the ESMF Executive and Advisory Boards and hosted their first meeting at NCAR in September 2002
- Submitted the first Annual Report for the ESMF project

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# Annual Scientific Report 2002

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### **Publications**

During Fiscal Year 2002, NCAR published over 500 refereed articles with approximately 540 university co-authors. We encourage you to visit each division's complete listing by using the navigation bar at the top of this page.



## Annual Scientific Report 2002

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### **Educational Activities**

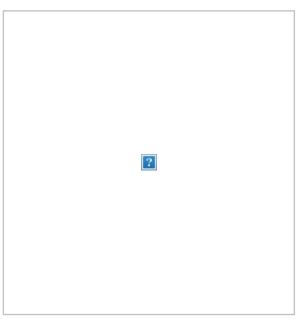
For over 40 years, NCAR has played a leadership role in advancing scientific knowledge of our planet's atmosphere, ocean, related biogeochemical systems, and Sun-Earth relationships. In addition, our studies of the global environment and the impacts of global change on society inform both scientists and policy makers. Outreach to a wide range of audiences and educational communities allows advances in scientific knowledge to be disseminated in order to educate students at all levels, as well as to enhance public science literacy. Through development of educational resources and technologies, professional development workshops, conferences, special events, public tours, and exhibits, the UCAR Office of Education and Outreach (E&O) works with internal and external partners to achieve this integration of research and education.

To view the 2002 NCAR Scientific Report on Education and Outreach, please click here.



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# **Director's Message**



Daniel McKenna, ACD Director

## The Atmospheric Chemistry Division's (ACD) Mission is:

- to understand the composition of the atmosphere, the processes that modify and control atmospheric composition, and how they may change in time due to natural and human induced changes.
- to provide relevant, reliable, accessible, unbiased, and timely information on atmospheric chemistry to government and society.
- to act as an intellectual resource and enabler to the wider atmospheric sciences community by the development of new capabilities and methodologies, and the planning and execution of complex field experiments.

We advance our scientific mission through field and laboratory experiments that test theory or address fundamental questions. To support these experiments we develop leading-edge instrumentation,

techniques, and observing systems to make new or better measurements. ACD also develops and maintains a hierarchy of numerical models that are applied to laboratory experiments, field campaigns, and other process studies. Our societal mission is further advanced through the timely dissemination of results in the scientific literature and to the public, by contributing to national and international assessments, and by providing direct input to policy-makers. Our community mission is advanced by the organization of large-scale activities and facilities and by the provision of community instrumentation and models. We assist in the scientific development of the next generation of atmospheric scientists by providing a wide range of formal and informal training opportunities.

ACD has three main research themes: tropospheric chemistry, middle atmosphere chemistry and dynamics, and biosphere-chemistry-climate interactions. The division is organized into 16 specialist groups whose individual missions cover a broad spectrum of instrumental, experimental and theoretical goals. Two groups undertake basic laboratory studies of gas-phase (Geoffrey Tyndall) and heterogeneous processes (David Hanson). Two groups use gas chromatography and mass spectroscopy techniques to measure a range of hydrocarbons, halocarbons, organic nitrates, and other species either from whole air samples (Elliot Atlas) or in situ samples (Eric Apel). Two groups (Fred Eisele and Christopher Cantrell) specialize in chemical ionization mass spectroscopy) techniques to measure a wide range of compounds, including the two important radical species hydroxyl (OH) and hydroperoxy (HO2) radicals. These measurements are complemented by the measurement of spectrally-resolved actinic fluxes allowing calculation of photolysis frequencies of a number of molecules of atmospheric importance (Richard Shetter). The tunable diode laser group measures formaldehyde (CH2O) and radical sources (Alan Fried). Biogenic trace gas fluxes to the atmosphere are determined by employing a variety of analytical techniques (Alex Guenther). Our measurement capabilities also include chemiluminescence measurement of many reactive and reservoir nitrogen species in the troposphere and lower stratosphere (Brian Ridley). Global (Anne Smith), regional, and process models (Sasha Madronich) have been developed. There are several groups that specialize in remote sensing of the atmosphere. Column abundances of several stratospheric species are retrieved from both ground-based sites and airborne platforms (William Mankin). John Gille leads our spaceborne remote sensing activities with the now-operational Measurement of Pollution in the Troposphere instrument (David Edwards) and the High Resolution Dynamics Limb Sounder instrument (Gille). Satellite data analysis and assimilation (William Randel) ensure good exploitation of the wealth of satellite data available now and in the future.

ACD is the lead division for NSF s Global Tropospheric Chemistry Program (GTCP). We also collaborate with NCAR s Climate and Global Dynamics Division (CGD), High Altitude Observatory (HAO), and Mesoscale and Microscale Meteorology Division (MMM) on NCAR s general circulation, regional, and whole-atmosphere community models. These interactions also require collaboration with the Scientific Computing Division. ACD works with the Atmospheric Technology Division (ATD) on instrumentation and field campaigns. Division staff are active participants in cross-NCAR programs such as the Advanced Study Program s Geophysical Turbulence Program and postdoctoral fellowships.

Division scientists also play an active role in many national and international community efforts, ranging from activities of the North American Research Strategy on Tropospheric Ozone (NARSTO) and International Global Atmospheric Chemistry (IGAC) to international ozone and climate assessments.



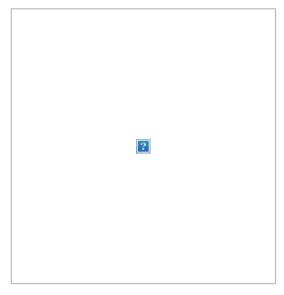
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## **Scientific Highlights**

### Global Modeling (GM)

### Increasing trend of mesospheric water

Using a 10-year data set from the UARS/HALOE instrument, Marsh et al. has found that mesospheric water has an increasing trend of about 1% per year, similar to the trend previously reported in the stratosphere. (*J. Geophys. Res.*, in press) In addition, it has been found that ozone measured at sunset has a strong negative trend that peaks at -4% per year around 75 km. The ROSE model calculations indicate that current photochemical understanding can account for a) the trend in sunset ozone, while there is no ozone trend at sunrise; b) the vertical structure of the observed ozone trend, which varies sharply with altitude, and c) the magnitude of the ozone trend, given the observed water changes.



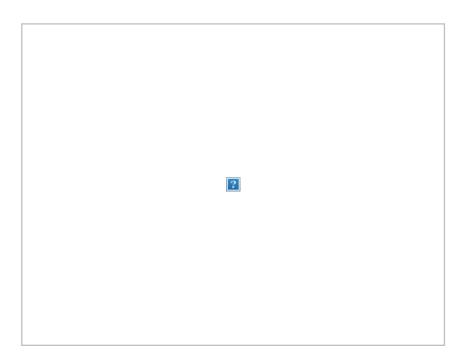
Monthly anomalies (filled circles) at 0.023 hPa (approx. 75 km) for a) ozone and b) water vapor. Data shown are for sunset observations between 17N and 52.5N. Solid line represents the linear trend in the data.

#### **Measurements, Standards and Intercomparisons (MSI)**

### Participation in the international non-methane hydrocarbon intercomparison experiment (NOMHICE)

The MSI Group (Eric Apel) contributes to understanding of biogeochemical cycling, atmospheric trace gases and tropospheric photooxidants. One of the major projects for the group last year was their participation in Task 4 of the international non-methane hydrocarbon intercomparison experiment (NOMHICE). This is the first time an international intercomparison has been conducted with a collected whole air sample. The results from this study have recently been submitted to the *J. Geophys. Res.* Atmospheres. Figure 1 below shows a summary of some of the important results from the study. For each analysis, the geometric mean ratio (i.e., the antilog of the mean of

the logs of the ratios, which is indicated by the symbols) indicates the average fractional systematic error of that analysis. The mean of the geometric mean ratios of the 30 analyses is 0.90, which indicates that, on average, the analyses were 10% lower than the NCAR-MSI reference concentrations. The average systematic errors of the individual analyses ranged from 55% low (analysis 27) to over a factor of 2 high (analysis 28). The geometric standard deviation of the ratios for each analysis (i.e., the antilog of the standard deviation of the logarithms of the ratios, which is indicated by the bars) gives a measure of the 1s precision of the measurements in the analysis.



### Stratospheric / Trophospheric Measurements (STM)

### Firn air sampling: Studies of historical trends of trace gases in the 20th century

Studies of the historical trend of tropospheric trace gases have continued in collaboration with William Sturges (University of East Anglia, UK), Jerome Chappellaz (Centre National de la Recherche Scientifique [CNRS], France), Jakob Schwander (University of Berne), James Butler and Steven Montzka (NOAA CMDL, Boulder). Historical trends are inferred from trace gas profiles trapped in firn air in polar regions. Depending on the rate of snow accumulation and the depth of the close-off layer (where porous firn becomes solid ice), trace gases from the early to mid-20th century may be sampled. This past year, the S/TM Group combined their analyses of NMHC from 2 firn cores in the Northern Hemisphere (Devon Island, Canada and NGRIP, Greenland) and several Antarctic firn cores (including S. Pole) [Figure 2]. As expected from contemporary distributions of NMHC, significantly higher levels of NMHC are found in the Northern Hemispheric samples compared to the Southern Hemisphere. A coherent trend in NMHCs from the mid-sixties to the present are observed in the two Northern Hemispheric firn sample sets, with similar features in the Southern Hemisphere. Atmospheric levels of NMHC showed an increase from the 1950s until the mid-1970s or early 1980s. Since that time there has been a consistent decrease in NMHC concentrations in the troposphere, presumably because of decreased emissions from more stringent environmental controls. Details of the relationship between inferred atmospheric history and emissions estimates are currently being examined to evaluate this hypothesis.

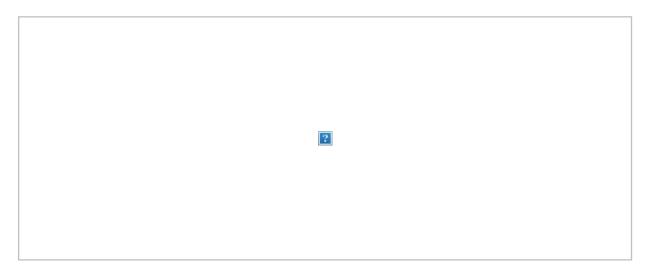
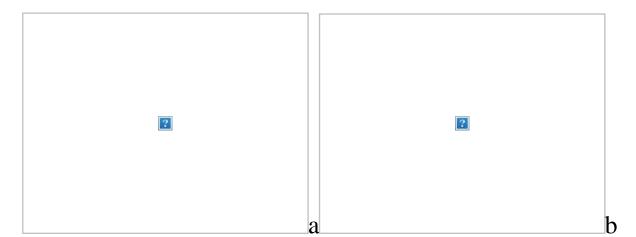


FIGURE 2.  $\clubsuit$  Historical trends of  $C_2$  and  $C_3$  hydrocarbons in the atmospheres of the Southern (left) and Northern (right) hemisphere inferred from firn air profiles at South Pole, Devon Island, and NGRIP.

### **Atmospheric Radical Studies (ARS)**

### Comparison of total peroxy radical levels

Observations of total peroxy radical (HO<sub>2</sub> + RO<sub>2</sub>) levels were compared with a measurement-constrained steady state model of radical concentrations for the geographical and temporal domain of the TOPSE (Tropospheric Ozone Production about the Spring Equinox) campaign (February-May, 2000; 40 to 85 degree north latitude). The data were averaged into two latitude bands: MLB or middle latitude band (40 to 60 degrees) and HLB or high latitude band (60 to 85 degrees). In Plate 1, panels a and b show the contour averaged observations, panels c and d shown the contour averaged steady state model results (coincident with the observations), and panels e and f show the contour averaged ratio of measurements to model results. The average ratios are 1.04 and 0.94 in the MLB and HLB, respectively.



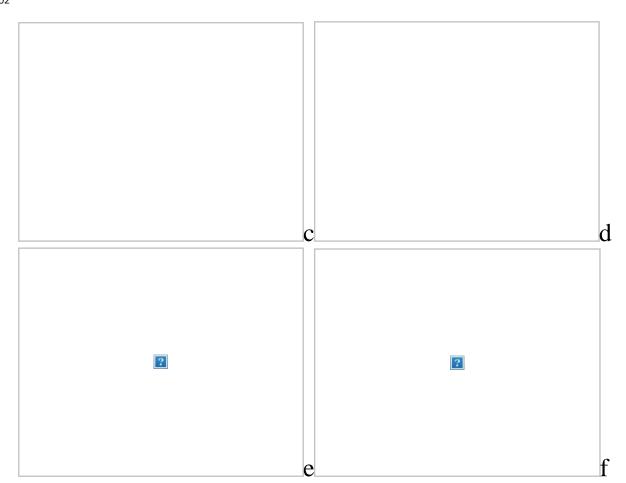


Plate 1. TOPSE peroxy radical concentrations (a,b) measured, (c,d) calculated from steady state model at the coincident measurements, and (e,f) ratio of coincident measured to steady state concentrations, for the MLB (left) and HLB (right) regions.

### Tunable Diode Laser (TDL) Spectroscopy

### Formaldehyde studies

The group participated in the TRACE-P 2001 airborne field campaign in part to extend detailed  $CH_2O$  measurement-model comparisons from high northern latitudes, successfully carried out during TOPSE, to the Asian Pacific region, a region where past studies have shown rather large  $CH_2O$  measurement-model discrepancies. This region, furthermore, is characterized by large frequent continental outflow events where Asian pollution affects large geographic regions of the remote Pacific Ocean. As  $CH_2O$  is intimately involved in radical production and cycling processes,  $CH_2O$  measurement-model comparisons are particularly important in attempts to understand the magnitude and extent of the affected remote areas.

Figure 1 illustrates the altitude dependence of our TRACE-P CH<sub>2</sub>O measurements and comparisons with the NASA Langley box model results.



Figure 1:  $CH_2O$  measurement and box model results from the TRACE-P mission for 8 altitude and 3 longitude bins: Western Pacific (110 to 150  $\spadesuit$  longitude), Central Pacific (150 to 200  $\spadesuit$  longitude) and Eastern Pacific (> 200  $\spadesuit$  longitude). The number of comparison points for each altitude range is indicated.

This plot, which is part of a comprehensive  $CH_2O$  measurement-model comparison study (Fried et al., TRACE-P special issue), illustrates excellent measurement-model agreement for 3 longitude bins for all altitudes > 3 km. However, in the Western Pacific 0 to 1 km range, where Asian outflow of pollution is most pronounced, the box model results underpredicts the measurements. Although this has been observed in other studies, the TOPSE 2000 and TRACE-P studies are perhaps the first such studies to employ comprehensive and verifiably accurate  $CH_2O$  measurements to further examine this effect in terms of box model shortcomings (i.e., steady-state break down and missing and/or under representative non-methane hydrocarbons (NMHCS)). Our TRACE-P analysis further examines measurement and model variances as an additional means of assessing model performance.

In the Central Pacific region, where large pollution outflow is no longer evident, the model results are significantly higher than measurements in the 1 2 km range. Examination of individual flight legs comprising the Central Pacific as well as the other two longitude bins, reveals a persistent model overestimation, which becomes obvious only during non-polluted conditions. Such behavior, which has not been previously reported, is thought to be due to oceanic uptake of CH<sub>2</sub>O. Further analysis in this area is underway.

Figure 2 further examines in more detail the  $CH_2O$  measurement-model comparisons for all 3 longitudes combined for the 8 to 12 km region. This represents the first such detailed  $CH_2O$  study in the 8 to 12 km region, a region where extra  $HO_x$  sources are thought to be important. Both the upper and lower traces indicate overall good measurement-model agreement for this important altitude region, with the exception of background and stratospherically-influenced air masses. In both cases, the model results underpredict the measurements, and the model variance collapses relative to measurements in the *All Comparisons* and *Elevated Precursors* categories. Although it is clear that our finite measurement detection limits (1-minute LOD of 15 to 50-pptv at 1s) contribute to extra measurement variance in all cases, one cannot discount the fact that the box model does not capture additional  $CH_2O$  production pathways in background and stratospherically-influenced air. It is interesting to note that the NASA box model underpredicts  $HO_x$  measurements in this regime, which is consistent with the need for additional  $HO_x$  sources from gases like  $CH_2O$ . We are presently working with NASA to further examine this aspect.

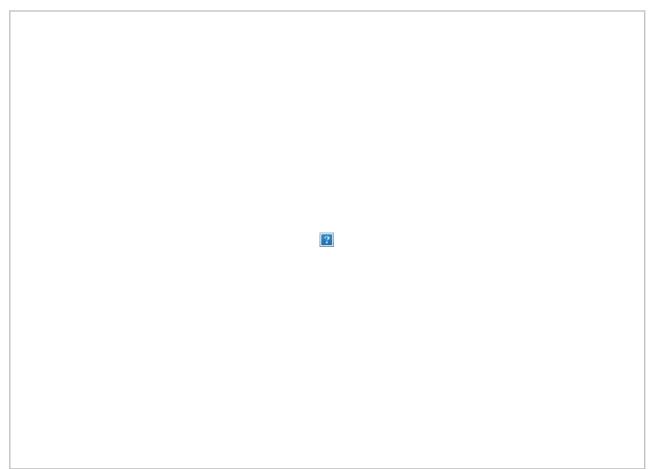
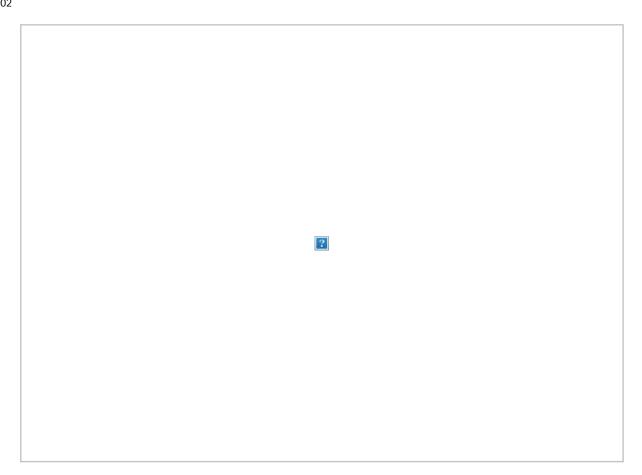


Figure 2: Time coincident measurement-model comparisons for the 8 to 12 km altitude region. The upper trace shows box and wisker plots (box: 25% to 75% of the data, wiskers represent 10% and 90% of the data, and the points show < 1% and > 99% outliers). The elevated and background air categories were determined based upon various NMHCs, CO, CH<sub>4</sub>, and aerosol concentrations, while the stratospherically-influenced air was determined based upon  $O_3$  and CO levels ( $O_3 > 100$  ppbv and CO < 80 ppbv). The bottom plot shows an overall histogram for the measurement-model differences in the 8 to 12km region, irrespective of the air mass type.

### **Biosphere & Atmosphere Interactions (BAI)**

### Boundary Layer CO<sub>2</sub> Vertical Profiles

Greenberg, Roger Hendershot, William Bradley, Prevost, Turnipseed, Potosnak, Harley and Guenther integrated an in-situ CO<sub>2</sub> analyzer into the NCAR-ACD tethered balloon profiling system in FY2002 and deployed the system in Manaus, Brazil, along with collaborators Julio Tota (University of Sao Paulo) and Antonio Nobre (Instituto Nacional de Pesquisas da Amazonia [INPA]), and Niwot Ridge Colorado, along with R. Monson (Univ. Colorado), Jielun Sun (NCAR-MMM), Britt Stephens, Steve Oncley and Tony Delaney (NCAR-ATD). The profiling system successfully characterized CO<sub>2</sub> gradients in the convective and nocturnal boundary layers and will be used to better understand dynamics of CO<sub>2</sub> exchange between terrestrial ecosystems and the atmosphere. The Niwot Ridge study was an interdivisional effort sponsored by the NCAR Biogeosciences program.



Nighttime Vertical Profiles of  $CO_2$  concentration measured above a tropical rainforest near Manaus Brazil using a tethered sampling system.  $\clubsuit$  Each profile represents a specific time (e.g., 105 am, 317 am, to 402 am, all times are local time).  $\spadesuit$  These profiles can be used to quantify the strong  $CO_2$  flux from the forest and the entrainment flux from above.  $\spadesuit$ 

### **Atmospheric Radiation Investigations and Measurement (ARIM)**

### Final TRACE-P actinic flux and photolysis frequency data

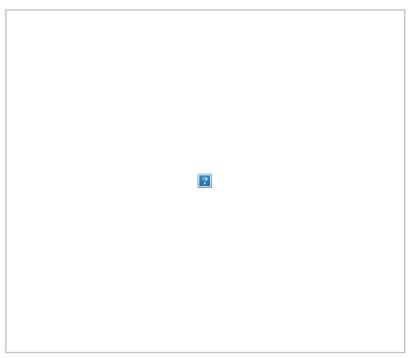
A large effort was put into final data reduction and analysis of the TRACE-P actinic flux data. At the request of other TRACE-P investigators, additional molecules were added to the data reduction effort. These included the oxygenated organics butanal, pentanal, acetaldehyde, methylethyl ketone, and glyoxal, which were measured for the first time on a GTE mission. ARIM personnel gave presentations on the effects of clouds and aerosols on photochemical data at TRACE P data workshops in October 2001 and June 2002. Further analysis of the photochemical data has led to a collaborative set of papers with Gregory Charmichael s group (University of Iowa) and James Crawford s group (NASA LaRC) on cloud and aerosol effects on the photochemistry of the Asian outflow. The ARIM group has taken the lead on Impact of Clouds on Photolysis Frequencies and Photochemistry during TRACE-P, Part I: Analysis using Radiative Transfer and Photochemical Box Models by Lefer, Shetter, Hall, Crawford, Jennifer Olson, You-Hua Tang, and Carmichael, to be submitted to a special TRACE P section of *J. Geophys. Res.* and are co-authors on Impact of Clouds on Photolysis Frequencies and Photochemistry during TRACE-P, Part II: Analysis using a 3-D Regional Chemical Transport Model.

### **Laboratory Kinetics (LK)**

### **Chemistry of Acetic and Peracetic Acid**

Acetic acid and peracetic acid are important trace constituents of tropospheric air and are present as the result of direct anthropogenic and biogenic emissions (acetic acid only) and as by-products of hydrocarbon oxidation processes. Removal of these two species from tropospheric air is likely controlled by deposition processes in the boundary layer, but gas phase processes are also expected to play a role, particularly in the free and upper troposphere. At present, there is essentially no data available on gas phase destruction of peracetic acid, and

discrepancies exist in the current database for acetic acid loss. The Group has recently obtained laboratory data on the photolysis rates for these species and the rate coefficients for their reaction with OH. Data on peracetic acid show that this compound behaves much like an organic hydroperoxide, with OH reaction and photolysis both occurring in the troposphere with time constants on the order of a week or two. Our studies of the OH/acetic acid rate coefficient alleviate a long-standing discrepancy in the literature. The results indicate that the rate coefficient has a negative temperature dependence, and that the lifetime for acetic acid removal via OH reaction is about one week.



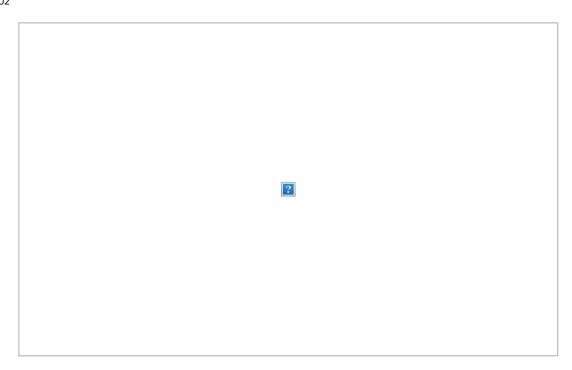
The figure shows ultraviolet absorption cross sections of gas-phase peracetic acid (solid line) compared to those in isooctane solution (diamonds), and gas-phase H2O2 (triangles), CH3OOH (squares), and HOCH2OOH (open circles).

### The Optical Techniques (OT)

### **Network for Detection of Stratospheric Change (NDSC)**

The Network for Detection of Stratospheric Change is a network of high quality ground based observing stations for early measurement of changes in the composition and state of the stratosphere and determination of their causes. In addition it provides high quality data for validating atmospheric models and for comparison with measurements from satellites. The group operates a Fourier transform infrared spectrometer at Thule, Greenland (76.53 N), one of the Network for Detection of Stratospheric Change (NDSC) primary stations. We have obtained data automatically whenever the weather was suitable and the sun was above the horizon, and have analyzed those data for column amounts of gases, including both stratospheric gases important in ozone chemistry and tropospheric gases related to climate change.

The shape of spectral lines in the infrared contains information on the height distribution of the absorber up to altitudes, typically 30 km, at which Doppler effects overwhelm pressure broadening. The Thule spectrometer has sufficient resolving power, about a million, to allow inversion of the line shape to produce a low resolution vertical profile. In collaboration with ACD Affiliate Scientist Aaron Goldman (University of Denver) and visitor Frank Hase (University of Karlsruhe [IFK]), the group has been developing the method for the inversion. The figure below shows a retrieved profile of HCl during Arctic spring; the profile was retrieved from fitting the HCl line shown in the left panel. The smooth profile on the right was the initial a priori profile, and the profile with the crosses is the retrieved profile showing HCl depletion in the lower stratosphere.



Measurement of Pollution in the Troposphere (MOPITT) Data Validation

Validation activities are essential at each level of the data processing to ensure a full understanding of the in-flight MOPITT performance, to allow characterization of measurement accuracy, precision, and resolution, and to point the way to needed improvements. In most of this validation activity, a step-by-step approach has been used starting with the simpler situations, learning from the results, before moving on to more complicated cases. The MATR aircraft instrument team (Alan Hills, Jianquo Nui, and Deeter) has continued studies using the 2001 flight data taken: (1) during April and May over the Oklahoma CART site, and (2) during November over three Western U.S. cities (Los Angeles, Las Vegas, and Denver).

These flights were supported with in-situ measurements by Paul Novelli (NOAA Climate Modeling and Diagnostics Laboratory [CMDL]). Kate Paulin, a student visitor from Oxford University, was also involved in this work. Emphasis has been placed on quantifying sources of radiance bias and noise for both the longwave LMC and PMC channels. Multi-level flight data has been used to characterize radiance biases. Currently, LMC and PMC retrieval results agree fairly well, although PMC retrieval results appear much noisier. Analysis of retrieval results for recent MATR measurements over western cities is underway.

At Level 0-1 there has been a careful examination of the instrument engineering data on a daily basis. The resulting calibrated radiances are being extensively compared with model calculations for special cases where the measurement scenes are believed to be well characterized. This work has led to studies by Deeter to characterize the way in which retrieval errors are related to radiance uncertainties. This activity has been especially important in the development of the Phase-2 data product. A manuscript detailing this validation effort is currently in preparation (Deeter et al.)

At level 2, Emmons, Valery Yudin, Deeter, and Jean-Luc Attie, a collaborator and frequent visitor from Laboratoire d'Aerologie, Toulouse, France, have continued the work of comparing individual retrieved CO profiles with in-situ measurements taken by Novelli's NOAA/CMDL group. Comparisons have also been made with CO total column retrievals from ground-based spectrometers, coordinated by Nikita Pougatchev (Christopher Newport University). These show good agreement in terms of seasonal trends. An example from one such study is shown in Figure 2a. The MOPITT total column composite data are shown for November 1-15, 2000. This is a time of high biomass burning in Africa which results in an emissions plume that stretches out into the Indian Ocean. The atmospheric CO is further enhanced by biomass burning in northwestern Australia. The high CO at this time of year is reflected in the ground-based FTIR CO total column measurements taken at Lauder, New Zealand, (Figure 2b) by Nick Jones, (University of Wollongong [NIWA] Australia). This is a good example of the way in which MOPITT measurement can provide the global context to local measurements. A manuscript detailing the Level 2 validation work is currently in preparation (Emmons et al.)

### The Atlanta Aerosol Nucleation And Real-time Characterization Experiment (Atlanta-ANARChE)

The University of Minnesota led this collaborative study involving NCAR and several universities. This study investigated, for the first time, both nucleation and ultrafine particle growth immediately after the gas-to-particle conversion process. The study took place at a ground-based field site in Atlanta, Georgia from July 22-September 4, 2002. NCAR's contribution included the measurement of the chemical composition of 5-15 nm diameter particles by a new technique called Thermal Desorption Chemical Ionization Mass Spectrometry (TDCIMS). NCAR scientists also measured OH, H and molecular ions and ion clusters.

The TDCIMS was recently built and tested in the POP laboratory in collaboration with Peter McMurry services research group (University of Minnesota) and is the only instrument presently capable of measuring the chemical composition of 5-15 nm particle at ambient concentrations in real time. A schematic of the instrument is shown below. The instrument combines recently developed nanoparticle separation and collection techniques, an area

of research in which the University of Minnesota is at the forefront, with highly sensitive chemical analysis provided by NCAR selected ion chemical ionization mass spectrometry technique. The TDCIMS is now capable of measuring the sulfate, nitrate, or ammonia content of 5-15 nm particles with a detection sensitivity of about 1 picogram of collected aerosol. It can also detect organics in ultrafine particles and improvements to the detection sensitivity in this area are presently underway.

Preliminary results of Atlanta-ANARChE suggest an extremely successful study that will contribute significantly to present understanding of homogeneous nucleation, ion induced nucleation and ultrafine particle growth, but additional analysis will be required before these findings can be confirmed.



### **Data Analysis and Assimilation (DAA)**

### **Global Positioning System (GPS)**

DAA has used temperature profiles derived from Global Positioning System (GPS) radio occultation measurements to study thermal variability of the tropical tropopause region. These novel GPS data are characterized by high vertical resolution (~0.2 km), and global sampling (especially advantageous in the tropics, where the radiosonde network is sparse). The key results demonstrate that much of the temperature variability in the tropical tropopause region is related to wave-like fluctuations, such as inertia-gravity waves or Kelvin waves. Furthermore, significant correlations are found between the GPS temperatures and daily, gridded outgoing longwave radiation (OLR) data (a proxy for tropical convection), providing independent confirmation of the GPS temperature fluctuations. The plot below illustrates the spatial structure of the temperature-OLR correlations, showing remarkably coherent hemispheric-scale temperature waves excited by convection. This work is an important step towards understanding and quantifying dynamical variability in the tropical tropopause region, and its influence on water vapor, cirrus and chemical constituents.

(Download figure at <a href="http://acd.ucar.edu/~randel/ASR\_2002.html">http://acd.ucar.edu/~randel/ASR\_2002.html</a>)

Caption: Height-longitude structure of temperature correlations with transient convection near the equator, derived from GPS temperature measurements and contemporaneous OLR data (a proxy for tropical convection). The correlations are calculated between the profile GPS temperature measurements and gridded OLR data, in order to isolate the longitudinal temperature response to localized convection (centered at the origin). Contours are +/- 0.2, 0.3, ..., and the sign convention is such that cold temperatures occur above enhanced convection, with warm anomalies to the east and west. The eastward-tilting wave variations with height over ~12-18 km are characteristic of an equatorially-trapped Kelvin wave. Note that the patterns are coherent over an entire hemisphere, showing that localized convection influences temperatures over 10, 000 km away! The dashed line at 17 km indicates the cold point tropopause (background temperature minimum).

### Whole Atmosphere Community Climate Model (WACCM)

WACCM has been used to investigate the "mesospheric temperature inversion" phenomenon. Model runs show clearly that these inversions arise from the rapid dissipation of planetary waves in the mesospheric surf zone, which leads to large temperature perturbations near 80 km that are in very good agreement with observations. These results provide a clear explanation of the winter inversion phenomenon, and highlight the usefulness of a comprehensive model like WACCM for middle atmosphere studies.

### **High-Resolution Dynamics Limb Sounder (HIRDLS)**

This year began to see the results of the long period of planning, design and development of the HIRDLS instrument. Gille, HIRDLS U.S. Principal Investigator, and the instrument development group of Michael Coffey and William Mankin (OT), with, Michael Dials, Aaron Lee, and Douglas Woodard (University of Colorado) were involved in the oversight and testing of the Engineering Model, and final reviews before shipment to Oxford University, to refine the calibration methods to be used on the flight instrument. Philip Arter (University of Colorado) spent several long periods in Oxford, helping to get the calibration facility completed on time.

The same group plus Nardi and Eden, was also deeply involved in the final stages of the fabrication of the Proto-Flight Model (PFM). Major efforts by Woodard to complete the Command and Telemetry Handbook, and by Dials to provide the associated database, essential for subsequent operation and testing of the instrument, enabled subsequent work to proceed. The whole group supported the thermal vacuum testing at Lockheed. Its rapid analysis and turn-around of test data greatly aided the process. The PFM was shipped to Oxford for calibration in the middle of August. All members of the instrument group have spent periods of a week or more working with the United Kingdom Principal Investigator, John Barnett, and colleagues (Chris Hepplewhite, John Whitney, Soji Oduleye and Robert Watkins), as well as students (Joseph Moorhouse and Daniel Peters). Primary contributions have been in data reduction, but they have also taken part in the shift rotations looking after the instrument and making observations. Initial results look quite good. This will continue for a period of about 3 months.

Planning for flight operations, and development of procedures to command the instrument computer have been begun by James Craft and Angie Williams (University of Colorado). These are being built on the foundation of procedures used during instrument test and calibration. The initial major test will be the SpaceCraft InterFace (SCIF-2) exercise next year.

### **Regional and Process Studies**

### Modeling of Atmospheric Short-Wave Radiation and Photochemical Processes

A new version of the Tropospheric Ultraviolet-Visible Model (TUV, version 4.2) was developed by Madronich. It now includes updated spectroscopic data bases for 67 atmospheric photolysis reactions and newly available data for the spectral sensitivity of UV damage to some biological tissues (e.g. ocular damage); improved radiative transfer parameterizations at UV-C wavelengths (100-280 nm, specifically in Lyman-a, Schumann-Runge continuum and bands, and the Herzberg spectral regions), allowing accurate calculations of radiation fields up to 120 km altitudes; and implementation of a more user-friendly interface which allows calculations to be made on a variety of platforms (e.g. UNIX, Windows<sup>TM</sup>).



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### **Research Summaries**

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- Atmospheric Radiation, Investigations and Measurements
- Stratospheric/Tropospheric Measurements
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- Global Modeling
- Photochemical Oxidation and Products

### ATMOSPHERIC TRACE GASES

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- Tunable Diode Laser Spectroscopy
- Atmospheric Radiation, Investigations and Measurements
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### STRATOSPHERIC OZONE AND UV-B

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### **CHEMISTRY - CLIMATE INTERACTIONS**

- Global Modeling
- Photochemical Oxidation and Products

### Measurements, Standards and Intercomparisons (MSI) Group

The MSI Group (Eric Apel) contributes to understanding of biogeochemical cycling, atmospheric trace gases and tropospheric photooxidants. One of the major projects for the group last year was their participation in Task 4 of the international non-methane hydrocarbon intercomparison experiment (NOMHICE). This is the first time an international intercomparison has been conducted with a collected whole air sample. The results from this study have recently been submitted to the *J. Geophys. Res. Atmospheres*. Figure 1 below shows a summary of some of the important results from the study. For each analysis, the geometric mean ratio (i.e., the antilog of the mean of the logs of the ratios, which is indicated by the symbols) indicates the average fractional systematic error of that analysis. The mean of the geometric mean ratios of the 30 analyses is 0.90, which indicates that, on average, the analyses were 10% lower than the NCAR-MSI reference concentrations. The average systematic errors of the individual analyses ranged from 55% low (analysis 27) to over a factor of 2 high (analysis 28). The geometric standard deviation of the ratios for each analysis (i.e., the antilog of the standard deviation of the logarithms of the ratios, which is indicated by the bars) gives a measure of the 1 precision of the measurements in the analysis.

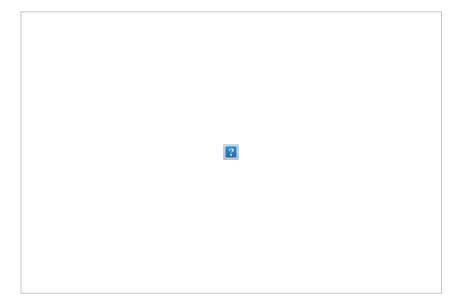


Figure 1. Results from the respective individual analyses of the Task 4 NOMHICE whole air sample. 30

analyses from 23 individual laboratories worldwide were considered in the study. Each dot indicates the result from a single NMHC ratioed to the reference (NCAR-MSI group) concentration. The symbols are coded according to the range of NMHCs analyzed and show the geometric mean ratio (i.e., the antilog of the mean of the logs of the ratios). The bar for each analysis shows the standard deviation of the logarithms of the ratios reported in the analysis. The left ordinate gives the natural logarithm of the ratios and the right ordinate gives the corresponding logarithmic scale of the ratios.

An average random error factor of 1.54 is indicated, i.e., approximately 2/3 of the measurements fell in the range 35% below to 54% above the reference concentrations. The average random error of the individual analyses varied from a factor of 1.12 (i.e., +/- 11%) for analysis 22 to a factor of 2.2 for analysis 28 (-55% to 120%). The overall results indicate that a number of research groups are able to accurately measure the NMHCs in an air sample; but for many groups significant problems remain, although progress has been shown through this program,. The results from this study have broad implications for the interpretation and modeling of NMHC measurements that have been obtained throughout the atmospheric research community.

Results were published on one of the most complete in-the-field isoprene chemistry experiments ever conducted. (Apel, Daniel. Riemer, Ian Faloona, D. Tan, Chris Geron, and William Brune, *J. Geophys. Res.*, 2002). A simple sequential reaction scheme model both confirmed laboratory kinetics studies of isoprene chemistry and provided insight into factors required for the successful implementation of field campaigns designed to study the oxidation of biogenic compounds.

Results were presented (IGAC 2002, Atomic Chlorine is an Oxidant in the Coastal Marine Boundary Layer and in Houston, Texas) on a novel experiment designed to measure for the first time unique isoprene-product tracers for chlorine chemistry in the troposphere. By accurately measuring the tracers, the group demonstrated that it is possible to estimate chlorine atom concentrations and hence the contribution of chlorine chemistry to ozone formation and the potential importance of this contribution is for regions with high chlorine sources for attaining the air quality standards set by the government.

To determine the presence and extent of CI chemistry in the coastal MBL and in the Houston urban area, the group measured via mass spectrometry specific tracers from isoprene oxidation by CI. Laboratory studies have shown that the reaction of isoprene with CI forms several unique tracers which could be used as evidence for CI chemistry. We investigated the isoprene oxidation process under ambient conditions in the coastal MBL near Miami, Florida and southeast of downtown Houston, Texas and were able to characterize the different oxidation processes that were occurring. Results confirm that CI is indeed an oxidant in both the coastal MBL and in the Houston urban area. Isoprene oxidation by OH and O<sub>3</sub> results in the formation of methacrolein (MACR), methyl vinyl ketone (MVK) and formaldehyde (CH<sub>2</sub>O). Isoprene oxidation by CI addition forms the unique reaction products 1-chloro-3-methyl-3-butene-2-one (CMBO) and several isomers of chloromethylbutenal (CMBA). 2-methylene-3-butenal (MBA) is formed as a result of H-abstraction by CI. CMBO and CMBA serve as robust tracers of CI chemistry.

One of the goals of the MSI Group is to develop instrumentation that is a benefit to ACD and to the research community. A fast gas chromatograph mass spectrometer for measuring alcohols, ketones, and aldehydes for Transport and Atmospheric Chemistry near the Equator (TRACE-P) was developed. In FY02, the MSI Group improved the time resolution of the instrument and extended the measurement capability to include a number of CFCs and NMCSs. Data has been analyzed and presented on the distribution off of the Asian continent of alcohols and carbonyls from measurements made during TRACE-P. Plans are to continue to improve the instrument in anticipation of the group sparticipation in the Megacity Impacts on Regional and Global Environments (MIRAGE) program.

Support of the Clouds/Convection and upper troposphere/lower stratosphere (UT/LS) Initiatives, as well as data analysis and manuscript preparation for TRACE-P, Texas Air Quality Study (TexAQS) 2000, and NOMHICE will continue.

### Stratospheric/Tropospheric Measurements (S/TM) Group

The Stratospheric/Tropospheric Measurements (S/TM) group (Elliot Atlas, Frank Flocke, Sue Schauffler, Stephen Donnelly, and Verity Stroud) investigates the sources, budgets, distribution and variations of atmospheric trace gases, with particular emphasis on those species related to the ozone formation and destruction processes in both the troposphere and the stratosphere. Sources and sinks of atmospheric organic nitrogen are receiving increased investigation in S/TM with the collaboration of an ASP post doctoral fellow, Kimberley Mace. Research investigations related to peroxyacetyl nitrate distributions and chemistry are conducted jointly with the Atmospheric Odd-Nitrogen (AON) group (Brian Ridley, Andrew Weinheimer) in ACD. Additional collaborations are described in the following narrative. An integral part of the S/TM program is to evaluate and develop state-of-the-art sampling and analytical facilities for trace gas measurement from different environments.

The S/TM group has been active in both field and laboratory investigations during the past several years. Analysis of the results of these investigations was a major emphasis during FY2002, and significant findings are highlighted in this report. A review of accomplishments in major field deployments and other projects is presented first.

The Intercontinental Transport and Chemical Transformation (ITCT) Project. The ITCT project is a research activity of the International Global Atmospheric Chemistry (IGAC) Program that directly addresses the tropospheric chemistry and transport of ozone, fine particles and other chemically-active greenhouse compounds (http://www.al.noaa.gov/WWWHD/Pubdocs/ITCT/2k2/). Scientists at the NOAA Aeronomy Laboratory (Fred Fehsenfeld, Michael Trainer, David Parrish, Gerd H&bler) were the primary organizers and planners of the ITCT activity, and NOAA provided partial support for S/TM participation. Briefly, the ITCT activity is aimed at understanding the long-range (intercontinental) transport of ozone and aerosols and the impact that this intercontinental transport has on regional climate and air-quality. The first field campaign was in April/May 2002 (ITCT 2k2) and it focused on the influence of Asian outflow on the U.S. west coast, on emissions from west oast urban centers and ship traffic, and on characterization of the atmospheric chemistry of the eastern North Pacific troposphere. The campaign included NOAA P3 aircraft flights out of Monterey, California and ground based measurements from Trinidad Head, California. S/TM measurements were exclusively from the aircraft platform, and measurements included PAN and related peroxyacyl nitrates (using an automated PAN gas chromatograph) and also a suite of trace gases from whole air sample collection.

In January-March, the PAN GC was repaired, refurbished, and upgraded prior to integration on the NOAA P3 in late March for deployment to California in April-May. Significant among the improvements were hardware and software changes that enabled unmanned operation of the GC, for the first time, in the ITCT mission. In addition, instrument tests and calibration comparisons between the NOAA and NCAR PAN instruments were conducted in collaboration with Jim Roberts of NOAA.

The ST/M whole air sampler was modified for ITCT to accommodate up to 80 samples per flight. The samples were collected automatically with a preprogrammed schedule; in addition, the flight director activated additional samples for increased temporal coverage, or for specific plume studies. Whole air samples were collected for analysis of a variety of organic trace gases, including methane, NMHC, halocarbons, organic nitrates, and selected sulfur species. Mission flight tracks were designed to examine regions characteristic of the background atmosphere, and regions impacted by specific point sources, larger urban sources, and long-range transport.

Measurements from whole air samples are being used to characterize the background atmosphere of the eastern North Pacific, to define chemical emissions from the west coast urban areas and to identify signatures of long-range trans-Pacific transport that impact the U.S. west coast. These analyses are in the early stages. As one example of the trans-Pacific transport observed during ITCT, Figure 1 shows the relationship of carbonyl sulfide (OCS) to carbon monoxide (CO) in studies from WIFE (Wildfire Experiment, Friedli et al., 2001), TRACE P (data in collaboration with Donald Blake et al., University of California at Irvine (UCI) and Glen Sachse (CO)), and from ITCT 2K2. Biomass burning is one significant source of OCS to the atmosphere, but the data from East Asia suggest that an additional strong source of OCS is collocated or co-emitted with CO. One possibility is the burning of high sulfur coal in the Asian region. While the exact source is still under investigation, the signature of Asian outflow is clearly defined by the relatively high ratio of OCS to CO compared to other known sources. This signature was clearly identified in at least one of the ITCT flights (5

May) when other tracers (NMHC, CO, PAN) were elevated, and when computer models predicted long-range transport of Asian air masses to the U.S. west coast. Tracer data clearly support the computer model predictions. In flight segments that clearly sampled plumes from forest fires (e.g. on the transit from California to Colorado), the characteristic signature of wildfires is observed.

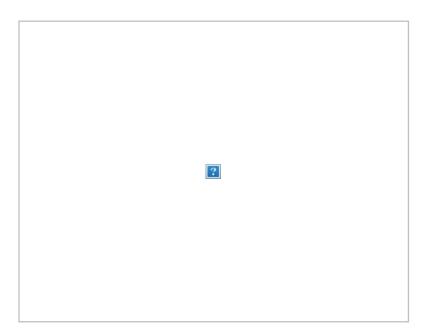


FIGURE 1. © OCS:CO relationships observed in Asian outflow (TRACE-P) and North American wildfires (WIFE) compared to observations over the West Coast of the U.S. during ITCT 2K2. © Observations of high levels of OCS relative to CO appear to be a characteristic signature of continental outflow from Asia, and this signature was observed in an air mass predicted by several 3-D chemical transport models to have traveled from Asia to the U.S. coast.

Transport and Chemistry Evolution over the Pacific (TRACE-P). Data from the NASA TRACE-P experiment conducted February to April, 2001 were analyzed in FY02, and these analyses focused on the influence of Asian pollution outflow on the tropospheric chemistry over the central and western Pacific Ocean. ♠ The campaign included 20 flights, covering the Western Pacific from about 10♠N to 40♠N latitude. ♠ Two aircraft were deployed, the NASA DC-8 and the NASA P-3. ♠ S/TM contributed two projects to the TRACE-P mission. These were trace gas analyses from whole air samples and in-situ analysis of PANs. Whole air samples were collected and analyzed by Blake♠s group. ♠ All samples were analyzed, and a subset was analyzed at NCAR for a variety of gases, including alkyl nitrates, halocarbons, hydrocarbons, and hydrochlorofluorocabons (HCFCs). ♠ Flocke and Weinheimer deployed an in-situ instrument on the P-3 that measured PAN, PPN, PiBN, APAN and MPAN.

Measurements from the whole air sampler were used to characterize trace gas signatures from different regions in Eastern Asia to determine if air masses from these source regions could be specifically identified by their respective signatures. Various statistical tests are being applied to the data to identify specific source characteristics. Significant differences in trace gas signatures were identified between air masses influence by Japan compared to those from mainland China and other regions. For example, high levels of vinyl chloride and selected chloroalkanes in sample near Japan reflect emissions from specific chemical production processes. Also elevated levels of HCFCs and other anthropogenic halocarbons were observed in or near large metropolitan areas along with CO and light hydrocarbons. On a broader scale, the widespread use of coal burning in the region was evident through high levels of carbonyl sulfide relative to carbon monoxide as mentioned earlier.

The photochemical evolution of alkyl nitrate formation from Asian source regions was clearly evident and the timescale for these processes is currently under examination. Evaluation of the evolution of alkyl nitrate measurements from TRACE-P was led by Isobel Simpson, University of California, Irvine (Simpson et al., 2002). They report that in young, highly polluted air masses, the ratio between the production rates of 3-pentyl

nitrate and 2-pentyl nitrate from n-pentane was 0.60-0.65. These measured ratios show excellent agreement with results from a field study in Germany (0.63 • 0.06), and they agree better with predicted ratios from older laboratory kinetic studies (0.63-0.66) than with newer laboratory results (0.73 • 0.08). Furthermore, the measured ratios of ethyl nitrate/ethane and 2-PrONO2/propane showed notable deviations from modeled values based on laboratory kinetic data, suggesting additional Asian sources of their alkoxy radical precursors. In contrast, the measured ratios of 1-propyl-, 2-butyl-, 2-pentyl- and 3-pentyl nitrate to their respective parent hydrocarbons were fairly close to modeled values.

Measurements from the whole air sampler were also used to characterize regions in the upper troposphere that were recently influenced by convection from marine areas. Methyl nitrate, methyl iodide, and bromoform are generally elevated in the marine boundary layer, especially in the tropics, relative to the mid and upper troposphere. Elevated levels of these compounds in the upper troposphere, together with back trajectories, were used to identify the influence of convective activity. Methyl nitrate, in particular, was found to be a more prominent indicator of tropical convective activity compared to either methyl iodide or bromoform.

Texas Air Quality Study (TexAQS) 2000. Data from the TexAQS 2000 field campaign (August/September 2000), was analyzed and published during FY02. TexAQS focused on obtaining an improved understanding of the processes that control the formation and distribution of fine particles and ozone in the Houston and southeast Texas areas. In particular, the study examined the relative importance of various local sources as well as local versus transported emissions on local and regional ozone chemistry. TexAQS 2000 addressed these issues through a series of coordinated measurements involving instrumented aircraft and a groundbased network of chemistry and meteorological measurements. The S/TM whole air sampler designed and built to fly on the NOAA WP-3D during the 1999 SOS campaign in Tennessee was modified and flown on the NCAR Electra. The whole air sampler was utilized during TexAQS 2000 to investigate specific plumes from industrial and power plant sources, and to characterize the trace gas composition in these plumes and in the surrounding area. The PAN, PPN, MPAN instrument was also deployed on board the NCAR Electra. Measurements from the whole air sampler revealed significant amounts of reactive hydrocarbons, primarily ethene and propene, in the plumes from specific industrial sources. �� High levels of alkanes were also seen, though these compounds contributed less to the photochemical reactivity of the plume compared to the alkenes and their carbonyl oxidation products. The high levels of alkenes in specific petrochemical plumes represented the highest mixing ratios of any trace gas measured from the whole air sampler. Pryan Wert and Alan Fried (ACD/TDLS) described the effect of these alkenes on formaldehyde (which they measured on board the Electra) and ozone production in these plumes [Wert et al., 2002]. They found formaldehyde and ozone production were greatly enhanced in petrochemical plumes compared with plumes dominated by power plant and mobile emissions. Tom Ryerson (NOAA/AL) found that the industry reported emissions of the alkenes were substantially lower than emissions inferred from measurements in the plumes [Ryerson et al., 2002] and suggests that reductions in reactive alkene emissions from petrochemical industrial sources are required to effectively address the most extreme ozone exceedences in the Houston metropolitan area.

Whole air sampler measurements were also used by Charles Brock (NOAA/AL) who concluded that photochemical oxidation of SO2 is the key process regulating particle mass growth in the plumes studied and that the presence of elevated levels of VOCs substantially enhanced particle growth [Brock et al., 2002]. Whole air sampler measurements of CO were also used by Dennis Nicks (NOAA/AL) to evaluate emissions of CO from electric utility power plants in east and central Texas [Nicks et al., 2002]. Correlations of the CO observations with measured CO2 and NOy indicated the CO emissions for several of the plants were significantly higher than reported and could represent up to an additional 30% of the total annual CO emissions from point sources for the state of Texas.

The PAN data from TexAQS 2000 presented an interesting chemical puzzle. The perspective obtained from a look at PAN-ozone and PAN-PPN correlations suggested that the hydrocarbon distribution supporting the ozone chemistry in Houston was not atypical when compared to other regions where measurements have been made by the S/TM Group (Arctic, Nashville, Asia). This appeared to conflict with the finding that Houston was very unique, at least for the high ozone events, in that light alkenes were primarily responsible for ozone formation in a manner not seen in other cities. This issue was addressed by applying the NCAR Master Mechanism, with its highly detailed hydrocarbon chemistry (including some additions relevant to the production of PANs), to model the production on PAN-type compounds. The hydrocarbon measurements

from the P3 were used to initialize the model. From these analyses, it was found that it is possible to produce normal-looking PAN-ozone and PAN-PPN correlations, even with a mix of hydrocarbons dominated by abnormally high levels of alkenes, provided these are present in the right distribution, consistent with the P3 hydrocarbon measurements.

SAGE III Ozone Loss and Validation Experiment (SOLVE). Whole air samples from SOLVE were analyzed to quantitatively describe the organic chlorine budget and the contributions from each species and each group to total organic chlorine [Schauffler et al., 2002]. Measurements of the mean age of air together with measurements of the organic chlorine containing compounds were used to calculate inorganic chlorine released from each compound since entry into the stratosphere. These calculations were used to quantitatively describe the inorganic chlorine budget. This experiment was a NASA-sponsored measurement campaign that focused on the processes controlling ozone levels at mid- to high- latitudes in the Northern Hemisphere. Measurements were made in the Arctic high-latitude region in December, 1999-March, 2000 using the NASA DC-8 and ER-2 aircraft, as well as balloon platforms and ground-based instruments. The flights were based out of Kiruna, Sweden. The ST/M whole air sampler (WAS) flew aboard the ER-2 and for this campaign the redesigned instrument was located in the centerline drop tank. The calculations were also used to determine the fractional chlorine release (FC) from each compound, which is the amount of chlorine released relative to the stratospheric entry mixing ratio for each sample. FC values for each compound relative to the FC value of CFC-11 are used in calculations of the amount of chlorine available for involvement in current and future stratospheric ozone loss. The FC values calculated for HCFCs 141b and 142b were significantly lower than previous estimates which results in significantly lower Ozone Depletion Potentials (ODPs) for these compounds. We are currently examining the effects on our FC calculations of varying the tropospheric trend and the parameters used to take into account stratospheric mixing (age spectrum). This work will provide a comprehensive description of our FC calculations and associated errors, which will be required in further evaluations of the ODPs of HCFCs 141b and 142b. S/TM whole air sampler measurements of HCFCs and HFCs (hydrofluorocarbons) from SOLVE were combined with our measurements from previous stratospheric campaigns to characterize stratospheric trends of these compounds. HCFCs and HFCs show rapid growth in the stratosphere and make significant contributions to the organic chlorine and fluorine budgets. Their growth in the stratosphere is maintained at a significant fraction of their rate of growth in the troposphere. HCFC and HFC mixing ratios from SOLVE were used to calculate the burden and partitioning of these trace gases in the troposphere and stratosphere for the year 2000. These values were then compared with annual and cumulative emissions to estimate the fractional distribution of these emissions in the troposphere and stratosphere.

Collaborative Isotopic Studies from Stratospheric Whole Air Samples. During recent stratospheric research campaigns, including STRAT, POLARIS, and SOLVE, a subset of whole air samples was collected for investigation of isotopic compositions of stratospheric trace gases. This work was initiated in collaboration with Kristie Boering (University of California, Berkeley). Sample aliquots from selected whole air samples were archived by Boering and colleagues, and isotopic analyses were conducted in the UCB laboratory and elsewhere. Isotopic studies include oxygen isotopes in stratospheric CO<sub>2</sub>, C and H isotopes in stratospheric methane, and H isotopes in hydrogen.

Measurements of the oxygen isotopic composition of stratospheric  $CO_2$  by Boering from ST/M whole air samples have shown anomalous enrichment in  $^{17}O$  and  $^{18}O$  [Boering et al., 2001]. These results and their correlations with measurements of  $N_2O$ ,  $O_3$ , and  $CO_2$  provide new observation-based constraints on the source of the fractionation that leads to the enrichment and on the stratospheric distribution of the anomalous fractionation. The results also lead to constraints on the use of the anomalous enrichment as a tracer of stratospheric chemistry and transport and on the magnitude of the flux of the anomalous signature in  $CO_2$  in the troposphere. Quantification of the anomalous isotopic flux to the troposphere is required for using the isotopic composition of  $O_2$  as an index of modern primary productivity on Earth [Boering et al., 2001].

Recent isotopic measurements by Stanley Tyler, University of California, Irvine and Andrew Rice (now at University of Washington) from samples collected by the ST/M whole air sampler during STRAT, POLARIS, and SOLVE of D and <sup>13</sup>C of stratospheric CH<sub>4</sub> represent the first of a kind of high precision D

measurements of stratospheric CH<sub>4</sub> by continuous flow isotope mass spectrometry and the largest data set of stratospheric D of CH<sub>4</sub> reported thus far [Rice et al., 2002]. Large isotope ratio shifts were observed for both C and H in stratospheric CH<sub>4</sub> relative to surface values. These shifts can be evaluated by considering the effects of Rayleigh fractionation, chemical sink factors, and transport effects. More detailed evaluation of the data with a 2-D chemical model can also provide insights about vertical amounts and distributions of OH, CI, and O(<sup>1</sup>D) and their kinetic isotope effects [McCarthy et al., 2002].

Molecular hydrogen isotopes have also been measured by Thom Rahn and John Eiler (California Institute of Technology, Pasadena) in a subset of the whole air sample archive (Rahn et al., 2002). Isotopic characterization of molecular hydrogen may help understand the various sources and sinks of this abundant atmospheric gas. Because of the dynamic production (CH<sub>4</sub> oxidation) and loss processes (oxidation) of hydrogen in the stratosphere, molecular hydrogen levels in the stratosphere remain relatively constant, but D/H ratio is dramatically altered. These data are currently being analyzed to define fractionation factors for the stratospheric oxidation processes. These data are also being analyzed by Michael McCarthy, University of California, Berkeley, to provide some constraint on the hydrogen isotope content of stratospheric water vapor.

Firn air sampling: Studies of historical trends of trace gases in the 20th century. Studies of the historical trend of tropospheric trace gases have continued in collaboration with William Sturges (University of East Anglia, UK), Jerome Chappellaz (Centre National de la Recherche Scientifique [CNRS], France), Jakob Schwander (University of Berne), James Butler and Steven Montzka (NOAA CMDL, Boulder). Historical trends are inferred from trace gas profiles trapped in firn air in polar regions. Depending on the rate of snow accumulation and the depth of the close-off layer (where porous firn becomes solid ice), trace gases from the early to mid-20th century may be sampled. This past year, the S/TM Group combined their analyses of NMHC from 2 firn cores in the Northern Hemisphere (Devon Island, Canada and NGRIP, Greenland) and several Antarctic firn cores (including S. Pole) [Figure 2]. As expected from contemporary distributions of NMHC, significantly higher levels of NMHC are found in the Northern Hemispheric samples compared to the Southern Hemisphere. A coherent trend in NMHCs from the mid-sixties to the present are observed in the two Northern Hemispheric firn sample sets, with similar features in the Southern Hemisphere. Atmospheric levels of NMHC showed an increase from the 1950s until the mid-1970s or early 1980s.♦ Since that time there has been a consistent decrease in NMHC concentrations in the troposphere, presumably because of decreased emissions from more stringent environmental controls. Details of the relationship between inferred atmospheric history and emissions estimates are currently being examined to evaluate this hypothesis.

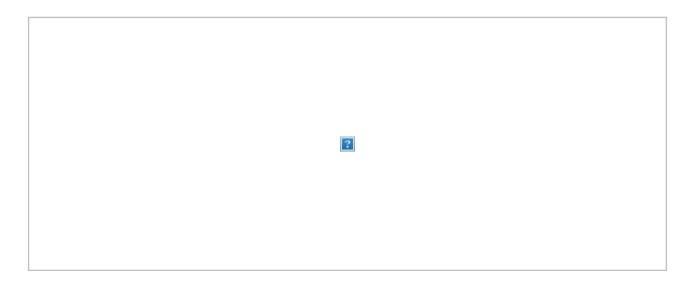


FIGURE 2.  $\clubsuit$  Historical trends of  $C_2$  and  $C_3$  hydrocarbons in the atmospheres of the Southern (left) and Northern (right) hemisphere inferred from firn air profiles at South Pole, Devon Island, and NGRIP.

Laboratory Studies: Organic Nitrate Formation. Previous collaboration with Ronald Cohen and Douglas Day (University of California, Berkeley) identified a wide variety of >C4 organic nitrates, including multifunctional nitrates (hydroxy and carbonyl nitrates), in the atmosphere of Blodgett Forest, California. These types of compounds may play a significant role in the budget and partitioning of reactive nitrogen, especially in an environment influenced by both urban and biogenic hydrocarbon emissions. To obtain a better understanding of the organic nitrate signature in forest environments and to evaluate analytical procedures for these complex nitrates, some basic laboratory investigations were initiated. The project is a collaboration with ACD AKP group (Geoffrey Tyndall and John Orlando) to investigate the formation of multifunctional or tertiary alkyl nitrates during the photooxidation of unsaturated or branched hydrocarbons, respectively, in the presence of NO. Preliminary experiments were carried out in AKP \$\displays 50-liter photoreactor. The groups were able to reproduce the alkyl nitrate formation rates and ratios expected for n-pentane, which can be used as a relative-rate standard to investigate other hydrocarbons. First results show that the yield of tertiary alkyl nitrates from isobutane and isopentane is much larger than presently reported in the literature. Preliminary experiments with a variety of C3-C5-alkenes and isoprene were carried out. First results include the finding that presently published data for the yield of isoprene nitrates obtained in smog chamber experiments may be biased in one direction by nitrates formed from dark chemistry (i.e. the reaction of isoprene with NO2) and in the other direction by losses of the thermally-labile tertiary hydroxynitrate, which is one of the main alkyl nitrate products of the isoprene oxidation in the presence of NO. Further experiments are planned using a flow-tube apparatus to eliminate problems associated with static chamber studies.

Analytical Development: LC/MS of water-soluble organics. As part of an effort to understand the fate of oxidized organic gases in the atmosphere, and to better characterize the chemical composition of organic matter in condensed phases (aerosol, rain water, cloud water, ice etc.), S/TM has begun development of a liquid interface/mass spectrometric measurement of atmospheric water-soluble organic compounds. Initial development has begun that is based on a prototype electrospray interface (Bear Instruments) with MS/MS capabilities. Basic operating parameters are being developed and system performance is being evaluated. Currently, we are comparing ultimate sensitivities of various electrospray introdution methods, including nanospray, nebulizer-assisted spray, and sonic spray interfaces.

## **Atmospheric Radical Studies (ARS) Group**

The Atmospheric Radical Studies Group (Chris Cantrell) is involved in the measurement and interpretation of peroxy radical levels in laboratory and atmospheric measurement situations. Activities this year have included the continued analysis and reporting of results from earlier studies and an intercomparison study with William Brune, Pennsylvania State University. The main analytical tool for these studies is the Peroxy radical Chemical Ionization Mass Spectrometer (PerCIMS) system, which is based on the chemical conversion of ambient peroxy radicals (HO2 and RO2) into a unique ion (HSO4) which can be quantified by mass spectroscopy. This instrument has been developed, characterized and improved over the past several years and has now been deployed in several field campaigns.

This work done in the ARS Group contributes to the study of tropospheric photooxidants by helping to understanding the details of the mechanisms of photochemical ozone formation, including the factors that affect changes in the abundance of ozone in the troposphere. Observations do not directly answer these questions, but serve as indicators of the quality of the understanding of the various mechanisms by which precursors are transformed into products and lead to the formation of ozone. New knowledge or confirmation of current understanding comes in part by using observations in conjunction with appropriate models of tropospheric photochemistry (including the steady state model that the group has developed). The role of aerosols in potentially perturbing photooxidation processes is of interest particularly as it relates to the uptake of peroxy (and other) radicals and the impact on the radiation environment that can change radical production rates.

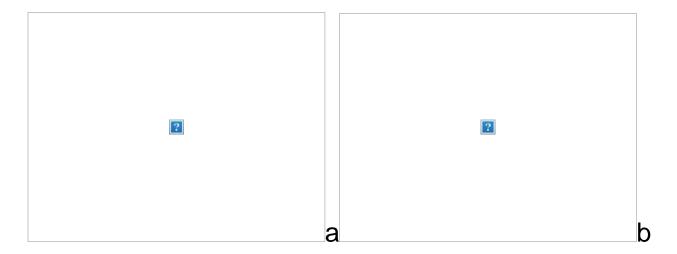
These observations could be an important component of an interdivisional observation program (such as the

emerging upper troposphere/lower stratosphere [UT/LS] interdivisional initiative and the Megacity Impacts on Regional and Global Environments [MIRAGE] program).

Peroxy radical observations aid in the understanding of the carbon cycle (Biocomplexity initiative), since they are key intermediates in the oxidation of organic compounds in the troposphere.

Data Analysis and synthesis. Intensive efforts have been made toward the analysis, interpretation and reporting of measurements of peroxy radicals and other species from the TOPSE (Tropospheric Ozone about the Spring Equinox) study from the winter and spring of 2000, and the TRACE-P (Transport and Chemical Evolution over the Pacific) campaign in February through April, 2001. Papers have been submitted related to the IPMMI (International Photolysis frequency Measurement and Modeling Intercomparison) campaign, in which ARS had a significant presence in collaboration with the Atmospheric Radiation Investigation and Measurements (ARIM) group of ACD (Richard Shetter and colleagues), and groups throughout the radiation community (e.g. Andreas Hofzumahaus, Forschungzentrum Juelich; Paul Monks, University of Leicester; Richard McKenzie, NIWA, New Zealand; James Crawford and John Barrick, NASA Langley; Steven Lloyd, Johns Hopkins; Greg Frost, NOAA and many others; http://acd.ucar.edu/~cantrell/ipmmi.html). The TOPSE experiment was an ACD-led campaign with significant university and national laboratory collaboration that was designed to understand the evolution of ozone and other trace gases during the winterto-spring transition in northern middle to high latitudes. • Cantrell was a co-Principal Investigator on this experiment, and led the activities to request the aircraft facility and coordinate the package of instruments that were deployed. The aircraft platform was deployed seven times for approximately one week each from early February to mid-May (2000). These included flights from Jefferson County airport to Churchill, Manitoba on to Thule, Greenland and north over the Arctic Ocean. Important measurements of a number of photochemical, tracer and remotely-sensed species were made that allow constraint of numerical models and tests of the understanding of tropospheric photochemistry and transport. This campaign and the subsequent data analysis and presentation involved collaboration with the TOPSE Science Team consisting of professors and researchers from universities and national laboratories (including Edward Browell, NASA Langley; Robert Talbot, University of New Hamshire; Rodney Weber, Georgia Tech; Donald Blake, University of California-Irvine: Brian Heikes, University of Rhode Island: Ronald Cohen, University of California-Berkeley and their associates; topse.acd.ucar.edu/people/). A first paper describing the peroxy radical budgets and ozone photochemistry has been accepted for a special TOPSE section of the J. Geophys. Res. • Atmospheres. • A second paper describing the details of the peroxy radical observations is in review.

Observations of total peroxy radical (HO<sub>2</sub> + RO<sub>2</sub>) levels were compared with a measurement-constrained steady state model of radical concentrations for the geographical and temporal domain of the TOPSE (Tropospheric Ozone Production about the Spring Equinox) campaign (February-May, 2000; 40 to 85 degree north latitude). The data were averaged into two latitude bands: MLB or middle latitude band (40 to 60 degrees) and HLB or high latitude band (60 to 85 degrees). In Plate 1, panels a and b show the contour averaged observations, panels c and d shown the contour averaged steady state model results (coincident with the observations), and panels e and f show the contour averaged ratio of measurements to model results. The average ratios are 1.04 and 0.94 in the MLB and HLB, respectively.



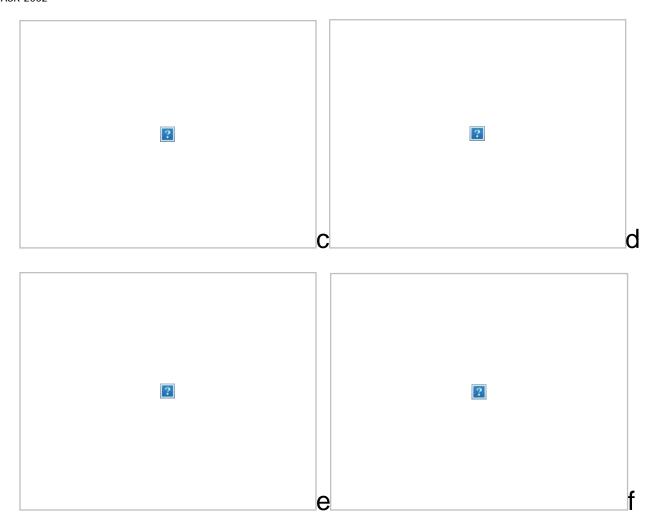


Plate 1. TOPSE peroxy radical concentrations (a,b) measured, (c,d) calculated from steady state model at the coincident measurements, and (e,f) ratio of coincident measured to steady state concentrations, for the MLB (left) and HLB (right) regions.

The TRACE-P campaign was a NASA-sponsored study designed to examine the outflow of trace gases from eastern Asia and their transformation during transport over the Pacific. Two aircraft (the NASA DC-8 and P-3B) were deployed with full suites of instrumentation to characterize the chemical, physical and aerosol environment. Most of the flights originated from two bases of operation: Hong Kong International Airport, China, and Yokota Air Base, Japan. This involved significant collaboration with the TRACE-P Science Team consisting of colleagues from universities and national laboratories (www-gte.larc.nasa.gov/trace/TP\_Science\_Team.htm), including mission scientists Daniel Jacob of Harvard, and lames Crawford of NASA Langley Research Center. Workshops were held to exchange preliminary results

James Crawford of NASA Langley Research Center. Workshops were held to exchange preliminary results, a special session of papers is in preparation for presentation at the Fall 2002 AGU meeting, and manuscripts are in progress. These include a paper describing peroxy radical measurements aboard the P-3B and their interpretation, to be submitted to a special section of *JGR-Atmospheres* this fall.

Measurements of total peroxy radical concentrations (HO<sub>2</sub>+RO<sub>2</sub>) and HO<sub>2</sub> concentrations were performed aboard the NASA P-3B aircraft during TRACE-P (Transport and Chemical Evolution over the Pacific), which took place February through April, 2001 over the Pacific basin with particular emphasis over the western Pacific Ocean region. An observation-constrained model was used to estimate these concentrations. The measured and modeled radical measurements are shown in Plate 2, averaged by the total production rate of radicals and the observed NO<sub>2</sub> concentrations. A simple description of this functional dependence was derived assuming that the radical loss could be represented by radical-radical and radical-NO<sub>2</sub> reactions.

Detailed laboratory studies of the effect of water vapor on the sensitivity of the PerCIMS (Peroxy Radical

Chemical Ionization Mass Spectrometer) have been performed. Part of the reason for these experiments is that other instrumentation for measurement of tropospheric peroxy radicals (chemical amplifier) suffers from a large decrease in sensitivity with relative humidity. Also, the PerCIMS depends on the presence of some water vapor for its inlet chemistry (for conversion of  $SO_3$  into  $H_2SO_4$ ). Plate 3 shows the relative response of PerCIMS to water vapor, indicating that there is no noticeable effect for water vapor concentrations greater than  $10^{15}$  cm<sup>-3</sup> (about 40 ppmv at the earth s surface) at room temperature. The drop in sensitivity at lower water vapor concentrations is likely due to incomplete conversion of  $SO_3$ . In the atmosphere, low water vapor levels are usually accompanied by low temperatures; the reaction of  $SO_3$  with water vapor becomes faster at lower temperatures.

In May and June, 2002, the PerCIMS instrument was deployed at a rural site near Pennsylvania State University for a comparative study (called PenSPeRC: Penn State Peroxy Radical Comparison) with the radical instrument of Dr. William Brune and his colleagues Dr. Xinrong Ren and Bob Lesher. Over several weeks, synthetic radical sources were exchanged and ambient air was sampled with the goal of uncovering any systematic problems with either instrument. In spite of some minor instrument problems, the study was very successful. Plate 4 shows a comparison of HO<sub>2</sub>+RO<sub>2</sub> measured with the NCAR PerCIMS instrument compared to that measured with the Penn State GTHOS instrument. The degree of correlation and agreement are remarkable, although perhaps unexpected since HO<sub>2</sub>+RO<sub>2</sub> should be somewhat (perhaps 50%) greater than HO<sub>2</sub> only. Further analysis of these data continues and follow on comparisons will be performed.

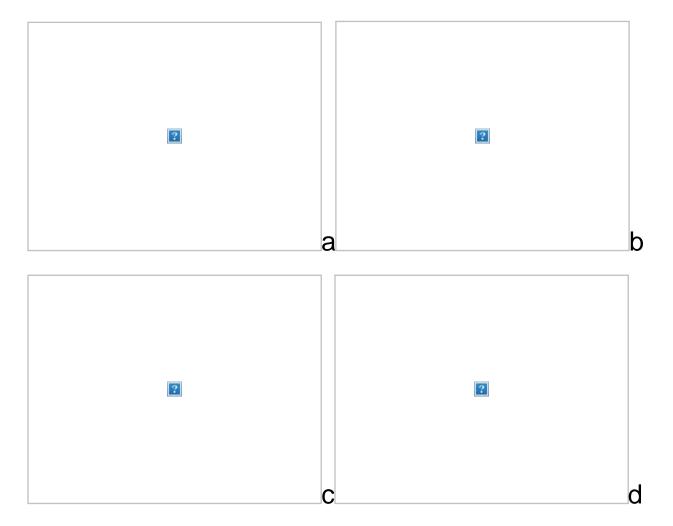


Plate 2. Measured (left) and modeled (right) bin averaged total peroxy radical concentrations ( $HO_2 + RO_2$ ) (panels a and b) and  $HO_2$  concentrations (panels c and d) for TRACE-P versus measured  $NO_2$  concentration. The curves are fits to the binned data based on a simple model of peroxy radical loss through radical-radical and radical-NO reactions. The colors represent the total radical production rate.

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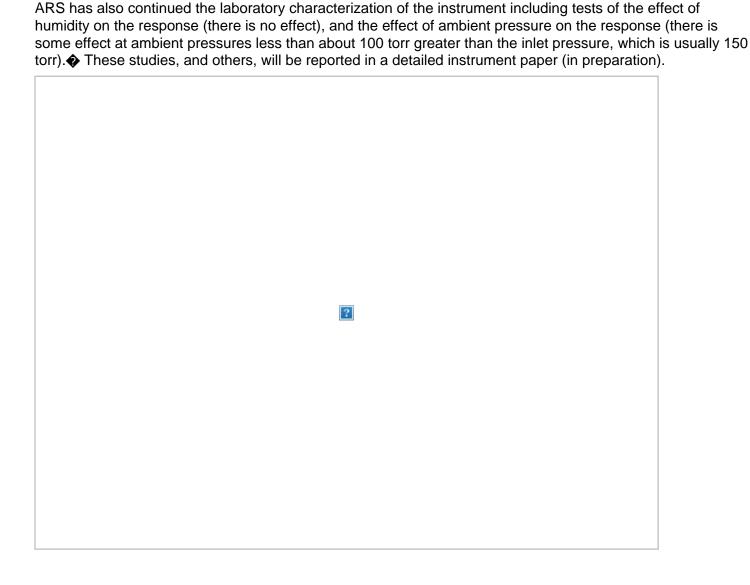


Plate 3. Relative response of PerCIMS tropospheric peroxy radical instrument to  $HO_2$  as a function of water vapor concentration present in the sampled air mass. The response is flat if room air is used for the sheath flow (in which ions are produced). If very dry air is used for the sheath, the response is flat until water vapor concentrations drop below about  $10^{15}$  cm<sup>-1</sup>. Shown for comparison is the calculated lifetime of  $SO_3$  radicals toward reaction with water vapor at room temperature. If this lifetime becomes long enough, then it would lead to a reduced measurement efficiency of this instrument.

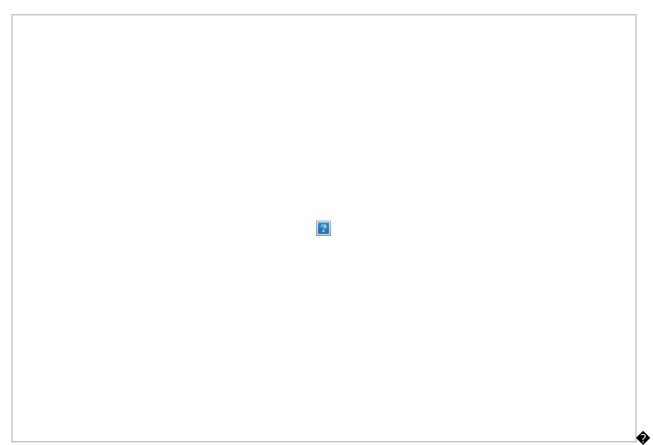


Plate 4.♠ Comparison of HO<sub>2</sub>+RO<sub>2</sub> measured by the NCAR PerCIMS instrument and the Penn State GTHOS HO<sub>2</sub> concentrations during the PenSPeRC study in May and June, 2002.

Field Campaigns. In May and June, 2002, the PerCIMS instrument was deployed at a rural site near Pennsylvania State University for a comparative study (called PenSPeRC) with the radical instrument of Brune and his colleagues, Xinrong Ren and Robert Lesher. Over several weeks, synthetic radical sources were exchanged, and ambient air was sampled with the goal of uncovering any systematic problems with either instrument. In spite of some minor instrument problems, the study was very successful. These data are currently being analyzed with the goal of a follow-on study in 2003, and inclusion of these results in an instrument description paper now in preparation.

Other Activities. MIRAGE Science Team (mirage-mex.acd.ucar.edu): ARS has been planning a future observational campaign to study to evolution of emissions from a developing Megacity (Mexico City), including facilities requests and involvement of the wider community. Collaborators include the Scientific Steering Committee members, Donald Blake (University of California, Irvine), Chris Cantrell (NCAR/ACD), Greg Carmichael (Iowa State University), Telma Castro (Universidad Nacional Autonomo de Mexico [UNAM]), Jerome Fast (DOE PNNL), Frank Flocke (NCAR/ACD), Robert Harriss (NCAR/ESIG), Mark Jacobson (Stanford University), Sasha Madronich (NCAR/ACD, chair), Mario Molina (Massuchusetts Institute of Technology [MIT]), L. Mireya Moya-Nunez (UNAM), Michael Trainer (NOAA/AL), Tom Warner (NCAR/RAP).

## **Tunable Diode Laser (TDL) Spectroscopy Group**

Throughout this past year as well as in previous years, the TDLS Group (Alan Fried, James Walega and dirk Richter) has focused on carrying out and analyzing highly sensitive and accurate aircraft measurements of formaldehyde (CH<sub>2</sub>O) in different atmospheric regimes. As many hydrocarbon reactions initiated by OH, O<sub>3</sub>, and/or CI involve CH<sub>2</sub>O as an intermediate, CH<sub>2</sub>O becomes important in further testing current understanding

of hydrocarbon oxidation mechanisms, as well as the consistency with the input OH concentrations employed in the models. In addition,  $CH_2O$  (through its decomposition) can be a major source of  $HO_2$  radicals, particularly in the mid to upper troposphere where radical production from  $O(^1D)$  with  $H_2O$  diminishes as the available  $H_2O$  vapor decreases with altitude. Elevated concentrations of  $CH_2O$  from convective transport as well as from in situ production may play a significant role in the production of  $HO_2$  radicals in the upper troposphere where current models indicate additional sources are necessary. Comparisons of  $CH_2O$  measurements with those from box model calculations in all atmospheric regimes are an important component for further assessing understanding of the processes discussed above. Unfortunately, measurement-model comparisons, even for remote background conditions where  $CH_4$  oxidation is the primary  $CH_2O$  precursor, have sometimes exhibited both positive and negative deviations. These discrepancies clearly point to gaps in our understanding of  $CH_2O$  production and destruction pathways, and, hence, in tropospheric oxidation processes.

There were numerous group accomplishments this past year regarding improvements in CH<sub>2</sub>O instrument performance and data analysis that address the issues discussed above. These include: (1) continued development of a difference-frequency based laser system in collaboration with Dirk Richter (now at ATD), and Frank Tittel (Rice University) for improved airborne measurements of CH<sub>2</sub>O and other gases; (2) data analysis and publication of the Texas 2000 study in collaboration with Bryan Wert ( graduate student at the University of Colorado), and William Potter (University of Tulsa); and (3) data analysis of the Transport and Atmospheric Chemistry near the Equator (TRACE-P) study in collaboration with scientists at NASA Langley, as well as the entire TRACE-P Science Team and Potter. In addition, TDLS has been successful in collaborating with James White (University of Colorado), with Tittel, Dave Carlson and Richter (ATD), and Dave Schimel (CGD/NCAR) to successfully acquire NSF biocomplexity funds to develop a high precision instrument to measure <sup>13</sup>CO<sub>2</sub>/<sup>12</sup>CO<sub>2</sub> ratios based upon a difference-frequency laser instrument. NCAR Director Opportunity Funds were also successfully acquired to support this new group initiative.

Rather than discuss each accomplishment in further detail, this report focuses on the results of the TDLS participation in the TRACE-P 2001 airborne field campaign. The group participated in this study in part to extend detailed CH<sub>2</sub>O measurement-model comparisons from high northern latitudes, successfully carried out during TOPSE, to the Asian Pacific region, a region where past studies have shown rather large CH<sub>2</sub>O measurement-model discrepancies. This region, furthermore, is characterized by large frequent continental outflow events where Asian pollution affects large geographic regions of the remote Pacific Ocean. As CH<sub>2</sub>O is intimately involved in radical production and cycling processes, CH<sub>2</sub>O measurement-model comparisons are particularly important in attempts to understand the magnitude and extent of the affected remote areas.

Figure 1 illustrates the altitude dependence of our TRACE-P CH<sub>2</sub>O measurements and comparisons with the NASA Langley box model results.

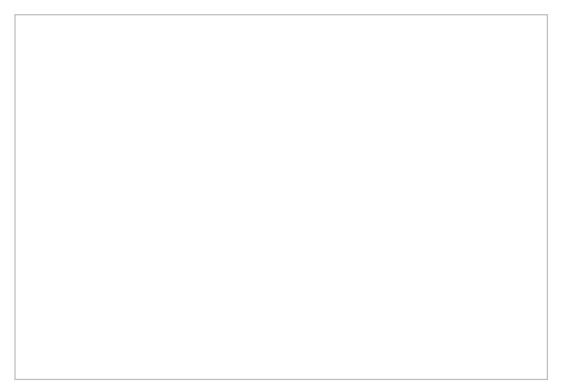


Figure 1: CH<sub>2</sub>O measurement and box model results from the TRACE-P mission for 8 altitude and 3 longitude bins: Western Pacific (110 to 150 longitude), Central Pacific (150 to 200 longitude) and Eastern Pacific (> 200 longitude). The number of comparison points for each altitude range is indicated.

This plot, which is part of a comprehensive CH<sub>2</sub>O measurement-model comparison study (Fried et al., TRACE-P special issue), illustrates excellent measurement-model agreement for 3 longitude bins for all altitudes > 3 km. However, in the Western Pacific 0 to 1 km range, where Asian outflow of pollution is most pronounced, the box model results underpredicts the measurements. Although this has been observed in other studies, the TOPSE 2000 and TRACE-P studies are perhaps the first such studies to employ comprehensive and verifiably accurate CH<sub>2</sub>O measurements to further examine this effect in terms of box model shortcomings (i.e., steady-state break down and missing and/or under representative non-methane hydrocarbons (NMHCS) ). Our TRACE-P analysis further examines measurement and model variances as an additional means of assessing model performance.

In the Central Pacific region, where large pollution outflow is no longer evident, the model results are significantly higher than measurements in the 1�2 km range. Examination of individual flight legs comprising the Central Pacific as well as the other two longitude bins, reveals a persistent model overestimation, which becomes obvious only during non-polluted conditions. Such behavior, which has not been previously reported, is thought to be due to oceanic uptake of CH<sub>2</sub>O. Further analysis in this area is underway.

Figure 2 further examines in more detail the  $CH_2O$  measurement-model comparisons for all 3 longitudes combined for the 8 to 12 km region. This represents the first such detailed  $CH_2O$  study in the 8 to 12 km region, a region where extra  $HO_x$  sources are thought to be important. Both the upper and lower traces indicate overall good measurement-model agreement for this important altitude region, with the exception of background and stratospherically-influenced air masses. In both cases, the model results underpredict the measurements, and the model variance collapses relative to measurements in the *All Comparisons* and *Elevated Precursors* categories. Although it is clear that our finite measurement detection limits (1-minute LOD of 15 to 50-pptv at 1s) contribute to extra measurement variance in all cases, one cannot discount the fact that the box model does not capture additional  $CH_2O$  production pathways in background and stratospherically-influenced air. It is interesting to note that the NASA box model underpredicts  $HO_x$  measurements in this regime, which is consistent with the need for additional  $CO_x$  sources from gases like  $CO_x$ . We are presently

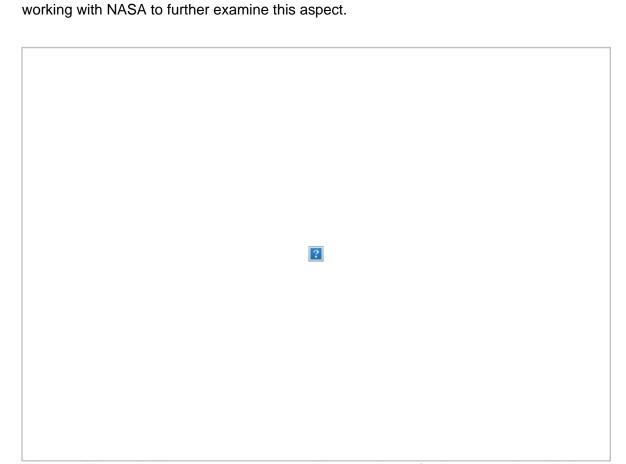


Figure 2: Time coincident measurement-model comparisons for the 8 to 12 km altitude region. The upper trace shows box and wisker plots (box: 25% to 75% of the data, wiskers represent 10% and 90% of the data, and the points show < 1% and > 99% outliers). The elevated and background air categories were determined based upon various NMHCs, CO, CH<sub>4</sub>, and aerosol concentrations, while the stratospherically-influenced air was determined based upon  $O_3$  and CO levels ( $O_3$  > 100 ppbv and CO < 80 ppbv). The bottom plot shows an overall histogram for the measurement-model differences in the 8 to 12km region, irrespective of the air mass type.

## **Biosphere-Atmosphere Interactions (BAI) Group**

The mission of the Biosphere-Atmosphere Interactions Group (Alex Guenther, James Greenberg, Peter Harley, Thomas Karl, Eiko Nemitz, Pierre Prevost, Ryan Schnell, Andrew Turnipseed, and Christine Wiedinmyer) is to advance understanding of the role of biosphere-atmosphere interactions in the Earth system and to predict the response to human perturbations. This is being accomplished through multidisciplinary field, laboratory and modeling studies of the processes controlling these interactions on various scales (e.g., leaf to canopy to landscape to global). Student and postdoctoral scientists working closely with the BAI group include Sreela Nandi (ASP), Mark Potosnak (ASP), Janne Rinne (University of Helsinki), Christoph Spirig (ETH Zurich), Emiliano Pegoraro (University of Edinburgh). FY2002 accomplishments and FY2003 plans include investigations of the natural Earth system and human perturbations and the development of community tools.

**Boundary Layer CO<sub>2</sub> Vertical Profiles.** Greenberg, Roger Hendershot, William Bradley, Prevost, Turnipseed, Potosnak, Harley and Guenther integrated an in-situ CO<sub>2</sub> analyzer into the NCAR-ACD tethered balloon profiling system in FY2002 and deployed the system in Manaus, Brazil, along with collaborators Julio Tota (University of Sao Paulo) and Antonio Nobre (Instituto Nacional de Pesquisas da Amazonia [INPA]), and

Niwot Ridge Colorado, along with R. Monson (Univ. Colorado), Jielun Sun (NCAR-MMM), Britt Stephens, Steve Oncley and Tony Delaney (NCAR-ATD). The profiling system successfully characterized CO2 gradients in the convective and nocturnal boundary layers and will be used to better understand dynamics of CO2 exchange between terrestrial ecosystems and the atmosphere. The Niwot Ridge study was an interdivisional effort sponsored by the NCAR Biogeosciences program.

TexAQS2000. Karl deployed an on-line proton-transfer-reaction mass spectrometry (PTR-MS) at one of the TEXAQS2000 ground sites and observed abundant levels of propene that were highly correlated with its oxidation products, formaldehyde and acetaldehyde, with typical ratios close to 1 in propene-dominated plumes. Data analysis conducted in FY 2002 demonstrates that tropospheric ozone production in Houston is most likely driven by low molecular weight alkene-NOx chemistry, as shown for propene-dominated air masses advected south from the Ship Channel. In the case of aromatic, nitrogen containing and various oxygenated species the high time resolution of the obtained dataset helped in identifying different anthropogenic sources (e.g. industrial from urban emissions) and testing current emission inventories. The results also show that emission inventories currently used for regional air models in the greater Houston-Galveston area need to be carefully reevaluated and updated and do not adequately reflect the status-quo. ❖

Mauna Loa Trace Gas Experiment. Karl deployed an on-line PTR-MS to the Mauna Loa Trace Experiment in 2001 and completed the data analysis in FY2002. Acetonitrile is one of the most abundant organic species in the stratosphere and therefore has a strong impact on stratospheric photochemistry. It is also thought to be exclusively emitted by biomass burning activities and therefore represents a distinct atmospheric marker. However, there is still a large uncertainty on loss mechanisms in the troposphere. We can clearly show that acetonitrile originated from biomass burning events in South East Asia. The dataset also demonstrates that ocean uptake is probably the most important loss process in the troposphere. This was shown with a simple ocean uptake model, suggesting a 20% undersaturation in the uppermost layers. A variability-lifetime analysis confirmed these results by showing that the actual lifetime of acetonitrile is on the order of 180 days, much lower than predicted by OH destruction (~1000 days).

Physiological and Biochemical Laboratory Studies. In collaboration with Ray Fall (University of Colorado, Boulder) Karl used a PTRMS in FY2002 to observe the kinetics of 13C-labeling of isoprene following exposure to 13CO2 and then the loss of 13C after a return to normal 12CO2 in oak (Quercus agrifolia) and cottonwood (Populus deltoides) leaves. For the first time, it was possible to observe the lifetimes of individually 13C-labeled isoprene species during these transitions, and to trace some of the label to the C3-allylic fragment of isoprene (CH2=CH(CH3)H+; masses 41-44, depending on number of 13C atoms). At steady state (under 13CO2), approximately 80% of isoprene carbon was labeled, with fully labeled isoprene as the major species (approximately 60%). The source of the unlabeled C is suggested to be extrachloroplastic, but not from photorespiration.

Emissions of acetaldehyde from tree leaves were also investigated. Bursts of acetaldehyde were released by sycamore, aspen, cottonwood and maple leaves following light-dark transitions. Labeling of leaf volatiles with 13CO2 suggested that the pools of cytosolic pyruvate, the precursor of acetaldehyde during periods of inhibited leaf mitochondrial respiration, were derived from both recent photosynthesis and cytosolic carbon sources. We suggest that releases of acetaldehyde during light-dark transitions immediately precede the light-enhanced-dark-respiration (LEDR) phenomenon seen in these leaves. Our results show that leaves of woody plants contribute reactive acetaldehyde to the atmosphere under different conditions: 1) metabolic conditions that promote excess leaf glycolysis and the pyruvate bypass; and 2) leaf ethanol oxidation resulting from ethanol transported from anoxic tissues.

Harley and Greenberg used PTRMS in FY2002 to investigate the light and temperature controls over leaf-level methanol and acetone emission. Hourly variations in methanol emission was strongly correlated with transpiration but controls over daily total emission appear to be more complex.

Emiliano Pegoraro (University of Edinburgh) worked with Harley, Wiedinmyer, Greenberg and Guenther to investigate the influence of drought and long term temperature variations on isoprene emission in the NCAR phytotron in FY2002. Isoprene was found to be much less sensitive to drought than is photosynthesis. However, isoprene emissions are greatly reduced by extended drought. Long term variations in temperature

were shown to be an important factor controlling isoprene emission.

Biogenic Trace Gas Fluxes over Temperate Forests. Above-canopy, trace gas fluxes were measured at two temperate forest sites as a component of a research program that contributes to, and is partially funded by, the NSF biocomplexity initiative. Karl, Turnipseed, Prevost and Guenther collaborated with Brian Lamb and Shelley Presseley (Washington State University) to compare several isoprene flux measurement techniques (eddy covariance, disjunct eddy covariance, relaxed eddy accumulation, disjunct eddy accumulation) during spring 2002 at the university of Michigan Biological Station (UMBS). Further data analysis will help in assessing future flux experiments and recommending experimental guidelines. In addition, oxygenated trace gas fluxes were measured using the PTR-MS method. These springtime observations complement fall measurements made in 2001 at this site. Methanol fluxes were enhanced due to rapid leaf expansion in spring. The data suggest that biogenic emissions of methanol and potentially other oxyVOCs are larger than previously thought.

Turnipseed tested several innovative systems for making eddy covariance measurements of important trace gases at the Niwot Ridge flux site that he maintains in collaboration with Monson. The systems evaluated in FY2002 included CO eddy covariance, with Teresa Campos (ACD/ARIM), NOy disjunct eddy covariance, with Jed Sparks (Cornell University), and ozone eddy covariance, with Alan Hills and Detlev Helmig (University of Colorado).

Biogenic Trace Gas Fluxes over Tropical Landscapes. Harley, Greenberg, and Guenther synthesized observations from a series of studies that were conducted in Amazonia during 1998 to 2001 as part of the Large-scale Biosphere Atmosphere (LBA) study. ♦ The results show that isoprene emissions from different regions of Amazonia range from more than a factor of 2 lower to more than a factor of two higher than what had been previously observed. ♦ These differences were shown to have substantial impact on regional photochemistry. Harley, Greenberg, and Guenther analyzed observations from the FY2000 SAFARI2000 study during FY2002. ♦ The results demonstrate that some savanna regions have extremely low biogenic VOC emissions while others have very high isoprene or monoterpene emission rates.

**Biogenic Aerosols.** Christoph Spirig (ETH Zurich), Greenberg, and Guenther analyzed observations from the FY2001 OSOA study during FY2002. OSOA collaborators include Thorsten Hoffman and Markku Kulmula (University of Helsinki). VOC measurements suggest that there is a substantial regional flux of monoterpenes that contribute to secondary organic aerosols. Vertical profiles measurements of particles indicate that aerosol growth occurs within the surface layer.

**Biogenic Emissions and Landcover Change.** Wiedinmyer, Guenther, Sam Levis, and Gordon Bonan (CGD) incorporated biogenic VOC emission algorithms into the NCAR CCSM-LSM and used the model to investigate the impact of landcover change on biogenic VOC emissions.

Wiedinmyer, Guenther, Xuexi Tie and Elisabeth Holland (ACD/Global Modelling) used the NCAR MOZART model to investigate the sensitivity of land management driven changes in biogenic VOC emissions on the tropospheric distribution of oxidants. The model predicts that plausible land management change scenarios could result in surface ozone and OH changes that exceed 30% over large regions.

**Regional and Global Modeling.** Guenther improved global emission estimates of isoprene and a-pinene and developed a global model of acetone and methanol emissions during FY2002 in collaboration with Wiedinmyer, Harley, Greenberg, Luanne Otter (University of Wittwatersrand), and Chris Geron (USEPA).

**Biogenic VOC Database.** Wiedinmyer organized a workshop and led the development of a biogenic VOC measurement database during FY2002 in collaboration with Guenther, Harley, Geron, Rei Rassmussen (Oregon Graduate Center) and Nick Hewitt (Lancaster University). The database is described in detail, and available on-line, at URL: bvoc.acd.ucar.edu.

Instrument development. Barry Lefer, Scott Eisele and Greenberg led the FY2002 development of a CIMS

system that is intended for measuring ammonia fluxes. The initial development has been completed and the instrument performance is being evaluated. Turnipseed, Prevost and Guenther led the FY2002 development of disjunct eddy flux samplers that will enable investigators to measure fluxes of VOC, NOy, ozone and other important trace gases. A prototype has been completed and evaluated in the field.

**Wildfire Emissions.** Greenberg, Friedli (ASP), Karl, Harley and Guenther exposed vegetation to intense heat in order to quantify emissions of flammable VOC and determine if they are important energy and mass inputs to wildfires by controlling the spatial and temporal evolution of the gaseous fuels influences fire dynamics and ignitability of the vegetation. Methanol was identified as the dominant oxygenated VOC emission.

#### **Atmospheric Odd Nitrogen (AON) Group**

Instrument Development/Field Work. The Atmospheric Odd Nitrogen Group (Brian Ridley, Andrew Weinheimer, Denise Montzka, David Knapp, and Frank Grahek) expertise is in measurements and analysis of NO, NO<sub>2</sub>, total reactive nitrogen (NO<sub>v</sub>), O<sub>3</sub>, and PAN and related homologues. Major modifications were made to an autonomous instrument capable of flying on the WB57 aircraft (or others) for measurements of NO, NO<sub>v</sub> and O<sub>3</sub>.�� The changes were made in conjunction with the ATD machine shop and engineering design facilities, as well as with design input from the NOAA Aeronomy Laboratory CIMS group (David Fahey and Ru-Shan. Gao). • A new data acquisition/control system and power supply were built and installed. A completely new sampling inlet system was constructed and fitted to allow measurement of (1) NO, (2) the NO<sub>v</sub> content of the gas phase plus that on particles having diameters less than 3-4 microns, and (3) the NO<sub>V</sub> content of the gas phase plus that on particles of all sizes. By taking into account the enhancement in the sampling of particles, and by looking at the difference between the signals from the two NO<sub>V</sub> channels, the NOy content of the larger particles can be determined, which are the dominant ones in cirrus clouds. The instrument flew successfully on 3 test flights from Texas and 14 flights to or from Key West, Florida as a contribution to the NASA-led Cirrus Regional Study of Tropical Anvils and Cirrus Layers-Florida Area Cirrus Experiment (CRYSTAL-FACE) project (Eric Jensen, NASA Ames, and Brian Toon, University of Colorado, were the mission scientists) (see http://cloud1.arc.nasa.gov/crystalface/ for detailed information). This very large multidisciplinary project (six aircraft and two ground stations) included participation from other divisions: • e.g., MMM (Andrew Heymsfield), RAF (Teresa Campos, David Rogers), ATD (the EDLDORA group) and a large number of scientists from universities and government agencies. The focus was on the microphysics/radiative properties/chemistry of cirrus clouds and especially those of the anvil outflow of thunderstorm over south Florida. Several flights were also dedicated to investigating the reactive constituent/long-lived tracer distributions in the tropical tropopause region and the mid-latitude tropopause region, furthering the group so goals to better understand the budgets of ozone and radical precursors in the upper troposphere and lower stratosphere, a region in which ACD is currently developing a research plan in conjunction with the new HIAPER facility. The flights within thunderstorm anvils also provided the opportunity to measure the production and vertical distribution of NO produced by lightning and to compare the results with our previous studies of thunderstorms over New Mexico and the Colorado plains. Since NOx is very often the rate limiting precursor of O3 production throughout the UT, global models of the O3 budget in the troposphere and its influence as a greenhouse gas are guite sensitive to their parameterizations of thunderstorms.

**Lightning Production of NO in Florida Thunderstorms.** A significant uncertainty in current global chemistry/transport models and their estimates of the tropospheric ozone burden is the input of NO<sub>x</sub> to the atmosphere by lightning activity. Current global estimates have a wide range of 2-20 Tg(N)/yr. The models are

also quite sensitive to how the NO<sub>x</sub> is distributed vertically by the deep convection since the lifetime of NO<sub>x</sub> increases strongly with altitude. NO<sub>x</sub> is also the rate-limiting constituent for production of tropospheric ozone in much of the middle and upper troposphere, the region where the ozone abundance has its largest influence as a greenhouse sax. During the recent NASA-sponsored CRYSTAL-FACE program, AON measured NO and total odd nitrogen (NO<sub>y</sub>) on board the WB-57 aircraft as it penetrated the anvil outflow regions of thunderstorms over southern Florida during the month of July. The results from a number of flights are shown below. In the case of no deep convection or electrical activity, mixing ratios of NO in this altitude range would be of the order of 100 parts per trillior or less. Clearly, the electrical activity has increased the mixing ratios by factors of 25-50 and this increase will have a large effect on ozone production as the outflow mixes over several lifetimes of NO<sub>x</sub>. By comparison with studies we have made in New Mexico and over Colorado, it appears from preliminary analyses that the Florida storms on average produce significantly higher mixing ratios. The three studies have also shown that a large fraction of the lightning produced NO<sub>x</sub> accumulates in the anvil outflow region rather than being distributed throughout the vertical extent of the storm.

#### Atmospheric Radiation Investigations and Measurement (ARIM) Group

Atmospheric Radiation Investigations and Measurement (ARIM) Group (Richard Shetter, Teresa Campos, Edward Riedel, Samuel Hall, and Barry Lefer) concentrated much of their effort this year on data reduction and analysis from several campaigns undertaken last year.

Final TRACE-P actinic flux and photolysis frequency data. A large effort was put into final data reduction and analysis of the TRACE-P actinic flux data. At the request of other TRACE-P investigators, additional molecules were added to the data reduction effort. These included the oxygenated organics butanal, pentanal, acetaldehyde, methylethyl ketone, and glyoxal, which were measured for the first time on a GTE mission. ARIM personnel gave presentations on the effects of clouds and aerosols on photochemical data at TRACE P data workshops in October 2001 and June 2002. Further analysis of the photochemical data has led to a collaborative set of papers with Gregory Charmichael s group (University of Iowa) and James Crawford s group (NASA LaRC) on cloud and aerosol effects on the photochemistry of the Asian outflow. The ARIM group has taken the lead on Impact of Clouds on Photolysis Frequencies and Photochemistry during TRACE-P, Part I: Analysis using Radiative Transfer and Photochemical Box Models by Lefer, Shetter, Hall, Crawford, Jennifer Olson, You-Hua Tang, and Carmichael, to be submitted to a special TRACE P section of J. Geophys. Res. and are co-authors on Impact of Clouds on Photolysis Frequencies and Photochemistry during TRACE-P, Part II: Analysis using a 3-D Regional Chemical Transport Model.

Development / Upgrade of Instrumentation. In order to better understand the effects of aerosols on photolysis frequencies and tropospheric photochemistry, steps were taken to develop a direct solar beam spectroradiometer for molecular slant column measurements and wavelength dependent aerosol optical depth measurements. These measurements will be used in radiative transfer modeling for comparisons with in situ actinic flux measurements to quantify wavelength dependent effects of different aerosol types on photolysis frequencies. These measurements will also be an important component of future studies like MIRAGE. A preliminary ground-based instrument has been designed, fabricated, and is in testing. The instrument is comprised of 3 subsystems: a narrow field of view optical collector, a microprocessor controlled 2-axis pointing system, and a scanning double monochromator detection system. ▶ Data reduction software has been written to produce direct irradiance spectra, slant ozone columns and aerosol optical depths from 290 to 750 nm in 1 nm increments. In addition to applications for understanding tropospheric photochemistry, wavelength dependent atmospheric optical depths, aerosol optical depths, and molecular slant column measurements (e.g., O₃ and NO₂) will be critical in validation activities for the series of satellite instruments that will be making tropospheric measurements. Satellite validation activities are becoming an integral component of

future NASA atmospheric chemistry programs, thus instruments that link these activities are important. Campos participated in several field experiments: Instrument Development and Education in Airborne Science (IDEAS), International H<sub>2</sub>O Project (IHOP), and Cirrus Regional Study of Tropical Anvils and Cirrus Layers - Florida Area Cirrus Experiment (CRYSTAL-FACE) airborne campaigns, and the ground-based Niwot Ridge Pilot Experiment (NRPE). The tunable diode laser hygrometer was modified by the manufacturer to improve the time response to 15-20 Hz sample rates. During the IDEAS project, the instrument demonstrated significantly improved performance, establishing its utility for eddy covariance flux measurements. This instrument was deployed on the NRL P3 during IHOP. CO and water vapor were measured during the CRYSTAL-FACE project on the CIRPAS Twin Otter, with the goal of characterizing boundary layer in situ tracers in the area of tropical convection formation. These observations were complementary to high altitude tracer measurements of convective outflow taken by the NASA WB-57 platform. Additionally, boundary layer water vapor flux measurements at and below cloud base provided insight into entrainment and cloud processes. During the NRPE, funded by the Biogeosciences Strategic Initiative and NCAR Director SOPPOPTURING CO fluxes were measured above the canopy by the method of eddy covariance.

Continued development and testing of actinic flux measurement techniques. A detailed analysis of optical collectors for actinic flux instrumentation revealed that the azimuthal response of these collectors is not always uniform, and that azimuthal response measurements are a critical screening tool to determine which heads are useful for actinic flux measurements. This testing is something that most other labs in this field do not usually do. In addition, ARIM continued the testing of diode array spectrometers for application to actinic flux measurements, with particular emphasis on methods to reduce the problem of straylight contamination in the UV-B. The most promising idea that we are trying to test is the use of an optical filter to reduce the UV-A and VIS radiation, while not impacting the UV-B wavelengths. The initial evaluation and testing of embedded controller data acquisition and control system for the scanning actinic flux spectroradiometers has shown that this small, lightweight, and low power data acquisition system can do everything the current rackmount PC systems can. These systems are crucial for unpressurized and limited payload aircraft platforms. Acquisition and control software has been written and tested in the laboratory. Further software development may yield additional speed improvements in the scan cycle time to allow for improved data frequency.

Participation in community research programs. A proposal to NASA Support Upper Atmospheric Research Program to participate with the newly developed Direct beam Irradiance Atmospheric Spectroradiometer (DIAS) in the second SAGE III Ozone Loss and Validation Experiment was submitted in May 2002. This program involves investigators from university and NASA laboratories. The ARIM group proposed to make slant ozone column and wavelength dependent aerosol optical depth determinations from the NASA DC-8 aircraft in Kiruna, Sweden during January and early February 2003. The proposal has been funded and the design, fabrication, and testing of an aircraft deployable instrument has begun.

Tropospheric Photooxidants. ARIM participated in a three-year collaborative research proposal entitled ♦ Collaborative Research: Impact of snow photochemistry on atmospheric radical concentrations at Summit, Greenland that was submitted to NSF Polar Programs. The primary objective of this research is to elucidate the processes that produce and consume OH and HO₂ radicals within and above sunlit snow over a wide range of environmental conditions and to improve our understanding of fast photochemistry within this unique environment. The proposal involves researchers from the University of New Hampshire, the University of California-Irvine, the University of California-Davis, Georgia Tech, the University of Arizona, and the Cold Regions Research Laboratory of the US Army. The ARIM group will be responsible for measuring actinic flux above the snow surface and at several depths within the snowpack during field seasons in the summer of 2003 and the spring of 2004. Funding has been has been approved.

The Group participated in a collaborative research proposal which was submitted to NSF Polar Programs for Antarctic research. Proposed is a four year &collaborative research program involving nine major institutions including Georgia Institute of Technology, University of New Hampshire, University of Colorado, University of Arizona, University of California Irvine, New Mexico State University, Rutgers University, NASA Langley Research Center, and NCAR / ACD. This program will include two major field studies in Antarctica that will be conducted during the Austral spring/summer months (i.e., November, December and early January). The broad-based goal of this program will be to enhance our understanding of the processes that

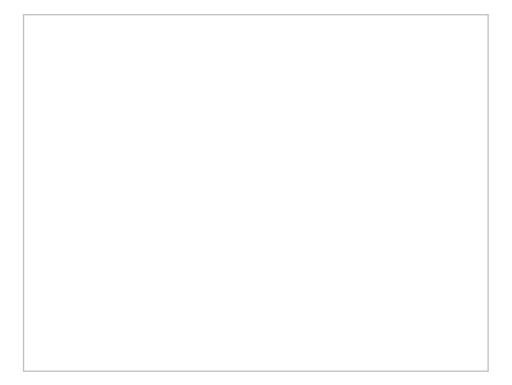
control tropospheric levels of HO<sub>x</sub>, NO<sub>x</sub>, sulfur, and other trace species over the Antarctic continent. The ARIM group proposed to determine photolysis frequencies from the NSF C-130 aircraft over the Antarctic continent during second field study in November and December 2006.

The ARIM Group participated in a pre-proposal to the National Science Foundation Integrative Graduate Education and Research Traineeship (IGERT) Program to foster the development of a graduate program at the University of Colorado Boulder, that is focused on field observations of atmospheric constituents and variables important in urban air quality and regional and global climate change. In order to achieve the depth of knowledge necessary to become leaders, these graduate students will carry out their projects in the laboratory of a senior investigator at one of the participating institutions. Each of these investigators will be someone with extensive experience with instrument development and field measurements. In addition to the ARIM group, this proposal involves Boulder based researchers from the following programs: Laboratory for Atmospheric and Space Physics (CU Boulder), Program in Atmospheric and Oceanic Sciences (CU Boulder), Department of Mechanical Engineering (CU Boulder), NOAA Aeronomy Laboratory, National Center for Atmospheric Research (RAF/ATD). If this pre-proposal is approved, the group will be invited to submit a full proposal in February 2003.

### **Laboratory Kinetics (LK) Group**

The Laboratory Kinetics Group (Geoffrey Tyndall and John Orlando) has continued its studies of the chemistry of oxygenated volatile organic compounds. Major progress has been made in the chemistry of the carboxylic acids and their derivatives, the esters.

Chemistry of Acetic and Peracetic Acid. Acetic acid and peracetic acid are important trace constituents of tropospheric air and are present as the result of direct anthropogenic and biogenic emissions (acetic acid only) and as by-products of hydrocarbon oxidation processes. Removal of these two species from tropospheric air is likely controlled by deposition processes in the boundary layer, but gas phase processes are also expected to play a role, particularly in the free and upper troposphere. At present, there is essentially no data available on gas phase destruction of peracetic acid, and discrepancies exist in the current database for acetic acid loss. The Group has recently obtained laboratory data on the photolysis rates for these species and the rate coefficients for their reaction with OH. Data on peracetic acid show that this compound behaves much like an organic hydroperoxide, with OH reaction and photolysis both occurring in the troposphere with time constants on the order of a week or two. Our studies of the OH/acetic acid rate coefficient alleviate a long-standing discrepancy in the literature. The results indicate that the rate coefficient has a negative temperature dependence, and that the lifetime for acetic acid removal via OH reaction is about one week. The figure shows ultraviolet absorption cross sections of gas-phase peracetic acid (solid line) compared to those in isooctane solution (diamonds), and gas-phase H<sub>2</sub>O<sub>2</sub> (triangles), CH<sub>3</sub>OOH (squares), and HOCH<sub>2</sub>OOH (open circles).



Chemistry of Esters. Esters such as formates and acetates can be released directly or produced photochemically in urban environments. In addition to their use as solvents, they can be formed in situ from the oxidation of ethers, which are being used increasingly in oxygenated automobile fuels. Hence, it is of interest to determine the lifetimes of these molecules, and to investigate the potential for formation of harmful products in the oxidation. It is also relevant to compare reactivity trends in the esters with those found in the carboxylic acids described above. In 2001, a study was published of the oxidation of methyl formate at 298 K. A reaction unique to esters was confirmed as occurring in this system, the alpha-rearrangement of the oxy radical.



In collaboration with Michael Hurley and Timothy Wallington (Ford Motor Company) and Andre Silva Pimentel (University of Michigan), LK has extended the study to the oxidation of methyl, isopropyl and t-butyl formate, and methyl acetate, all as a function of temperature. In the studies of methyl formate and methyl acetate, the activation energy for the alpha ester rearrangement was measured for the first time and shown to be around 12 kcal/mol, supporting quantum mechanical calculations made recently by Theodore Dibble (State University of New York [SUNY], Syracuse).

Mechanistic studies of isopropyl and t-butyl formate using chlorine atoms as the oxidant showed that the corresponding methyl-substituted radicals probably isomerize rather than decompose.

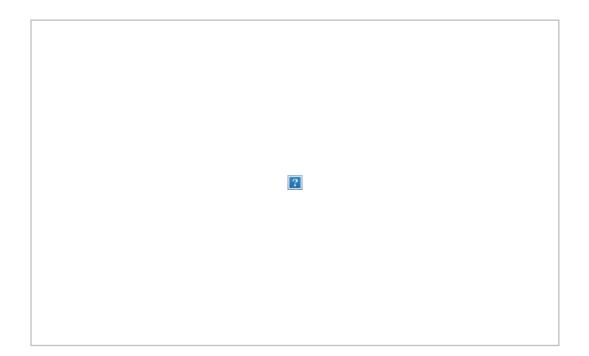
The occurrence of these unusual 5-membered transition states was confirmed in further calculations by Dibble. Products observed were CO2, acetone and formaldehyde from t-butyl formate, while isopropyl formate also led to substantial formation of formic acetic anhydride. When OH radicals were used to initiate of the reaction, the same suite of products was observed, although in the case of isopropyl formate there was strong evidence that attack at the central carbon atom was enhanced over what is predicted from simple empirical correlations. On the basis of these and other results, there is reason to believe that current theories of reaction rates do not adequately describe the kinetics of OH with oxygenated species.

## **Optical Techniques (OT) Group**

The Optical Techniques (OT) Group (William Mankin, Michael Coffey and James Hannigan) uses infrared spectroscopy, both in situ and remote sensing, to investigate problems of atmospheric chemistry and related issues. The group develops and uses airborne and ground-based instruments such as Fourier transform spectrometers and laser spectrometers for measurements of atmospheric composition.

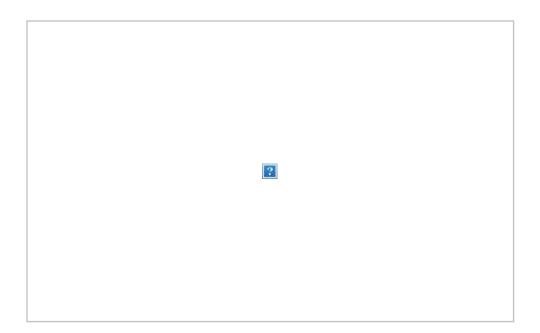
The Network for Detection of Stratospheric Change is a network of high quality ground based observing stations for early measurement of changes in the composition and state of the stratosphere and determination of their causes. In addition it provides high quality data for validating atmospheric models and for comparison with measurements from satellites. The group operates a Fourier transform infrared spectrometer at Thule, Greenland (76.53 N), one of the Network for Detection of Stratospheric Change (NDSC) primary stations. We have obtained data automatically whenever the weather was suitable and the sun was above the horizon, and have analyzed those data for column amounts of gases, including both stratospheric gases important in ozone chemistry and tropospheric gases related to climate change.

The shape of spectral lines in the infrared contains information on the height distribution of the absorber up to altitudes, typically 30 km, at which Doppler effects overwhelm pressure broadening. The Thule spectrometer has sufficient resolving power, about a million, to allow inversion of the line shape to produce a low resolution vertical profile. In collaboration with ACD Affiliate Scientist Aaron Goldman (University of Denver) and visitor Frank Hase (University of Karlsruhe [IFK]), the group has been developing the method for the inversion. The figure below shows a retrieved profile of HCl during Arctic spring; the profile was retrieved from fitting the HCl line shown in the left panel. The smooth profile on the right was the initial a priori profile, and the profile with the crosses is the retrieved profile showing HCl depletion in the lower stratosphere.

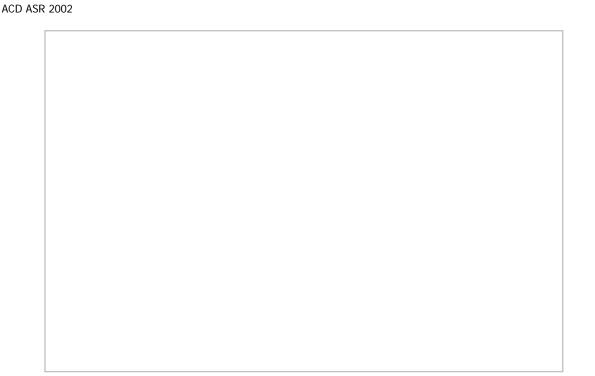


OT participated in the SAGE Ozone Loss and Validation Experiment (SOLVE), during the winter and spring of 2000. On board the NASA DC-8, several thousand spectra in and near the Arctic vortex were recorded, using an airborne Fourier transform spectrometer which had been substantially modified and improved for the experiment. The spectra show absorption lines of more than a score of gaseous species. The spectra has been analyzed for numerous species with emphasis on those which are involved in the heterogeneous chemistry and ozone loss in the cold polar vortex. The data show that strong activation of chlorine occurs during the winter when PSC swere abundant, and that some denitrification was also present, although it was not as widespread as it was in the Antarctic vortex. The observations from SOLVE were similar to those from our earlier Arctic campaigns. The figure below shows a result indicative of the chemistry of the winter vortex, specifically activation of chlorine, resulting in the observed decrease in the HCI/HF ratio within the

vortex. The HCI/HF ratio has declined over the last decade, as indicated by the decrease between Airborne Arctic Stratospheric Expedition (AASE) (1989), AASE2 (1992), and SOLVE (2000), due to the increasing fraction of stratospheric chlorine from anthropogenic sources. The reduction of the ratio inside the vortex, compared to observations outside the vortex, indicates the chlorine activation with about two-thirds of the total HCI column having been heterogeneously converted into active chlorine.



During the SAGE Ozone Loss and Validation Experiment (SOLVE), the Group recorded several thousand spectra in and near the Arctic vortex during the winter and spring of 2000. PSC were common during the January flights, but were absent in March. In addition to the spectral absorption lines of many gaseous species, the spectra contain broad absorption features due to the PSC particles. Working with the data from January and March, David Glandorf (University of Colorado) in collaboration with the OT Group and with Margaret Tolbert and Owen B. Toon (University of Colorado) has deduced the relative absorption due to PSC at a number of frequencies at which gaseous absorption is minimal; he has compared these absorption features to spectra of PSC computed from optical constants determined in the laboratory. He has concluded that the observations best match a mixed cloud containing crystalline nitric acid trihydrate particles and liquid droplets of nitric acid solutions; the mixed phase cloud is consistent with lidar observations (Edward Browell, NASA Langley Research Center) showing mixed layers of depolarizing and non-depolarizing particles. The figure shows the comparison of the observations with the mixed phase cloud; clouds using solid particles of nitric acid dihydrate do not match the observations nearly as well.



### Global Modeling (GM) Group

The Global Modeling (GM) Group (Anne Smith, Elisabeth Holland, Douglas Kinnison, Daniel Marsh, and Stacy Walters) primary focus is to investigate the chemistry of the atmosphere using global numerical models. The group engages in development and application of models for the troposphere and middle atmosphere, related studies using global observational data, and development of algorithms for treating specific processes within the models.

Using a 10-year data set from the UARS/HALOE instrument, Marsh et al. has found that mesospheric water has an increasing trend of about 1% per year, similar to the trend previously reported in the stratosphere. (*J. Geophys. Res.*, in press) In addition, it has been found that ozone measured at sunset has a strong negative trend that peaks at -4% per year around 75 km. The ROSE model calculations indicate that current photochemical understanding can account for • a) the trend in sunset ozone, while there is no ozone trend at sunrise; b) • the vertical structure of the observed ozone trend, which varies • sharply with altitude, and c) the magnitude of the ozone trend, given the observed water changes.



Monthly anomalies (filled circles) at 0.023 hPa (approx. 75 km) for a) ozone and b) water vapor. Data shown are for sunset observations between 17N and 52.5N. Solid line represents the linear trend in the data.

The MOZART model has been applied in the TOPSE field campaign to provide "real-time" calculations of the chemical conditions, and to analyze the ozone and  $NO_x$  budgets of the measurement and the model result. The effect of hydrolysis on  $NO_x$  and ozone concentrations are studied by the MOZART model. The results show that during TOPSE; with hydrolysis, modeled NOx concentrations are close to the measured values. This comparison provides evidence that the hydrolysis of  $N_2O_5$  on sulfate aerosol plays an important role in controlling the tropospheric  $NO_x$  and  $O_3$  budgets. The calculated reduction of NOx attributed to this reaction is more than 90% in winter at high latitudes over North America. Because of the reduction of  $NO_x$ ,  $O_3$  concentrations are also decreased. Tie, et al. (*J. Geophys. Res.*, in press; Emmons, et al., submitted to *J. Geophys. Res.*).

One puzzle has been understanding the response of stratospheric ozone to the 11-year variation in solar flux. Analysis of long-term ozone observations from SAGE and SBUV indicate that there are two areas of maximum response in midlatitudes, and that ozone has a negative response in the tropical lower stratosphere. However, theory predicts the largest response in the Tropics and a positive ozone perturbation everywhere. A series of experiments with the SOCRATES 2-dimensional model have provided an explanation for discrepancy. The short data period plus the timing of two tropical volcanoes at a 9-year interval during the observational record partially explains the problem. In addition, the QBO signal, which is well-known to be the largest forcing of interannual ozone variability, cannot be adequately removed from the available data. The residual of volcanic and QBO ozone variations contaminate the observational analysis and appear to be responsible for the discrepancy between observations and models. (Hyunah Lee, *J. Geophys. Res.*, in press)

## **Measurement Of Pollution In The Troposphere (MOPITT) Group**

The Terra satellite Measurement Of Pollution In The Troposphere (MOPITT) experiment is a joint Canadian-US effort to measure and interpret the global distributions of tropospheric carbon monoxide (CO) and methane (CH4). (The Group includes U.S. P.I. John Gille, David Edwards, Charles Cavanaugh, Jarmei Chen, Cheryl

Craig, Merritt Deeter, Louisa Emmons, Gene Francis, David Grant, Ben (Shu-Peng) Ho, Boris Khattatov, Deborah Mao, Danile Packman, Barbara Tunison, Juying Warner and Danel Ziskin) NCAR is responsible to NASA for the continued development of the data reduction algorithms and for operational data processing at every stage from instrument counts to calibrated radiances, through to globally-retrieved carbon monoxide vertical profiles and methane total columns. MOPITT version 3 provisionally validated tropospheric CO profiles are currently being processed and delivered to NASA for scientific use by the international science community. This is the first dataset of its kind, and represents a significant advance in satellite remote sensing of the troposphere.

The MOPITT group has been active in 3 main areas this year: (1) continued improvement of the data reduction algorithms, data processing, and delivery of the final products to NASA for later distribution to the community; (2) validation of the MOPITT data with independent correlative measurements to accurately assess data quality; and (3) use of the MOPITT data in tropospheric chemistry and transport studies. More information about the MOPITT project can be found at <a href="http://www.eos.ucar.edu/mopitt/">http://www.eos.ucar.edu/mopitt/</a> and <a href="http://www.atmosp.physics.utoronto.ca/MOPITT/home.html">http://www.atmosp.physics.utoronto.ca/MOPITT/home.html</a>.

Production of the MOPITT Version 3 Data Product. In the years leading up to launch, the ACD MOPITT group developed the tools necessary to receive and process the instrument measurements. After launch, additional effort in this area was required in order to properly understand the complexity of the instrument and to fully characterize the measurements which showed some unexpected artifacts. The elements of this processing capability and the people responsible, are: the data handling interfaces and protocols between NCAR and the NASA centers which receive and archive the satellite data and the ancillary meteorological data (Ziskin and Chen); the Level 0-1 processor which calibrates the instrument counts to produce geolocated radiances (Ziskin, Mao, Chen); and the Level 1-2 processor which comprises a forward model which provides a full simulation of the MOPITT measurement, a cloud detection algorithm, and a retrieval algorithm (Edwards, Francis, Warner, Deeter, Ho, Gille, and Grant). The retrieval combines information from the measurements, the forward model, and previous measurements which define the current understanding of the atmosphere, to obtain the most likely CO profile or CH<sup>4</sup> column consistent with the measured MOPITT signal.

Work has continued on the characterization of the MOPITT radiances and the development of improved algorithms. This culminated in the release of a new version 3 CO data product to the community. The data for the mission Phase 1, before the instrument cooler failure in April 2001, have been designated as provisionally validated and suitable for quantitative scientific research. This was announced by the MOPITT PI James Drummond during the IGARSS'02 meeting in Toronto, Canada in July 2002. Several major developments made this possible. During the last year, Ho has worked on issues related to instrument noise and recent improved understanding allowed the recovery of 40% of the MOPITT data which had to be removed from the previous data version 2 due to excessive noise. The problem of radiance biases at 4.7 micrometers that were noted soon after launch were also successfully resolved by Deeter, Francis, Edwards and Gille, with a redefinition of the modeling of the optical filters. This work is detailed in the paper Deeter, et al., *J. Atmos. Oceanic Tech.*, in press. A new radiance calibration strategy was also implemented by Edwards, Francis, and Ziskin, which resulted in improved retrievals compared to validation measurements. A cloud detection scheme was developed by Warner that makes use of signal information from MOPITT in conjunction with the cloud mask produced by the Terra/MODIS instrument. This has enabled the CO retrievals to be extended to higher latitudes where the cold underlying surface usually causes problems for thermal sensors.

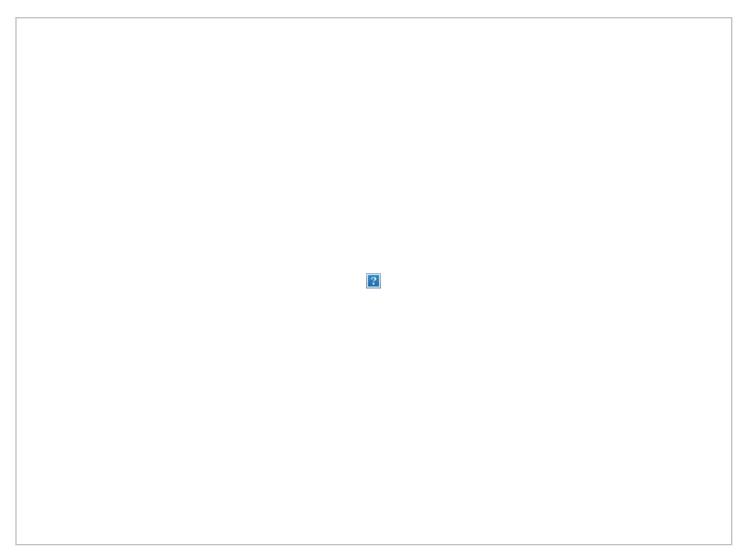


Fig. 1 shows an example of the combined MOPITT 700 hPa data for the first twelve days of November 2000. Global coverage is almost complete in three days, although no retrieval is possible in those regions of persistent cloud cover. Elevated CO levels associated with industrial pollution are evident in the northern hemisphere, with significant Asian outflow into the Pacific Ocean. Particularly evident in this figure are the plumes of CO due to biomass burning CO in southern Africa and South America. This highlights the utility of the MOPITT data in studying this important forcing of tropical tropospheric chemistry.

**Development of a Phase-2 Data Product**. In April 2001, the MOPITT instrument experienced the failure of one of its two coolers. This led to the loss of 4 of the 8 channels. In the last year, the MOPITT team has worked hard to overcome this setback and to produce a CO profile product using the radiances from the remaining 4 channels. Although the channels associated with each of the two coolers were designed to have some redundance, the team had relied most heavily on the channels that were lost in the pre-cooler problem (Phase 1) retrievals. Deeter led the effort to reconfigure the retrieval for the available post-cooler loss (Phase 2) signals. This has required careful examination of the calibrated radiances to account for small biases that have a significant impact on the retrieval. A Phase-2 CO profile product, without any apparent loss of vertical resolution compared to the Phase-1 period, has recently been delivered to NASA.

**MOPITT Data Validation.** Validation activities are essential at each level of the data processing to ensure a full understanding of the in-flight MOPITT performance, to allow characterization of measurement accuracy, precision, and resolution, and to point the way to needed improvements. In most of this validation activity, a step-by-step approach has been used starting with the simpler situations, learning from the results, before moving on to more complicated cases. The MATR aircraft instrument team (Alan Hills, Jianquo Nui, and

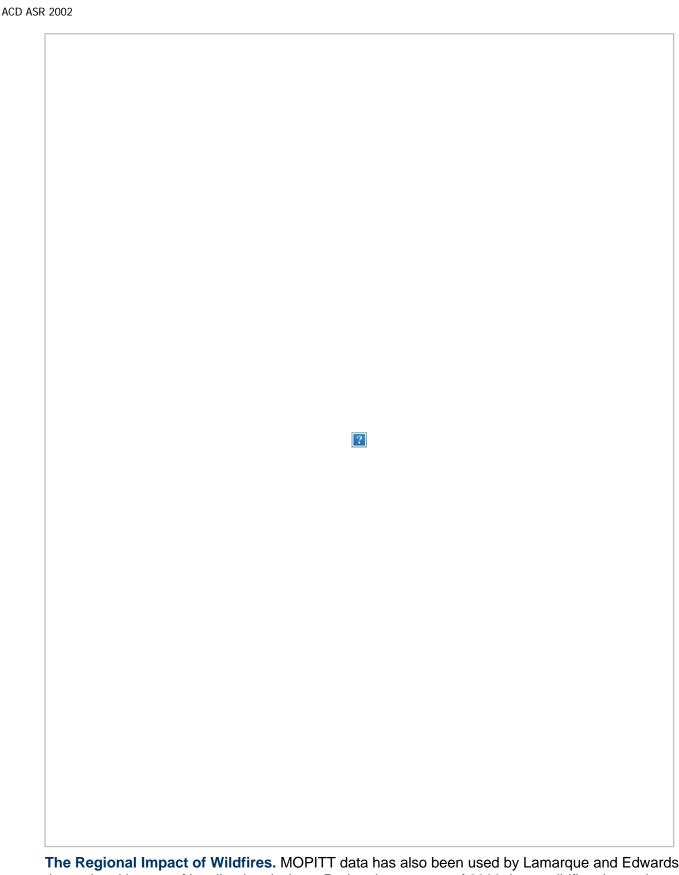
Deeter) has continued studies using the 2001 flight data taken: (1) during April and May over the Oklahoma CART site, and (2) during November over three Western U.S. cities (Los Angeles, Las Vegas, and Denver). These flights were supported with in-situ measurements by Paul Novelli (NOAA Climate Modeling and Diagnostics Laboratory [CMDL]). Kate Paulin, a student visitor from Oxford University, was also involved in this work. Emphasis has been placed on quantifying sources of radiance bias and noise for both the longwave LMC and PMC channels. Multi-level flight data has been used to characterize radiance biases. Currently, LMC and PMC retrieval results agree fairly well, although PMC retrieval results appear much noisier. Analysis of retrieval results for recent MATR measurements over western cities is underway.

At Level 0-1 there has been a careful examination of the instrument engineering data on a daily basis. The resulting calibrated radiances are being extensively compared with model calculations for special cases where the measurement scenes are believed to be well characterized. This work has led to studies by Deeter to characterize the way in which retrieval errors are related to radiance uncertainties. This activity has been especially important in the development of the Phase-2 data product. A manuscript detailing this validation effort is currently in preparation (Deeter et al.)

At level 2, Emmons, Valery Yudin, Deeter, and Jean-Luc Attie, a collaborator and frequent visitor from Laboratoire d'Aerologie, Toulouse, France, have continued the work of comparing individual retrieved CO profiles with in-situ measurements taken by Novelli's NOAA/CMDL group. Comparisons have also been made with CO total column retrievals from ground-based spectrometers, coordinated by Nikita Pougatchev (Christopher Newport University). These show good agreement in terms of seasonal trends. An example from one such study is shown in Figure 2a. The MOPITT total column composite data are shown for November 1-15, 2000. This is a time of high biomass burning in Africa which results in an emissions plume that stretches out into the Indian Ocean. The atmospheric CO is further enhanced by biomass burning in northwestern Australia. The high CO at this time of year is reflected in the ground-based FTIR CO total column measurements taken at Lauder, New Zealand, (Figure 2b) by Nick Jones, (University of Wollongong [NIWA] Australia). This is a good example of the way in which MOPITT measurement can provide the global context to local measurements. A manuscript detailing the Level 2 validation work is currently in preparation (Emmons et al.)



During TRACE-P, MOPITT data over the western Pacific were provided in near real-time for use in flight planning for the NASA DC-8 and P-3B aircraft. This demonstrates the utility of satellite data for providing the global context to local measurement goals during intensive field campaigns. Figure 3a shows MOPITT CO data at 700 hPa for the last week of February, 2001. Plumes originating from biomass burning in southeast Asia and from industrial regions in China are clearly evident. Through model simulations using analyzed winds, the effect of meteorology on plume development may be investigated. Figure 3b shows ozone profile measurements made by the TRACE-P aircraft on February 27, 2001, at 20 N, 170 -190 E. This indicates a strong plume near 700 hPa. A corresponding enhancement can be seen in the MOPITT CO field at the same location, with the indication that this is due to a break-off from the main plume that is caught in a local anticyclonic circulation in the region of the in-situ measurements. The long-range transport of Asian outflow and the impact on global air quality is being investigated by Emmons, Gille, Yudin, and Edwards.



The Regional Impact of Wildfires. MOPITT data has also been used by Lamarque and Edwards to examine the regional impact of localized emissions. During the summer of 2000, large wildfires burned more than a million acres over the Northwest and Rocky Mountain regions of the U.S., with particularly high intensity in Idaho and Montana. During the last 10 days of August 2000, large fires were active in the region between 44-46 N, 113-117 W. An indication of the location and extent of the fires is provided by AVHRR observations analyzed by the United States Forest Service. Figure 4a shows daily maps of the 1.1 km x 1.1 km AVHRR-derived burnt areas during August, and indicates a large increase in the number and extent of fires over the last 2 weeks of the month, mostly in Idaho and Montana.

west, bringing fai CO values over the fires, the MOPITT concentrations.	en from the average rly low values of CO, he Idaho-Montana bo concentrations reachigh CO values are sarge-scale transport.	approximately 8 order coincides vehicle to 250 ppb still found 500 km	0-120 ppbv, into ery well with the v, indicating at l downwind, eas	o the Idaho r e location of t east a doubli stward and n	egion. The locathe fires. In the ing of the local orthward, of the	ation of high wake of the CO e fires,
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The corresponding 2-week binned MOPITT data are shown in Figure 4b for the second half of August. At this

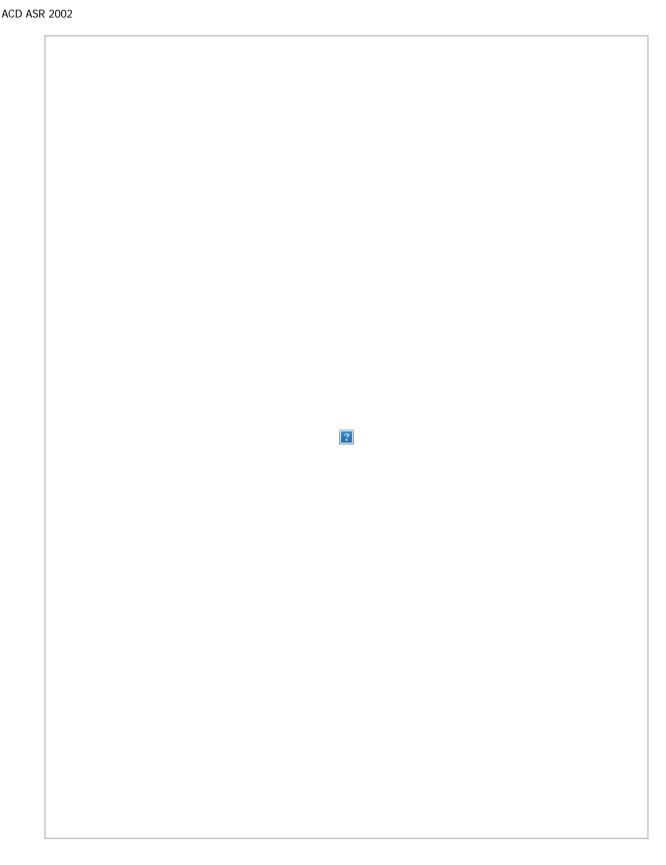
Using Tropospheric Satellite Remote Sensing Measurements to Investigate Tropical Ozone Formation. The combination of satellite retrievals of CO, NO<sub>2</sub>, aerosol, fire and lightning flash counts, can provide a powerful method for investigating the production of ozone precursors. Edwards, Lamarque, Emmons, and Gille, have used these sensor data in conjunction with in-situ measurements and chemical transport modeling to investigate the impact of biomass burning on tropical chemistry and to help explain the observed

tropospheric ozone distribution over the Atlantic.

There has been considerable interest in the recent literature regarding the apparent Atlantic tropical tropospheric ozone `paradox' [Thompson et al., 2000; 2001]. This can be summarized as follows: Most of the African Northern Hemisphere (NH) biomass burning in January and February occurs north of the intertropical convergence zone (ITCZ), while the maximum in most of the satellite-derived tropical tropospheric ozone (TTO) columns is observed in the southern hemisphere (SH) tropical Atlantic, south of the ITCZ. Apart from requiring a mechanism of significant ozone precursor production and inter-hemispheric transport across the ITCZ, it is also hard to reconcile this behavior with modeling studies and in-situ measurements which generally show high tropospheric ozone in regions of intense burning.

The mean MOPITT CO mixing ratio over Africa and the Atlantic for January 20-27, 2001, at 700 hPa, is shown in Figure 5a. The importance of biomass burning as a source of CO over northern equatorial Africa is readily apparent, and the northern extent of the plume correlates well with satellite observations of savanna fires. Emissions from the region of maximum burning in eastern Africa are generally transported southwest by the prevailing Harmattan flow to the ITCZ where convection takes place, and the plume ends up over southern central Africa or out in the Gulf of Guinea. Emissions from the fires in western Africa are advected westwards out into the Atlantic, suggesting that the ITCZ in this region presents a stronger barrier to interhemispheric transport. Once in the free troposphere, the CO from west Africa forms a strong plume that is caught in the tropical easterlies. MOPITT data show that this plume is persistent during the months December, 2000 - April, 2001, and that long-range transport carries CO to South America. Part of this plume crosses to the Pacific Ocean, while part is circulated over Amazonia. The absence of a significant CO plume in the southern tropical Atlantic suggests that it is unlikely that the north African fires are the origin of the observed Total Ozone Mapping Spectrometer (TOMS) TTO maximum.

Further information about ozone precursor distributions is provided by the ERS-2/GOME instrument. The January, 2001, mean residual tropospheric NO<sub>2</sub> vertical column is shown in Figure 5b. This can be compared directly with the MOPITT CO, and shows good correlation with the peak CO concentrations over the fire locations. The westward extent of the NO<sub>2</sub> plume over the equatorial Atlantic is not as great due to the shorter lifetime. Also evident are the significant levels of NO<sub>2</sub> over southern Africa where very few fire counts are observed at this time. Elevated levels are also seen over South America and out into the southern Atlantic. The absence of significant low altitude CO plumes in these regions suggests a possible lightning source of NO<sub>2</sub> in the mid-troposphere. Further evidence of this is provided by the fact that the areas of highest lightning flash density from other satellite observations corresponds well with the Global Ozone Monitoring Experiment (GOME) NO<sub>2</sub> observations. The resulting ozone would be advected westwards into the Atlantic, and may be one component of the ozone maximum observed in the TOMS TTO. This conclusion has been confirmed with a modeling analysis using the MOZART-2 chemistry transport model (CTM). This investigation has included the collaboration of Jean-Luc Attie and Jean-Pierre Cammas (Observatoire Midi Pyrenees, Toulouse, France), and Andreas Richter (University of Bremen, Germany). It has been accepted for publication in *J. Geophys. Res.* 



Data Assimilation and Inverse Modeling. The MOPITT modeling team (Khatattov, Lamarque, Yudin) has continued work on the assimilation of MOPITT data, profiles and total column independently, in the MOZART-2 global chemistry-transport model. The forecast model error specification has been revised in the assimilative code, and the theoretical aspects of the new error covariance model now include uncertainties in the analyzed winds, cloud mass fluxes, surface fluxes, and chemical production and loss. The assimilation takes into account the full information from averaging kernels. This in turn allows retrievals to be mapped to a regular time/space grid using sequential assimilation, and is very important in facilitating comparison of MOPITT measurements with other correlative data, especially when there is not an exact coincidence in time

and location.

Gabrielle Petron (graduate student from the University of Paris working in the MOPITT team), has led an investigation of inverse modeling using the MOPITT data and the MOZART-2 model to constrain surface fluxes of carbon monoxide and assess the accuracy of emission inventories. This work has also involved the collaboration of Claire Granier (University of Paris). Until now, the inverse modeling of CO sources had been limited by the complexity of the CO budget and by the small number of in situ observations. The MOPITT instrument provides almost global coverage of the tropospheric CO distribution every 3 days. The inverse modeling tool previously developed for the inverse modeling of CO sources using in situ measurements has been adapted and optimized to use the MOPITT data and the MOZART-2 model with analyzed winds. Statistical properties of the observation matrix linking a set of surface sources of CO to the observed distribution at 700 hPa are presented and discussed in a paper which will be submitted shortly. A bayesian synthesis inversion of the emissions of CO has been performed for the period June 2000-January 2001. The results, although quite promising, suggest a strong sensitivity of the solution to the a priori emissions inventory used in the model. Figure 6a shows the modeled CO distribution at 700 hPa using a priori emissions, Figure 6b shows the modeled CO distribution at 700hPa using optimized emissions obtained from the inversion of the MOPITT data, and Figure 6c shows the MOPITT data at 700hPa. The modified emissions are seen to bring the model and satellite results into closer agreement. More recent estimates of CO emissions will be used in the near future, and CMDL data will enable validation of the results.

### **Heterogeneous Chemistry (HC) Group**

The Heterogeneous Chemistry Group (David Hanson) studies the chemistry and physics of aerosol particles. This includes investigating their rates of formation (nucleation) and also, after they have grown to become long-lived particles, the uptake and reaction of gas-phase species on their surfaces. These processes can be key factors in the Earth's climate system and in atmospheric chemistry. Here, laboratory research is focused on the rates and mechanisms of nucleation and particle chemistry involving sulfuric acid, water, and ammonia vapors. Some gas-phase oxidation studies have also been undertaken using some of the techniques that are used for the heterogeneous chemistry studies.

In the past year, key parameters in the physical chemistry of aerosol particles were measured, particularly the mass accommodation coefficient of NH<sub>3</sub> on dilute sulfuric acid. This study provides information that is in major disagreement with previous work. This controversy is not resolved, but if HC s measurements are substantiated, there will be serious repercussions for the data analysis procedure of the previous work. This might have far reaching implications in that many of the other chemical systems reported by this group might have to be re-investigated.

The Group continues to work on laboratory techniques pioneered in ACD to explore particle nucleation at the molecular cluster level. The molecular cluster measurement technique was used to study species formed in the  $H_2SO_4/H_2O/NH_3$  system.

Preliminary experiments on the study of peroxy radicals using proton transfer mass spectrometry have begun. A new flow tube that can be illuminated with ultraviolet lights to photolyze  $Cl_2$  (or, in due course, HONO or other alkyl nitrite) has been mated to the mass spectrometer. Results from experiments with the cylcohexyl peroxy and the cyclopentyl peroxy radicals show the capability to detect these radicals and their subsequent products upon reaction with NO.

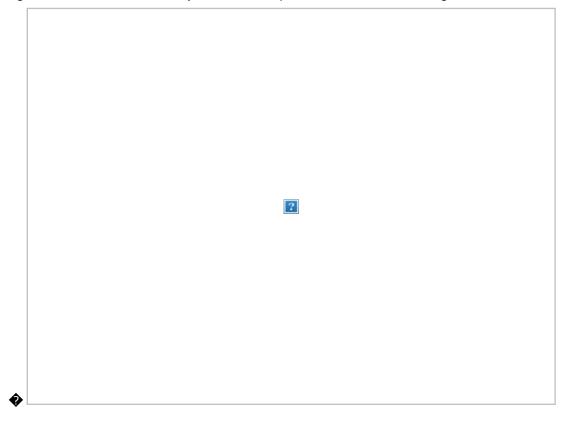
# **Photochemical Oxidation and Products (POP) Group**

The Photochemical Oxidation and Products Group studies fast photochemistry, sulfur chemistry, ion chemistry, particle nucleation, and the chemical composition of ultrafine particles. Its members include Fred Eisele, Roy Leon Mauldin, James Smith, Edward Kosciuch, Bruce Henry, and Katharine Moore (ASP).

The Atlanta Aerosol Nucleation And Real-time Characterization Experiment (Atlanta-ANARChE). The University of Minnesota led this collaborative study involving NCAR and several universities. ♦ This study investigated, for the first time, both nucleation and ultrafine particle growth immediately after the gas-to-particle conversion process. ♦ The study took place at a ground-based field site in Atlanta, Georgia from July 22-September 4, 2002. ♦ NCAR ♦ s contribution included the measurement of the chemical composition of 5-15 nm diameter particles by a new technique called Thermal Desorption Chemical Ionization Mass Spectrometry (TDCIMS). ♦ NCAR scientists also measured OH, H₂SO₄, SO₂, and molecular ions and ion clusters. ♦

The TDCIMS was recently built and tested in the POP laboratory in collaboration with Peter McMurry research group (University of Minnesota) and is the only instrument presently capable of measuring the chemical composition of 5-15 nm particle at ambient concentrations in real time. A schematic of the instrument is shown below. The instrument combines recently developed nanoparticle separation and collection techniques, an area of research in which the University of Minnesota is at the forefront, with highly sensitive chemical analysis provided by NCAR selected ion chemical ionization mass spectrometry technique. The TDCIMS is now capable of measuring the sulfate, nitrate, or ammonia content of 5-15 nm particles with a detection sensitivity of about 1 picogram of collected aerosol. It can also detect organics in ultrafine particles and improvements to the detection sensitivity in this area are presently underway.

Preliminary results of Atlanta-ANARChE suggest an extremely successful study that will contribute significantly to present understanding of homogeneous nucleation, ion induced nucleation and ultrafine particle growth, but additional analysis will be required before these findings can be confirmed.



enhancements of OH and H<sub>2</sub>SO<sub>4</sub> were commonly observed at the edges of plumes. As a result, nucleation events were also often observed in these same transition regions. An nighttime flight out of Midway Island also led to the unique discovery of nighttime production of MSA and H<sub>2</sub>SO<sub>4</sub> in the remote lower troposphere. Again, the observation of nucleation correlated with the high H<sub>2</sub>SO<sub>4</sub> concentrations gives even further support to this unexpected finding. Combined with previous results suggesting the nighttime production of DMSO, this study demonstrates that oxidation in the remote marine troposphere can occur at fairly rapid rates at night via one or more mechanisms that remain undefined. TRACE-P also resulted in the first NASA/GTE multi-aircraft instrument intercomparison, which was highly informative and will hopefully provide the basis for similar comparisons on future flight missions. The results of this study are also included in one of the 4 papers mentioned above.

Data analysis for the second ISCAT campaign (which is a collaborative Georgia Institute of Technology/NCAR study also involving several other universities) has also been carried out, and the final data submitted to the ISCAT data archive. A first author paper is also in preparation, along with several co-authored papers describing the results of this study. Highlights include 24 hour averaged OH concentrations comparable to tropical marine boundary layer values. The elevated OH is a consequence of elevated NO, which is photochemically produced in the snow and released into the atmosphere at a fairly constant (light dependent) rate. These summertime NO concentrations are controlled primarily by mixing into higher layers of the troposphere and can vary by more than an order of magnitude over the period of a day. Good agreement was also observed for the OH:(HO<sub>2</sub> + RO<sub>2</sub>) ratio on a day of maximum NO variation. Gas phase H<sub>2</sub>SO<sub>4</sub> and MSA concentrations were observed to be extremely low most of the time, suggesting that reactive sulfur gases are oxidized prior to reaching the polar region.

**Instrument Development.** A variety of new instrument development projects or instrument improvement efforts have also been underway this past year. • The recently developed TDCIMS has undergone several improvements over the past year, after which it performed its first measurements of ambient aerosols this past spring and then went on to play a central role in the success of this summer s ANARChE field study. The TDCIMS is now capable of measuring the sulfate, nitrate, or ammonia content of ultrafine particles with a detection sensitivity of about 1 picogram of collected aerosol. • It can also detect organics in ultrafine particles and improvements to the detection sensitivity in this area are presently underway. The transmission efficiency of this instrument for 4-5 nm particles has been both improved and well characterized. • Also, a high efficiency unipolar charger has been built and coupled to the TDCIMS system to further enhance sensitivity, especially for very small particles. In the TDCIMS technique, only particles that are charged can be measured, and particle charging efficiency drops dramatically as the particles decreased in size into the 3-5 nm size range. This charger increases sensitivity about a factor of 5 over what would be possible using common charging methods. Measurement of aerosols from outside the laboratory was performed after the completion of the above improvements. Along with observation of significant ammonium and sulfate content in Boulder air, these showed a surprisingly large amount of semi-volatile nitrate. This instrument got its first real test in the ANARChE campaign discussed above, and proved invaluable in determining ultrafine particle composition and growth mechanisms. At the completion of this study, the TDCIMS instrument resumed measurements of aerosols in Boulder to better understand their nitrate and organic content. • A paper describing this instrument was recently written (Voisin, et al., Aerosol Sci. Technol., in press) and a second is in preparation.

A separate, but related, instrument development effort involves the design and development of a high throughput ion trap mass spectrometer. Ion traps have an advantage over conventional mass spectrometers in that they can trap ions over a wide range of masses and then either mass analyze them or preferentially fragment them and analyze the resulting daughter ions in a period of time that is short compared to the collection time. They can thus provide a mass spectrum or daughter ion mass spectrum in the same time in which a conventional mass spectrometer would analyze a single ion mass. The disadvantage is that the ion trapping efficiency is quite low, typically a few percent. An experimental ion trap instrument was built and successfully operated this year providing a high-resolution mass spectrum. An octopole ion guide has recently been installed in front of the trap to enhance throughput. This and many other improvements will be tested shortly. If successful, this ion trap development project will dramatically speed up our measurements of organic compounds of fine and ultrafine particles, and will provide a valuable analytical tool for other

applications involving trace gas analysis.

Another area of instrument development is an aircraft measurement for gas phase ammonia. Ammonia is an important part of the reactive nitrogen budget and can also play a central role in particle nucleation, growth, and particle reactivity. An ion source has been built and coupled to a low pressure drift tube reaction region somewhat similar to a PTRMS instrument, except that the drift tube has smooth walls that are compatible with using a laminar sheath gas flow and it has a nearly wall-less entrance port. Such a laminar sheath flow can be used to keep the sampled air away from the instrument walls where ammonia can be absorbed and then later reemitted. The new ion source reactor was initially installed on the 4 channel aircraft instrument for laboratory testing and was then moved to the 2 channel mass spectrometer which participated in the Atlanta study so that it could be briefly tested in the field. It was used to measure ammonia in Atlanta, but the results have not yet been analyzed.

Considerable time has also been spent on improvements to the four channel mass spectrometer. Improved OH calibration techniques are being developed which use a recently constructed 184.9 nm light source and a solid state NIST diode that has only recently became available. New procedures are also being tested to reduce scatter in both the OH, H<sub>2</sub>SO<sub>4</sub> and MSA calibration and measurement data. As a fourth channel (NH<sub>3</sub>) is being developed for this instrument, additional down-sizing and streamlining of the electronics and plumbing for the other 3 channels has also been undertaken.

## **Data Analysis and Assimilation (DAA) Group**

The Data Analysis and Assimilation group (William Randel, Andrew Gettelman, Boris Khattatov, Steven Massie, Laura Pan, and Fei Wu) focuses on analysis and interpretation of global constituent data sets obtained from satellite observations, in conjunction with meteorological data analyses. Recent work has included studies of the dynamical and chemical behavior of the tropical tropopause region (including variability of cirrus clouds), global ozone variability, the behavior of water vapor in polar regions, and the assimilation of chemical measurements from satellites.

Global Positioning System (GPS). DAA has used temperature profiles derived from Global Positioning System (GPS) radio occultation measurements to study thermal variability of the tropical tropopause region. These novel GPS data are characterized by high vertical resolution (~0.2 km), and global sampling (especially advantageous in the tropics, where the radiosonde network is sparse). The key results demonstrate that much of the temperature variability in the tropical tropopause region is related to wave-like fluctuations, such as inertia-gravity waves or Kelvin waves. Furthermore, significant correlations are found between the GPS temperatures and daily, gridded outgoing longwave radiation (OLR) data (a proxy for tropical convection), providing independent confirmation of the GPS temperature fluctuations. The plot below illustrates the spatial structure of the temperature-OLR correlations, showing remarkably coherent hemispheric-scale temperature waves excited by convection. This work is an important step towards understanding and quantifying dynamical variability in the tropical tropopause region, and its influence on water vapor, cirrus and chemical constituents.

#### (Download figure at <a href="http://acd.ucar.edu/~randel/ASR\_2002.html">http://acd.ucar.edu/~randel/ASR\_2002.html</a>)

Caption: Height-longitude structure of temperature correlations with transient convection near the equator, derived from GPS temperature measurements and contemporaneous OLR data (a proxy for tropical convection). The correlations are calculated between the profile GPS temperature measurements and gridded OLR data, in order to isolate the longitudinal temperature response to localized convection (centered at the origin). Contours are +/- 0.2, 0.3, ..., and the sign convention is such that cold temperatures occur above enhanced convection, with warm anomalies to the east and west. The eastward-tilting wave variations with height over ~12-18 km are characteristic of an equatorially-trapped Kelvin wave. Note that the patterns are coherent over an entire hemisphere, showing that localized convection influences temperatures over 10, 000 km away! The dashed line at 17 km indicates the cold point tropopause (background temperature minimum).

Randel collaborated with Richard Stolarski (NASA Goddard) to quantify correlations between column ozone and large-scale circulation of the stratosphere, the latter quantified by the so-called Eliassen-Palm (EP) flux. The EP flux in the lower stratosphere quantifies the wave forcing of the stratospheric Brewer-Dobson circulation, which is reflected in global-scale ozone transport. This study used global observations from 1979-2000 to quantify the correlations, and isolate their spatial and seasonal variability. The key results showed that EP flux variations are strongly correlated with column ozone tendency during winter and spring over midlatitudes and polar regions (see an example), accounting for a high fraction of interannual variability in both hemispheres. Furthermore, the correlations were combined with observed decadal changes in EP flux to quantify the contribution of changing dynamics to decadal ozone trends; results showed that 20-30% of the NH midlatitude ozone trends over 1979-2000 could be explained by 'trends' in wave driving.

Randel contributed to the 2002 UNEP/WMO Stratospheric Ozone Assessment as a co-lead author (along with Martyn Chipperfield, University of Leeds, United Kingdom) for Chapter 4: Global ozone: Past and Future. This involved an update of global ozone observations, a synthesis of model studies to quantify understanding of past ozone changes, and updated predictions of future ozone changes. The executive summary was released in August 2002, and the full report will be distributed at the beginning of 2003.

Steve Massie led several studies aimed at understanding variability of cirrus clouds near the tropical tropopause. Cirrus is of interest for several reasons, for its effects on the tropospheric radiation balance and also because it is related to the amount of water vapor that enters the stratosphere. One study quantified the distribution and variability of tropical cirrus clouds near the tropopause (derived from Stratospheric Aerosol and Gas Experiment [SAGE] II and Halogen Occultation Experiment [HALOE] satellite observations) in relation to large-scale tropical convection. Seasonal variations of cirrus follow those of deep convection. Correlation studies and trajectory simulations demonstrated that about half the cirrus were 'close' (within 1000 km) to deep convective events, while half were 'distant' (thus probably not directly forced by deep convection). A second study showed the first observational evidence of a decrease in tropical cirrus clouds after the eruption of Mt. Pinatubo in 1991.

Massie collaborated with Kwong-Mog Lee (National Institute of Environmental Research, Korea) and Jae Park (NASA Langley) on the analysis of ILAS polar stratospheric cloud (PSC) extinction spectra. This work attempts to identify PSC composition types from the Improved Limb Atmosphere Spectrometer (ILAS) data. Massie also collaborated with Aaron Goldman (Denver University), and other spectroscopists from the U.S. and foreign universities and government labs, to update the HIgh-resolution TRANsmission (HITRAN) spectroscopy data base. Massie continues work with the HIRDLS group, providing aerosol spectral model data for incorporation into the HIRDLS retrieval code.

Laura Pan used the Chemical Lagrangian Model of the Stratosphere (ClaMS) to investigate stratosphere-troposphere exchange and mixing in the vicinity of the subtropical jet. The model results are combined with Light Detection and Ranging (LIDAR) measurements of ozone and Microwave Temperature Profiler (MTP) measurements of thermal tropopause during SONEX mission to investigate the transport and mixing in the vicinity of the subtropical jet. Potential vorticity (PV) fields generated using a simple advection (Reverse Domain Filling) technique are compared to the results from advection with mixing to examine the mixing time/length scale that produces a structure comparable to the observations.

Khattatov leads ACD efforts in chemical data assimilation. During the last year the group has extended efforts to derive variability and distributions of global sources of tropospheric carbon monoxide emissions from MOPITT data. This effort relies on using the global CTM MOZART2 and its adjoint. Most important practical and scientific results are derivations of global distributions of surface sources for all months of 2000 when MOPITT data are available. Computational requirements somewhat limit our ability to derive surface sources of CO on a high-resolution grid. Therefore during the next year we are planning to switch to a new technique of inverse modeling that will allow us to increase both the spatial and temporal resolution as well as facilitate error analysis.

Whole Atmosphere Community Climate Model (WACCM). WACCM has been used to investigate the "mesospheric temperature inversion" phenomenon. Model runs show clearly that these inversions arise

from the rapid dissipation of planetary waves in the mesospheric surf zone, which leads to large temperature perturbations near 80 km that are in very good agreement with observations. These results provide a clear explanation of the winter inversion phenomenon, and highlight the usefulness of a comprehensive model like WACCM for middle atmosphere studies.

WACCM has also been used to study the generation and seasonal behavior of the 2-day wave in the mesosphere and lower thermosphere. Aside from the tides, the 2-day wave is the most important source of high frequency variability in this region driong the solstice seasons. Model results indicate that the 2-day wave arises from baroclinic instability of the summer mesospheric jet, which explains its strong seasonal variability. The instability also excites other atmospheric normal modes, including the 5-day wave.

The structure and seasonal variability of the atmospheric tides has been investigated using WACCM. The model produces realistic migrating tides, as well as non-migrating components at the diurnal period and its harmonics. The latter are shown to be strongly forced by the variability of convective heating in the tropical troposphere associated with the diurnal cycle. Initial results have been presented at the EPIC Symposium in Kyoto (March, 2002), and a comprehensive paper describing our results is in preparation.

## **High-Resolution Dynamics Limb Sounder (HIRDLS) Group**

The focus for the High Resolution Dynamics Limb Sounder (HIRDLS) Group (John Gille, Cheryl Craig, Chris Halvorson, Lawrence Lyjak, Alyn Lambert, Rashid Khosravi and Douglas Kinnison) is a space-borne infrared limb-scanning radiometer designed to sound the upper troposphere, stratosphere, and mesosphere.

Instrumentation Development . The instrument is a 21-channel infrared limb-scanning radiometer, scheduled to fly on the Aura spacecraft as part of NASA's Earth Observing System (EOS) in early 2004. ♦ Its objectives are to make measurements of temperature, ozone, water vapor, 8 other species of chemical, radiative or tracer interest, with unprecedented resolution and coverage, for a period of 5 years or longer. ♦ Coverage will be from the upper troposphere (~ 8 km) to the mesopause and above, and from pole to pole. ♦ By making vertical limb scans at a range of azimuths from the orbital plane, uniform global coverage can be obtained with a nominal horizontal spacing of profiles (E-W and N-S) of 500 km, and with vertical resolution of ~ 1 km. ♦ Additional background information can be found at http://www.eos.ucar.edu/hirdls/. A strong focus of these measurements is the upper troposphere and lower stratosphere (UT/LS), including the exchange of tracers and dynamical quantities between the troposphere and stratosphere, and the climatic effects associated with them.

This year began to see the results of the long period of planning, design and development of the HIRDLS instrument. Gille, HIRDLS U.S. Principal Investigator, and the instrument development group of Michael Coffey and William Mankin (OT), with, Michael Dials, Aaron Lee, and Douglas Woodard (University of Colorado) were involved in the oversight and testing of the Engineering Model, and final reviews before shipment to Oxford University, to refine the calibration methods to be used on the flight instrument. Philip Arter (University of Colorado) spent several long periods in Oxford, helping to get the calibration facility completed on time.

The same group plus Nardi and Eden, was also deeply involved in the final stages of the fabrication of the Proto-Flight Model (PFM). Major efforts by Woodard to complete the Command and Telemetry Handbook, and by Dials to provide the associated database, essential for subsequent operation and testing of the instrument, enabled subsequent work to proceed. The whole group supported the thermal vacuum testing at Lockheed. Its rapid analysis and turn-around of test data greatly aided the process. The PFM was shipped to Oxford for calibration in the middle of August. All members of the instrument group have spent periods of a week or more working with the United Kingdom Principal Investigator, John Barnett, and colleagues (Chris Hepplewhite, John Whitney, Soji Oduleye and Robert Watkins), as well as students (Joseph Moorhouse and Daniel Peters). Primary contributions have been in data reduction, but they have also taken part in the shift rotations looking after the instrument and making observations. Initial results look quite

good. This will continue for a period of about 3 months.

Planning for flight operations, and development of procedures to command the instrument computer have been begun by James Craft and Angie Williams (University of Colorado). These are being built on the foundation of procedures used during instrument test and calibration. The initial major test will be the SpaceCraft InterFace (SCIF-2) exercise next year.

Algorithm and Software Development. Lambert led the efforts of Khosravi and Lee in the extension, optimization and testing of the retrieval algorithms. Their schemes now allow for the inclusion of the contributions of the information from all 21 channels to the retrievals of temperature, the 10 trace species, and now cases in which aerosol effects are included. A test comparison with the other Aura instruments using synthetic data showed that the HIRDLS results were extremely good, and meeting or exceeding expectations.

These algorithms are being converted into operational code by the group led by Kenneth Stone (University of Colorado), and including Cavanaugh, Craig, Charlie Krinsky and Brent Petersen (University of Colorado). The Science Investigator-led Processing System (SIPS) was designed, partially implemented by Thomas Lauren and Greg Young (University of Colorado); early phase testing by Vince Dean (University of Colorado) has been quite successful to date.

Validation of the unprecedented data from HIRDLS and the other instruments on the Aura spacecraft will require careful planning. NCAR hosted a meeting of the Aura Science Team in September that focused on defining missions that would use the synergism between aircraft and satellite observations to carry out important scientific investigations while providing opportunities to validate the satellite observations. Gille, co-investigators James Holton (University of Washington), and Brian Toon (University of Colorado) as well as Kinnison were active in presenting HIRDLS plans and needs.

## Regional and Process Studies (RPS) Group

The Regional and Process Studies (RPS) Group (Sasha Madronich, Xuexi Tie, Mary Barth [joint appointment with MMM], Peter Hess, Rolando Garcia, Stacy Walters, and Julia Lee-Taylor) research focuses on developing and refining models used for determining atmospheric processes

Modeling of Atmospheric Short-Wave Radiation and Photochemical Processes. A new version of the Tropospheric Ultraviolet-Visible Model (TUV, version 4.2) was developed by Madronich. ♦ It now includes updated spectroscopic data bases for 67 atmospheric photolysis reactions and newly available data for the spectral sensitivity of UV damage to some biological tissues (e.g. ocular damage); improved radiative transfer parameterizations at UV-C wavelengths (100-280 nm, specifically in Lyman-a, Schumann-Runge continuum and bands, and the Herzberg spectral regions), allowing accurate calculations of radiation fields up to 120 km altitudes; and implementation of a more user-friendly interface which allows calculations to be made on a variety of platforms (e.g. UNIX, Windows<sup>TM</sup>).

A study comparing recent measurements of actinic fluxes and photolysis rates within snow to those computed with the TUV model has been completed by Julia Lee-Taylor and Madronich. The comparisons show fairly good agreement over a wide range of snow types and amounts of contaminants (mostly soot). A manuscript describing this work has been accepted for publication. (Lee-Taylor, J. and S. Madronich, *J. Geophys. Res.*, accepted.)

Tie and Madronich have completed a version of TUV suitable for on-line radiative transfer calculations in 3D models. This fast-TUV (FTUV) model has the same physics as the TUV model, except that the wavelength gridding between 121-750 nm is reduced from 140 intervals to 17. The differences in calculated tropospheric photolysis frequencies between TUV and FTUV are generally smaller than 5%.

Tie, Madronich, Walters, and Phil Rasch [CGD] and Bill Collins [CGD]) using FTUV and sub-grid vertical distributions of clouds in MOZART show that, compared to a cloud-free atmosphere, globally averaged tropospheric photolysis frequencies are enhanced by ca. 10-15%. ♦ This leads to a ~20% increase in the global mean OH concentration, a reduction in the CH₄ lifetime from 11 years (clear sky) to 9 years (cloudy sky), an 8% increase in globally averaged tropospheric O₃ concentrations, and improvement in the comparison of model vs. observed surface CO concentrations. ♦

The TUV model was used (by Lee-Taylor and Madronich) to create an updated climatology of biologically-active UV radiation at the surface. Previously, the TOMS/Nimbus-7 total  $O_3$  column and cloud reflectivity (at 380 nm) data was used to calculate a global climatology for the years 1979-1992. The new study also incorporates data from two newer satellites (Meteor-3 and Earth-Probe), thus extending the coverage to the year 2000, and allowing evaluation of decadal changes due to changes in stratospheric  $O_3$  and cloud cover. The results show that decadal changes in clouds can affect surface UV radiation trends by amounts similar, and sometimes larger, than trends in stratospheric  $O_3$ .

**Modeling of Tropospheric Oxidant Processes**. Bernard Aumont (University of Paris) and Madronich continued the development of fully explicit chemical mechanisms for the atmospheric fate of volatile organic carbon (VOC). VOCs and their oxidation intermediates play a key role in the budgets of tropospheric  $O_3$ ,  $HO_x$ , and  $NO_x$ , and probably contribute to the formation of organic aerosols. Although their cumulative importance is widely acknowledged, the estimated number of intermediates far exceeds that for which direct laboratory measurements are available. We have developed a computer code to generate explicit reaction pathways and the associated kinetics for the oxidation of specified VOCs. This code uses structure-activity relations to estimate rate constants and products of previously unstudied reactions, and includes control parameters for systematic reduction of the number of reactions and species. As expected (but previously not quantified), a large number of intermediate species is generated, increasing quasi-exponentially with the size of the precursor molecule.

Summer Sands (SOARS student) and Madronich analyzed air quality data for Mexico City, as measured at 32 surface locations by the Red Autom tica de Monitoreo Atmosf rico (RAMA) network over 14 years (1986-1999). Although  $NO_x$  levels were high, typically in the range 50-100 ppb, diurnally averaged concentrations of  $Ooldsymbol{O}_3$  were seen to correlate positively with  $NO_x$  levels, suggesting that in Mexico City the production of  $Ooldsymbol{O}_3$  is still  $NO_x$ -sensitive. This is in contrast to many U.S. cities (e.g. Los Angeles), and probably results from the very high VOC levels present in Mexico City.

Craig Stroud (ASP) and Madronich have updated the NCAR Master Mechanism (MM) with improved calculations of photolysis rate coefficients, new kinetic and mechanistic data, and development of a more user-friendly interface. The MM was used to carry out detailed simulations of photochemical processing during the TOPSE field campaign. Ozone production was found to be a strong function of  $NO_x$  and  $H_{\diamondsuit 2}O$  concentrations, as well as the seasonal changes in the available actinic radiation. The results indicate net  $O_3$  destruction for the 1-3 km layer and net  $O_3$  production for the 3-6 km layer throughout the campaign. Peroxyacetyl nitrate (PAN) was found to be the major reactive nitrogen species, in agreement with observations. Pernitric acid (HNO<sub>4</sub>, which was not observed directly) was also found to be important in sustaining the observed NOx concentrations.

**Regional Chemistry Transport Modeling.** ACD  $\spadesuit$  s regional chemistry-transport model (HANK) was used to simulate the spatial distribution and temporal evolution of  $O_3$  and other tropospheric compounds measured during the TOPSE field campaign. Model results show that the springtime  $O_3$  maximum is due primarily to  $O_3$  photochemically produced in the troposphere during the winter months, while in the summer the concentrations of  $O_3$  decrease due to photochemical destruction.  $\spadesuit$  Downward transport of  $O_3$  from the stratosphere to the troposphere, previously thought to be a major factor in the springtime  $O_3$  maximum, is found to be only a minor contributor. (Emmons, L., et al., *J. Geophys. Res*, submitted).  $\spadesuit$  Changes in transport alone between winter and summer explain many of the differences observed in the distribution of CO.  $\spadesuit$  (A.

Klonecki, et al., J. Geophys. Res., accepted.)

A study of pollution transport from Asia across the Pacific Basin to Hawaii, using the HANK model and its adjoint, was completed. The results showed the importance of lofting of pollutants by synoptic storms in Eastern Asia, followed by upper tropospheric transport and chemical transformations, in determining elevated pollutant concentrations observed in Hawaii. (P. G Hess and T. Vukicevic, *J. Geophys Res*, submitted.)

Effect of Boundary Layer Processes on Chemical Species Distributions. Barth and Edward Patton (Pennsylvania State University) used an LES model to examine how vertical mixing above an isoprene-emitting canopy affects the kinetics of O<sub>3</sub> photochemistry. The results show strong sensitivity to the choice of chemical mechanism, indicating that the highly reactive intermediate species generated from isoprene tend to compensate for the loss of reactivity caused by incomplete mixing of isoprene with atmospheric oxidants.

Cloud Chemistry Process Studies. Barth, Sanford Sillman (University of Michigan), Rynda Hudman (Harvard University), Mark Jacobson (Stanford University), Cheol-Hee Kim (National Institute of Environmental Research, Korea), Anne Monod (Laboratoire Chimie et Environnement, France), and Jinyou Liang (California Air Resources Board) analyzed the results from the cloud chemistry photochemical box model intercomparison. Generally good agreement was found between models used by the various participants.

Barth analyzed cloud-scale numerical simulations of the 10 July 1996 Stratosphere-Troposphere Experiments: Radiation, Aerosols and Ozone (STERAO)-Deep Convection experiment, focusing on the budgets of aqueous and gas phase  $H_2O_2$  and  $CH_2O$ . Results show that depletion of  $H_2O_2$  in the cloud droplets is offset by chemical production in the gas phase thus creating very little effect on total  $H_2O_2$  concentrations. For  $CH_2O$ , gas phase chemistry was found to be dominant near cloud base, but both aqueous and gas processing was important near cloud top.

**MOZART: Model for Ozone and Related chemical Tracers.** A new version of MOZART, MOZART-2 has been developed, and comparisons with observations show generally good agreement for the distribution (seasonal, spatial gradients) of tropospheric O<sub>3</sub>, NO<sub>x</sub>, HNO<sub>3</sub>, CO, and the lifetime of CH<sub>4</sub> (9.5 yrs, compared to the IPCC estimate of 9.6 years). (Lawrence Horowitz, et al., *J. Geophys. Res.*, submitted).

MOZART-2 was used to assimilate MOPITT retrieved CO profiles during the March-December 2000 period. The results of the assimilation, not yet published, were used by NASA as a tool for visualizing intercontinental transport.

MOZART simulations were performed using National Center Environmental Prediction (NCEP) meteorological fields to study O<sub>3</sub> chemistry over the South Atlantic basin in conjunction with observations of CO from MOPITT and other satellite measurements. More accurate model results were achieved by re-distributing the emissions from biomass burning according to fire count observations from satellite. The influence of biomass burning and lightning on the region was examined by performing model simulations with the emissions from biomass burning and lightning each perturbed. Results show that biomass burning and lightning both contribute to O<sub>3</sub> production over the South Atlantic in January, but at different locations and altitudes. (D. Edwards et al., *J. Geophys. Res.* submitted).

The MOZART model has been used extensively in the interpretation of the TOPSE observations, leading to a number of important conclusions: 1) Comparison of measured and simulated  $NO_x$  reconfirmed the importance of the loss of  $N_2O_5$  on aerosols. However, in regions with low aerosol loading, the model tended to underestimate the  $NO_x$  measurements, suggesting that the  $NO_y$  budget is not yet understood in the remote troposphere. 2) Stratosphere-troposphere exchange was found to be a relatively minor component in the budget of tropospheric  $O_3$  (north of  $30 \diamondsuit N$ ), with in-situ photochemical production and loss being more important. During winter and early spring, low  $H_2O$  concentrations result in net  $O_3$  production. In late spring, higher  $H_2O$  concentrations lead to net  $O_3$  destruction. The average age of CO is generally large

during the winter months over North America. The exception is in the lower tropospheric polar regions where the winter circulation transports fresh emissions from Europe. During the spring months, increased venting from the boundary layer and increased oxidation decrease the average age of CO.

MOZART was also used for chemical forecasts for the Intercontinental Transport and Chemical Transformations (ITCT) field campaign during late winter and spring of 2002. A series of simulations are currently underway estimating the impact of Asian emissions on  $O_3$  levels over the United States, and the interannual variability of this impact.



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(Note: Bold = university authors; \* = institutional authors; ^ = private corporation authors.)

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# **Educational Activities**

## **Teaching Arrangements**

- Eric Apel, Adjunct Associate Professor, University of Miami
- John Gille, Adjoint Professor, University of Colorado
- ♦ John Gille, Adjunct Professor, State University of New York at Stony Brook
- John Gille, Lecturer, Scuola Superiore Guglielmo Reiss Romoli
- Barry Lefer, Lecturer, University of Colorado, Boulder
- William Randel, Lecturer, Colorado State University
- Juying Warner, Lecturer, Massachusetts Institute of Technology

## **Advising on Graduate Research**

- Alan Fried (Bryan Wert), University of Colorado, Boulder
- Alex Guenther (Christoph Spirig), Swiss Federal Institute of Technology, Switzerland
- Jean-Francois Lamarque (Gabrielle Petron), University of Paris
- Alyn Lambert (Graham Ewen), University of Oxford, United Kingdom
- Sasha Madronich (Katja Dzepina), Rudjer Boskovic Institute, Croatia
- Sasha Madronich (Maria Micheletti), University of Rosario, Argentina
- Sasha Madronich (Daniel Lack), School of Natural Resource Sciences, Australia
- Sasha Madronich (Lester Alfonzo), Universidad Nacional Atmosfera, Mexico
- William Randel (Meijong Park), Seoul National University, Korea
- Geoffey Tyndall (Camilla Bacher), University of Copenhagen
- ♦ XueXi Tie (Wen Fang Lei), Texas A&M University
- XueXi Tie (GuoHui Lei), Texas A&M University

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#### **Member of Thesis Committee**

- Mary Barth (Amy Stuart), Stanford University
- Alan Fried (Bryan Wert), University of Colorado, Boulder
- Rolando Garcia (Natalia Calvo), Universidad Complutense de Madrid, Spain
- John Gille (Katherine Paulin), Oxford University, United Kingdom
- Alex Guenther (Christoph Spirig), Swiss Federal Institute of Technology, Switzerland
- Peter Harley (Jennifer Funk), State University of New York at Stony Brook
- Anne Smith (KimCierpic), University of Colorado, Boulder

- Juying Warner (Edward Hyer), University of Maryland
- XueXi Tie (Wen Fang Lei), Texas A&M University
- XueXi Tie (Guohui Lei), Texas A&M University
- Peter Hess (Wen Fang Lei), Texas A&M University

#### PARTICIPATION IN OTHER EDUCATIONAL PROGRAMS

## Significant Opportunities in Atmospheric Research and Science (SOARS)

The SOARS program is designed to further science education and provide access to careers in the atmospheric and related sciences for students of minority groups that are historically under-represented in the science community. Each student is teamed with a science mentor, a communications mentor and a community mentor. In FY02, ACD hosted the following students:

- ♦ Shaan Bliss, Science Mentor: Alex Guenther/Lee Klinger; Communication Mentor: Sue Schauffler
- Olusegun Goyea, Science Mentor: Chris Cantrell/Gavin Edwards; Communication Mentor: Barry Lefer
- Theresa Johnson, Science Mentor: Alex Guenther/Elisabeth Holland
- Ernesto Munoz, Science Mentor: Alan Fried
- Amber Reynolds, Science Mentor: Daniel Marsh; Communications Mentor: Mary Barth
- Summer Sands, Science Mentor: Sasha Madronich; Communications Mentor: Julia Lee-Taylor
- **Tamara Singleton**, Science Mentor: William Mankin
- Rei Ueyama, Science Mentor: Steven Massie
- ♠ Melanie Zauscher, Science Mentor: Frank Flocke/Craig Stroud/Andrew Weinheimer

## **Internship Program, Louis Pasteur Institute**

ACD participates in a program with the Louis Pasteur Institute in France for students who have completed a degree in instrument design. The program is designed to increase the students experience, technical skills and language skills and to give them an opportunity to function independently. The students work half-time at NCAR for an eight-month period with one of the science groups in the division. Last year, ACD hosted the following students:

Vincent Kennel, Mentor: Eric Apel

Nadege Schwaller, Mentor: Elliot Atlas

## **Mentoring**

- Eric Apel mentored 2 students from Broomfield High School in an independent research class.
- ◆ <u>Teresa Campos</u> coached 2 University of Colorado students as part of L. Avallone ◆s instrumentation class during the IDEAS mission, helping them to gain experience in CO and CO<sub>2</sub> airborne instruments.
- Teresa Campos developed and presented the first stage of training of RAF technicians in the routing maintenance of the TDL hygrometer.
- William Mankin mentored a middle school teacher (formerly with LEARN) and her class on ground level ozone.
  The students won a competition using this information.
- Barry Lefer participated in the Denver Museum of Nature and Science Stars (Space Teens Ask Real Scientists) program where high school students interview and videotape local scientists who are engaged in earth science research.

- Daniel Marsh gave a talk to students at the American Meteorological Society s First Student Conference
- Steven Massie gave presentations on greenhouse warming at the Adams District 50 Denver school and at an elementary school in San Lorenzo, California
- James Smith assisted an undergraduate student at University of California-Berkeley in defining an independent study project.



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# **Community Service**

## **Editorships of Peer-Reviewed Journals**

- ♦ Elliot Atlas, North American Editor, Journal of Atmospheric Chemistry, 2002-present
- ♦ Chris Cantrell, Associate Editor, Journal of Geophysical Research ♦ Atmospheres, 2001-present
- ◆David Edwards, Editor, Journal of Quantitative Spectroscopy and Radiative Transfer, 2000-present
- ♦ Alan Fried, Co-Guest Editor, Applied Physics B, 2002
- ♦ Alex Guenther, Editorial Board, Atmospheric Chemistry and Physics, 2002-present
- ♦ Alex Guenther, Editorial Board, Atmospheric Environment, 2000-present
- Alyn Lambert, Co-Editor, European Geophysical Society Journal Atmospheric Chemistry and Physics, 2001-present
- ♦ William Randel, Associate Editor, Journal of the Atmospheric Sciences, 1999-present

## **Workshops and Colloquia**

- ♦ Alan Fried, symposium organizer and conference chair, 2002 SPIE Conference
- James Smith, invited speaker, Gordon Research Conference on Biogenic Hydrocarbons and the Atmosphere, 2002
- Anne Smith, organizer, TIMED-CEDAR Workshop, 2002
- Juying Warner, participant, IGBP-IGAC/BIBEX, 2002
- Christine Wiedinmver, NCAR Climate and Global Change Geoscience Education Workshop, 2002
- ♦ Christine Wiedinmyer, IGAC/GEIA/BVOC Workshop, 2002
- Douglas Kinnison, NASA EOS AURA Science and Validation Workshop, 2002
- ◆ <u>Douglas Kinnison</u>, NCAR WACCM Workshop, 2002

#### Service on Scientific Committees and Panels

## **Chris Cantrell**

- AGU Atmospheric Sciences Section Nominations Committee (provide/solicit nominations for section positions, special colloquia and awards), 1995-present
- ♦IGAC ACE<sup>ED</sup> Education Committee (organize atmospheric chemistry education programs, particularly for 3<sup>rd</sup> world countries), 1999-present

## **Cheryl Craig**

NASA SEEDS Study Advisory Panel for the Standards of Near-Term Missions (provide NASA with input on standards development), 2001-2002

#### **David Edwards**

- NASA Earth System Science Pathfinder Mission Advisory Panel, 2002
- Alan Fried
- Conference on Tunable Diode Laser Spectroscopy, Technical Program Committee, 2002.
- Rocky Mountain Optical Society, Board of Trustee
- Program Committee, International Topical Meetings, 2002-2004

#### John Gille

SPARC Science Steering Group (organizes SPARC activities, initiates and review projects), 1992present

#### Alex Guenther

- Gordon Conference Chair, (conference on biogenic VOC in the atmosphere), 2002
- ♦IGBP/IGAC Steering Committee (atmospheric chemistry and environmental education), 2002-present
- ♦IGBP/IGAC Steering Committee (biosphere-atmosphere trace gas exchange),2002-present Steve Massie
- American Meteorological Society Committee on Middle Atmosphere (helps plan conferences related to middle atmosphere), 2000-2003

#### William Randel

- National Research Council Board on Atmospheric Sciences and Climate, 2001-2003
- American Geophysical Union, Chair of the Atmospheric Dynamics Committee Anne Smith
- NASA, Science Working Group for TIMED satellite, 1993-present

## **Community Service**

- **♦** Eric Apel collaborated with the non-profit organization, EILI network, to provide through the web an informational resource about air quality issues to the public
- Mike Coffey, James Walega and Barry Lefer participated in the Boulder Valley School District Science Fair
- Alex Guenther was the rapporteur for the planning meeting to develop IGBP program on interactive land ecosystem atmosphere processes
- ♦ Lee Mauldin is the organizer of the ACD formal seminar series and the informal ACD research reports
- ♦ William Randel was the co-lead author for the 2002 UNEP/WMO Ozone Assessment
- <u>Richard Shetter</u> participated in a pre-proposal to the National Science Foundation Integrative Graduate Education and Research Traineeship Program to foster the development of a graduate program at the University of Colorado, Boulder.

#### **Awards**

- ♦ John Orlando was awarded a Vellux Visiting Professor Fellowship by the University of Copenhagen
- William Randel and co-authors received the Norbert Gerbier Outstanding Publication Award from the World Meteorological Organization
- Geoffrey Tyndall received the AMS Special Award made to a team of editors for the AMS Glossary of Meteorology, 2<sup>nd</sup> Edition.

#### **ACD Web-Based Services**

The ACD Web (<a href="http://www.acd.ucar.edu/">http://www.acd.ucar.edu/</a>) site is maintained by Garth D�Attilo. There is a digital library of many of the posters prepared by ACD personnel. It is also possible to download several data sets or model codes from the Web. Monitoring of hits to ACD web sites was instituted in February, 2001. ACD averages about 3000 hits per day, more than 50% of which are from outside NCAR.

- The TUV code developed and maintained by Sasha Madronich is now available in several formats over the Web.It can be downloaded to run on several computer platforms, including Windows.Monitoring indicates that there have been 500 unique downloads from all over the world, which are now on a TUV users mailing list. (<a href="http://www.acd.ucar.edu/TUV/">http://www.acd.ucar.edu/TUV/</a>).
- Several other models are available for download, in particular the MOZART suite of models (http://acd.ucar.edu/models/MOZART/).Additionally, one may access and download emission inventory data sets compiled at ACD.
- A new data archive concept was developed for the TOPSE missions. Throughout the extended TOPSE mission, data was made available by both instrument and modeling groups soon after each deployment and was posted on the TOPSE Web site (http://topse.acd.ucar.edu/). The full archive of data is open for public access.

## **Atmospheric Models Developed and Available to the Community**

TUV:Tropospheric Ultraviolet-Visible radiation model  MM:NCAR Master	Spectral (121-750nm) irradiance and actinic flux, photolysis rate coefficients, and biologically/radiometrically pertinent radiation.  Radiative transfer solved by two-stream or multi-stream discrete ordinates methods in pseudo-spherical geometry. User-selected wavelength and vertical resolution. Recently extended to stratosphere.  0-D model with detailed tropospheric chemistry including ca.
Mechanism	5000 reactions among ca. 2000 species, Gear solver, TUV-based photolysis rates.
SOCRATES	Surface to 120 km; 5 latitude, 1 km altitude; 1-day transport with 3-hour chemistry time steps; 60 chemical species and 150 reactions; PSC and aerosol chemistry; diurnal cycle; detailed solar and terrestrial radiation; planetary wave model; gravity wave, tides, and QBO parameterizations; semi-Lagrangian transport.
HANK:Regional Chemical Transport Model	3-D regional episodic CTM, meteorological inputs from the NCAR/Penn State mesoscale model (MM5); detailed parameterizations of physical processes (e.g. advection, convective transport; photolytic radiation). Time step 240 s, chemistry of 50 species, 123 reactions (27 photolysis), wet and dry deposition. Variable vertical and horizontal resolution, with 3-level nesting of higher resolution for selected regions.
IMAGES	3-D global CTM; surface to 50mb; 5 x 5, 25 levels; time step of 1 day; 40 species, 150 reactions; semi-Lagrangian transport; climatological dynamics.
MOZART	3-D global CTM; There are 3 versions. The resolution of the MOZART model is variable (i.e., depends on meteorological fields employed). All versions of MOZART use a time step is 20 minutes. 50-60 species are included with approximately 200 reactions.
MOZART-1	Now available and can be downloaded from the web. This version was designed for scientific questions relating to the troposphere. MOZART-1 has typical horizontal resolution of 2.8 x 2.8 and 35 vertical levels (50km). Semi Lagrangianadvective transport.

MOZART-2	An updated version of MOZART-1, will be released for use to a small group in April 2001. After documentation has been completed, it will be made available on the NCAR ACD website. MOZART-2, like MOZART-1 has horizontal resolution of 2.8 • x 2.8 • and 35 vertical levels (50km). MOZART-2 uses finite volume advective transport based on the MATCH model developed by Phil Rasch (CGD).
MOZART-3	Contains the same chemical, dynamical, and physical processes as MOZART-2, but with simplified tropospheric chemistry and with the addition of processes representative of the stratosphere and mesosphere; still under development and will not be ready for release until January 2002. Typical horizontal resolution 2.8 x 2.8 , with approximately 50 vertical levels.30 species and 50 reactions and stratospheric PSC and aerosol chemistry.