

GAME/Tibet field campaign in 1998. Different spatial patterns in delta-18O were found between active and break phases of Indian monsoon activity. During a break phase, low delta-18O with relatively low d-excess (<15) values were observed at all observational sites south of Tanggula mountain on the plateau, indicating that water vapor directly transported from the south over the Himalaya reached the central region of the plateau. Decrease in delta-18O from south to north on the plateau was insignificant, which indicates a high contribution of recycled water. During an active phase, low delta-18O with relatively low d-excess was observed in the region between the Himalaya and Nyainqentanghla mountain, indicating direct transport of water vapor from the south to this region, while high delta-18O with high d-excess value was observed in the region between Nyainqentanghla and Tanggula mountains. High delta-18O and high d-excess values were observed when water vapor was transported from the west or north. Water vapor with unusually high delta-18O and high d-excess may be formed by dynamic fractionation of water with low delta-18O in convective clouds in the ITCZ.

### A31C-0058 0830h POSTER

#### Pollution Sources Over the Grand Canyon and Canyonlands National Parks

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To investigate pollution sources that are degrading the visibility of two national parks, Grand Canyon National Park, AZ, and Canyonlands National Park, UT, daily samples of total suspended particulates (TSP), PM<sub>2.5</sub>, trace gases, and organic compounds were collected in the two parks in the summer (July) of 2001 and winter (December-January) of 2001-2002. Factor analysis results show a number of anthropogenic signals (e.g., smelters) in the summer air over the Grand Canyon. In winter, the Grand Canyon samples revealed an aged pollution signal, which was probably transported from long distance, and a local source. In contrast, Canyonlands has less distinctive pollution signals in summer compared with winter. Summer air there shows an aged pollution source, evidence for smelter impacts on the concentrations of rare-earth elements and other metals, and a titanium source. More individual pollution signals were identified from the winter samples at Canyonlands (e.g., coal combustion and smelters). Our chemical and meteorological data clearly indicate that the main long-range transport pathway for pollution in summer is via southwesterly winds at both national parks; this implicates western Arizona as a likely source region. In winter pollution comes from the Salt Lake area via northerlies or northwesterlies.

### A31C-0059 0830h POSTER

#### Can Large Windfarms Affect Local Meteorology?

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A numerical model was used to explore the possible impacts of large windfarms in the Great Plains region on the local meteorology over synoptic timescales under typical summertime conditions. Wind turbines were approximated as sinks of energy and sources of turbulence. A virtual windfarm was created using an array of such turbines. Results show that windfarms significantly slow down the wind at the turbine hub-height level. Additionally, the turbulence generated by rotors create small-scale eddies that enhance vertical mixing of momentum, heat and scalars usually leading

to a warming and drying of the near-surface air and reduced surface sensible heat flux. This effect is most intense in the early morning hours when the hub-height level wind speed is the strongest due to the nocturnal low-level jet. The impact on evapotranspiration is small.

### A31C-0060 0830h POSTER

#### Solar cycle signals in northern hemisphere wave activity

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Although there have been many indications of solar cycle influence on the Earth's climate from observational and statistical studies, the physical mechanism of Sun-Climate connections is thus far still unclear. One generally agreed, but unproved theory suggests that solar UV variation affects stratospheric ozone, which in turn affects stratospheric temperature and circulations. The stratospheric changes then propagate downward to the troposphere through modulation of tropospheric wave propagation and wave-mean flow interactions. To examine to what extent this theory is valid, we search for atmospheric regions where dynamical quantities including wave fluxes show, if any, the strongest apparent solar cycle. Based on the NCEP/NCAR Reanalysis data since 1979, we find that during solar maxima the northern hemisphere waves tend to be refracted more equatorward near the subtropical jet region, and wave forcing tends to enhance polar westerly wind. The meridional eddy heat flux also shows signals of solar cycle modulation in subpolar stratosphere, but the phase is somewhat different. Statistical and composite techniques are used to distinguish solar cycle effects from other external forcings, and to determine significance levels of analyzed solar signal in the dynamical quantities.

### A31C-0061 0830h POSTER

#### Synoptic Meteorology of U.S. Southwest-Great Plains Summer Precipitation

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In this study, daily synoptic weather patterns are examined for simultaneous precipitation characteristics of bioclimatic subregions of the Southwest U.S. and Great Plains. The bioclimatic regions take into account gradients caused by differences in topography, continentality, and diurnal precipitation characteristics; such gradients result in great differences in precipitation total that have ramifications for decision makers. Precipitation and synoptic patterns were analyzed for subregions with strong inverse precipitation correlations. Subregional precipitation characteristics (i.e., wetness or dryness) and associated synoptic patterns were defined based on the percent raininess from the raw regional precipitation data for the period from 1948 through 2002. Percent raininess is defined as the percent of stations in the region reporting measurable daily rainfall. Wet days are defined as those during which at least 60% of stations report daily rainfall; dry days are defined as those during which 0% of stations report daily rainfall. Midtropospheric synoptic meteorological patterns and atmospheric moisture (specific humidity) were examined for all days determined to be dry in a Southwest subregion of interest and dry in a corresponding Great Plains region of interest (dry-dry), and for all other possible combinations between these regions (i.e., wet-wet, wet-dry, dry-wet). Examination of the synoptic patterns associated with these combinations for subregions with strong inverse summer season precipitation correlations indicates that a wide variety of synoptic patterns can lead to simultaneous inverse precipitation in the subregions. In addition, a variety of synoptic patterns can lead to simultaneous wetness or dryness in these distant subregions. The findings of this research are at times dramatically different than past results reported in the literature. A number of examples and comparisons will be shown.

### A31C-0062 0830h POSTER

#### Alternate Energy from the Desert

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Due to rapid growth of the world's population and more demands for energy, and due to limited amount of fossil fuels (which provide 95 % of the world's energy needs), harnessing of alternate energy sources such as solar and wind power should be considered. In addition to the mountain passes with usually high wind, vast and flat desert areas could be good candidates for harvesting both solar and wind power. We set up a weather station in the middle of a desert, approximately 65 km east-west by 130 km north-south, located at Dugway (40°08' N, 113°27' W, 1124 m above mean sea level) in northwestern Utah, USA, in 1999. This station measured the incoming (Rsi) and outgoing (Rso) solar or shortwave radiation using two CM21 Kipp & Zonen pyrrometers (one inverted), the incoming (Rli or atmospheric) and outgoing (Rlo or terrestrial) longwave radiation, using two CG1 Kipp & Zonen pyrrometers (one inverted), and the net (Rn) radiation using a Q\*7 net radiometer (Radiation Energy Balance System, REBS). We also measured the 3-m wind speed (U3) and direction (R.M. Young wind monitor) and precipitation (Campbell Sci., Inc.) and some other weather parameters. The measurements were taken every two seconds, and averaged into 20-min, continuously, throughout the year. The two-year (January 2000 - December 2001) period comparisons of global or solar radiation and windiness with two other stations in central (Hunter) and northern (Logan) Utah, indicate higher average solar radiation [Rsi, Dugway = 601 MJ / (m<sup>2</sup>-month) vs. Rsi, Hunter = 5371 MJ / (m<sup>2</sup>-month) and Rsi, Logan = 516 MJ / (m<sup>2</sup>-month)] and much higher 10-m average wind (UDugway = 478 km/d vs. UHunter = 323 km/d and ULogan = 275 km/d) throughout the period over the desert. These data reveal the possibility of simultaneously harvesting these two sources of clean energies at this vast and uniform desert area. Keywords: Desert, energy, radiation balance, solar and wind energies, windiness.

### A31D MCC: Level 1 Wednesday 0830h

#### Chemistry and Composition of the Troposphere I Posters (joint with B, GC)

*Presiding:* A H Goldstein, University of California; P Novelli, NOAA Climate Modeling and Diagnostics Laboratory

### A31D-0063 0830h POSTER

#### Development of an in situ gas chromatograph - mass selective detector for the purpose of studying long-range pollution transport from Asia

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In September 2002, we began work on the development and construction of an automated, 3 channel gas chromatograph (GC) with a mass selective detector (MSD) and two electron capture detectors (ECDs). The instrument will be placed at a Pacific CMDL station (Mauna Loa or Trinidad Head), and will make continuous measurements of a variety of chemical species with a wide range of lifetimes, including chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), methyl halides, non-methane hydrocarbons (NMHCs), peroxyacetyl nitrate (PAN), nitrous oxide, and sulfur hexafluoride. The primary goal

is to characterize the episodic long-range transport of pollution from Asia. We have completed development of a cryogenic trapping system for pre-concentrating samples for the MSD channel. We present a comparison and characterization of two types of traps, one with a one-inch section of Porapak Q as the adsorbent material, and one with 6 mg of Carboxen 1003 and 4 mg of Carboxen 1000. We discuss the suitability of each of these traps for our intended research. We also present our progress on other aspects of the measurement system, including a dynamic dilution system for calibration of PAN measurements on one of the ECD channels, and a discussion of the science issues involved in choosing the deployment location.

#### A31D-0064 0830h POSTER

##### Negative Ion Chemical Ionization Mass Spectrometric Technique for the Detection of Atmospheric Molecular Halogens

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As a greenhouse gas and regulated pollutant, tropospheric ozone not only impacts regional air quality but also global climate. At the same time, it is essential as it determines, in part, the oxidizing capacity of the atmosphere. In light of this, understanding ozone depletion events that occur over the Arctic Ocean and in the marine boundary layer is important in predicting the future state of the atmosphere. Halogen chemistry is thought to play an important role in these ozone destruction events, but the sources and reservoirs of halogen atoms are not well understood. Molecular halogens (Cl<sub>2</sub>, Br<sub>2</sub>, and BrCl) have been identified as potentially important photolytic precursors to halogen atoms, but instrumentation for their detection has thus far precluded routine study and understanding of the production of the molecular halogens in the Arctic. The development of a negative ion chemical ionization mass spectrometric technique for the detection of ambient molecular halogens will be discussed. The technique uses electron impact of nitromethane to produce NO<sub>2</sub><sup>-</sup>, which through an electron transfer ion molecule reaction in a quadrupole ion trap, produces the molecular anion of the corresponding molecular halogen. The rate constant of the reaction Br<sub>2</sub> + NO<sub>2</sub><sup>-</sup> (relative to the published rate constant of Cl<sub>2</sub> + NO<sub>2</sub><sup>-</sup>) was determined to be 1.4 ± 0.4 × 10<sup>-9</sup> cm<sup>3</sup>/molecule-s. Sample introduction into the mass spectrometer, standardization methods, and preconcentration techniques will also be discussed.

#### A31D-0065 0830h POSTER

##### A new instrument to measure UV extinction profiles and photolysis frequencies in a snowpack environment

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A new profiling irradiance spectroradiometer measured ultraviolet (UV) radiation at four to five depths in the surface snowpack during a seven-week campaign at Summit, Greenland (Summer 2003). The UV photons were collected by a small irradiance head with a Teflon diffuser and transmitted through a UV-VIS fiber optic into a scanning 1/8-meter double monochromator and detected with a UV sensitive photomultiplier. One complete scan of the UV-VIS radiation between 290-420 nm took less than 30 seconds. Five different fibers (i.e., five different depths) were serially sampled using a stepping motor and micropositioning slider to create a penetration profile every 2.5 minutes. Simultaneous atmospheric actinic flux data from a synchronized above snow scanning spectroradiometer was used to identify periods when the incident downwelling UV intensity changed during a depth profile. The UV penetration distance was calculated as an *e*-folding depth (the depth over which the monochromatic UV irradiance decreases by a factor of *e*). After measuring the angular response of the irradiance entrance optics and assuming that the in-snow radiation environment was isotropic, it is possible to scale up from irradiance to actinic flux. Fourteen different photolysis frequencies (including  $\gamma\text{NO}_3^-(aq)$ ) were calculated from the snowpack actinic flux data. These data can then be used to add to our understanding of snowpack photolytic

processes that produce gas phase NO and/or NO<sub>2</sub> and are speculated to result in the snowpack production of other important photochemical species (such as HONO, HCHO, HOOH, etc.) in snow-covered environments.

#### A31D-0066 0830h POSTER

##### Altitude Controlled Balloons for Atmospheric Research

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Research balloons are one of the most economical and efficient means of carrying scientific payloads into the atmosphere. With their unparalleled combination of altitude range and flight duration, balloon platforms are the workhorse of modern weather forecasting and play a key role in studies of the climate, chemistry, and physics of planetary atmospheres. Recent technological advances promise to further increase the importance balloons and airships in atmospheric research. We present a new altitude-controlled balloon that can be scaled to a wide range of payloads and is capable of extremely long duration flights. Through model analysis and flight data, we demonstrate the utility of this new balloon for tracking air parcels, performing atmospheric soundings, and building satellite-like constellations for environmental monitoring.

#### A31D-0067 0830h POSTER

##### Preparation of Gravimetric Standards for Measurements of Atmospheric O<sub>2</sub>/N<sub>2</sub> Ratio and Reevaluation of Atmospheric O<sub>2</sub> Concentration

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Great concern has been increased about the measurements of the variations in atmospheric O<sub>2</sub> concentration because they give us crucial information about the carbon cycle. The changes in the atmospheric O<sub>2</sub> concentration are usually reported as relative deviations of O<sub>2</sub>/N<sub>2</sub> ratio from a reference gas. However, there is no reference gas of which absolute O<sub>2</sub> concentration is determined at ppm level. Therefore each laboratory uses ambient air filled into cylinders or flasks as own reference gases. In this study, gravimetric mixtures containing natural levels of CO<sub>2</sub>, Ar, O<sub>2</sub> and N<sub>2</sub> gases were prepared in 10-L high-pressure aluminum cylinders to develop absolute scale for the O<sub>2</sub> measurements. The mole fractions of individual components, calculated from the weights determined by a highly precise balance, were compared with analyzed values of CO<sub>2</sub>, Ar, and (O<sub>2</sub>+Ar)/N<sub>2</sub>. The precision of the gravimetric O<sub>2</sub> concentration was estimated to be about 3 ppm from the 14 gravimetric mixtures. The gravimetric O<sub>2</sub> scale was applied to the atmospheric O<sub>2</sub> measurements from air samples collected at Hateruma Island. The results showed that the annual mean in 2001 was by about 70 ppm lower than the global mean O<sub>2</sub> concentration reported by Machta and Hughes (1970).

#### A31D-0068 0830h POSTER

##### Comparison of the NIST Ozone, Nitric Oxide and Nitrogen Dioxide Standards

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Comparison of the NIST primary nitrogen dioxide (NO<sub>2</sub>), nitric oxide (NO) and ozone (O<sub>3</sub>) standards were conducted using gas-phase titration of ozone with nitric oxide. NO, NO<sub>2</sub> and O<sub>3</sub> were monitored *in situ* using chemiluminescence detection (CD), laser induced fluorescence (LIF) and UV photometry, respectively.

The observed correlation between the chemical loss of NO and O<sub>3</sub> and formation of NO<sub>2</sub> during titration experiments was within 1% at troposphericly relevant mixing ratios (40-200 ppbv) indicating that NIST O<sub>3</sub>, NO and NO<sub>2</sub> standards are accurate to within 1%. Prospects for improving on these experiments are discussed.

#### A31D-0069 0830h POSTER

##### Non-Controlled Emission of VOCs from Arico's Landfill, Tenerife, Canary Islands

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Landfills are important sources of CH<sub>4</sub> as well as other trace gas components to the environment. A large number of organic volatile components (VOCs) are present as tracers in landfill gases, and they are considered to be carcinogenic and toxic. In order to control the emissions of these contaminants to the atmosphere, extraction systems to recover biogas are installed in landfills. However, a significant amount of these emissions could be released to the atmosphere through the surface environment in a diffuse form, also known as a non-controlled emission of landfill gases. The aim of this study is evaluate the non-controlled emission of VOCs from Arico's landfill.

The Arico landfill has an extension of 0.35 km<sup>2</sup>, and about 1,546 tons of municipal solid waste (MSW) is daily deposited. A biogas extraction system was installed at the Arico landfill between 1998 and 1999. A non-controlled VOCs emission survey of 133 sampling sites was carried out during August, 2002. Surface CO<sub>2</sub> efflux measurements were performed by means of a portable NDIR spectrometer and according to the accumulation chamber method. Surface CO<sub>2</sub> efflux ranged from 1 to 10,580 gm<sup>-2</sup>d<sup>-1</sup>. At each sampling site, surface landfill gas samples were collected at 40 cm deep using a metallic probe. These gas samples were analyzed within 24 hours by means of GC-MS. Non-controlled emission rate of VOCs were estimated by multiplying surface CO<sub>2</sub> efflux times (VOCs)<sub>i</sub>/CO<sub>2</sub> weight ratio at each sampling site, respectively. The spatial distributions of VOCs at the Arico's landfill showed a different distribution pattern for each volatile component and it is related to actual use of the landfill. Taking into consideration the spatial distribution of the VOCs efflux values as well as the extension of the landfill, the non-controlled emission of VOCs to the atmosphere by Arico's landfill was estimated about 2108 Kgd<sup>-1</sup> of which 1638 Kgd<sup>-1</sup> are BTEX emissions.

URL: <http://www.iter.es>

#### A31D-0070 0830h POSTER

##### One Year of Continuous In-Situ NMHC Measurements in Rural Ontario, Canada

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Speciated in-situ measurements of 37 Nonmethane Hydrocarbon compounds (C<sub>2</sub> to C<sub>8</sub>) are routinely made at the Centre for Atmospheric Research Experiments (CARE) in Egbert (Southern Ontario, Canada). CARE is home to one of Environment Canada's six regional enhanced air quality monitoring sites and is located in a rural setting, approximately 70 km north of the city of Toronto. The site is impacted by both urban/industrial air masses from the South and relatively unpolluted continental air masses from the Northwest. NMHC measurements have been made at this site since March, 2001 at a frequency of 6-8 samples per day. We report here the data from April, 2002 - March, 2003. The fully automated measurements are made by means of a liquid nitrogen-cooled glass bead pre-concentration trap and multi-column capillary Gas Chromatography/Flame Ionization Detection. Detection limits range from 5 to 16 parts per trillion by volume with an air sampling volume of 930 mL. Routinely reported are mixing ratios of the C<sub>2</sub> and C<sub>3</sub> alkanes,

alkenes, and alkynes. C4 and C5 alkanes and alkenes including isoprene (2-methyl-1,3-butadiene), C6 alkanes, benzene, toluene, and xylene isomers. We discuss diurnal and seasonal trends in the data. Back trajectory calculations are used to indicate source profiles and to estimate the impact of Arctic air masses on this site. The amount of photochemical processing from various source directions is estimated using hydrocarbon ratio data. Anomalous C7 and C8 aromatic data are investigated to assess the possible impact of local sources on the site.

#### A31D-0071 0830h POSTER

##### Measurement of CO, NO, NO<sub>2</sub>, Organic Compounds and PM<sub>10</sub> at a Motorway Location in an Austrian Valley During a Twelve Hour Blockade Period

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Proton transfer reaction mass spectrometry (PTR-MS) was used during a twelve hour motorway blockade (25th October 2002, 12:00 - 24:00) to detect key chemical compounds in the air. Located within the Inn valley (Tirol, Austria), the monitoring site has restricted dilution conditions for air pollutants and high traffic sources. In-situ measurements took place over an eleven day period (encompassing the one day road-block) during which time detection of certain aromatic compounds was conducted. Additionally, continuous routine CO, NO and NO<sub>2</sub> levels were monitored and detection of PM<sub>10</sub> was carried out. The period of traffic absence showed a dramatic decrease of NO, PM<sub>10</sub>, as well as the aromatics, showed a corresponding but slower decrease throughout this period. Analysis of data separated into weekdays and weekends showed significant reductions of NO<sub>x</sub> and PM<sub>10</sub> at the weekends, when fewer heavy duty vehicles (HDV) use the motorway, indicating them as being the dominant source of these two pollutants. Principal components analyses (PCA) for the separated data support this. The aromatics in the PCA are clustered together, suggesting their source as being predominantly from light duty vehicles. A mean concentration of benzene over the measurement period was found to be 0.9 ppbV; below the annual 1.5 ppbV EU limit, to be reached by 2010 but above the annual mean target level of 0.78 ppbV set by the Oesterreichischen Akademie der Wissenschaften (Austrian Academy of Sciences). NO<sub>x</sub> and PM<sub>10</sub> showed mean values over the entire campaign of 189  $\mu\text{g m}^{-3}$  and 24.5  $\mu\text{g m}^{-3}$  respectively.

#### A31D-0072 0830h POSTER

##### On-line Monitoring of VOCs at a High Mountain Site in the German Alps (Schneefernerhaus, Zugspitze)

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In the frame of the Schneefernerhaus Aerosol & Reactive Nitrogen Experiment (SCAVEX) a Proton-Transfer-Reaction Mass Spectrometer was installed on the Environmental Research Station Schneefernerhaus (47.42° N, 10.99° E, 2650 m a.s.l.). The Schneefernerhaus is situated about 300 m below the peak of the Zugspitze in the German Alps. From 28th October 2002 to 12th March 2003 the remotely operated PTR-MS instrument measured a series of volatile organic compounds (VOCs) including oxygenates (methanol, acetaldehyde, acetone, methyl ethyl ketone), aromatics (benzene, toluene, alkyl substituted benzenes) and the biomass burning tracer acetonitrile. PTR-MS measurements on high mountain sites can be used to identify

air masses with very different chemical characteristics, which have originated in the planetary boundary layer or have undergone long-range transport in the free troposphere. First results will be presented in this paper.

#### A31D-0073 0830h POSTER

##### Seasonal change of NMHCs (nonmethanehydrocarbons) and halocarbons from winter to spring in East Asia observed during the PEACE (Pacific Exploration of Asian Continental Emission) aircraft measurement campaigns

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Recent population growth and rapid economic development in Asia has had a great impact on the amount and composition of gas emissions from Asia. To investigate the impact of these Asian emissions on local and regional air quality and climate, an airborne observation campaign PEACE (the Pacific Exploration of Asian Continental Emission) phases-A and B were conducted in January and April - May 2002, respectively. The concentrations of NMHCs (nonmethanehydrocarbons) and halocarbons were obtained by whole air sampling and subsequent gas chromatography analysis in the laboratory. Quantified onboard the aircraft were CO, CO<sub>2</sub>, O<sub>3</sub>, NO, NO<sub>2</sub>, NO<sub>y</sub>, H<sub>2</sub>O, SO<sub>2</sub>, aerosols, and condensation nuclei. The experiments were conducted along the East Asian coast, with PEACE-A and B representing the local winter and spring weather conditions, respectively. For most of the trace gases whose major atmospheric sink is OH oxidation, observed mixing ratios were much lower during PEACE-B compared to PEACE-A because of the more active photochemistry during spring-time. By contrast, some compounds showed higher mixing ratios in the upper troposphere for PEACE-B than PEACE-A, indicating more effective convection and transport of pollutants from the source regions during the spring-time. For compounds which have biogenic sources, the seasonal variation in the source strengths are indicated. The timescale of the transport in each season was estimated using the ratios of short-lived gases vs. more stable compounds. The results from PEACE are compared to those from the TRACE-P campaign (one of the NASA/GTE projects conducted from February to April 2001 in western Pacific). This comparison highlights the transition from winter to spring, as well as the range of annual trace gas variability in the region.

URL: <http://atmchem.eorc.nasda.go.jp/GLACE/PEACE/htdocs/index.html>

#### A31D-0074 0830h POSTER

##### Airborne Measurements of Halocarbons During the 2003 COBRA - North America Study

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During May and June 2003, we made thousands of in situ measurements of seven halocarbons (CFC-11, CFC-12, CFC-113, CH<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub>, CBrClF<sub>2</sub>, and CHCl<sub>3</sub>) and other important atmospheric gases in the boundary layer and free troposphere over the USA and Canada as part of the 2003 CO<sub>2</sub> Budget and Regional Airborne - North America (COBRA-NA 2003) study. Our goal was to compile a geographically extensive set of mixing ratio data for these gases from which their emissions could be determined at the regional to continental scale. Two 11,000 km racetracks around the USA and Canada were completed during this study, along with several regional flights in the northeastern and southern central USA. Our interest in quantifying contemporary halocarbon emissions in the USA and Canada stems from the prohibited production and consumption of these ozone-depleting substances in the Montreal Protocol for Substances that Deplete the Ozone Layer and its Amendments. Developed countries in compliance with the Protocol have not produced the halocarbons we measured (excluding CHCl<sub>3</sub>) since before 1996, yet modern emissions persist from reservoirs (banks) of these chemicals. Halocarbon emissions in developed nations are increasingly difficult to estimate because their once ubiquitous sources have diminished, both in magnitude and spatial uniformity, limiting the accuracy of regional and continental-scale emission estimates derived from localized measurements. Our broad-ranging data set for the USA and Canada lead to improved estimates of large-scale halocarbon emissions in these countries.

URL: <http://www.fas.harvard.edu/~cobra>

#### A31D-0075 0830h POSTER

##### Atmospheric Carbon Tetrachloride - A Conundrum?

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Carbon tetrachloride (CCl<sub>4</sub>) is a significant ozone-depleting gas in the atmosphere that has been decreasing in concentration at just under 1 ppt y<sup>-1</sup> (< 1% y<sup>-1</sup>) over the past decade. This turnover and decrease in reported mixing ratio can be attributed to lowered production as agreed upon by the parties signing the Montreal Protocol on Substances that Deplete Stratospheric Ozone. The rate of decline, however, is inconsistent with available information regarding the production and atmospheric lifetime of this gas. Other useful information for CCl<sub>4</sub> is in the interhemispheric difference, which has changed little since the initial turnover in mixing ratio. This is unlike that of the CFCs and methyl chloroform (CH<sub>3</sub>CCl<sub>3</sub>), for which the interhemispheric difference in mixing ratio has become smaller, in some cases rapidly, with the decline in emissions in the mid-1990s. This suggests that emissions of CCl<sub>4</sub> continue to be significant, particularly in light of the lowered estimates for the atmospheric lifetime of CCl<sub>4</sub>. This seeming paradox raises a number of questions, not just regarding production and emission, but also about the calculated lifetimes of atmospheric trace gases. The lifetime of CCl<sub>4</sub> from losses solely within the atmosphere currently is calculated at 35(21-43) y. Recently reported losses to the ocean have reduced the lifetime estimate to 26(17-36) y and an even more recent estimate of losses to soils reduces the lifetime further to 20(13-32) y. These newly reported losses of CCl<sub>4</sub> force a re-examination of the magnitudes and distributions of the sources and sinks of this gas. This poster presents some new data and an evaluation of what is known and unknown with regard to the budget of atmospheric CCl<sub>4</sub>, highlighting uncertainties and the need for additional research to reduce them. Montzka, S. A., et al., Controlled substances and other source

gases, Chapter 1, in Scientific Assessment of Ozone Depletion: 2002, Global Ozone Res. and Monitor. Proj., Vol. No. 47, World Meteorol. Organ., Geneva, Switzerland, 2003. Yvon-Lewis, S. A., and J. H. Butler, Effect of oceanic uptake on atmospheric lifetimes of selected trace gases, *J. Geophys. Res.*, 107(D20), 4414, doi:10.1029/2001JD001267, 2002. Happell, J. D., and M. P. Roche, Soils: A global sink of atmospheric carbon tetrachloride, *Geophys. Res. Lett.*, 30(2), 1088, doi:10.1029/2002GL015957, 2003.

URL: <http://www.cmdl.noaa.gov>

### A31D-0076 0830h POSTER

#### Trace gas sources and distributions across the tropical Atlantic Ocean lower atmosphere

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A research cruise of the R/V METEOR was conducted during October-November, 2002, along a transect from South America to Africa along approximately 10°N, with a jog to the equator in the Eastern Atlantic section. Trace gases were measured in-situ and from stainless steel canisters collected throughout the cruise. Trace gas measurements included CO, ozone, C1-C5 hydrocarbons, numerous halocarbons, HFCs, HCFCs, alkyl nitrates, and selected sulfur compounds. In this presentation we will examine the factors influencing the distribution and sources of trace gases in the marine boundary layer of the tropical Atlantic Ocean. The variety of trace gases measured during the experiment contain signatures of different source types including marine emission, biomass burning, industrial and anthropogenic activity, and interhemispheric exchange. Background marine conditions were encountered in the Western Atlantic, with little evidence of recent continental sources and limited emission of trace gases from marine biogenic sources. The transect to the equator from 10°N showed increasing evidence of marine biogenic emissions, particularly of light alkyl nitrates. The Eastern Atlantic contained a more complex distribution of tracers. Air mass transport from the north and east across North Africa showed evidence of mixtures of industrial tracers, biomass burning emissions, and strong indication of emissions of halocarbons from productive coastal waters along the African shelf.

### A31D-0077 0830h POSTER

#### The influence of long-range transport of pollution on the annual cycles of carbon monoxide and ozone

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During 2001-2002, carbon monoxide and ozone measurements were made at Cheeka Peak, Washington, a remote site on the northwestern tip of the contiguous U.S. These observations were combined with a global model, GEOS-CHEM, to yield information on the controlling factors of CO and ozone concentrations in different seasons. Previous CO-ozone measurement campaigns at Cheeka Peak (spring, 1997 and 1998) relied upon isentropic back trajectories to classify the data by source region. In this paper however, we show that GEOS-CHEM is a superior tool because it incorporates emission strengths, mixing/diffusion, and chemical processes, and gives a better agreement with the measurements. Two outputs from GEOS-CHEM were the most useful in classifying the data: the amount of

CO from European+Asian pollution ("LRT" for long-range transport), and the amount of CO produced from the oxidation of CH<sub>4</sub> and biogenic hydrocarbons ("Ox" for oxidation CO). LRT is the dominant source of CO from Jan. - Jun., whereas Ox dominates from Jul. to Oct. Peaks in LRT usually show a corresponding peak in measured CO. Ozone production and/or destruction during LRT events is dependent on a myriad of factors and is thus not well correlated with CO. Periods where Ox is enhanced generally show a decrease in CO and ozone concentrations compared to LRT-dominant times. When these Ox-events occur in the winter and spring, they are associated with transport from more southerly latitudes, which brings cleaner oceanic tropical air masses exposed to higher oxidation rates and a greater time since land contact (aged pollution). Hourly CO measurements from all seasons in 2001-2002, and the springs of 1997 and 1998, are well correlated ( $r=0.88$ ) with the ratio LRT/Ox, indicating that these two parameters account for roughly 78% of the variability in CO. Ozone correlates to LRT/Ox less well:  $r=0.70$ , or 50% of the variability in ozone is accounted for by LRT/Ox.

### A31D-0078 0830h POSTER

#### Measurements of Toxic Trace Substances in Ambient Air of Gosan, Jeju in Korea

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Atmospheric concentrations of persistent organic pollutants (POPs) and heavy metals have been measured at Gosan, Jeju in Korea twice a year since November 2001. Gosan is a representative background site in Korea and was a super site during ACE-Asia. Purposes of this work were to monitor the background concentrations of POPs and heavy metals in Korea and to assess the effect of long-range transport of these substances. Target substances were POPs in the Stockholm Convention and heavy metals as well as PAHs and PM<sub>2.5</sub>. Criteria pollutants and meteorological variables were monitored at co-located stations operated by the government. As of the end of August 2003, measurements have been made six times; each measurement period lasted about two weeks. The data analysis for the first two measurements was completed, whose preliminary results for POPs were presented at the last fall meeting (*Eos. Trans. AGU*, 83(47), Fall Meet. Suppl., Abstract A52B-0116, 2002). During the 1st measurement period in November 2001, high concentration of pollutants similar to that in urban areas was observed at Gosan. This high concentration was thought caused by emission from the nearby area. At the end of the 2nd measurement period in spring 2002, a large-scale Asian dust swept. However, concentration of major hazardous pollutants was lowered probably because of scavenging and dilution effects accompanied by Asian dust. In the 3rd measurement period, two typhoons exerted influences; one was direct and the other was indirect. In spite of large variation of the origin of air mass came to the site, pollutant concentration did not vary so much.

### A31D-0079 0830h POSTER

#### Naphthalene and Naphthoquinone: Distributions and Human Exposure in the Los Angeles Basin

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Naphthalene is the simplest and most abundant of the polycyclic aromatic hydrocarbons (PAHs). Naphthalene is found primarily in the gas-phase and has been detected in both outdoor and indoor samples. Evaporation from naphthalene-containing products (including gasoline), and during refining operations, are important sources of naphthalene in air. Naphthalene is also emitted during the combustion of fossil fuels and wood, and is a component of vehicle exhaust. Exposure to high concentrations of naphthalene can damage or destroy red blood cells, causing hemolytic anemia. If inhaled over a long period of time, naphthalene may cause kidney and liver damage, skin allergy and dermatitis, cataracts and retinal damage, as well as attack the central nervous system. Naphthalene has been found to cause cancer as a result of inhalation in animal tests. Naphthoquinones are photooxidation products of naphthalene and the potential health effects of exposure to these quinones are a current focus of research. We are developing and applying models that can be used to assess human exposure to naphthalene and its photooxidation products in major air basins such as California South Coast Air Basin (SoCAB). The work utilizes the Surface Meteorology and Ozone Generation (SMOG) airshed model, and the Regional Human Exposure (REHEX) model, including an analysis of individual exposure. We will present and discuss simulations of basin-wide distributions of, and human exposures to, naphthalene and naphthoquinone, with emphasis on the uncertainties in these estimates of atmospheric concentrations and human exposure. Regional modeling of pollutant sources and exposures can lead to cost-effective and optimally health-protective emission control strategies.

### A31D-0080 0830h POSTER

#### Sunlight Mediated Biogeochemical Dynamics of Mercury in the Everglades Aquatic Ecosystem: A Case Study

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Competition of photochemical reduction of Hg(II) with methylation process may reduce local Hg toxicity in aquatic ecosystems as the produced dissolved gaseous mercury (DGM) can be emitted back to the atmosphere. Diel changes of DGM levels in natural freshwaters driven by sunlight have been observed widely, especially in the large northern lakes. The Florida Everglades aquatic ecosystem is a special wetland ecosystem, which receives rich solar radiation and strong influence of aquatic plants (e.g., cattails and sawgrass) but generally has still water with enriched organic matter. Biogeochemical cycling of Hg in this system has been of special interest because of involvement of both photochemical redox of Hg and solar-driven transport of DGM by the aquatic vegetation. We here report a study of sunlight-mediated biogeochemical dynamics of aquatic Hg in a natural area of the Everglades in a cool season (late February and early March) and a warm season (early June). The DGM levels were found to be very low both in the cool season ( $4.1 \pm 2.2$  (1.1-8.6) pg/L,  $n = 17$ ,  $T = 20 \pm 2.5$  °C) and in the warm season ( $3.9 \pm 1.5$  (1.4-8.0) pg/L,  $n = 19$ ,  $T = 25 \pm 1.8$  °C), exhibiting little seasonal change over the time studied. These values were all much lower than those found in summer season in the northern lakes (20-72 pg/L), in a southern small lake in Cookeville, TN (e.g., 39 pg/L in early Aug.), and in the Everglades ENR (4-33 pg/L). Only moderate to very weak diel trends were observed (e.g., highest daily difference between max and min DGM = 3.7 pg/L). In situ incubations of freshwater samples in sunlight led to moderate increases in DGM production (e.g. from 4.4 to 18 pg/L in 3.4 h), but dark incubations of initially solar-exposed water samples showed significant decreases in DGM (e.g., from 9.8 to 1.2 pg/L in 5 h). Spike of 1000 pg/L Hg(II) led to only moderate increases of DGM (e.g., from 6.7 to 32 in 10 min and to 54 pg/L in 54 min), while little enhancing effect of Fe(III) on photochemical production of DGM was seen, in contrast to the large positive effect of Fe(III) seen in some northern lake waters. These data collectively suggest that oxidation loss of produced DGM could play a significant role in Hg photochemical dynamics in the system studied. Yet, in addition to the oxidation, sunlight-driven transport of DGM

by the aquatic plants must be considered in order to explain the unusually low DGM levels and related observations. Further study on the driving forces and mechanism for Hg biogeochemistry in the ecosystem is highly of interest.

### A31D-0081 0830h POSTER

#### Core Atmospheric Measurements at the Summit, Greenland Environmental Observatory: GEOSummit

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A program is being implemented for long-term measurements of the Arctic atmosphere, snow and other Earth system components at the Summit, Greenland Environmental Observatory (GEOSummit), located at an elevation of 3100 m on the Greenland ice sheet. GEOSummit was the site of the Greenland Ice Sheet Project 2 (GISP2) ice core studies, completed in 1993, and has been a site of atmospheric, snow, and other geophysical measurements ever since. It is currently the only high-altitude site for atmospheric and related measurements in the Arctic. Many of these measurements, previously made intermittently at GEOSummit, resumed on a continuous basis beginning in summer 2003 and will be made publicly available. Core atmospheric and snow measurements provide a baseline for the continued operation of GEOSummit as a long-term site for year-round disciplinary and interdisciplinary measurements and research. Because changes in Arctic atmospheric circulation are cyclic over 4-5 year or longer times, long-duration measurements are being made available to understand circulation and to place observed changes in a long-term perspective. The availability of the GEOSummit measurements encourages and facilitates multi-disciplinary research by providing a high-quality core of baseline observations. The current program continues and expands the core baseline measurements at GEOSummit for a five-year period, beginning in summer 2003. GEOSummit is currently a partnership between NSF-OPP, NOAA-CMDL, and investigators from Denmark, Germany and Switzerland. Baseline measurements include meteorology, radiation, tropospheric and aerosol chemistry, snow properties and snow chemistry as well as carbon cycle compounds, chlorofluorocarbons, radiation, and ozone. Average water accumulation at GEOSummit is 21 g cm<sup>-2</sup> y<sup>-1</sup>, with annual patterns varying significantly from year to year. The mean annual temperature is -30 °C, varying between -70 and 0 °C. Near-surface summertime ozone averages 55 ppbv. Aerosol fluxes and atmospheric gas concentrations (e.g., O<sub>3</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>) exhibit characteristic annual cycling.

URL: <http://www.geosummit.org>

### A31D-0082 0830h POSTER

#### Seasonal differences in snow chemistry from the vicinity of Mt. Everest, central Himalayas

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During August and September, 1998, fresh snow samples were collected in the East Rongbuk (ER) Glacier on the northern slope of Mt. Everest over an elevation range 5800-6500 m. Three snowpits were sampled in the ER glacier at an elevation of 6400m, 6500m, and 6500 m in August 1998, May 2000, and October

2002, respectively. Snow chemical data from fresh snow and snowpit samples from the ER Glacier are shown to be consistent with earlier results reported by other researchers from the vicinity of Mt. Everest. Among major ions, calcium has the most striking seasonal differences: non-monsoon snow calcium concentration is one order of magnitude higher than monsoon value. A large seasonal difference characterizes fresh snow sulfate but does not seem to persist in snowpit samples probably as a consequence of post-depositional ion elution. Non-monsoon snow sodium, potassium, and chloride are close to two times higher than monsoon snow for both fresh snow and snowpit samples. Magnesium has distinct seasonal variations in snowpit samples and a four fold higher concentration in non-monsoon snow than that in monsoon snow. Seasonal differences in major chemical composition in snow over the Mt. Everest region provide a definitive indicator for precisely dating ice cores and as a consequence are essential in reconstructing the history of climate change and atmospheric chemistry in this region.

### A31D-0083 0830h POSTER

#### Linkage Issues Between Global Tropospheric Chemistry Model and Regional Air Quality Model

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One of key problems of regional air quality models, such as U.S. EPA's CMAQ, is finding accurate initial and boundary conditions for the simulations. Most popular method for this is running a regional air quality model at a coarser resolution with seasonal profile data and surface emissions input for a long-enough period of time for the spin-up process. However, the procedure is not able to account for the change in the boundary conditions due to certain air pollution long-range transport events. For this reason, we attempt to use outputs of global tropospheric chemistry model simulations to provide the reasonable boundary conditions for the regional air quality simulations. To provide the initial and boundary conditions for regional modeling, we have used the GEOS-CHEM model to link with CMAQ. To link the GEOS-CHEM output in the Latitude-Longitude coordinates at 2°X2.5 of horizontal resolution and 48 vertical layers to the CMAQ in the Lambert-Conformal coordinate at 36kmX36km horizontal resolution over the US-continental domain and 23 vertical layers, it is necessary to perform the horizontal and vertical interpolations. Chemical species mapping is needed because of the different chemistry reaction mechanisms are used such as the O<sub>3</sub>-NO<sub>x</sub>-hydrocarbon chemistry in GEOS-CHEM and CB4 and SAPRC99 in CMAQ. In this study we discuss issues in linking the global and regional scale models, such as compatibility of model dynamics, differences in emissions data used and effects of different chemical mechanisms between GEOS-CHEM and CMAQ. To investigate the effects of using GEOS-CHEM output as initial and boundary conditions instead of the profile data on regional CMAQ simulations we have conducted 4 sensitivity CMAQ simulations for the combination of using GEOS-CHEM output and profile data for the boundary conditions and with the CB4 and SAPRC99 as the chemical mechanisms. Analysis shows that there were no significant differences in wind fields and O<sub>3</sub> distributions between the GEOS of the NASA DAO in GEOS-CHEM and MM5 in CMAQ. We also compared emissions inputs used for the GEOS-CHEM and CMAQ, in particular for the NO<sub>x</sub> and VOC species. To verify the CMAQ results after linking with GEOS-CHEM, we have compared the CMAQ results of each simulated cases with AIRS data.

### A31D-0084 0830h POSTER

#### Relationships between crustal records from three ice cores in West Antarctica and atmospheric circulation

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Using NCEP/NCAR Reanalysis data, we investigate the relationships between crustal ion (nssCa<sup>2+</sup>: non sea-salt Ca<sup>2+</sup>) concentrations from three West Antarctica ice cores: Siple Dome (SD), ITASE00-1 (IT001) and ITASE01-5 (IT015), and the climatic factors: air pressure/geopotential height, zonal (u) and meridional (v) wind strength. Linear correlation analyses between nssCa<sup>2+</sup> concentrations and air pressure, wind fields for the recent 50 years indicate that the SD nssCa<sup>2+</sup> variation is positively correlated with spring (SON) circumpolar zonal wind, while the IT001 nssCa<sup>2+</sup> has positive correlation with circumpolar zonal wind during the whole year ( $r > 0.3$ ,  $p < 0.01$ ). Intensified Southern Westerlies circulation is conducive to transport more crustal aerosols to both sites. Further correlation analyses between nssCa<sup>2+</sup> concentrations and atmospheric circulation for SD and IT001 suggest that the high inland plateau (e.g. IT001) is largely influenced by the transport from the upper troposphere. The IT015 nssCa<sup>2+</sup> is negative correlated with westerly wind in October and November, suggesting that the stronger westerly circulation may weaken the transport of crustal species to IT015. Results of correlation of nssCa<sup>2+</sup> in three ice cores with Antarctic Oscillation (AAO) index are agreed well with those of winds. NssCa<sup>2+</sup> concentrations are also related to ENSO variability in which higher crustal species corresponds with stronger ENSO event.

### A31E MCC: Level 1 Wednesday 0830h

#### Climate II Posters (joint with GC)

**Presiding:** M Herzog, University of Michigan; M J Prather, University of California, Irvine

### A31E-0085 0830h POSTER

#### Modes of Climate Variability Under Climate Change Scenarios

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This combined observational and modeling study concerns how patterns of variability including the El Niño Southern Oscillation (ENSO), the Arctic Oscillation-North Atlantic Oscillation (AO-NAO), the Pacific North American Pattern (PNA) and the Western Pacific Pattern (WP) may be modified by climate change. Possible modifications to these teleconnection patterns, including changes in amplitude, frequency, duration, and spatial pattern, are analyzed. The signature and influence of these teleconnection patterns on diagnostics including surface air temperature, precipitation, zonal and meridional wind, geopotential height, storms, and the fluxes of heat and momentum are also explored. Analytical techniques include correlation and compositing of NCEP reanalysis data from two periods: 1) 1958-1998, and 2) 1979-1998. Model data from the Goddard Institute for Space Studies (GISS) AGCM, driven with 1) current and 2) enhanced greenhouse forcing are compared as well.

### A31E-0086 0830h POSTER

#### A New Approach to Global Surface Temperature Study

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A new approach to global surface temperature study was investigated. A complete set of non-orthogonal Thermal Decay Modes of Climate (TDM) was derived from a two dimensional linear Energy Balance Climate Model (EBCM). This EBCM includes the distribution of land and sea surface characteristics explicitly and was solved in two dimensions on the sphere as a series of time (or frequency) dependent mode amplitudes. The amplitudes of these modes have temporal characteristics which are purely decaying exponential with time constants that are proportional to the sensitivity of an individual mode to external perturbations. Experiments, such as the reconstruction of the geographical distributions of seasonal cycle and variance, suggest that the TDM of 2D EBCM fit the present climate very well. The decomposition may provide a new way of analyzing surface temperature data. The new analyses should make it possible to infer the sensitivity of the real climate to external perturbations.