

a 7.3 TgN/yr biogenic soil source that is consistent with previous inventories based on the extrapolation of small-scale measurements, but is a factor of two larger than process-based models. The large soil source inferred from GOME observations supports the idea that both biomass burning and biogenic sources significantly contribute to the ozone enhancement originating from Tropical Africa.

A31D-04 0930h

Satellite Remote Sensing of Ozone-NOx-VOC Sensitivity

Randall V Martin^{1,2} (902-494-3915; randall.martin@dal.ca)

Arlene Fiore³ (arlene.fiore@noaa.gov)

Aaron Van Donkelaar¹ (adonkela@dal.ca)

¹Department of Physics and Atmospheric Science, Dalhousie University, Halifax, NS B3H 3J5, Canada

²Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, United States

³Atmospheric and Oceanic Sciences Program, Princeton University, Princeton, NJ 08542, United States

We present a novel capability in satellite remote sensing with implications for air pollution control strategy. Uncertainty in the relation between surface ozone and its two main precursors, nitrogen oxides (NO_x=NO+NO₂) and volatile organic compounds (VOCs) remains a primary obstacle to improving surface air quality. The design of control strategies for surface ozone has been impeded by limited observations of ozone-NO_x-VOC sensitivity. We show that the ratio of formaldehyde to tropospheric nitrogen dioxide columns is an indicator of the relative sensitivity of surface ozone to emissions of NO_x and VOCs. Space-based observations of the ratio from the GOME satellite instrument reveal that surface ozone is more sensitive to emissions of NO_x than of VOCs throughout most of the Northern Hemisphere during summer. Exceptions include Los Angeles and industrial areas of Germany. A seasonal transition occurs in the fall when surface ozone becomes less sensitive to NO_x and more sensitive to VOCs.

A31D-05 0945h

Seasonal and Diurnal Cycles of Nitrogen Oxides on the Western Slope of the Sierra Nevada

Jennifer G Murphy¹ (510-642-8001; jgmurphy@berkeley.edu)

Delphine K Farmer¹

Douglas A Day¹

Paul J Wooldridge¹

Ronald C Cohen¹

¹Department of Chemistry, University of California, Berkeley, CA 94720, United States

Air quality is often worse in remote areas downwind of cities than in the urban areas themselves. Accurate, long-term measurements of the precursors and byproducts of ozone production are needed to understand the composition and transport of photochemical smog and to evaluate potential control strategies. Thermal dissociation laser-induced fluorescence (TD-LIF) was used to make continuous, sensitive measurements of the mixing ratios of NO₂, total peroxy nitrates (EPNs), total alkyl nitrates (ΣANs), and HNO₃ at two sites on the western slope of California's Sierra Nevada. Observations at Blodgett Forest (1315 m) are made from a tower above a 12-year old ponderosa pine plantation while observations at Big Hill (1850 m) are made from an exposed hilltop. The sites are located 20 km apart and are both subject to daytime upslope winds that transport polluted air from the Sacramento Valley. The diurnal and seasonal cycles of reactive nitrogen at the two sites are examined, as are relationships between the classes of NO_y and O₃, particulate matter, CO and meteorological variables. The observations provide new constraints on the complex interplay between chemistry, transport, and atmosphere-biosphere interaction occurring in the region.

A32A CC: 520 D Wednesday 1030h

Tropospheric Chemistry (Mixed Phase) (joint with B, GC)

Presiding: R V Martin, Dalhousie University; J Thornton, University of Toronto

A32A-01 1030h

The 2003 North American Blackout: An Accidental Experiment in Air Chemistry

Russell R. Dickerson¹ (301.405.5364;

russ@atmos.umd.edu); Lackson T Marufu¹ (marufu@atmos.umd.edu); Brett F Taubman¹ (taubman@atmos.umd.edu); Bryan Bloomer¹ (blkoomer@atmos.umd.edu); Charles A Piety¹ (charles@atmos.umd.edu); Bruce G Doddridge¹ (bruce@atmos.umd.edu); Jeffrey T. Stehr¹ (stehr@atmos.umd.edu)

¹The University of Maryland, Dept. Meteorology, College Park, MD 20742, United States

Airborne observations over central Pennsylvania on August 15, 2003, about 24 h into massive blackout in North America, revealed significant reductions in SO₂ (90%), O₃ (50%), and aerosol loading (70%), relative to values measured outside the blackout region and over the same location the year before. CO and light-absorbing particles were unaffected; the single scattering albedo during the blackout was 0.85. Ground level O₃ decreased by 38 ppb; visibility increased by >40 km. Reported emissions of SO₂ and NO_x from upwind power plants were reduced to 34 and 20% of normal. The substantial improvement in air quality during the blackout provides strong evidence that the transport of emissions from power plants hundreds of km upwind plays a dominant role in levels of O₃ and haze over eastern North America.

A32A-02 1045h

Reaction Probabilities for HO₂ Loss on Aqueous Aerosol

Joel A Thornton¹ (416-946-7359; jthornto@chem.utoronto.ca)

Jonathan P. D. Abbatt¹ (416-946-7358; jabbatt@chem.utoronto.ca)

¹Department Of Chemistry University of Toronto, 80 St. George St., Toronto, ON M5S 3H6, Canada

The heterogeneous loss of HO₂ on aerosols has been predicted to dominate the total loss of HO_x radicals in some regions of the troposphere impacted by heavy aerosol loading. However, appropriate values for the net reactive uptake of HO₂ to tropospheric aerosol have yet to be experimentally determined in many cases. For this purpose, we have constructed an aerosol flow tube coupled to a chemical ionization mass spectrometer and aerosol sizing instrumentation to study the heterogeneous chemistry of HO₂ in the presence of aqueous sub-micron aerosol at room temperature. Mass accommodation coefficients were determined on 50 wt% H₂SO₄ aerosol and super-saturated aqueous (NH₄)₂SO₄ aerosol (RH=40%) to be greater than 0.5 by doping these aerosol with Cu(II) which catalyzes the conversion of HO₂ to H₂O₂. Measured reaction probabilities for HO₂ on 50 wt% H₂SO₄ aerosol without Cu(II) were less than 0.01. In contrast, reaction probabilities of 0.1-0.2 were obtained for HO₂ loss on aqueous (NH₄)₂SO₄ aerosol buffered to a pH of 5. We discuss the relevant condensed-phase properties and chemical mechanisms that might explain these differences in kinetics, and we address the implications and applicability of our results to tropospheric oxidant chemistry.

A32A-03 1100h

Tropospheric partitioning of nitric acid between the gas and fine particle phases

Mark A Zondlo¹ (1-505-984-1322;

mzondlo@swsciences.com); Fred L Eisele^{2,3}; R. Lee Mauldin²; Ed Kociuch²; Christopher A Cantrell²; Rodney J Weber³; Yin-Nan Lee⁴; Yilin Ma³

¹Southwest Sciences, 1570 Pacheco Street Suite E-11, Santa Fe, NM 87505

²NCAR / ACD, 1850 Table Mesa Drive, Boulder, CO 80305

³Georgia Institute of Technology, School of Earth and Atmospheric Sciences, Atlanta, GA 30332

⁴Brookhaven National Lab, Mail Stop 815E, Upton, NY 11973

Nitric acid plays numerous roles in tropospheric photochemistry and in the composition of aerosol particles. Unfortunately, quantifying these roles has been complicated by the difficulty in measuring both gas phase and particulate phase concentrations. In particular, gas phase nitric acid is efficiently removed by atmospheric particles, but quantifying these roles has been difficult. Measurements of gas phase nitric acid and fine (less than 1.3 micron diameter) particulate phase nitrate were made over the western and central Pacific during the NASA TRACE-P experiment in spring 2001. By examining the amount of gas phase nitric acid relative to the total amount of nitric acid (defined as gas phase nitric acid plus particle phase nitrate), the partitioning of nitric acid between the phases could be examined as a function of numerous variables. In the marine boundary layer, approximately half of the nitric acid was tied up in the aerosol phase, qualitatively consistent with heterogeneous loss of nitric acid on sea-salt particles. Above the marine boundary layer, the percentage of nitric acid in the gas phase increased to greater than 90% at 400 mb. No significant trends were noted longitudinally in either the free troposphere or in the marine boundary layer. A striking dependence, however, was noted versus absolute water concentration or dewpoint. Gas phase nitric acid accounted for 90% of total HNO₃ at very dry conditions (dewpoints less than -30C) but gradually decreased to less than 40% at dewpoints near 20C. To separate the effects of dew point versus relative humidity, the data was sorted into relatively smaller temperature bins. For the coldest temperature bin (245-255 K) as well as the warmest one (285-295 K), only slight increases in aerosol nitrate partitioning were observed as relative humidity increased dramatically from 15% to 95%. The partitioning results will be discussed in the context of laboratory studies which have observed significant increases in the uptake of HNO₃ on mineral/dust aerosol as a function of water vapor. Finally, the measurements of the partitioning of HNO₃ will be compared to results from global aerosol chemistry models. Generally, global chemical aerosol models seem to underpredict the partitioning of nitric acid in the aerosol phase, although inclusion of sea salt particles improves the agreement somewhat.

A32A-04 1115h

The CCN activity of internally mixed organic-inorganic particles: the effect of solubility and surface tension on particle activation

Keith Broekhuizen¹ (416-946-7359; kbroekhu@chem.utoronto.ca)

Pradeep Kumar² (020 - 25697752; ppk@physics.unipune.ernet.in)

Jonathan Abbatt¹ (416-946-7358; jabbatt@chem.utoronto.ca)

¹University of Toronto, Department of Chemistry 80 St. George St., Toronto, ON M5S 3H6, Canada

²University of Pune, Department of Atmospheric and Space Sciences, Pune 411007, India

The ability of internally mixed organic-inorganic aerosols to act as cloud condensation nuclei (CCN) will be discussed. Internally mixed particles were produced through a variety of methods, including particle coating and atomization of mixed solutions. These experiments were designed to address several key questions concerning particle activation. How does surface tension play a role and can a surface active organic species impact activation? Does a trace amount of a highly soluble species impact the activation of organic particles of moderate to low solubility? Can the activation properties of ammonium sulfate be "shut off" through coating with an inactive organic species? To systematically address these issues, the CCN activity of various mixed particles such as ammonium sulfate(AS)/oleic acid, AS/stearic acid, AS/adipic acid, AS/hexanoic acid and others have been studied. These results are among the first to specifically address the effect of surface tension on CCN activity in the laboratory.

A32A-05 1130h

3-D Simulation of Aerosol Physics and Chemistry Within a Convective Cloud

Annica ML Ekman¹ (1-617-452-5994; annica@mit.edu)

Chien Wang¹ (1-617-253-5432; wangc@mit.edu)

Julian Wilson² (39-0332-785204; julian.wilson@jrc.it)

Johan Ström³ (46-8-674-7287; johan@itm.su.se)

¹Massachusetts Institute of Technology, 77 Massachusetts Avenue, EAPS, Bldg. 54-1413, Cambridge, MA 02139, United States

²Institute for Environment and Sustainability, European Commission, DG JRC, Ispra, VA 21020, Italy

³Institute for Applied Environmental Research, Stockholm University, Frescativägen 54, Stockholm 10691, Sweden

Convective clouds provide an efficient mechanism for transporting aerosols to the upper troposphere. Although observational data in the upper troposphere are still limited, the few measurements available all indicate the existence of high concentrations of small particles, possibly due to the vertical transport related to deep convection. In addition, with sufficiently low temperature, high relative humidity, and relatively high concentrations of aerosol precursors; the outflow regions of convective clouds are likely areas for new aerosols to form, adding even more particles to the upper troposphere. In order to simulate convective cloud transport along with cloud processing of aerosols we have developed a 3-D cloud-resolving model with an interactive explicit aerosol module. A baseline simulation suggests good agreement in the upper troposphere between modeled and observed results including concentrations of aerosols in different size ranges, mole fractions of key chemical species, and concentrations of ice particles. A set of 34 sensitivity simulations has been carried out to investigate the sensitivity of modeled results to the treatment of various aerosol physical and chemical processes in the model. The size distribution of aerosols is proved to be an important factor in determining the aerosols' fate within the convective cloud. Nucleation mode aerosols ($0 < d < 5.84$ nm) are quickly transferred to the larger modes as they grow through coagulation and condensation of H₂SO₄. Accumulation mode aerosols ($d > 31.0$ nm) are almost completely removed by nucleation and impact scavenging. However, a substantial part (up to 10% of the boundary layer concentration) of the Aitken mode aerosol population (5.84 nm $< d < 31.0$ nm) reaches the top of the cloud and the free troposphere. The sensitivity simulations performed indicate that in order to sustain a vigorous storm cloud, the supply of CCN must be continuous over a considerably long time period of the simulation. Hence, the treatment of the growth of particles is in general more important than the initial aerosol concentration itself.

A32A-06 1145h

Infrared Study of Water Adsorption on Na-Montmorillonite

Elizabeth K Frinak¹ (303-492-1433; frinak@colorado.edu)

Courtney D Mashburn¹ (303-492-1433; mashburn@colorado.edu)

Margaret A Tolbert¹ (303-492-3179; margaret.tolbert@colorado.edu)

¹Department of Chemistry and Biochemistry & CIRCES, Campus Box 216, Boulder, CO 80309, United States

It is estimated that 350 Tg/yr of mineral aerosol particles are available for long range transport. A large fraction of transported mineral aerosol is composed of clays, such as smectite and kaolinite group clays. Because of its unique ability to expand upon addition of water, we have chosen to study the adsorption of water to Na-montmorillonite, a member of the smectite group, under conditions representative of the earth's troposphere. In addition to our studies of these particles as surfaces for heterogeneous chemistry, these particles are also being investigated in other laboratories for their potential as cloud condensation nuclei and for their interference in infrared satellite measurements of temperature. Na-montmorillonite has also been studied as a possible component of the surface of Mars. We have used a Knudsen cell equipped with transmission Fourier transform infrared (FT-IR) spectroscopy to quantify water adsorbed to Na-montmorillonite as a function of temperature and relative humidity. We find at 200 K and 220 K, the water content of the clay increases from 42 mg H₂O/g clay at 15% relative humidity to 111 mg H₂O/g clay at 58% relative humidity with respect to water. These results are in excellent agreement with room temperature, gravimetric measurements. This suggests that although water adsorption to Na-montmorillonite depends strongly on relative humidity there is not a strong temperature dependence. Comparisons to the existing Martian studies, potential relevance to satellite measurements and the implications of our results to tropospheric chemistry will be discussed.

A33A CC: 220 C-E Wednesday 1330h

Tropical Water Vapor: New Understanding and New Challenges III Posters (joint with H, OS, GC)

Presiding: I Folkins, Dalhousie University; S Sherwood, Yale University

A33A-01 1330h POSTER

Water Vapor and Cirrus in the Tropical Tropopause Layer Observed by UARS

Hannah L Clark (0033561079767; hannah.clark@cnrm.meteo.fr)

Meteo France, 42, Avenue Gaspard Coriolis, Toulouse 31057, France

The Microwave Limb Sounder (MLS), an instrument on the Upper Atmosphere Research Satellite (UARS), is sensitive to water vapor in the tropical tropopause layer. We exploit a new dataset from MLS which has enhanced vertical resolution and gives new insights into the vertical structure of water vapor between 215 and 56 hPa. The Cryogenic Limb Array Etalon Spectrometer, another of the instruments on UARS is sensitive to sub-visible cirrus formation in the region of the tropical tropopause. Cirrus clouds play an important role in the dehydration of this region and can contribute to the destruction of ozone. Combining these datasets, we investigate the seasonal and intraseasonal variability of water vapor and cirrus and the implications for stratosphere-troposphere exchange.

A33A-02 1330h POSTER

Asymmetry and Non-linearity in Upper Tropospheric Humidity Variability

Elizabeth Jane Kennett¹ (44-207-594-8210; elizabeth.kennett@imperial.ac.uk)

Ralf Toumi¹ (44-207-594-7668; r.toumi@imperial.ac.uk)

¹Physics Department, Imperial College, Blackett Laboratory, Prince Consort Road, South Kensington, London SW7 2BZ, United Kingdom

Changes in upper tropospheric humidity (UTH) are important in understanding the climatic response to increased anthropogenic forcing. This paper explores the asymmetry and non-linearity in the response of subtropical UTH to tropical intraseasonal forcing. HIRS (High Resolution Infrared Sounder) UTH data with pentad time resolution, spanning the period January 1979 to December 1998, were used and compared with ERA-40 (European Centre for Medium-Range Weather Forecasts 40 year Reanalysis) UTH and dynamical fields. During northern winter, subtropical UTH anomalies, varying on intraseasonal timescales, propagate eastwards from northern Africa to the central Pacific. These anomalies are associated with the Rossby response to tropical intraseasonal heating in a baroclinic atmosphere. There is a discontinuity in the propagation of moist anomalies over the Tibetan Plateau, whilst dry anomalies show reduced propagation in the lee. This is consistent with the expected evolution of cyclones and anticyclones incident on high topography. Correlations of five-day mean UTH show no significant linear correlation between moist anomalies over Indonesia and subtropical anomalies to the north. This appears to be explained by the limitation of dry anomalies in the region of low ambient vorticity south of the East Asian Jet Stream.

A33A-03 1330h POSTER

Evaporative Moistening Above and Below the Melting Level

Ian Folkins (902-494-1292; Ian.Folkins@dal.ca)

Dept. of Physics and Atm. Sci., Dalhousie University, Halifax, NS B3H 3J5, Canada

Convective Downdrafts that occur above the 5 km melting level are physically different from those that occur below the melting level. Above 5 km, evaporative moistening tends to be self limiting. Because the evaporation of falling ice quickly brings the tropical atmosphere to saturation locally, the overall rate of evaporative moistening becomes dynamically controlled by the rate at which deep convective regions can import dry air from non convective regions and export humid air to the subtropics. Below the 5 km melting level, the relative humidity of a neutrally buoyant downdraft tends to stay the same or decrease (from its point of origin). This implies that, although an increase in the

downdraft mass flux below the melting level still requires a convergent inflow of air, there is no requirement that this air be dry. This air can therefore arise from a localized mid-level circulation associated with cumulus congestus clouds.

A33A-04 1330h POSTER

Insights into tropical water vapor using stable isotopes

Andrew Gettelman (303-497-1887; andrew@ucar.edu)

National Center for Atmospheric Research, 1850 Table Mesa Drive, Boulder, CO 80304, United States

Stable isotopes of water (H₂-18O and HDO) provide an integrated history of condensation and evaporation processes in the atmosphere due to large temperature dependent fractionation. In the upper tropical troposphere, these isotopes can be used to help us understand the sources and sinks of tropical water vapor and condensate. This work presents an analytic model of water and its isotopes, and compares it to observations from the CRYSTAL-FACE experiment in July 2002. The results indicate that the upper tropical troposphere contains a large amount of water lofted as ice, and highlights the role of convection in maintaining the water vapor distribution in the upper troposphere. The role of convection in hydrating and dehydrating the tropical upper troposphere is discussed. The implications for stratospheric humidity and for water vapor and high cloud feedbacks on climate are also discussed.

A

A33A-05 1330h POSTER

Sensitivity improvements in measurement of water vapor isotopic composition in the upper troposphere and lower stratosphere

Elisabeth J Moyer¹ (617 495-5922;

moyer@huarp.harvard.edu); Joshua B Paul²; Gregory S Engel¹; Larry B Lapon¹; David S Sayres¹; Thomas F Hanisco¹; James G Anderson¹

¹Dept. of Chemistry & Chemical Biology, Harvard University, Cambridge, MA 02138, United States

²NovaWave Technologies, 230 Twin Dolphin Dr., Redwood City, CA 94065, United States

There has been much interest in the scientific community in using the isotopic composition of water vapor in the uppermost troposphere and lower stratosphere as a tool to understand the transport and control of water vapor in these regions. The effectiveness of that tool is however a function of the capabilities of the instruments available to measure it. The only model scenarios that can be differentiated are those whose isotopic differences exceed the resolution of the measurements, both in terms of precision and of spatial resolution. We describe here a new in-situ instrument designed specifically for measurement of water vapor isotopes that provides an order of magnitude improvement in sensitivity over previously available technology. The Harvard ICOS (Integrated Cavity Output Spectroscopy) Isotope Instrument is an aircraft-borne absorption spectrometer, approximately 1 meter in length but with an effective absorption pathlength of 4 km, a factor of 40 longer than those in traditional Herriott cell spectrometers. The resulting improved measurement sensitivity allows scientifically useful measurements on a 1 s timescale, providing 200 m horizontal resolution from typical high-altitude aircraft. Estimated total measurement precision is 2%, equivalent to 10 per mil in typical tropopause-region conditions. This precision is required for addressing issues such as the seasonal cycle of water vapor isotopic composition in the lower stratosphere, which could range from virtually absent to as much as 80 per mil, depending on the mechanisms dehydrating air entering the stratosphere. We present model results for different scenarios and demonstrate that the instrument capabilities are sufficient to provide useful discrimination between them. The instrument is scheduled for first flight in autumn of 2004.

A33A-06 1330h POSTER

Upper Tropospheric Water Vapor from AIRS Measurements: Comparison to ARM Sondes

Annamarie Eldering¹ (818-354-4941; Annmarie.Eldering@jpl.nasa.gov)

Eric J Fetzer¹ (818-354-0649; Eric.J.Fetzer@jpl.nasa.gov)

Fredrick William Irion¹ (818-393-4337; Fredrick.Irion@jpl.nasa.gov)

Stephen S Leroy¹ (818 354-4545; Stephen.S.Leroy@jpl.nasa.gov)