

common at times in the aerosol over these oceans. It is generally believed that the numerous sulfate-containing particles in the atmospheric boundary layer at remote marine sites were formed by homogeneous nucleation of sulfuric acid in the free troposphere. In the absence of cloud removal processes, they there grew large enough to act as CCN. It is assumed that air interchanges between free troposphere and boundary layer account for their presence in the latter. Aqueous oxidation of sulfur dioxide in cloud drops would add to their sulfur content. The identification in the boundary layer of airborne particles and polymer gels clearly of marine origin, suggests an additional, and more direct, pathway to CCN formation. Because CCN concentrations may have a strong influence on climate, the relative importance of these two methods of CCN formation requires further study. In the central Arctic in summer, the lack of communication between the free troposphere and the surface air means that the marine bioaerosol will be the more important source.

**A22A-05 1150h INVITED**

**Investigation of Electrobiological Properties of Bioaerosols**

Gediminas Mainelis<sup>1</sup> (732-932-7166; mainelis@envsci.rutgers.edu)

Maosheng Yao<sup>1</sup> (732-932-4945; myao@envsci.rutgers.edu)

Hey Reoun An<sup>1</sup> (732-932-4945; hran@eden.rutgers.edu)

<sup>1</sup>Rutgers University, 14 College Farm Rd Dept. of Environmental Sciences, New Brunswick, NJ 08901, United States

Exposure to bioaerosols, especially to pathogenic or allergenic microorganisms, may cause a wide range of respiratory and other health disorders in occupational and general populations. One of bioaerosol characteristics - electric charge - can greatly influence their deposition in sampling lines and collection devices. The magnitude of electric charge carried by inhaled particles can have a significant effect on their deposition in the lung. In addition, electric charge may affect role of bioaerosols as ice and cloud condensation nuclei; charge (or electrical mobility) can control bioaerosol movement in electrical fields, such as created by power lines. Electrical charge is also important for the development of bioaerosol samplers that utilize electrostatics for particle collection - this technique has been shown to be more "gentle" collection method than traditionally used impactors and impingers. Our previous studies have shown that airborne environmental bacteria, such as *Pseudomonas fluorescens* and *B. subtilis* var. *niger*, have a net negative charge, with individual cells carrying as many as 10,000 elementary charge units, which sharply contrasted with low electrical charges carried by non-biological test particles. We have also found that magnitude and polarity of electrical charge can significantly affect viability of sensitive bacteria, such as *P. fluorescens*. In our continuing exploration of electrobiological properties of bioaerosols, we investigated application of electrostatic collection method for concurrent determination of total and viable bioaerosols, and also analyzed the effect of electrical fields on microbial viability. In our new bioaerosol collector, the biological particles are drawn into the sampler's electrical field and are concurrently deposited on an agar plate for determining viable microorganisms, and into a ELISA plate for determining total collected microorganisms. Experiments with *B. subtilis* var. *niger* and *P. fluorescens* vegetative cells have shown that on average 80 percent of airborne bacteria entering the sampler were removed from the air onto the plates when the sampler operated at 8 L/min and used collection voltage of -1,500V. From 15 to 25 percent of all bacteria entering the sampler were enumerated by the culture technique. Use of electrostatic analysis techniques may require application of strong electrical fields which could be damaging to biological particles. In our experiments, the airborne *P. fluorescens* bacteria were exposed to electric fields of 10kV/cm for 30 seconds, which did not result in viability reduction. In contrast, more than 90 percent of the *P. fluorescens* cells have been killed when the microorganisms were first deposited on filters and then exposed to positive electrical field of 15 kV/cm for at least 15 minutes. Electrical fields of 5 and 10 kV/cm also achieved similar effect when bacteria were exposed for 120 min. The exposure of bacteria to negative electrical fields resulted in even higher rates of inactivation. The *B. subtilis* var. *niger* bacteria proved to be harder and 10 percent viability reduction was achieved with the use of 15kV/min for 2 hours. The obtained results demonstrate the importance of electrical charges and fields in behavior, collection and control of bioaerosols. The field studies will have to be performed to confirm laboratory findings.

**A22B CC: 520 D Tuesday 1030h**

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

**Presiding: A Gettelman, National Center for Atmospheric Research; S Sherwood, Yale University**

**A22B-01 1030h INVITED**

**Tropical tropopause water isotopes in a GCM: Sensitivity to cloud processes and stratosphere-troposphere exchange**

Gavin A Schmidt<sup>1</sup> (212 678 5627; gschmidt@giss.nasa.gov)

Georg Hoffmann<sup>2</sup> ((33) 1 69.08.46.72; hoffmann@lscs.saclay cea.fr)

Yongyun Hu<sup>1</sup> (212-678-5534; yhu@giss.nasa.gov)

<sup>1</sup>NASA GISS and Center for Climate Change Research, Columbia University, 2880 Broadway, New York, NY 10025, United States

<sup>2</sup>Laboratoire des Sciences du Climat et de l'Environnement, D.S.M. Orme des Merisiers C.E. Saclay, Gif-sur-Yvette 91191, France

Water isotopes ratios ( $\delta^{18}O$ ,  $\delta D$ ) are very sensitive tracers of the history of the water in the atmosphere. For example, depletion of heavy isotopes in convective plumes can be extreme and thus isotope ratios can be used to discriminate between upwelled and in-situ condensation. We present results with state-of-the-art GCMs that include water isotopes in every aspect of the modelled water cycle, including the relatively sophisticated prognostic cloud water scheme. These models also have reasonable representations of the stratospheric circulation and so can be used to look at the processes involved in stratosphere-troposphere exchange. We demonstrate that the models show a similar range of variability near the tropical tropopause to that seen in recent data, and that the zonal mean values are less depleted than a simple Rayleigh distillation column would suggest. Importantly, we show that the isotopes can be sensitive to uncertain details of the cloud parameterizations and thus may help in improving and validating cloud schemes in models.

**A22B-02 1050h**

**The Lofting and Sublimation of HDO-Rich Ice in Cumulonimbus Anvils**

Jamison A Smith<sup>1</sup> (303-735-3521; jamison.smith@colorado.edu)

Owen B Toon<sup>2</sup>

Andrew S Ackerman<sup>3</sup>

Eric J Jensen<sup>3</sup>

<sup>1</sup>Laboratory for Atmospheric and Space Physics, University of Colorado, 392 UCB, Boulder, CO 80309, United States

<sup>2</sup>Laboratory for Atmospheric and Space Physics, Program in Atmospheric and Oceanic Sciences, University of Colorado, 392 UCB, Boulder, CO 80309, United States

<sup>3</sup>NASA Ames Research Center, Earth Science Division, Mail Stop 245-4, Moffett Field, CA 94035, United States

We employ a three-dimensional large eddy simulation with bin-resolved microphysics to simulate the distribution of water isotopomers within deep convective clouds. Deep convection produces vertical profiles of HDO vapor that deviate significantly from the Rayleigh distillation model. These deviations are caused by the lofting of HDO-rich cloud ice within convective updrafts and the subsequent sublimation of this lofted ice in cumulonimbus anvils. The model results agree qualitatively with in situ measurements obtained during the CRYSTAL/FACE field campaign. Together, the in situ measurements and simulation results provide a key step to understanding the isotope ratios of water vapor in the stratosphere and the dehydration mechanisms operating during stratosphere/troposphere exchange.

**A22B-03 1105h**

**Dehydration in the Tropical Tropopause Layer: Implications from UARS MLS**

William G Read<sup>1</sup> (818 354 6773; bill@mls.jpl.nasa.gov)

Dong L Wu<sup>1</sup> (818 353 1954; dwu@mls.jpl.nasa.gov)

Joe W Waters<sup>1</sup> (818 354 3025; joe@mls.jpl.nasa.gov)

Hugh C Pumphrey<sup>2</sup> (+44 131 650 6026; hcp@met.ed.ac.uk)

<sup>1</sup>Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, Ca. 91109, United States

<sup>2</sup>Department of Meteorology, University of Edinburgh, James Clerk Maxwell Building, King's Buildings, Mayfield Road, Edinburgh EH9, 3JZ, United Kingdom

Measurements of H<sub>2</sub>O from the Microwave Limb Sounder (MLS) on the Upper Atmosphere Research Satellite (UARS) are used to investigate the structure of H<sub>2</sub>O in the near tropopause region and dehydration mechanisms in the tropical tropopause layer (TTL). The new MLS data are consistent with convective input of H<sub>2</sub>O into the bottom of the TTL followed by slow ascent with a maximum relative amplitude in the seasonal cycle occurring near the tropopause nearly in phase with the tropopause temperature seasonal cycle. The relative amplitude of the seasonal cycle shows a minimum at 121 hPa in the upwelling moist phase. These features are reproduced with the 'cold-trap' dehydration hypothesis. Seasonal maps show wettest tropical 100 hPa H<sub>2</sub>O co-located with continental convection.

**A22B-04 1125h**

**What are the changes in stratospheric water vapor?**

Karen H Rosenlof (303 497-7761; krosenlof@al.noaa.gov)

NOAA Aeronomy Laboratory, Mail Stop R/AL6 325 Broadway, Boulder, CO 80305, United States

Increases have been noted in Northern Hemisphere middle latitude stratospheric water vapor over an extended period of time in a variety of instrument records. However, the changes are neither linear nor continuous. In particular, since 2000, a significant decrease has been observed in tropical HALOE water vapor measurements in the 100-70 hPa layer. Similar decreases in the lower stratosphere are also seen in the frost balloon observations taken by the NOAA Climate Monitoring and Diagnostics Laboratory in Boulder, Colorado, USA. (40N) and the POAM and SAGE-II satellite records. In this presentation, data from these varied instrument records will be shown, and possible mechanisms for the observed temporal changes discussed.

**A22B-05 1140h**

**Dehydration at the Tropical Tropopause Over the Indian Ocean**

Susanne Rohs<sup>1</sup> (49-2461-614353;

s.rohs@fz-juelich.de); Juergen Beuermann<sup>1</sup> (49-2461-614353; j.beuermann@fz-juelich.de); Iulia Gensch<sup>1</sup> (49-2461-616933; i.gensch@fz-juelich.de); Martina Kraemer<sup>1</sup> (49-2461-613238; m.kraemer@fz-juelich.de); Robert A. MacKenzie<sup>2</sup> (44-1524-593970; R.MacKenzie@lancaster.ac.uk); Cornelius Schiller<sup>1</sup> (49-2461-15272; c.schiller@fz-juelich.de); Vladimir Alexandrovich Yushkov<sup>3</sup> (7-501-4086150; vladimir@cao.mipt.ru)

<sup>1</sup>Institut für Stratospherische Research (ICG-I) Forschungszentrum Juelich GmbH, Leo-Brandt-Str., Juelich 52425, Germany

<sup>2</sup>Department of Environmental Science Lancaster University, LA1 4YQ, Lancaster, United Kingdom

<sup>3</sup>Central Aerological Observatory, 49-71 Moscow str., Moscow region, Dolgoprudny 141700, Russian Federation

During the APE-THESOO campaign in February/March 1999 high-resolution in-situ measurements were carried out onboard the Russian M-55 Geophysica high altitude aircraft, based on the Seychelles (-4.7° N, 55.3° E) in the western Indian Ocean. In the potential temperature range from 340 - 430 K, 36 individual (quasi)-vertical profiles of temperature, the gas-phase and total water cloud particles, and ozone were obtained. The height of the tropopause and the hypogopause were highly variable for the investigated period. We attribute this to short and local perturbations to the seasonal cycle. The cold point tropopause was located at a potential temperature range from 365 - 403 K. Minimum temperatures were very low (183 - 194 K), leading to saturation mixing ratios at the tropopause of

1.1 - 8.4 ppmv. The hypopause was located on average 4 K above the tropopause with water vapour mixing ratios of 1.2 - 4.1 ppmv. These very low mixing ratios are comparable to those found in previous studies in the 'fountain region' over Micronesia. For 70 % of the vertical profiles, ice saturation was found in a wide range around the tropopause. Predominantly the saturation was corroborated by concurrently detected clouds up to the altitude of the cold point, providing evidence of active dehydration. We identify three common types of vertical profiles: coincident hypopause and cold point at relatively low potential temperatures, associated with a cirrus deck; coincident hypopause and cold point at relatively high potential temperatures, associated with thin subvisible cirrus; and unsaturated, cloud-free, profiles without a pronounced relationship between hypopause and cold point. Characteristics such as extension, number density, frequency distribution of relative humidity over ice of the cirrus clouds were different for these categories which allows to infer their different origin. The low water vapour ratios and the existence of saturation support the hypothesis that the Tropical Tropopause layer (TTL) over the western Indian Ocean is a region where air masses are dehydrated to very low values during their transport into the stratosphere.

## A23A CC: 220 C-E Tuesday 1330h Tropospheric Chemistry Posters (joint with B, GC)

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

### A23A-01 1330h POSTER

#### Chemical Feedbacks in Inverse Modelling of Emissions Using the Adjoint of a CTM

Jean-Francois J. Muller<sup>1</sup> (32-2-373 0366;  
jfm@oma.be)

Jenny Stavrakou<sup>1</sup> (32-2-373 6766; jenny@oma.be)

<sup>1</sup>Belgian Institute for Space Aeronomy, Avenue Circulaire 3, Brussels 1180, Belgium

In order to optimise the emissions of ozone precursors (CO, NO<sub>x</sub>, hydrocarbons) in the IMAGES global chemical transport model, we apply the adjoint technique. Misfits between modelled and measured concentrations are quantified by introducing the cost function and looking for a solution that corresponds to its minimum. The minimum of the cost function is calculated via an iterative procedure that makes use of the adjoint model operator, that is, the gradient of the cost function with respect to a set of control parameters to be optimised. The advantage of the adjoint model technique compared to other inversion methods is that no linear response of the calculated concentrations to changes in the emissions is assumed. Furthermore, the emissions of several chemical compounds can be varied and optimised simultaneously and the chemical feedbacks existing between different chemical compounds can be explicitly taken into account. These features are very important for compounds like CO and NO<sub>x</sub> which have common emission sources (like biomass burning), and are strongly inter-related through the chemistry of the OH radical. In the present study, the control parameters to be optimised are the annual emissions of CO, NO<sub>x</sub> and a few NMVOCs over large regions and for different broad categories. Making use of the emission inventories for the year 2001, we present the results for emission optimisations performed using different combinations of the following observational datasets considered for the same year: ground-based (NOAA/CMDL) measurements of CO concentrations, MOPITT-derived distribution of CO (total or partial) columns, and GOME-derived distributions of NO<sub>2</sub> tropospheric columns. Finally, optimised concentrations will be compared to independent observations provided by aircraft campaigns.

### A23A-02 1330h POSTER

#### Effects of Evolving Size Distributions on Biomass Burning Aerosol Properties in Southern Africa Smoke Plumes

Rebecca L. Matichuk<sup>1</sup> (303-492-2829;  
matichuk@lasp.colorado.edu)

Owen B. Toon<sup>1</sup> (303-492-1534;  
brian.toon@lasp.colorado.edu)

Peter R. Colarco<sup>2</sup> (301-614-6382;  
peter.colarco@gsfc.nasa.gov)

Jamison A. Smith<sup>1</sup> (303-492-6946;  
jamison.smith@colorado.edu)

<sup>1</sup>Laboratory for Atmospheric and Space Physics, Program in Atmospheric and Oceanic Sciences, University of Colorado 311 UCB, Boulder, CO 80309, United States

<sup>2</sup>Earth System Science Interdisciplinary Center, University of Maryland-College Park NASA Goddard Space Flight Center Code 916, Greenbelt, MD 20771, United States

We investigate the importance of aerosol optical properties when employing a realistic smoke aerosol size distribution in an offline three-dimensional chemical transport model used to simulate the evolution of smoke aerosols from biomass burning fires. Our model is driven by assimilated meteorology from the NCEP/NCAR reanalyses and is initialized with measurements collected during the Southern African Aerosol Regional Science Initiative campaign (SAFARI 2000). The model uses a bin representation of a smoke aerosol size distribution and allows aerosols to age by coagulation and hydration. We consider two cases for our simulation: one in which we transport an aerosol particle size distribution that evolves by coagulation and hydration, and another in which we simply transport the mass of the aerosol species and assume its optical properties. The smoke aerosol optical thickness and single scattering albedo at 500 nm were calculated from the model results for both of these cases and compared to Total Ozone Mapping Spectrometer (TOMS) aerosol index, the MODIS aerosol optical thickness, and the aerosol optical thickness, particle size distribution, and single scattering albedo retrieved from Aerosol Robotic Network (AERONET) sun/sky photometers. The results from this study will be useful in future applications relating to the optical properties of evolving smoke aerosols from biomass burning fires.

### A23A-03 1330h POSTER

#### Environmental Partitioning and Reactivity of Polybrominated Diphenylethers

Inez Hua<sup>1</sup> (hua@ecn.purdue.edu)

Laura Iraci<sup>2</sup> (liraci@mail.arc.nasa.gov)

Chad Jafvert<sup>1</sup>

Juan Bezares-Cruz<sup>1</sup>

<sup>1</sup>Purdue University, School of Civil Engineering, West Lafayette, IN 47907, United States

<sup>2</sup>NASA Ames Research Center, Atmospheric Chemistry and Dynamics Branch, Moffett Field, CA 94035, United States

Polybrominated diphenyl ethers (PBDEs) are an important class of flame retardants. Annual global demand for these compounds was over 67,000 metric tons in 2001. PBDEs have recently been extensively investigated as environmental contaminants because they have been detected in air, sediment, and tissue samples from urban and remote areas. Important issues include quantifying PBDE partitioning in various environmental compartments, and elucidating transformation pathways. The partitioning of PBDE congeners to aerosols was estimated for 16 sites in the United States, Canada, and Mexico. The aerosol particles were PM<sub>2.5</sub>, the total suspended particle (TSP) concentration varied between 3.0 - 55.4 μg m<sup>-3</sup>, and the organic fraction ranged from 11 - 41%; these data are published values for each site. It is estimated that the largest fraction of each PBDE associated with the aerosol particles occurs in Mexico City, and the smallest fraction in Colorado Plateau. Although the organic fraction in Mexico City is about 60% of that observed in the Colorado Plateau, the TSP is larger by a factor of about 18.5, and it is the difference in TSP that strongly influences the fraction of particle-bound PBDE in this case. PBDE partitioning to PM<sub>2.5</sub> particles also varies seasonally because of temperature variations. For the less brominated congeners, the percentage that is particle-bound is relatively low, regardless of air temperature. In contrast, the heavier congeners exhibit a significant temperature dependence: as the temperature decreases (fall, winter) the percentage of PBDE that is particle-bound increases. The partitioning calculations complement experimental data indicating that decabromodiphenyl ether (DBDE) dissolved in hexane transforms very rapidly when irradiated with solar light. DBDE is the most highly brominated PBDE congener (10 bromine atoms) and occurs in the commercial formulation which is subject to the largest global demand.

### A23A-04 1330h POSTER

#### Regional Modeling of Stable Carbon Isotope ratio of non Methane Hydrocarbons

Farida - Dehghan<sup>1</sup> ((416) 960-0872; farida@yorku.ca)

Diane V Michelangeli ((416) 736-2100 x77713;  
dvm@yorku.ca)

<sup>1</sup>Farida Dehghan, Department of Earth and Atmospheric, York University, Petrie 4700 Keele Street, Toronto, ON M3J 1P3, Canada

The study of stable isotope ratio ( $\delta^{13}C$ ) can be useful to understand the history of an air parcel that include sources, mixing and photochemical processing. The 3D regional model (MC2AQ) was modified (with two different resolution, 21.2km and 5.3km) to include isotope information for Propene, Toluene, Propane, Benzene, Xylenes, and Isoprene. These compounds (both  $^{12}C$  and  $^{13}C$ ) were included as tracers in the model reacting only with OH, with no feedback on the main chemistry. This model structure can help to constrain the OH concentration. The kinetic isotope effect (KIE) was included for the reactions with OH. The results show that the  $\delta^{13}C$  varies with emissions: when emissions are high the  $\delta^{13}C$  is close to that of the sources, and as the air parcel moves away from the sources the  $\delta^{13}C$  gets heavier due to the chemical processing. We see a clear diurnal pattern in the  $\delta^{13}C$  after removing the effect of the sources. This is an indication of the effect of the processing by OH. The results show that the vertical gradient of  $\delta^{13}C$  depends on the lifetime and the KIE of the hydrocarbons. The back trajectories of the stable isotope ratio ( $\delta^{13}C$ ) were determined to study the history of each hydrocarbon independently using the average photochemical age. The results can help in the determination of the possible sources of individual hydrocarbons and the effects of mixing and dilution during the parcel advection. The back trajectory analysis of  $\delta^{13}C$  provides information of the possible locations of the sources of the compounds being investigated. The model was also set up to study the effect of the different emission type (area sources or point sources) of NMHCs on  $\delta^{13}C$ , using this method can help us to identify the fractionation and location of these two sources.

### A23A-05 1330h POSTER

#### Development and validation of a reduced mechanism for the oxidation of alpha-pinene

Jean-Francois J. Muller<sup>1</sup> (32-2-373 0366;  
jfm@oma.be)

Manuel Capouet<sup>1</sup> (32-2-373 6768; manuc@oma.be)

<sup>1</sup>Belgian Institute for Space Aeronomy, Avenue Circulaire 3, Brussels 1060, Belgium

Atmospheric monoterpenes are important due to their high reactivity and to their large emissions into the atmosphere. The emissions and chemistry of  $\alpha$ -pinene (as representative for the monoterpenes) are included in several tropospheric CTMs, but in a very simplified and unsubstantiated way. Recently Peeters and co-workers have developed a detailed mechanism for the gas phase oxidation of  $\alpha$ -pinene and pinaldehyde down to their primary products by OH (Peeters et al., 2001; Fantechi et al., 2002) and ozone (preliminary unpublished mechanism). Since this mechanism includes thousands of chemical reactions, its reduction into a condensed mechanism of reasonable size is required for global or regional modeling. The methodology we propose for this purpose is based on 1/ the grouping of multifunctional products into classes of similar physical characteristics and chemical reactivities in the atmosphere, 2/ the use of generic peroxy radicals to represent the NO to NO<sub>2</sub> conversions, and 3/ the appropriate validation by comparison with the explicit mechanism and with laboratory measurements. Both the explicit and reduced mechanisms have been implemented in a box model. In addition, a module describing the gas/particle partitioning of the semi-volatile products has been developed and coupled to the gas-phase model. The estimation of the gas/particle partitioning coefficients is based on a parameterization of the temperature dependent saturation vapor pressures for the compounds produced in the mechanism. We present comparisons of the model results using both mechanisms with laboratory experiments, including Yu et al. (1999) for the ozonolysis and Nozriere et al. (1999) for the oxidation by OH. The temperature dependence of secondary organic aerosol is tested against the measurements by Takekawa et al. (2003).

### A23A-06 1330h POSTER

#### Uptake of Gas-Phase Nitric Acid by Water-Ice Surfaces

Maria Ullerstam<sup>1</sup> (416-946 7359;  
mullerst@chem.utoronto.ca)

Jonathan P Abbatt<sup>1</sup> (416-946 7358;  
jabbatt@chem.utoronto.ca)

<sup>1</sup>University of Toronto, 80 St George Street, Toronto, ON M5S 3H6, Canada

Nitric acid is a widespread molecule found in the atmosphere. It is mainly removed from the troposphere by wet or dry deposition. In colder regions such as the upper troposphere and tropopause where cirrus clouds are formed nitric acid can also be scavenged by cirrus ice particles. The uptake of gas-phase nitric acid by