

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

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In order to optimise the emissions of ozone precursors (CO, NO_x, 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_x 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_x 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 NO₂ 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

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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

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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_{2.5}, the total suspended particle (TSP) concentration varied between 3.0 - 55.4 μg m⁻³, 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_{2.5} 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

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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

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Atmospheric monoterpenes are important due to their high reactivity and to their large emissions into the atmosphere. The emissions and chemistry of α -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 α -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 NO₂ 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

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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

water-ice films has been re-examined with a coated-wall flow tube coupled to a chemical-ionization mass spectrometer (CIMS) at 228K. Previous flow tube studies of this system have shown little dependence of the uptake over the partial pressure regime studied. In these studies the initial, short-term uptake has been the focus and the long term uptake has not been quantified. In this experimental setup it was possible to study the uptake of nitric acid at lower partial pressures resulting in a more atmospherically appropriate determination of the adsorption isotherm and the long term uptake has also been addressed. Measurement of the initial uptake coefficient representing a lower limit will also be presented. Finally, possible burial of nitric acid into the bulk of the ice during continuous growth of the ice film has been studied. In the atmosphere ice particles will be subject to cycles of evaporation and condensation which could cause the nitric acid to be encapsulated into the particle, especially since the major part of the adsorption has been proven to be irreversible. This could enhance the ice particles capacity of scavenging nitric acid.

A23A-07 1330h POSTER

Comparative Analysis of the Surface Ozone Regime Over Russia and Europe

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The data of the measurements of the surface ozone concentration (SOC) at several Russian cities, in TROICA expeditions, data of EMEP network as well as the results of LOTOS model application were used to compare the main characteristics of ozone spatial and temporal variability over Russia and Europe. To carry out this investigation the number of new methods of data analysis were developed and applied. Their complex application gave us possibility to separate clearly the contribution of photochemical processes having mainly periodical component (daily and seasonal). Hence more attention could be paid to the dynamical mechanism impacting SOC regime, their spatial and temporal variability including trends estimation. Spectral windowing application to the filtered database of EMEP network showed that among the different processes providing annual and shorter variability the main part (about 40% of dispersion) is governed by local and synoptical scale processes in the range of 2-7 days. At the same time the spatial distribution of these percentage contribution is non-uniform over Europe. One of the important mechanisms providing this type of variability as well as the longer ones is air transport. To study the impact of air transport the correlation fields were calculated for the transport indices using 2D NILU trajectories and SOC at EMEP network. They showed that at the Eastern border of Europe the growth of the westerlies provides not the decrease but the growth of observed SOC. This approach was used to study the features of the zonal and meridional transport, its seasonal characteristics and annual variability. Moreover at Kislovodsk High Mountain Station the changes of the transport patterns can partly explain even observed trend of SOC. Comparison of the regime at the different locations using TROICA data shows that in the most of Russian cities ozone destruction is observed. The generation of the surface ozone is only possible in the cases of combination of natural and anthropogenic emissions (like forest fires episodes in Moscow region in summer 2002). The spatial structure of the surface ozone over the European Russia was obtained with the application of LOTOS model (TNO) evaluated for 1997. It showed much more uniformity of the SOC fields over Russia with the high concentrations in rural regions in comparison with industrial ones. This conclusion is in a good agreement with the measurements of TROICA expedition. The work is carried out under the support of INTAS grant 01-0016 and RFBR 03-05-64712.

A23A-08 1330h POSTER

Perspectives on African Ozone from Sondes, Dobson and Aircraft Measurements

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We have been studying variability in ozone over Africa using data from ozonesondes (vertical profiles from surface to stratosphere), aircraft (the MOZAIK dataset with cruise altitude and landing/takeoff profiles) and the ground (Dobson spectrophotometer total ozone column measurement). The following may give context for ozone investigations during AMMA: 1. Total ozone measurements since 1989 show considerable variability in mean value among the African stations in Algeria, Kenya, Egypt, South Africa, as well as in seasonal cycles and year-to-year. Trends are not evident. 2. The impacts of convection, stratospheric injection, biomass burning and lightning appear in ozone sounding profile data. Time-series analysis and case studies point to periodic influences of long-range interactions with the Atlantic ("ozone paradox," wave-one") and Indian Oceans. 3. Tropospheric ozone variations, observed in tropospheric profiles and integrated column amount, follow general seasonal patterns but short-term variability is so strong that simple averages are inadequate for describing "climatology" and statistical classification approaches may be required.

URL: <http://croc.gsfc.nasa.gov/shadow>

A23A-09 1330h POSTER

Aerosol Modelling as External and Internal Mixtures in Southern Ontario During the Summer Time

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Aerosol can be modeled either under an internal mixed (IM) or an external mixed (EM) scheme. In general, under the IM-scheme, particles with the same size share the same hygroscopic properties. In contrast, under the EM-scheme, particles with the same size are allowed to have various hygroscopic properties. Using the modified version of Community Aerosol and Radiation Model for Atmospheres (CARMA) from the NASA-Ames Research Center; the landuse types, meteorological and emission data from the Mesoscale Compressible Community Air Quality (MC2AQ) model; and the parameterized natural inorganic aerosol emissions, we simulate aerosol microphysics in Southern Ontario during the period of July 1st-5th, 1999. This study compares the different impacts of the IM- and EM-schemes on air quality modelling with respect to the evolution of the aerosol size distribution and composition. A dry deposition algorithm is implemented into CARMA. This study adopts the dry deposition parameterization from the Canadian Aerosol Module (Zhang 2001). It is able to simulate deposition velocity as a function of the meteorological variables such as temperature, pressure, relative humidity and wind velocity, the particle radius and the local landuse categories. Two types of emissions are included in this study. Anthropogenic emissions as PM_{2.5} and PM₁₀ provided by MC2AQ and sea salt emissions as a function of particle size and meteorology (Monahan et al., 1986). Three locations with various landuse categories are being studied in detail with respect to aerosol size distribution and composition. The 1st location has no water, 64% trees and 2.7% urban; the 2nd location has 48% water, 12% trees and 0.9% urban; and the 3rd location has 100% water. These 3 locations have different evolution of aerosol size distributions and compositions resulting from different deposition velocities, sea salt and anthropogenic emission amounts. In order to examine the ability of IM- and EM-schemes to keep track of aerosol composition, the corresponding aerosol composition at 4am, 2pm and 6pm of each day are plotted. The results of the model simulations will be compared and conclusion will be drawn regarding the usefulness of both schemes.

URL: <http://www.agu.org.yorku.chiu>

A23A-10 1330h POSTER

Beyond BC and OC: A Preliminary Global Emission Inventory of What Really Matters

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Carbonaceous aerosols, including black carbon (BC) and organic carbon (OC), make up a large fraction of the atmospheric aerosols and affect the radiative balance of the earth either by directly scattering and absorbing solar radiation or through indirect influence on cloud optical properties and cloud lifetimes. Fossil fuels, biofuels, and open biomass burning are the major sources of BC and OC. Although there are hundreds of different organic species in aerosols, global climate models treat organics as one 'compound' and the emissions of OC are often simply derived by multiplying BC emissions with OC/BC ratio. Because different combustion practices play an important role in determining emission rate of BC and OC to the atmosphere, estimates of carbonaceous aerosol emissions are very uncertain both regionally and globally. We present a global emission inventory of primary carbonaceous aerosols that has been designed for global climate modeling purpose. The inventory considers emissions from fossil fuels, biofuels, and open biomass burning. Fuel type, combustion type, and emission controls, and their prevalence on a regional basis are combined together to determine emission factors for all types of carbonaceous aerosols. Since one single organic 'compound' is not sufficient to represent all the organics in aerosols, we propose a preliminary classification for organic aerosols based on structural and optical properties. We provide broad classes aiming at global models instead of very detailed classifications, which are not amenable for use in global-scale models due to the calculation cost. OC is broken down into several groups with varied absorption and water solubility properties. Because our inventory tabulates emissions from specific sources, we can make use of data available from source characterization. The uncertainty in emissions is constructed and we discuss how this uncertainty translates to radiative forcing. The uncertainty of emissions results from factors including emission rates, speciation of particulate matter, prevalence of different technologies, and activity rates. Finally, the direction of future development of the carbonaceous aerosol global inventory will be discussed.

A23A-11 1330h POSTER

Interannual to Synoptic Scale Variability in Intercontinental Transport

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Intercontinental transport (ICT) represents pathways of atmospheric flow responsible for dispersion of air pollutants e.g. ozone and aerosols that play vital roles in regional air quality and climate change. Temporal variations in atmospheric dynamics influence behavior of ICT. Here, we investigate interannual to synoptic scale variability in ICT using a source-receptor relationship. We performed a 10-year online' simulation of eight Rn-like tracers (one global and seven regional) using Finite Volume General Circulation Model. Six-hourly model output archived from this simulation is analyzed for surface concentration, vertical profile and column amount of all tracers on various timescales at 50 regional receptors placed around the globe. We quantified the contributions from the seven source regions to global tracer distribution at these receptors. In addition, we will present a statistical description of tracer distributions and regional contributions representing the 10-year simulation period.

A23A-12 1330h POSTER

NARSTO Data Available from NASA Langley Atmospheric Sciences Data Center

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North American Research Strategy for Tropospheric Ozone (NARSTO) data are available from the NASA Langley Atmospheric Sciences Data Center (ASDC). The NARSTO data products contain ground-based and laboratory aerosol and gases measurements from select urban and regional environments. The primary mission of NARSTO is to coordinate and enhance scientific research and the assessment of tropospheric ozone behavior, with the central programmatic goal of determining workable, efficient, and effective strategies for local and regional ozone management. NARSTO is an ongoing project. Currently the data are available for May through September 1995, March 1997 through March 1998 and June 26, 1999 through July 1, 2003. The NASA Langley ASDC is the permanent archive for NARSTO data. More information is available at <http://eosweb.larc.nasa.gov>.

URL: <http://eosweb.larc.nasa.gov>

A23A-13 1330h POSTER

Nitration of Methanol to Methyl Nitrate in H₂SO₄/HNO₃/H₂O Solutions: Implications for Aerosol Chemistry

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The liquid phase reaction of methanol with nitric acid to yield methyl nitrate under atmospheric conditions has been investigated using infrared spectroscopy. When methanol and nitric acid are taken up by acidic particles, this nitration reaction is expected to occur in the upper troposphere and lower stratosphere. The methyl nitrate produced is much less soluble than nitric acid, suggesting that aerosol-phase reaction may reduce removal of nitric acid by wet deposition. Methyl nitrate will be subsequently photolyzed to regenerate NO₂, thus this reaction may have important implications for the NO_x budget. Experiments in 45, 50 and 60 wt% sulfuric acid solutions between 10 and 30° indicate that the rate of product formation increases with temperature; the activation energy of the reaction is 130 kJ/mol and 90 kJ/mol for 50 and 60 wt% sulfuric acid solutions, respectively. The reaction was found to be linearly dependent on methanol at all acidities investigated. Methyl nitrate production rates increase exponentially with acidity within the regime studied. Preliminary calculations suggest that for perturbed tropospheric conditions, the rate of methyl nitrate production is approximately 0.3 ppt/hr. This reactive pathway could significantly affect tropospheric nitric acid and methyl nitrate levels during the lifetime of aerosol particles.

A23A-14 1330h POSTER

High Order Finite Volume Methods for the numerical simulation of atmospheric transport processes

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The set of conservation laws governing reactive flow describes a complex physical system in which the fluid dynamics is coupled with local processes such as chemical reactions or phase changes. In order to solve this very complex set of equations in an efficient and accurate manner we first discretize the spatial derivatives using the finite volume technique with appropriate limiters to assure monotonicity of the scheme. The discussion of the discretization of the spatial terms is performed on an arbitrary unstructured triangular mesh. The system of semi-discrete ordinary differential equations obtained following the discretization of

spatial terms is then solved using an appropriate numerical method. In the case of reaction-advection-diffusion equations we use a high order semi-implicit Runge-Kutta scheme. The most interesting aspect of this approach is the elimination of the need for operator splitting. The high order Finite Volume scheme is applied for the simulation of atmospheric transport processes on an icosahedral geodesic mesh. The performance of the proposed method is first evaluated using a set of simple advective tests. In the second step, the method is applied for the simulation of the polar stratospheric vortex and tropospheric chemistry.

A23A-15 1330h POSTER

Empirical combination of aerosol optical depth from transport models, satellite retrievals and ground observations

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It is now well established that natural as well as anthropogenic aerosols affect the global radiation balance by direct and indirect effects. However, due to their short lifetime and the complex physical and chemical processes involved, aerosols display large temporal and spatial variations and information of aerosol properties on global scale is scarce. In recent years, numerous efforts have been undertaken to obtain such information by methods of satellite remote sensing, model simulations, and ground observations. In this study an attempt is being made to merge aerosol optical depth from three different independent sources. Used will be global observations from the MODIS instrument on the Terra satellite; observations from the AERONET network; and simulations from GOCART chemical transport model. An empirical method is presented which keeps the large-scale spatial and temporal variation patterns derived from satellite and model results, and at the same time, regulates the amplitude by the more accurate ground point measurements. The methodology was implemented with a two year time record when simultaneous observations from all three sources were available, to obtain a global distribution of AOD.

A23A-16 1330h POSTER

Reactions of Volatile Furandiones, Aldehydes and Water Vapor in Secondary Organic Aerosol Formation and in Gas Chromatography Analysis

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Volatile furandiones and aldehydes are important atmospheric oxidation products of simple aromatic compounds found in gasoline. A mechanism of secondary organic aerosol formation by furandiones was identified using particle chamber observations and FTIR measurements of model condensed phases. Growth of inorganic seed aerosol was monitored by scanning mobility particle sizing in the presence of humidity and high concentrations of 2,5-furandione (maleic anhydride), 3-methyl-2,5-furandione (citraconic anhydride), benzaldehyde, and trans-cinnamaldehyde. Particle growth began when the gas-phase saturation level of each organic compound (relative to its pure liquid) and water vapor, when summed together, reached a threshold near one. This threshold implies that equilibrium is established between the gas phase and a newly formed, mixed condensed phase containing both organic compounds and water. This equilibrium appears to be governed by Raoult's Law, where the vapor pressure of each component is reduced proportionally to its mole fraction in the condensed phase. However, bulk liquid phase experiments showed that these organics are immiscible with water at the mole fractions expected in the particle phase in our chamber experiments. Thus, non-reactive condensation of these compounds into a mixed organic / aqueous phase is ruled out. Instead, we show that reactions between furandiones and water produce unusually strong dicarboxylic acids:

cis-methylbutenedioic acid (citraconic acid) and cis-butenedioic acid (maleic acid). Bulk phase pH microprobe and FTIR attenuated total reflectance measurements demonstrated that an aqueous phase is rapidly acidified during exposure to furandiones. In addition, the presence of furandiones also greatly increased benzaldehyde solubility. This solubility increase has two causes. First, the entry of maleate (or methylmaleate) ions into the water layer lowers the polarity of the phase. Second, the increase in acidity may enhance reactivity at the aldehyde functional group. Thus the uptake of both furandiones and aldehydes onto particles in the presence of humidity appears to be reaction-dependent. When subjected to normal GC injector temperatures, the cis-butenedioic acids produced in these reactions recycle back to furandiones with much greater ease than similar alkanedioic or trans-alkenedioic acids. This production of volatile compounds during GC analysis could cause large artifacts in gas / particle phase distribution measurements if chemical derivatization techniques are not employed.

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A23A-17 1330h POSTER

Secondary Organic Aerosol Formation by Reactive Condensation of Glyoxal and Water Vapor

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The formation of secondary organic aerosol particles by particle-phase reactions is currently of great interest. Glyoxal has been identified as a significant component in the particle phase in recent smog chamber aromatic oxidation studies. This is surprising because glyoxal has a high vapor pressure and phase partitioning theory would predict that it remain almost entirely in the gas phase. Growth of inorganic seed aerosol in a particle chamber was monitored by scanning mobility particle sizing during addition of gas-phase glyoxal and small amounts of water vapor. Glyoxal was observed to condense on inorganic seed aerosol at concentrations that are at least 100 times below its vapor pressure. This behavior can be explained by a chemical reaction: glyoxal is known to polymerize when exposed to water vapor. This polymerization may be a general mechanism for secondary aerosol formation by alpha-dicarbonyl compounds. The reactivity of hydrated and polymerized forms of glyoxal during analysis by gas chromatography was assessed. Hydrated glyoxal was found to convert to glyoxal at even slightly elevated temperatures in GC injection ports. We then showed that breakdown of solid-phase glyoxal trimer dihydrate, forming gas phase glyoxal and water vapor, occurs at temperatures just above 50 °C, the boiling point of glyoxal. These observations suggest that reports of particle-phase glyoxal are likely caused by GC sampling artifacts, and that the actual particulate species are instead polymerized forms of glyoxal. It does not appear that chemical derivatization protects glyoxal polymers from thermal breakdown during GC analysis. The existence in the particle phase of glyoxal polymers with negligible vapor pressures, rather than volatile glyoxal, is consistent with phase partitioning theory.

A23A-18 1330h POSTER

Analysis of Seasonal and Inter-Annual Variability in Trans-Pacific Transport

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We use the global Model of Ozone and Related Tracers, version 2 (MOZART-2) driven with NCEP winds to conduct a simulation from 1991-2002 of the transport of nine continental tracers with uniform emissions and 2-week lifetimes. The purpose of our analysis is to both evaluate the meteorological component of the inter-annual variability of trans-Pacific transport and to derive an algorithm by which we can predict the transport. For each region emissions we first define average seasonal time-scales for transport in order to describe the average time necessary for each regional tracer to travel from its source to a location downwind. We next define a 'transport potential', the percentage of a tracer emitted from a region that is transported

across a meridional plane in the Pacific, and an 'influence potential', the percentage of a tracer emitted from a region that enters into the boundary layer or free troposphere over the United States. These 'potentials' permit a quantification of the seasonal and inter-annual variability in transport of each regional tracer and their relative contribution to the composition of downwind air masses due to the variability of meteorology. Maximum trans-Pacific transport occurs in winter and spring. The East Asian and former Soviet Union regions have the largest transport potential across the Pacific and have the largest influence potential on the U.S. boundary layer composition while the European region is of secondary importance. East Asian and Indian tracers have the largest trans-Pacific transport potential and influence potential in the U.S. free troposphere. Transport and influence potentials are both larger in the free troposphere than in the boundary layer. Vertical subsidence over the continental U.S. is an important entry route for foreign tracers, particularly in winter. Focusing on the East Asian tracer we find that maximum transport occurs at approximately 40°N in the lower to mid-troposphere. Although significant inter-annual variability in transport exists, we find that neither the North Pacific Index nor the Southern Oscillation Index is adequate for predicting the inter-annual variability in trans-Pacific transport. However, using a combination of area weighted indices of surface pressure over the Pacific we are able to accurately predict the seasonal and inter-annual variability in trans-Pacific transport of the East Asian tracer.

A23B CC: 520 F Tuesday 1330h Stratospheric Composition and Dynamics I

Presiding: D F Rault, NASA Langley
Research Center; S M Melo,
University of Toronto

A23B-01 1330h

Chemistry-Climate Modelling of Ozone Throughout the Middle Atmosphere

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To address issues associated with stratospheric ozone changes and their coupling to climate requires the use of comprehensive models that can properly represent all the relevant physical processes and interactions. The Canadian Middle Atmosphere Model (CMAM) is based on the state-of-the-art CCCma GCM, and includes a comprehensive on-line stratospheric photochemistry that is fully interactive with the radiation. Thus, CMAM is ideally suited for representing the climate coupling between troposphere and stratosphere and its interaction with stratospheric ozone changes. The model is run at T32L65 resolution, with no degradation of tropospheric resolution compared to that of the host tropospheric GCM, and with a lid at ~95km to avoid contamination from upper boundary effects. A key requirement is to validate CMAM in terms of its ability to properly represent the key physical processes and interactions. To that end, results from multi-decade simulations will be presented and compared with observations to show the model's capability to give a comprehensive representation of the current state of the overall climate system from the surface to the mesopause region. The analysis will focus on various aspects of the general circulation and the ozone distribution, including coupled chemical-dynamical variability, and highlight the role of the ozone radiative feedback on the circulation in the polar vortex region.

A23B-02 1345h

Polar Stratospheric Cloud Properties Observed in the Arctic

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Polar stratospheric clouds (PSCs) were observed in the Arctic with an airborne lidar during the recent SAGE-III (Stratospheric Aerosol and Gas Experiment) Ozone Loss and Validation Experiments (SOLVE-I in 1999-2000 and SOLVE-II in 2003) and the earlier Airborne Arctic Stratospheric Experiment in 1989 (AASE-I). In all campaigns the airborne lidar operated from the NASA DC-8 aircraft and used multiple laser wavelengths to obtain aerosol scattering ratio (ASR) measurements at 1064, 610, and 311 nm and aerosol depolarization measurements at 610 and 1064 nm (note that in SOLVE-II the 1064 nm depolarization channel was unavailable due to additional requirements for simultaneous nadir measurements). Optical properties and spatial extent of the background stratospheric aerosols and PSCs were measured during all the campaigns with the results from the AASE-I campaign leading to the discovery of two sub-types of nitric acid trihydrate (Type-1) PSCs. The Type-1a PSCs were found to contain large solids with high depolarization, low wavelength dependence of backscattering (WDB), and low ASR, which reflects low number densities, and the Type-1b PSCs were found to contain small liquid aerosols with very low/zero depolarization, moderate WDB, and moderate ASR. Also, the ASR of the Type-1a PSCs is not much greater than the ASR of the background sulfate aerosols, particularly at 610 nm, and this will modify the average optical characteristics of the PSCs if not properly accounted for. There are differences in the average optical characteristics of the Type-1a and 1b PSCs observed during these campaigns; however, there are many PSC observations whose properties fall in between the characteristics of the Type-1a and 1b PSCs. In situ measurements have indicated that many PSCs may be mixtures of Type-1a and Type-1b aerosols. An analysis of the airborne lidar depolarization and WDB data shows that the optical properties of these PSCs are consistent with a mixture of the Type-1a and 1b aerosols, and the relative amounts of their contribution to the average optical properties of the mixture can be estimated. Results on Type-1a, Type-1b, and Type-1a/b mixtures observed during the SOLVE campaigns are discussed and compared with results from the AASE-I campaign, and a self-consistent interpretation of the Type-1 PSC characteristics is presented.

A23B-03 1400h

The Interaction Between Chemistry and Dynamics in a Climate Model during Antarctic ozone depletion events

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The CMAM is a general circulation model with a top at ~95 km with comprehensive on-line stratospheric chemistry. As part of the WMO report (Austin et al 2003) we have made several 20 year time slice runs for current and future atmospheric and ocean surface conditions. We have analysed these time slices scenarios with a view to characterizing the variability of the timing and magnitude of ozone loss due to the of the Antarctica spring-summer stratospheric Vortex. We find that the dynamical influences are important and can alter the modelled ozone depletion in a significant fashion. Our analysis points to the need for a better characterization within all models of the actual wave forcing (planetary waves and gravity waves) for the time period of the climate being represented so that the model can reproduce the right vortex evolutionary character and hence ozone loss, for the right reasons. Thus, it is necessary to define scenario conditions in a more rigorous fashion in order to simulate the complex interactions between dynamics, chemistry and physics which produce particular ozone loss episodes.

A23B-04 1415h

SCIAMACHY on ENVISAT: Results From the First Years in Space.

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SCIAMACHY (Scanning Imaging Absorption spectrometer for Atmospheric Cartography) is a passive remote sensing instrument, and is a German, Dutch and Belgian contribution to the ESA-ENVISAT. The SCIAMACHY instrument comprises eight spectral channels and records spectra simultaneously from 220 to 2380 nm. SCIAMACHY makes measurements of the back scattered and reflected light coming from the atmosphere in nadir and limb viewing geometries, but also observes solar and lunar occultation at high latitudes. Inversion of the measurements of SCIAMACHY yields information about the amounts and distributions of

atmospheric constituents (gases, aerosols and clouds). In this presentation, results about the mesospheric, stratospheric and tropospheric distributions of constituents will be reported. Case studies of relevance will be discussed.

URL: <http://www.iup.physik.uni-bremen.de>

A23B-05 1430h

Detecting ozone recovery: data, models and techniques

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Decline in total column ozone amounts has been observed over the past several decades throughout much of the world. Due to international legislation to limit the production of ozone depleting substances, we can now expect a recovery of the ozone layer. Looking for early signs of recovery requires a careful understanding of the data, the techniques available to identify a change and the magnitude and fingerprint of the changes we are expecting. All three issues will be briefly covered in this presentation. Data available for both total column and vertically resolved ozone levels will be reviewed. A distinction will be made between looking for positive trends, a change in previously negative trends and a return to unperturbed levels. Some insight into the signature of recovery is known from currently available models. Both the qualitative and quantitative features of these models will be discussed in light of recent data.

A23B-06 1445h

Interhemispheric differences in the trends of the stratospheric long-lived tracers during the last decade

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Long-lived chemical species were analyzed to investigate the temporal variations of mixing ratios in the stratosphere during 1992-2002 based on the data observed by HALOE. The characteristic features observed in the mixing ratios of CH₄, HF and H₂O are similar in the middle latitude region in the stratosphere. Those features include the annual, interannual as well as the secular trends. The trends observed in all three tracers show the same feature of the interhemispheric differences. It is implied that the reason of this difference is due to the change of the global-scale stratospheric circulation. To verify this implication the increase of the interhemispheric asymmetry was investigated by relating the long-term variations of observed tracers with the residual mean meridional circulation and the stratospheric wave activities. The interhemispheric differences shown in the tracer mixing ratio is in good agreement with the change in the residual circulation, which has been strengthening in the last decade in the Northern Hemisphere. This change of residual circulation is caused by the increase of the upward-propagating planetary waves in the Northern Hemisphere. The difference in the trends of the planetary waves between the Northern and Southern Hemispheres seems to be another feature of the global climate change.