

fire characterization was not a major consideration in the design of the early satellite-borne remote sensing instruments, such as AVHRR. Therefore, although they are able to provide fire location information, they are not adequately sensitive to variations in fire strength or size, because their thermal bands used for fire detection saturate at the lower end of fire radiative temperature range. As such, hitherto, satellite-based emission estimates employ proxy techniques using satellite derived fire pixel counts (which do not express the fire strength or rate of biomass consumption) or burned areas (which can only be obtained after the fire is over). The MODIS sensors, recently launched into orbit aboard EOS Terra (1999) and Aqua (2002) satellites, have a much higher saturation level and, not only detect the fire locations 4 times daily, but also use their 4 micron channel temperatures to measure the at-satellite fire radiative energy (which is a measure of the fire strength). Also, MODIS measures the optical thickness of smoke and other aerosols. Preliminary analysis shows appreciable correlation between the MODIS-derived rates of emission of fire radiative energy and smoke over different regions across the globe. These relationships hold great promise for deriving emission coefficients, which can be used for estimating smoke aerosol emissions from MODIS active fire products. This procedure has the potential to provide more accurate emission estimates in near real-time, thereby broadening opportunities for various active fire disaster management applications such as alerts, evacuation and, smoke dispersion forecasting.

A22C-1086 1330h POSTER

The impact of the 1998 boreal forest fires on oxidant chemistry in the global troposphere

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The highest surface measurements of northern mid and high latitude CO in the past 15 years were recorded in the summer and fall of 1998. These high values have been linked with anomalously large boreal forest fires associated with El Nino conditions. To study the impact of these forest fires on oxidant chemistry in the global troposphere, we use the GEOS-CHEM global 3-D model driven by biomass burning emissions of trace gases derived from AVHRR firecount data. We compare model results for CO using two independently derived fire products with column data and with concentration measurements at CMDL monitoring sites. To probe the effects of the increased fire activity on OH and ozone, we study the differences between model runs using emissions specific to 1998 and using annual mean biomass burning emissions.

A22C-1087 1330h POSTER

In-situ aircraft and remotely sensed observations of pyrogenic plumes over southern Africa biomass burning regions during SAFARI 2000

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As a part of the SAFARI 2000 validation effort, a series of research flights were coordinated with Terra and TOMS satellite overpasses. Many flights were conducted in regions profoundly affected by biomass burning plumes. This paper explores the relationship between remotely sensed aerosol products from Terra and in-situ aircraft observations made within these pyrogenically impacted areas. In-situ aircraft point data

were scaled up to the size of MODIS data pixels. Several correlations were found between aircraft measurements of trace gases and aerosols and the MODIS derived aerosol measurements. Results of comparisons with MISR and TOMS data are also presented. Column averages obtained during aircraft vertical profiles as well as averages stratified by altitude are presented and illustrate the importance of understanding the vertical structure of the atmosphere for proper data interpretation. As a result, the in-situ aircraft measurements and the remotely-sensed data are linked to meteorological parameters including the location of absolutely stable layers and synoptic conditions in an effort to better understand atmospheric controls on these plumes. Overall these comparisons provide a more robust understanding of column aerosol measurements and the factors that control the vertical distribution of pyrogenic products.

A22C-1088 1330h POSTER

Trace gas emissions from boreal forest fires - 1995 to 2002

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A new data set on area burned in eastern Russia developed from satellite observations has allowed us to develop estimates of trace gas emissions from boreal forest fires for the period of 1995 to 2002. This data set contains information on emissions on a 1 by 1 degree grid at weekly time steps and therefore can be used as a source term for specific fire events in the boreal forest region. During the study period, an average of 9.8 million ha (Mha)/year burned, ranging between 3.0 Mha and 15.6 Mha. In this paper, we will present the results of an approach developed to estimate emissions by merging area burned information with data sets depicting the spatial distribution of fuels and using models of combustion efficiency based on expected fire type (crown, surface, ground) that varied during the growing season. We estimate that an average of 209 Tg of carbon/year (range of 51 to 371 Tg) were released by boreal fires, including 68 Tg/year of CO (range of 50 to 122 Tg). Most of the emissions (80%) are from fires in Russia. There are also clear seasonal patterns to the emissions signature. During low fire years, there is a bi-modal seasonal distribution, with 25% of seasonal emissions occurring in both May and July. During large fire years, while the early season peak still occurs, the majority of seasonal emissions (40%) occur during large fires in August.

A22C-1089 1330h POSTER

Unexpectedly High Aerosol Load in the Free Troposphere Observed With Raman Lidar in Central Europe in Spring/Summer 2003

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We present spectrally resolved backscatter and extinction coefficients, particle optical depths, Ångström exponents, extinction-to-backscatter ratios, and depolarization ratios of strongly enhanced particle loading in the free troposphere. The observations were made with Raman lidar at 355 and 532 nm wavelength at Leipzig (51.3° N, 12.4° E), Germany. Particle extinction coefficients were 5–30 Mm⁻¹ in the free troposphere from May to July, 2003. These numbers result in particle optical depths of 0.03–0.12 at the ultraviolet and visible wavelengths. In May and early June distinct aerosol layers could be observed above the boundary

layer, which typically was between 3 and 7-km height. By the end of June and in July the aerosol distribution became vertically more homogeneous and reached up to the tropopause. On the basis of satellite imagery and backward trajectory analysis it is most likely that severe forest fires in Siberia in early spring 2003 caused this enhanced free tropospheric background. Additional significant sources of the observed aerosols may have been strong forest fires in western Canada in the summer 2003.

A22D MCC: 3016 Tuesday 1340h

Biogenic Reactive Trace Compounds and Their Role in Atmospheric Chemistry and Climate III (joint with B, OS)

Presiding: J Rudolph, Centre for Atmospheric Chemistry, York University; L T Iraci, NASA Ames Research Center

A22D-01 1340h INVITED

Quantifying biogenic VOC emissions over North America using formaldehyde column observations from space

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Formaldehyde (HCHO) columns measured from space using solar UV backscatter allow mapping of reactive hydrocarbon emissions. Our study focuses on North America, where isoprene provides the dominant contribution to HCHO during summer months. Using seven years (1995–2001) of HCHO column data from the GOME satellite instrument we show that the seasonal and interannual variability of HCHO over North America is consistent with known factors that drive regional-scale isoprene emissions. Our previous work has highlighted discrepancies between isoprene emissions derived from GOME and current inventories. These discrepancies are addressed by performing a detailed simulation of oxidant chemistry using the GEOS-CHEM global 3-D model, driven by a new-generation biogenic emission inventory. The contributions from other VOCs, in particular the terpenes, to the GOME HCHO data is also examined. An emission inventory of isoprene calculated from GOME HCHO data is presented with its estimated uncertainties. We evaluate these emissions using in situ measurements of isoprene flux and HCHO concentrations.

A22D-02 1355h

Climate Induced Changes in Biogenic Emissions - Global Chemical and Radiative Effects

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A number of key biogenic emissions are temperature-sensitive. Thus, future climate and temperature changes may lead to changes in the emissions

of naturally occurring species such as N₂O, NO_x, CH₄, and isoprene. Once in the atmosphere, these gases react to form other gases and aerosols and feedback to alter the earth's radiative balance. We examine the possible influence of climate change and the accompanying change in biogenic emissions on upper tropospheric/lower stratospheric species distributions. Specifically, we use a three-dimensional, global chemistry/transport/deposition model (IMPACT). IMPACT contains over 300 prognostic tropospheric and stratospheric reactions. Reactions appropriate for the stratosphere include those for O_x, NO_y, ClO_y, HO_y, BrO_y, SO_x, and CH₄ and their oxidation products. The model also accounts for methane-produced water vapor in the stratosphere. Reactions appropriate for the troposphere include those for O₃, OH, PAN, NO, NO₂, CO, CH₄, HNO₃, SO_x, H₂SO₄, isoprene, ethane, propane, C₄-5 alkanes, C₆-8 alkanes, ethene, propene, ketones (including acetone), formaldehyde, acetaldehyde, higher aldehydes, and their products. We simulate both a baseline scenario and a scenario in which temperature increases 1 - 4 degrees C. The prescribed temperature increase is allowed to alter the emissions of a number of biogenic species: N₂O, soil NO_x, lightning NO_x, CH₄, and isoprene. The resulting effects on key tropospheric and stratospheric species are calculated, and possible changes in radiative forcing are estimated.

A22D-03 1410h

Evaluation of PROPHET and Ameri-Flux Measurements Obtained Over the Period 1998 to 2003 for Evidence of Ozone Effects on CO₂ and Isoprene Fluxes

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Significant increases in surface ozone have been observed in recent decades, particularly in both urban and rural areas in the Northern Hemisphere. Although considerable work has been done to elucidate the effects of ozone on plant physiology, there have been relatively few modeling studies assessing ozone effects on ecosystems and only one large-scale fumigation study involving elevated levels of both CO₂ and O₃ is underway. Very little is known about the subsequent effects of ozone exposure and deposition on biogenic emissions. With increasing emissions of reactive nitrogen oxides and thus increasing levels of surface ozone expected for the foreseeable future, the effects of ozone on ecosystem function must be more thoroughly studied so that we may quantitatively assess impacts on carbon cycling and storage. Measurements of ambient ozone, meteorological parameters, and isoprene fluxes (1997 - 2003), CO₂ and H₂O fluxes (1998 - 2003), and O₃ fluxes (2002

and 2003) were obtained at the Program for Research on Oxidants: Photochemistry, Emissions, and Transport (PROPHET) and AmeriFlux Towers at the University of Michigan Biological Station. We examine these data for evidence for possible effects of ozone. In particular, it appears that ambient O₃ levels may influence the observed relationship between isoprene emissions and sensible heat flux, where there is a high degree of correlation but the slopes vary day-to-day. As well, we attempt to sort out the influences of ozone and soil moisture on CO₂ fluxes. We also assess the relative levels of ozone foliar uptake and deposition by evaluating the behavior of ozone fluxes during periods when it is likely that stomata close mid-day. An assessment of year-to-year variability for these 7 growing seasons is also provided.

A22D-04 1425h

The Role of Atmospheric Organic Nitrogen in Forest Nitrogen Cycling

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Changes in the global climate and atmosphere cause significant effects to the biosphere. Forests respond to these global changes in various ways which all can affect their ability to store carbon, which in turn impacts climate change. Many temperate latitude forests are nitrogen-limited. A current working hypothesis is that atmospheric nitrogen compounds that are deposited to the canopy may be directly utilized by the plant as a nitrogen source. A significant fraction of atmospheric reactive nitrogen that can be deposited is organic. Organic nitrogen deposition is not well characterized nor have the ecological consequences been assessed. Our hypothesis is that organic nitrogen deposition to the canopy is significant, and that that nitrogen is utilized by trees. Fumigation experiments were conducted with 14N and 15N-labeled organic nitrates (focusing on 1-nitrooxy-3-methyl butane as a surrogate for isoprene nitrates) to determine if and how that nitrogen gets incorporated into the leaves by detecting the 15N-labeled leaf amino acids. This research builds on work completed during past summer intensives as part of the Program for Research on Oxidants: Photochemistry, Emissions, and Transport (PROPHET), and begins the next stage of research as part of the Biosphere Atmosphere Research & Training program (BART) at the University of Michigan Biological Station (UMBS). The overall goal of the new effort, the Biosphere Exchange of Atmospheric Carbon and Odd Nitrogen (BEACON) program, is to evaluate the interactive roles of the atmosphere and forest in the coupling of the carbon and nitrogen cycles.

A22D-05 1440h

The Role of Dimethyl Sulfoxide in the Reductive Dissolution of Iron in Marine Aerosols

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Very little is known about the effects of atmospheric iron (Fe) deposition from aeolian dusts into the remote oceans and the role it plays as a key nutrient for photosynthesis in marine phytoplankton in high nutrient low chlorophyll (HNLC) waters. Several *in situ* iron fertilization studies in HNLC regions have reported increases in chlorophyll *a* concentrations, nutrient and carbon uptake, and the release of various biogenic gases which have the potential to directly and indirectly impact global climate. Of particular interest in the present study is the indirect effect of dimethyl sulfoxide (DMSO) as part of a positive feedback cycle that may exist between such biogenically derived reduced sulfur compounds and crustal derived iron in the atmosphere over remote oceanic regions. To determine whether DMSO can lead to larger atmospheric concentrations of bioavailable iron in the form of Fe(II), photochemical simulation experiments were carried out using synthetic ferrihydrite (Fe₅HO₈-4H₂O) in the presence of DMSO. During these experiments DMSO oxidation products, such as methane sulfonic acid (MSA), methane sulfonic acid (MSIA), and sulfate (SO₄²⁻), were quantified by

means of ion chromatography (IC), while Fe(II) was determined spectrophotometrically by complexation with ferrozine. Preliminary results suggest that current ambient DMSO levels are too low to play a significant role in the reductive dissolution of iron hydroxide in aerosol particles. However, increased DMSO levels may enhance bioavailability of iron, thus potentially closing the gap in the positive feedback cycle.

A22D-06 1455h

Tropospheric Aerosol Formation Rates From Dimethylsulfide Oxidation

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Biogenically emitted dimethylsulfide (CH₃SCH₃, DMS) is the largest natural and second largest overall source of atmospheric sulfur. In the atmosphere DMS is oxidized by a complex mechanism to a variety of gaseous species, including H₂SO₄. Gas-phase sulfuric acid has an extremely low vapor pressure, and so it contributes to aerosol and, subsequently, cloud formation under special conditions. The DMS-aerosol-cloud link is complicated by the non-linearity of aerosol nucleation and the spatial disparity between high DMS concentrations, which occur near the surface, and low temperatures conducive to aerosol formation, which occur in the upper troposphere. Global distributions of gaseous H₂SO₄ are estimated from simulations of DMS chemistry using the 3D Model of Atmospheric Transport and Chemistry. The model contains the major DMS-related sources and sinks (oceanic emissions, wet and dry deposition, photochemical conversion, and scavenging by background aerosols). Uncertainties inherent in DMS oxidation are also considered by using two different chemical mechanisms (5-reaction parameterized and 46-reaction comprehensive schemes). For confidence, the modeled H₂SO₄ is compared with gas-phase measurements from ACE-1 and PEM Tropics-A. Along with temperature and relative humidity, the DMS-derived sulfuric acid is used to compute H₂SO₄-H₂O binary nucleation (BN) rates throughout the troposphere. This analysis shows that DMS oxidation does not lead to appreciable aerosol formation through BN in most of the lower troposphere. More specifically, between 60°S and 60°N in the lowest 1 km both DMS mechanisms produce BN rates of less than 10⁻⁵ particles cm⁻³ s⁻¹. These low rates indicate that an additional process such as ternary nucleation is likely required to explain particle formation in the lower troposphere. In the upper troposphere the H₂SO₄ levels are low, yet sufficient enough to induce BN when combined with the cold upper tropospheric temperatures. Just below the tropical tropopause, both DMS mechanisms yield BN rates that exceed 1 particle cm⁻³ s⁻¹. These large tropical upper tropospheric nucleation rates provide evidence that the DMS cycle may serve as an important source of natural aerosols to the lower stratosphere, which may have relevance to climate and the ozone layer.

A22D-07 1510h

Direct Eddy-correlation Measurements of DMS Fluxes and Exchange Coefficients in the Equatorial Pacific

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In the marine atmosphere the emission of dimethylsulfide gas (DMS) is thought to be a major factor in the production of aerosols that control cloud reflectivity. The sea/air flux of DMS has been constrained mostly by budget methods that rely on assumptions about the fate of DMS in the ocean or atmosphere. Area-averaged parameterizations of these fluxes in terms of wind speed alone cannot explain all of the variability, because a) wind speed is only one factor affecting the exchange velocity (roughness, surface films, bubble spectra, and

mean-square wave slope are others), and b) the parameterizations are based on observations that cannot resolve fluxes on time scales of less than a day. We measured the flux of DMS on an hourly time scale in the Eastern Equatorial Pacific from the NOAA ship R/V Ronald H. Brown, using an atmospheric pressure ionization mass spectrometer (APIMS) with an internal isotopically-labeled standard. Both standard and ambient concentrations were measured at 20 Hz. We also measured the seawater DMS concentration with a purge and trap system, so that we could compute the DMS exchange coefficient (flux/interfacial concentration difference). We will compare our transfer coefficients with those from three commonly used parameterizations and with those reported from the GASEX data sets.

A22D-08 1525h

Direct and Indirect Measurements of DMS, Ozone, and CO Fluxes Over the Eastern Pacific Ocean

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The second Dynamics and Chemistry of Marine Stratocumulus experiment (DYCOMS-II) was an integrated investigation of the stratocumulus topped boundary layer regime off the coast of Baja California using the NCAR C-130. While the suite of chemical measurements was relatively scant, the application of a novel, fast technique for measuring dimethyl sulfide (DMS) was employed to great advantage in constraining the dynamic exchange between the strongly capped marine boundary layer (MBL) and the free troposphere above. This exchange parameter, the entrainment velocity, in concert with the surface flux, plays a principal role in controlling the abundance and diurnal behavior of DMS, and most other trace gases, in the MBL worldwide. By measuring the fluxes of DMS and ozone with direct eddy-correlation methods the entrainment rates were determined with unprecedented accuracy, thereby allowing an inference to be made of the oceanic carbon monoxide emissions. The observed fluxes of DMS and ozone are found to be in line with previous estimates and measurements, but the carbon monoxide fluxes are substantially larger than others reported in the literature. Furthermore, very strong horizontal gradients of DMS were observed on almost every flight and indicate patchy emissions upwind of the target area, the orientation of which is not easily explicable from patterns of oceanic primary production.

A22E MCC: 3018 Tuesday 1340h Integrating Aerosol Measurements and Models IV (joint with OS, GC)

Presiding: K A Prather, University of California, San Diego; G R Carmichael, University of Iowa

A22E-01 1340h INVITED

Results of ACE 1, ACE 2, AEROSOLS99, INDOEX, TARFOX, and NEAQS: What Have We Learned? Where Do We Go From Here?

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Since 1995, a series of international field experiments has focused on the measurement of aerosol properties in marine regions downwind of continental emissions. A goal of these experiments has been the characterization of regional aerosol properties and their controlling processes in order to improve estimates of aerosol direct and indirect radiative forcing. The first Aerosol Characterization Experiment (ACE1) purposefully steered clear of any continental plumes in order to

characterize the "background" aerosol upon which anthropogenic perturbations could be imposed. ACE2 focused on the European plume, INDOEX (Indian Ocean Experiment) on the plume emanating from the Indian subcontinent, ACE Asia on the Asian plume, and TARFOX (Tropospheric Aerosol Radiative Forcing Observational Experiment) and NEAQS (New England Air Quality Study) on the eastern U.S. plume. In addition, measurements of dust and biomass burning aerosols from Africa were made the Atlantic Aerosols99 cruise. With the exception of TARFOX, all experiments included the shipboard sampling of aerosol chemical, physical, and optical properties. The shipboard sampling was done with standardized protocols to minimize sampling biases and to make the data from the different regions directly comparable. Regional aerosol properties from the North American, European, African, Asian, and Indian plumes will be compared and the major findings from these experiments will be presented. Properties that will be compared include the relative contribution of the dominant chemical components to aerosol mass and light extinction, the absolute concentrations of the chemical components, light scattering and absorption by the aerosol, single scattering albedo, and aerosol optical depth. Since TARFOX was an aircraft study we include only data collected at altitudes less than 300 m. In addition to using standardized sampling protocols on the ship, over-determined data sets were collected so that a measured aerosol property such as aerosol mass or light extinction could be compared to mass or extinction calculated from an independent set of measurements. Hence, internal consistency in the data sets could be checked, sources of uncertainty could be identified and quantified in the measurement and model methods, and our understanding of regional aerosol properties could be objectively assessed. Based on these closure studies, successes of the experiments will be discussed as well as some of the areas where improvements are needed in measurement and modeling capabilities.

URL: <http://saga.pmel.noaa.gov>

A22E-02 1410h

DMS oxidation: effects of halogens and of increased sea salt alkalinity.

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The oxidation of DMS is the main source of SO₂, MSA, and non-sea-salt sulfate (nss) in the clean marine boundary layer (MBL). Recently the importance of BrO - in addition to OH and NO₃ - has been suggested as oxidant for DMS. Furthermore HOCl_{aq} and HOBr_{aq} can increase the oxidation of S(IV) to S(VI) in aerosol and cloud particles. Chlorine and bromine in the MBL are derived from seasalt aerosol. We investigated the importance of these processes for the chemistry of the MBL and possible climate links with the one-dimensional chemical and microphysical model MISTRA-MPIC. BrO plays a very significant role as oxidant even under very low mixing ratios of 0.5 pmol mol⁻¹. We found that still significant uncertainty exists in the kinetics of DMS oxidation especially with regard to the endproducts of DMS oxidation. Under most conditions that we studied the net effect of halogens, especially under cloudy conditions, is an increase in particulate sulfur (MSA plus nss) and decrease of precursors for the formation of new CCN. In field experiments at Baring Head, New Zealand, it was found that supermicron sea salt aerosols were enriched several fold in their alkalinity resulting from ocean surface layer biogenic sources. Extrapolation of these Baring Head results to typical open ocean lower MBL conditions indicate that supermicron sea salt aerosol alkalinity is enriched by a factor of 100 - 150% compared to deeper ocean water. This would lead to increased alkalinity in the seasalt aerosol and therefore an enhancement of the importance of the nss production by O_{3, aq}. Our model runs show a non-linear response of the oxidation by O_{3, aq} with increasing alkalinity due to saturation effects. In the model runs with increased alkalinity O_{3, aq} dominates the total nss production.

A22E-03 1425h

Non-Seasalt Sulfate (NSS) Production by O₃-Oxidation in Seasalt Aerosols under Clear Sky Conditions: Implications for Modeling of Global Marine Boundary Layer NSS and of New Particle Production

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Aqueous-phase mechanisms can explain a portion of the coarse aerosol NSS (heterogeneous O₃ oxidation and halogen chemistry in the water associated with seasalt aerosols)/found in the MBL. NSS data were collected at Baring Head, New Zealand during clear sky and normal cloudiness conditions. The clear sky coarse aerosols - a unique data subset - encountered little cloud, had substantial excess alkalinity from marine biogenic sources, and contained over 8 nmol NSS m⁻³; normal cloudiness coarse aerosols contained 5 nmol NSS m⁻³. Up to 90% of the clear sky coarse aerosol NSS (70-80% for normal cloudiness cases) was due to O₃-oxidation within seasalt aerosols. For typical global open ocean conditions this biogenic source introduces 100% to 150% added alkalinity beyond that from bulk seawater. The MISTRA model was used to assess the magnitude of S oxidation by O₃ in seasalt aerosols due to this added alkalinity. For a doubling of alkalinity, the % contribution to S oxidation increases 2.5x, causing O₃ oxidation to dominate over halogen chemistry and H₂O₂ oxidation. A major implication of this S oxidation by O₃ in seasalt aerosols is that new particle production from biogenically-derived oceanic S is severely limited in the MBL.

A22E-04 1440h

Aerosol Mixing State Inferred From Highly Time Resolved Composition Measurements And an Aerosol Thermodynamic Model: Case Studies From ACE-Asia And TRACE-P

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In this study highly time-resolved bulk aerosol composition data recorded from airborne measurements during TRACE-P P3B Flight #10 and ACE-ASIA C130 Flight #6 are used to investigate the extent of fine particle mixing among various inorganic aerosol particle constituents. First, a biomass-burning plume, roughly 3-4 day old, superimposed on a background aerosol recorded in the Philippine Sea during the NASA TRACE-P experiment is investigated. Focusing on the fine particle NO₃-, SO₄2-, K+, and NH₄+ system, the observed correlations suggest the existence of a fine mode K+-NO₃- aerosol. Because K+-NO₃- is thermodynamically less favored than 2K+-SO₄2- in a mixture of NO₃-, SO₄2-, K+, and NH₄+, the correlations suggest that aerosols could be composed of biomass burning particles (KNO₃) mixed externally with the background (NH₄)₂SO₄ aerosols. A "closed-mode" thermodynamic aerosol simulation predicts a degree of external mixing of 60 to 100 % is necessary to achieve the observed ionic associations. The same methodology is applied to a dust aerosol plume mixed with polluted urban and sea-salt aerosols recorded in the marine boundary layer of the Yellow Sea during the ACE-ASIA mission. The aerosol simulation carried out assuming various degrees of external mixing between dust and urban particles indicates the observed 2NH₄+SO₄2- association only exists when most of fine-mode dust particles exist externally. In this case, the degree of external mixing is estimated to be between 72 % and 100 %.