

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 (ACE 1) purposefully steered clear of any continental plumes in order to

characterize the "background" aerosol upon which anthropogenic perturbations could be imposed. ACE 2 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 %.

A22E-05 1455h

The Need for Closer Integration of Measurements and Models - Results from Modeling Aerosols in the East Asia Outflow

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East Asia outflow contains primary aerosols arising from diverse sources including: wind-blown mineral dust, biomass/biofuel burning, sea salt spray, and combustion and construction. The outflow also contains large amounts of secondary particles (e.g., sulfate, nitrate and ammonium), which are produced from processes involving gas-phase pollutants emitted in East Asia. The TRACE-P and ACE-ASIA experiments have produced a comprehensive observation-based characterization of the aerosol and their precursors in East Asia. A three-dimensional regional scale model that incorporated an on-line, size-resolved, aerosol thermodynamics model (SCAPE-II) was used (STEM-2K3) was used to study the aerosol ion distributions, and factors that influence the composition-size relationships, in the East Asia outflow during the TRACE-P and ACE-ASIA periods. Results from the model were compared with various observations, and used to study how the aerosol composition changed as air masses travel off the continent and out over the western Pacific. The results presented in this paper indicate that present day models have substantial interpretive and diagnostic capabilities. However the results also point out that improvement in our predictive capability will require substantial reductions in uncertainties, and that closer integration of models and measurements is clearly needed. These issues will be the focus of this paper.

A22E-06 1510h

Change in Mixing State of the Global Aerosol Since Pre-Industrial Times

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The magnitude of the radiative effect of individual chemical aerosol components is sensitive to how they are mixed among the particles. Using a global chemical transport model we show that the increase in emissions of aerosol particles and their precursor gases have caused important changes in aerosol formation processes, and hence the aerosol mixing state. Whereas in pre-industrial times the conversion of gaseous precursors followed by nucleation was the dominant mechanism for particle production over large parts of the globe, today the direct emission of anthropogenic black carbon particles with subsequent condensation of condensable material predominates. The latter process has led to particles that are chemically more complex (more internally mixed) today than in pre-industrial times. We review the measurements that allow us to test the model calculations. They include direct measurements such as single particle mass spectroscopy, an indirect ones such as tandem humidity differential mobility analysis. The available measurements seem to confirm the present day predominance of internally mixed particles, as suggested by the model results. We therefore argue that assessments of the present and future radiative forcing of aerosols and hence sound climate change mitigation policies, must evaluate changes in the emissions of individual aerosol components in terms of their effect on the complete aerosol mixture, rather than just that component alone.

A22E-07 1525h

Simulation of the Intercontinental Transport, Aging, and Removal of a Boreal Fire Smoke Plume

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Back trajectories suggest that an elevated absorbing aerosol plume observed over Oklahoma in May 2003 can be traced to intense forest fires in Siberia two weeks earlier. The Fire Locating and Modeling of Burning Emissions (FLAMBE) product is used to estimate smoke emissions from those fires. The Model for Integrated Research on Atmospheric Model Exchanges (MIRAGE) is used to simulate the transport, aging, radiative properties, and removal of the aerosol. The simulated aerosol optical depth is compared with satellite retrievals, and the vertical structure of the plume is compared with in situ measurements. Sensitivity experiments are performed to determine the sensitivity of the simulated plume to uncertainty in the emissions vertical profile, mass flux, size distribution, and composition.

A22F MCC: 3018 Tuesday 1600h

Integrating Aerosol Measurements and Models V (joint with OS, GC)

Presiding: G R Carmichael, University of Iowa; J Penner, University of Michigan

A22F-01 1600h INVITED

Formation and Growth of Sulfate Particles During Long-Range Transport From Asia to North America

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Fast response measurements of particle size distributions, bulk submicron particle composition, and single particle composition were made aboard the NOAA WP-3D research aircraft over the eastern Pacific Ocean and the western coast of North America. Simultaneous measurements of gas-phase tracers and photochemically reactive compounds, and meteorological analyses, show convincing evidence of long-range transport of layers of aerosol particles from anthropogenic and biomass-burning sources in east and southeast Asia. High concentrations of particulate sulfate and gas-phase H₂SO₄ observed during one transport event were interpreted with the aid of a numerical model of particle formation and growth. The simulation indicates that the particles were formed over the mid-Pacific via gas-to-particle conversion following long-range transport of SO₂ through a midlatitude wave cyclone. This work points to the complexity and diversity of particles transported over intercontinental distances, and the importance of quantitatively understanding the transport and chemistry of both particles and partially soluble precursor gases through cloud systems to estimate the properties and global impacts of the transported aerosol.

URL: <http://www.al.noaa.gov/WWWHD/Pubdocs/ITCT/2k2/>

A22F-02 1630h

Oxygen Isotopic Anomaly in SO₄ and NO₃ Aerosol as a Tracer of Chemistry During Trans-Pacific Pollution Transport

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Sulfate and nitrate are prominent aerosol components in the marine atmosphere, and their budgets are partly controlled by global anthropogenic emissions. Long-range transport of pollution is a phenomenon that highly complicates the marine atmosphere chemistry, as chemical, microphysical and transport processes interact closely, and can alter the radiative and biogeochemical budgets of the atmosphere. Oxygen isotopes of SO₄ and NO₃, and especially the isotopic anomaly ($\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.5 \cdot \delta^{18}\text{O}$), represent a highly specific tracer of the formation pathways of SO₄ and